Available online at http://ijcpe.uobaghdad.edu.iq and www.iasj.net
Iraqi Journal of Chemical and Petroleum Engineering
Vol.23 No.2 (June 2022) 1 – 8
EISSN: 2618-0707, PISSN: 1997-4884

Kinetics and Energetic Parameters Study of Phenol Removal from Aqueous Solution by Electro-Fenton Advanced Oxidation Using Modified Electrodes with PbO_2 and Graphene

Rowaida N. Abbas and Ammar S. Abbas

Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad, Iraq

Abstract

The Electro-Fenton oxidation process is one of the essential advanced electrochemical oxidation processes used to treat Phenol and its derivatives in wastewater. The Electro-Fenton oxidation process was carried out at an ambient temperature at different current density (2, 4, 6, 8 mA/cm^2) for up to 6 h. Sodium Sulfate at a concentration of 0.05M was used as a supporting electrolyte, and 0.4 mM of Ferrous ion concentration (Fe^{2+}) was used as a catalyst. The electrolyte cell consists of graphite modified by an electrodepositing layer of PbO_2 on its surface as anode and carbon fiber modified with Graphene as a cathode. The results indicated that Phenol concentration decreases with an increase in current density, and the minimum Phenol concentration obtained after 6 h of electrolysis at 8 mA/cm^2 is equal to 7.82 ppm starting from an initial concentration about 155 ppm. The results obtained from the kinetic study of Phenol oxidation at different current density showed that the reaction followed pseudo first-order kinetics regarding current density. Energetic parameters like specific power consumption and current efficiency were also estimated at different current density. The results showed that an increase in current density caused an increase in the specific power consumption of the process and decreased current efficiency.

Keywords: Wastewater, Phenolic pollutants, Electro-Fenton oxidation, Graphene, Carbon fiber

Received on 03/04/2022, Accepted on 22/05/2022, published on 30/06/2022

https://doi.org/10.31699/IJCPE.2022.2.1

1- Introduction

Hydrocarbon pollutants are spilling and leaking during exploration, manufacture, refining, transportation, and storing of products in several industries, causing pollution by these hydrocarbons [1]. Among these hydrocarbon pollutants, monoaromatic hydrocarbons are strong environmental pollutants, persistent, and priority organic contaminants due to their high stability in the environment [2]. Wastewater containing aromatic hydrocarbon is recalcitrant, more harmful than aliphatic components, and toxic to biological treatment [3, 4]. The most dangerous aromatic components in refinery wastewater are Phenol and phenolic derivatives [5].

Phenols are aromatic compounds enclosing one or more hydroxyl groups attached to the aromatic ring, and they are barely degraded by nature and remain a danger to the environment. Phenol has been placed on the list of essential pollutants according to Environmental Protection Agency (EPA) and European Agency (EU) that causes extreme toxicity for human and aquatic life [6]. Phenolic compounds can accumulate in human and animal tissue and inhibit the synthesis and copying of Deoxyribonucleic Acid (DNA) in a cell, and it prevents the reparation of DNA in diploid human fibroblast [7, 8].

In some cases, high concentration Phenol becomes mortal and causes burns and hurtful influence on the lung and liver, and hurt the central nervous system [9]. The rules by EPA to lower Phenol content in wastewaters to less than 1 mg/L, and according to the World Health Organization (WHO) recommendation, the permissible concentration of phenolic contents in potable waters is 0.001 mg/L [10], while the EU assigned that a maximum permitted limit of less than 0.0005 mg/L for Phenol in all of its forms [11].

Great interest has been raised today to reduce these pollutants from industrial wastewater before discharge into aqueous environments to ensure harmless removal to the ecosystem and avoid legal problems [12].

Generally, there are two primary stages of wastewater treatment; The first is the pre-treatment step that consists of mechanical and physicochemical treatments. This pre-treated effluent goes into advanced treatment. Primary treatment is important because it prevents the purification equipment from damaging and lowering its efficiency by particulate matter pollutants and can be achieved by mechanical, physical, and chemical methods [13]. The next treatment step is advanced wastewater treatment which aims to remove and mineralize organic pollutants or reduce the contaminants in wastewater to the allowable limit before discharging.

Corresponding Authors: Name: Rowaida N. Abbas , Email: rowida.abbas1307d@coeng.uobaghdad.edu.iq, Name: Ammar S. Abbas, Email: ammarabbas@coeng.uobaghdad.edu.iq

These processes are bioremediation [14], adsorption [15], membrane separation [16], microwave catalytic wet air oxidation [17], photocatalytic degradation [18], chemical oxidation [19], electrochemical oxidation process [20].

