Spectrum Journal of Innovation, Reforms and Development
Volume 51, May 2026 | **ISSN (E): 2751-1731**
Website: www.sjird.journalspark.org

ASSESSING THE ABILITY OF THE ELECTRO-OXIDATION TECHNIQUE TO REMOVE HYDROCARBONS FROM EFFLUENT WASTEWATER FROM THE AL-MUTHANA PETROLEUM REFINERY

Huda Kadhim Hasan 1
Husham M. Al. Tameemi 2
1,2 Department of Chemical Engineering,
College of Engineering, University of AL-Qadisiyah, AL-Qadisiyah, IRAQ
Drhuda718@gmail.com 1
husham.mohammed@qu.edu.iq 2

Abstract
In this study, the anodic oxidation approach was applied to remove organic hydrocarbon from effluent wastewater from Al-Muthana petroleum refinery. The treatment process was achieved using a batch tubular electro-reactor of 1 liter in volume consisted of two concentric graphite electrodes. Impact of current density, pH and addition of NaCl were studied. The optimum operation conditions could be obtained when the operation is carried out at a current density of 8 mAcm-2, pH of 6.0, and addition 1g/L of NaCl for 120 min starting from an initial chemical oxygen demand (COD) of 800 ppm which results in COD removal efficiency (RE%) of 84.3% with a COD discharge lower than 150ppm. The result showed that the electro-oxidation process was applied efficiently for the treatment of hydrocarbons - loaded wastewater. This technique can be applied in the treatment processes of wastewater produced from petroleum refineries with high performance, low cost, and simple operation

Keywords: Wastewater, Electro-oxidation method; COD; Cell current density; Organic compounds removal.

Introduction

Nowadays, the main challenge faced by different industrial sectors is how to treat wastewaters generated from them, because these wastewaters contain various complex pollutants in addition to their huge amount systems. Oil refineries are considered one of the most important Iraqi industries in which huge amounts of water are used through various processes such as distillation, thermal cracking, hydro-treatment, and cooling with desalination systems [1]. It was found that the volume of effluent resulting from the operation of the oil refinery is about 1.6 times the amount of crude oil used in operation. In addition, the percentage of wastewater discharged is around 85% of the amount of fresh water utilized in refinery process. Hence, the treatment of this wastewater is necessary to reuse it again and to prevent environmental pollution [2].

Depending on the plant configuration, production method, and used oil source, the generated wastewater characteristics vary accordingly [3]. Nevertheless, most of the generated wastewaters contain high concentrations of aromatic and aliphatic pollutants which lead to adverse effect on the environment [4]. Therefore, the adoption of a feasible, low-cost and effective approach to treat these effluents should be considered.

Various methods have been used to treat refinery wastewater which include coagulation [4], chemical oxidation [5], adsorption [7], biological methods [6], advanced oxidation processes [3], membrane treatment [8], and electrochemical methods [9, 10].

Generally, these traditional methods only transfer contaminants from one phase to another and suffer from low efficiency in operation. In addition, the selection of any of these methods depends entirely on the characteristics of the wastewater and the ultimate goal in case it is to be reused or discharged. Among these methods, electrochemical processing plays an important role because of its many advantages such as versatility, selectivity, and cheap methods [11]. Also, these systems do not depend on the source of the wastewater or its characteristics, as the reaction can be controlled through any value of the current available in these systems [12].

Anodic oxidation is found in electrochemical treatment systems which is receiving more attention in the treatment of oily wastewater. It depends on the producing of a powerful oxidizing agent ($OH^{\bullet}$) on the surface of the anode which has the