Three ways could treat wastewater containing organic contaminants: complete oxidation of these organic compounds to form carbon dioxide and water, converting its chemical structures to another structure that is degraded easily, and the final way is the partial oxidation of these organic pollutants to form less toxic substance and biodegradable substance [21].

Electrochemical treatment is one of the cleaner methods and eco-friendly environmental protection strategies and promising technologies for treating organic pollutants, especially Phenol from aqueous solutions [22]. Electrochemical technologies have many advantages that make them preferred in treating petroleum refinery wastewater, such as compatibility with the environment, adaptability, energy efficiency, selectivity, safety, flexibility to automation, and cost-effectiveness [23, 24]. Whenever the conventional oxidation processes become inadequate in treating wastewater, Advanced Oxidation Processes (AOPs) are used. AOPs replace conventional oxidation because the oxidation rate is prolonged, and the pollutants resist chemical oxidation or oxidize partially, forming contaminants of high toxicity [25]. In these processes, oxidation is attainted by hydroxyl radicals (•OH) generated electrochemically, which have a robust ability to oxidize. •OH, is strongest than other chemical oxidants and the strongest inorganic oxidant after fluorine [26]. The reaction rate velocity of these processes is high, and •OH is oxidized organics faster than ozone. So, the advanced electrochemical oxidation process is commonly used in treating the poisoning of organic pollutants such as Phenol in industrial wastewater like coking wastewater, papermaking wastewater, and refinery wastewater [23, 27].

The Electro-Fenton oxidation process is one of the most critical AOPs as it reduces the cost and the risk of transportation of hydrogen peroxide in the traditional Fenton process. The Electro-Fenton oxidation process involves the combination of addition Ferrous ion and electro-generated of H_2O_2 in-situ. Also, the electro-Fenton is environmentally friendly and does not produce secondary pollutants due to that the electricity used is clean and pollution-free [28, 29]. Hydrogen peroxide is produced by a two-electron reduction of oxygen at the appropriate cathodic potential on particular electrodes (Eq. 1) [30].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

•OH and •OOH are generated in the solution with the addition of Fe^{2+} as catalyst (Eqs. (2) and (3)). Then, •OH and •OOH can attack and initiate the oxidation of pollutants (RH), as shown in Eq. (4) [30].

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \qquad (3)$$

$${}^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \qquad (4)$$

Fe^{2+} ions are regenerated electro-catalytically through the Fenton process by one-electron reduction of Fe^{3+} Eq. (5).

$$\mathrm{Fe}^{3+} + e^- \rightarrow Fe^{2+} \qquad (5)$$

The electrodes used in the oxidation processes are one of the most critical factors that determine the efficiency and selectivity of the removal efficiency and affect mechanisms and products [31]. The electrode material's performance variance is different in its ability to generate hydroxyl radicals and is affected by the side reaction at the electrode surface and in the bulk solution [32].

Carbonous electrodes are commonly utilized as anodes in wastewater treatment because they provide high surface area per unit volume. Carbonous electrodes such as graphite have porous substrates and corrosion resistance and can be easily covered by electrodeposition of active materials on their surface, such as PbO_2 [29, 33]. The cathode material is also an important factor in the electrochemical oxidation processes of organic pollutants, especially in the electro-Fenton processes, because hydrogen peroxide is produced by cathodic reduction of dissolved oxygen or air. The essential cathodes that using to increase the rate of hydrogen peroxide production in these processes are graphite (G), carbon fiber (CF), carbon felt, carbon black [34-36], carbon nanotube [37], Graphene (GN) [38].

The present work investigates electrochemical oxidation techniques for Phenol in an aqueous solution by using an electrochemical cell consisting of graphite modified by electrodeposition of PbO_2 on its surface as anode and CF modified by GN as a cathode. The Electro-Fenton oxidation technique was used in the treatment process at a different current density (CD). Also, reaction kinetics and energetic parameters were calculated and discussed.

2- Experimental Work

All chemicals used in experiments were of the reagent grade, and there was no need for further purification, and distilled water was used to prepare all aqueous solutions. CF (purchased from OEM with 0.2 mm thickness and 3k yarn size) modified by GN was used as a cathode, and PbO_2 on G (imported from Graphite India Limited (GIL)) was used as anode in the electro-Fenton oxidation process.

The electrolytic solution of Phenol removal experiments consisted of 400 mL of 150 ppm Phenol solution. The process was carried out in an open, undivided Perspex cell of 400 mL volume. The two electrodes' dimensions are (3*10 cm), and the distance between them was 3 cm.

The mixing of 200 rpm was achieved by using an electrical gearbox stirrer (Heidolph). Sodium Sulfates was used as supporting electrolyte with a concentration of 0.05 M to improve the electrolyte conductivity. A catalytic amount of $FeSO_4.7H_2O$ was added before electrolysis started with a concentration of 0.4 mM. The current remained constant during each experiment, and different CD was used (2, 5, 8 mA/cm^2) and supplied by a direct current (DC) power supply (KORAD KA3005D). Compressed air (Resun ACO-001 Electromagnetic Air Pump) was bubbled in the treated solution with a flow rate of 1 l/min for 20 minutes and remained for the electrolysis time until the experiment was completed. A schematic drawing of the electro-Fenton oxidation system is shown in Fig. **1**.

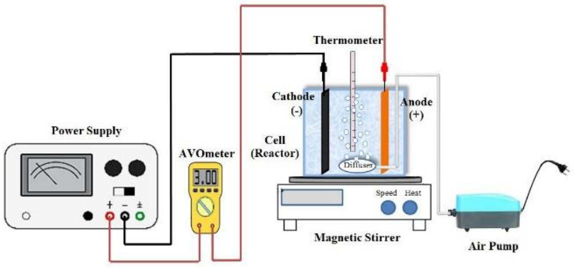

Fig. 1. The electro-Fenton oxidation system

The experiments were carried out at ambient temperature, and the pH of the solution was adjusted initially at 3 by using concentrated sulfuric acid to optimize the production of hydrogen peroxide in acidic media that is saturated with dissolved oxygen. Samples were withdrawn before and after electrolysis for up to 6 hours, and the Phenol concentration was measured using an ultraviolet-visible spectrophotometer (Thermo Genesys 10 UV Electron Corporation Madison W153711). The COD of the final treating solution after 6 h of electrolysis is also determined.

3- Results and Discussions

3.1. Effect of the CD of Phenol Concentration

The electro-Fenton oxidation process was carried out at different CD (2, 4, 6, 8) mA/cm^2, and Ferrous ion concentration (Fe^{2+} = 0.4 mM), supporting electrolyte consisted of sodium sulfate (Na_2SO_3 = 50 mM) and at ambient temperature. The results of Phenol concentration were recorded for up to 6 hours, plotted in Figures (2). The Phenol concentrations were 20.49, 16.27, 12.05, and 7.83 ppm after 6 hours of electrolysis at 2, 4, 6, and 8 mA/cm^2 of CD, respectively, as shown in Fig. **2**. It is clear that increases in CD lead to decreasing Phenol concentration. The reason is that increasing CD from 2 to 8 mA/cm^2 leads to improving the rate of organic pollutants degradation. Increasing organic degradation with CD is due to an increase in the amount of hydrogen peroxide generated electrochemically through the electrolysis. When the amount of hydrogen peroxide increases, the hydroxyl radical (•OH) increases to enough amount to react with the organic pollutants that existed in the treated solution, leading to minimize the Phenol concentration [39, 40]. Our results agree with the results of other researchers [41, 42].

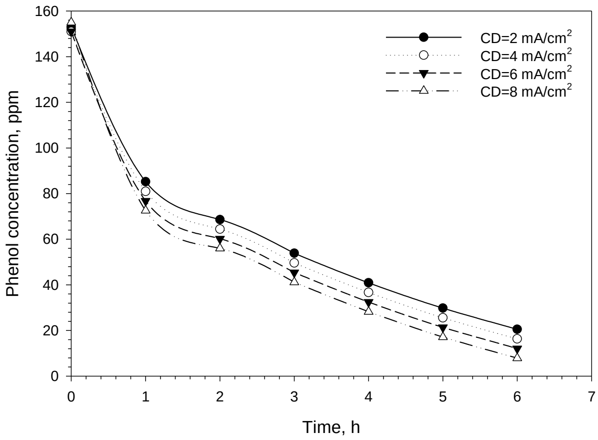

Fig. 2. The effect of applied CD on Phenol concentration, Fe^{2+} = 0.4 mM, Na_2SO_3 = 50 mM, and initial pH = 3

3.2. Kinetic study of Phenol removal by the electro-Fenton process

The deterioration kinetics of Phenol in simulated wastewater was estimated at different CD (2, 4, 6, 8 mA/cm^2), and 0.4 mM of Fe^{2+}. The electro-Fenton oxidation reaction can be represented generally by Eq. (6).

$$Ph + {}^{\bullet}OH \rightarrow CO_2 + H_2O \tag{6}$$

Assuming that the •OH concentration was constant with the experimental time because it is generated simultaneously by Eq. (2), the reaction rate kinetics model can be written as Eq. (7).

$$\frac{-d[Cph_t]}{dt} = k_{obs}[Cph_t]^n \tag{7}$$

where C*ph* is phenol concentration and k_{obs} is the observe rate constant.

The oxidation reaction on the PbO_2 anode and modified CF cathode was determined as the pseudo first-order rate expression and was estimated by non-linear regression for the kinetics data. The regression results and the obtained correlation coefficients (R^2) indicated that the Phenol removal reaction followed first-order kinetics for different CD. The obtained reaction rate constants were tabulated in Table **1**. As CD increasing, the reaction rate constant (k) increases due to increasing of •OH generation, which controls the oxidation reaction speed, and the reaction happens in bulk away from the anode [43].

Table 1. Rate constants of Phenol degradation by electro-Fenton oxidation process at ambient temperature 0.4 mM Fe^{2+}, and different CD

CD, mA/cm^2	k, 1/h	R^2, -
2	0.3390	0.9922
4	0.3690	0.9931
6	0.4092	0.9931
8	0.4674	0.9912

3.3. Energetic parameters: current efficiency (CE) and specific power consumption (SPC)

Energetic parameters such as CE and SPC also calculated for electro-Fenton oxidation process at different current density. SPC as a function of the consumed electrical charge Q (Ah/L) calculated and the results shown in Figure (3). CE at each CD calculated based on COD removal after 6 h of electrolysis and the results shown in (Table 2). These energetic parameters are commonly used to compare and assess electrochemical treatment techniques [44]. The CE donates to the interpretation of the change in the oxidative capacity of the process of electrochemical treatment with the applied current used (I), cell potential (V), and the removed amount of the pollutant (ΔCOD) during the electrolysis time (t), as shown in Eq. (8) [45].

$$CE = \frac{V\left(\Delta COD\right)F}{8It} \tag{8}$$

where F is the Faraday constant (96485.33 C/mol)

The amount of energy consumption in the system driven by electric energy is estimated via SPC for electrolysis of a specific volume of treated solution (Vs) by Eq. (9) [45].

$$SPC = \frac{VIt}{V_s \Delta Conc.} \tag{9}$$

At the lowest value of CD (2 mA/cm^2), the CE (%) is the highest value, and it is equal to 17.59. Increasing CD promotes the removal efficiency of the electro-Fenton oxidation process and decreases CE (%). The least value of CE (%) is achieved at a higher value of CD and it is equal to 4.78 after 6 h of electrolysis. Our results agree with the previous study [46].

SPC in (kW h/kg) increased proportionally as Q increased with time (Figure 3). The highest value of SPC was obtained when Q is equal to 3.6 Ah/L after 6 h of electrolysis. The reason is that the gradual formation of intermediate is more difficult to oxidize and needs more time [47]. High CD increases the cell voltage, which means high power will be consumed. Our results confirm with other researchers [46, 48] as they found the SPC for electro-Fenton oxidation processes in the same range.

Table 2, CE for COD removal via electro-Fenton oxidation over of PbO_2 on G as anode and GN on CF as cathode at different current density after 6 h of electrolysis

CD, mA/cm^2	COD removal	CE %
2	82.2725	17.59
4	84.6425	9.05
6	87.0125	6.20
8	89.3825	4.78

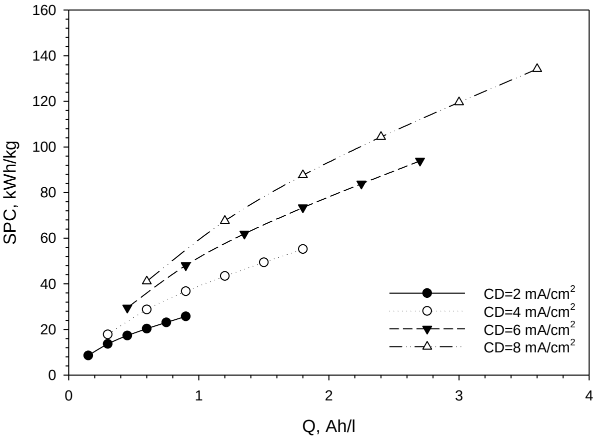

Fig. 3. The effect of the consumed specific charges on the SPC at 0.4mM Fe^{2+}, and different CD for Phenol removal by the electro-Fenton oxidation process

4- Conclusion

Electro-Fenton oxidation technique utilized to treated phenol and phenolic derivatives in diluted aqueous solution with a concentration of 155 ppm. The experiments carried out in a cell consist of PbO_2 on G as anode and GN on CF as cathode. Different current densities were applied to the system in the range between 2 to 8 mA/cm^2 and the results recorded up to 6 hours of electrolysis. The results showed that increasing in CD leads to decrease Phenol concentration because high CD improves the generation of hydrogen peroxide, thereby increasing the •OH that attacks and degrades the organic species. Kinetic study of the oxidation reaction showed that the reaction is pseudo first order kinetic at different CD. Energetic parameter results present that increasing in CD leads to increase in SPC and the highest SPC obtained is about 134.2 (kW h/kg) at 8 mA/cm^2 after 6 h of treatment. Increasing in CD cause to decrease in CE, and the reason is the formation of persistent intermediates and the highest CE was obtained at the lowest CD.

References

[1] S. J. Varjani, E. Gnansounou, and A. Pandey, "Comprehensive review on toxicity of persistent organic pollutants from petroleum refinery waste and their degradation by microorganisms," *Chemosphere*, vol. 188, pp. 280–291, 2017, doi: 10.1016/j.chemosphere.2017.09.005.

[2] S. J. Varjani and V. N. Upasani, "A new look on factors affecting microbial degradation of petroleum hydrocarbon pollutants," *Int. Biodeterior. Biodegrad.*, vol. 120, pp. 71–83, 2017, doi: 10.1016/j.ibiod.2017.02.006.

[3] X. Y. Li, Y. H. Cui, Y. J. Feng, Z. M. Xie, and J. D. Gu, "Reaction pathways and mechanisms of the electrochemical degradation of phenol on different electrodes," *Water Res.*, vol. 39, no. 10, pp. 1972–1981, 2005, doi: 10.1016/j.watres.2005.02.021.

[4] S. Randazzo, O. Scialdone, E. Brillas, and I. Sirés, "Comparative electrochemical treatments of two chlorinated aliphatic hydrocarbons. Time course of the main reaction by-products," *J. Hazard. Mater.*, vol. 192, no. 3, pp. 1555–1564, 2011, doi: 10.1016/j.jhazmat.2011.06.075.

[5] A. S. Abbas, M. H. Hafiz, and R. H. Salman, "Indirect Electrochemical Oxidation of Phenol Using Rotating Cylinder Reactor," *Iraqi J. Chem. Pet. Eng.*, vol. 17, no. 4, pp. 43–55, 2016.

[6] A. Medel, E. Bustos, K. Esquivel, L. A. Godínez, and Y. Meas, "Electrochemical incineration of phenolic compounds from the hydrocarbon industry using boron-doped diamond electrodes," *Int. J. Photoenergy*, vol. 2012, 2012, doi: 10.1155/2012/681875.

[7] N. V. Pradeep *et al.*, "Treatment of Sugar Industry Wastewater in Anaerobic Downflow Stationary Fixed Film (DSFF) Reactor," *Sugar Tech*, vol. 16, no. 1, pp. 9–14, 2014, doi: 10.1007/s12355-013-0227-8.

[8] P. Praveen and K. C. Loh, "Simultaneous extraction and biodegradation of phenol in a hollow fiber supported liquid membrane bioreactor," *J. Memb. Sci.*, vol. 430, pp. 242–251, 2013, doi: 10.1016/j.memsci.2012.12.021.

[9] F. Karim and A. N. M. Fakhruddin, "Recent advances in the development of biosensor for phenol: A review," *Rev. Environ. Sci. Biotechnol.*, vol. 11, no. 3, pp. 261–274, 2012, doi: 10.1007/s11157-012-9268-9.

[10] H. B. Senturk, D. Ozdes, A. Gundogdu, C. Duran, and M. Soylak, "Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study," *J. Hazard. Mater.*, vol. 172, no. 1, pp. 353–362, 2009, doi: 10.1016/j.jhazmat.2009.07.019.

[11] H. Jiang, Y. Fang, Y. Fu, and Q. X. Guo, "Studies on the extraction of phenol in wastewater," *J. Hazard. Mater.*, vol. 101, no. 2, pp. 179–190, 2003, doi: 10.1016/S0304-3894(03)00176-6.

[12] A. Olusegun *et al.*, "We are IntechOpen , the world ' s leading publisher of Open Access books Built by scientists , for scientists TOP 1 %," *Intech*, vol. i, no. tourism, p. 38, 2012, doi: 10.1016/j.colsurfa.2011.12.014.

[13] F. Renault, B. Sancey, P. M. Badot, and G. Crini, "Chitosan for coagulation/flocculation processes - An eco-friendly approach," *Eur. Polym. J.*, vol. 45, no. 5, pp. 1337–1348, 2009, doi: 10.1016/j.eurpolymj.2008.12.027.

[14] A. Chavan and S. Mukherji, "Treatment of hydrocarbon-rich wastewater using oil degrading bacteria and phototrophic microorganisms in rotating biological contactor: Effect of N:P ratio," *J. Hazard. Mater.*, vol. 154, no. 1–3, pp. 63–72, 2008, doi: 10.1016/j.jhazmat.2007.09.106.

[15] M. H. El-Naas, S. Al-Zuhair, and M. A. Alhaija, "Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon," *Chem. Eng. J.*, vol. 162, no. 3, pp. 997–1005, 2010, doi: 10.1016/j.cej.2010.07.007.

[16] W. Raza, J. Lee, N. Raza, Y. Luo, K. H. Kim, and J. Yang, "Removal of phenolic compounds from industrial waste water based on membrane-based technologies," *J. Ind. Eng. Chem.*, vol. 71, pp. 1–18, 2019, doi: 10.1016/j.jiec.2018.11.024.

[17] Y. Sun, Y. Zhang, and X. Quan, "Treatment of petroleum refinery wastewater by microwave-assisted catalytic wet air oxidation under low temperature and low pressure," *Sep. Purif. Technol.*, vol. 62, no. 3, pp. 565–570, 2008, doi: 10.1016/j.seppur.2008.02.027.

[18] Y. Hou, J. Qu, X. Zhao, P. Lei, D. Wan, and C. P. Huang, "Electro-photocatalytic degradation of acid orange II using a novel TiO2/ACF photoanode," *Sci. Total Environ.*, vol. 407, no. 7, pp. 2431–2439, 2009, doi: 10.1016/j.scitotenv.2008.12.055.

[19] Y. Yavuz, A. S. Koparal, and Ü. B. Öğütveren, "Phenol removal through chemical oxidation using Fenton reagent," *Chem. Eng. Technol.*, vol. 30, no. 5, pp. 583–586, 2007, doi: 10.1002/ceat.200600377.

[20] X. Duan, F. Ma, Z. Yuan, X. Jin, and L. Chang, "Electrochemical degradation of phenol in aqueous solution using PbO2 anode," *J. Taiwan Inst. Chem. Eng.*, vol. 44, no. 1, pp. 95–102, 2013, doi: 10.1016/j.jtice.2012.08.009.

[21] R. G. Saratale, K. J. Hwang, J. Y. Song, G. D. Saratale, and D. S. Kim, "Electrochemical oxidation of phenol for wastewater treatment using Ti/PbO2 electrode," *J. Environ. Eng. (United States)*, vol. 142, no. 2, pp. 1–9, 2016, doi: 10.1061/(ASCE)EE.1943-7870.0001007.

[22] A. Ali, M. Hewehy, X. Chen, G. Huang, and J. Wang, "Electrochemical Reduction / Oxidation in the Treatment of Heavy Metal Wastewater" "Electrochemical reduction/oxidation in the treatment of heavy metal wastewater." *Journal of Metallurgical Engineering (ME) Volume* 2, no. 4 (2013).

[23] Z. Tasic, V. K. Gupta, and M. M. Antonijevic, “The mechanism and kinetics of degradation of phenolics in wastewaters using electrochemical oxidation,” *Int. J. Electrochem. Sci.*, vol. 9, no. 7, pp. 3473–3490, 2014.

[24] S. Ben Abdelmelek, J. Greaves, K. P. Ishida, W. J. Cooper, and W. Song, “Removal of pharmaceutical and personal care products from reverse osmosis retentate using advanced oxidation processes,” *Environ. Sci. Technol.*, vol. 45, no. 8, pp. 3665–3671, 2011, doi: 10.1021/es104287n.

[25] E. Brillas, I. Sire, and M. A. Oturan, “Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton ’ s Reaction Chemistry,” pp. 6570–6631, 2009.

[26] J. Krýsa, D. Mantzavinos, P. Pichat, and I. Poulios, “Advanced oxidation processes for water/wastewater treatment,” *Environ. Sci. Pollut. Res.*, vol. 25, no. 35, pp. 34799–34800, 2018, doi: 10.1007/s11356-018-3411-2.

[27] P. Jin, R. Chang, D. Liu, K. Zhao, L. Zhang, and Y. Ouyang, “Phenol degradation in an electrochemical system with TiO 2/activated carbon fiber as electrode,” *J. Environ. Chem. Eng.*, vol. 2, no. 2, pp. 1040–1047, 2014, doi: 10.1016/j.jece.2014.03.023.

[28] S. Parsons, “Advanced Oxidation Processes for Water and Wastewater Treatment,” *IWA Publ.*, 2004.

[29] E. Rosales, M. Pazos, M. A. Longo, and M. A. Sanromán, “Electro-Fenton decoloration of dyes in a continuous reactor : A promising technology in colored wastewater treatment,” vol. 155, pp. 62–67, 2009, doi: 10.1016/j.cej.2009.06.028.

[30] M. Zhou, Q. Yu, L. Lei, and G. Barton, “Electro-Fenton method for the removal of methyl red in an efficient electrochemical system,” *Sep. Purif. Technol.*, vol. 57, pp. 380–387, 2007, doi: 10.1016/j.seppur.2007.04.021.

[31] R. A. Torres, W. Torres, P. Peringer, and C. Pulgarin, “Electrochemical degradation of p-substituted phenols of industrial interest on Pt electrodes. Attempt of a structure-reactivity relationship assessment,” *Chemosphere*, vol. 50, no. 1, pp. 97–104, 2003, doi: 10.1016/S0045-6535(02)00487-3.

[32] A. Urtiaga, I. Ortiz, Á. Anglada, A. Urtiaga, and I. Ortiz, “Contributions of electrochemical oxidation to waste-water treatment: Fundamentals and review of applications,” *J. Chem. Technol. Biotechnol.*, vol. 84, no. 12, pp. 1747–1755, 2009, doi: 10.1002/jctb.2214.

[33] R. M. Farinos, R. L. Zornitta, and L. A. M. M. Ruotolo, “Development of three-dimensional electrodes of PbO2 electrodeposited on reticulated vitreous carbon for organic eletrooxidation,” *J. Braz. Chem. Soc.*, vol. 28, no. 1, pp. 187–196, 2017, doi: 10.5935/0103-5053.20160162.

[34] M. Pimentel, N. Oturan, M. Dezotti, and M. A. Oturan, “Phenol degradation by advanced electrochemical oxidation process electro-Fenton using a carbon felt cathode,” *Appl. Catal. B Environ. 83*, vol. 83, pp. 140–149, 2008.

[35] A. Özcan, Y. Şahin, A. S. Koparal, and M. A. Oturan, “Degradation of picloram by the electro-Fenton process,” *J. Hazard. Mater.*, vol. 153, no. 1–2, pp. 718–727, 2008, doi: 10.1016/j.jhazmat.2007.09.015.

[36] J. Liu, X. Sun, P. Song, Y. Zhang, W. Xing, and W. Xu, “High-Performance Oxygen Reduction Electrocatalysts based on Cheap Carbon Black, Nitrogen, and Trace Iron,” *Adv. Mater.*, vol. 25, no. 47, pp. 6879–6883, 2013, doi: 10.1002/adma.201302786.

[37] A. Thiam, M. Zhou, E. Brillas, and I. Sirés, “Two-step mineralization of Tartrazine solutions: Study of parameters and by-products during the coupling of electrocoagulation with electrochemical advanced oxidation processes,” *Appl. Catal. B Environ.*, vol. 150–151, pp. 116–125, 2014, doi: 10.1016/j.apcatb.2013.12.011.

[38] T. Liu, K. Wang, S. Song, A. Brouzgou, P. Tsiakaras, and Y. Wang, “New Electro-Fenton Gas Diffusion Cathode based on Nitrogen-doped Graphene@Carbon Nanotube Composite Materials,” *Electrochim. Acta*, vol. 194, pp. 228–238, 2016, doi: 10.1016/j.electacta.2015.12.185.

[39] N. Beqqal, M. S. Yahya, M. El Karbane, A. Guessous, and K. El Kacemi, “Kinetic study of the degradation/mineralization of aqueous solutions contaminated with Rosuvastatin drug by Electro-Fenton: Influence of experimental parameters,” *J. Mater. Environ. Sci.*, vol. 8, no. 12, pp. 4399–4407, 2017, doi: 10.26872/jmes.2017.8.12.464.

[40] Gökkuş, N. Yıldız, A. S. Koparal, and Y. Yıldız, “Evaluation of the effect of oxygen on electro-Fenton treatment performance for real textile wastewater using the Taguchi approach,” *Int. J. Environ. Sci. Technol.*, vol. 15, no. 2, pp. 449–460, 2018, doi: 10.1007/s13762-017-1404-1.

[41] Z. I. Abbas and A. S. Abbas, “Optimization of the electro-fenton process for cod reduction from refinery wastewater,” *Environ. Eng. Manag. J.*, vol. 19, no. 11, pp. 2029–2037, 2021, doi: 10.30638/eemj.2020.192.

[42] Y. Yavuz, A. S. Koparal, and Ü. B. Öğütveren, “Treatment of petroleum refinery wastewater by electrochemical methods,” *Desalination*, vol. 258, no. 1–3, pp. 201–205, 2010, doi: 10.1016/j.desal.2010.03.013.

[43] S. Li, D. Bejan, M. S. McDowell, and N. J. Bunce, “Mixed first and zero order kinetics in the electrooxidation of sulfamethoxazole at a boron-doped diamond (BDD) anode,” *J. Appl. Electrochem.*, vol. 38, no. 2, pp. 151–159, 2008, doi: 10.1007/s10800-007-9413-2.

[44] J. R. Bolton, K. G. Bircher, W. Tumas, and C. A. Tolman, “Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems,” *Pure Appl. Chem.*, vol. 73, no. 4, pp. 627–637, 2001, doi: 10.1351/pac200173040627.

[45] Z. I. Abbas and A. S. Abbas, "Oxidative degradation of phenolic wastewater by electro-fenton process using MnO2-graphite electrode," *J. Environ. Chem. Eng.*, vol. 7, no. 3, p. 103108, 2019, doi: 10.1016/j.jece.2019.103108.

[46] D. S. Ibrahim, "Electrochemical Oxidation Treatment of Petroleum Refinery Effluent," *Int. J. Sci. &Engineering Res.*, vol. 4, no. 8, pp. 0–5, 2013, doi: 10.14299/00000.

[47] B. Boye, M. M. Dieng, and E. Brillas, "Anodic oxidation, electro-Fenton and photoelectro-Fenton treatments of 2,4,5-trichlorophenoxyacetic acid," *J. Electroanal. Chem.*, vol. 557, pp. 135–146, 2003, doi: 10.1016/S0022-0728(03)00366-8.

[48] C. A. Martínez-Huitle, S. Ferro, and A. De Battisti, "Electrochemical incineration in the presence of halides," *Electrochem. Solid-State Lett.*, vol. 8, no. 11, pp. 35–39, 2005, doi: 10.1149/1.2042628.

دراسة الحركية والمعلمات النشطة لإزالة الفينول من محلول مائي مخفف بواسطة أكسدة الكترو–فنتون المتقدمة باستخدام الأقطاب الكهربائية المعدلة بـ PbO_2 والجرافين

رويدة نزيه عباس وعمار صالح عباس

قسم الهندسة الكيمياوية, كلية الهندسة, جامعة بغداد, بغداد, العراق.

الخلاصة

عملية أكسدة الكترو–فنتون هي إحدى عمليات الأكسدة الكهروكيميائية الأساسية المتقدمة المستخدمة في معالجة الفينول ومشتقاته في مياه الصرف الصحي. تم إجراء عملية أكسدة الكترو–فنتون في درجة حرارة المختبر و بأستخدام كثافات تيار مختلفة (2 ، 4 ، 6 ، 8 مللي أمبير / سم 2) لمدة تصل إلى 6 ساعات. تم استخدام كبريتات الصوديوم بتركيز 0.05 مولار كمحلول كهربائي داعم ، و استخدم 0.4 ملي مولار من تركيز الأيونات الحديدية (Fe2 +) كمحفز. تتكون خلية المعالجة الكهربائية من الجرافيت المعدل بواسطة ترسيب طبقة من PbO2 على سطحها كأنود وألياف كربون معدلة باستخدام الجرافين ككاثود. أشارت النتائج إلى أن تركيز الفينول يتناقص مع زيادة كثافة التيار ، والحد الأدنى لتركيز الفينول المتحصل عليه بعد 6 ساعات من التحليل الكهربائي عند 8 مللي أمبير / سم 2 يساوي 7.82 جزء في المليون بدءا من التركيز الاولي للفينول الذي يساوي تقريبا 155 ppm. أظهرت النتائج المتحصل عليها من الدراسة الحركية لأكسدة الفينول عند كثافات تيار مختلفة أن التفاعل يتبع حركية من الدرجة الأولى. كما تم تقدير المعلمات النشطة مثل استهلاك الطاقة المحدد و الكفاءة الحالية بكثافات تيار مختلفة. أظهرت النتائج أن الزيادة في كثافة التيار أدت إلى زيادة في استهلاك الطاقة المحدد للعملية و انخفاض كفاءة التيار.

الكلمات الدالة: مياه الصرف الصحي ، ملوثات الفينول ، أكسدة إلكترو–فينتون ، الجرافيت ، ألياف الكربون.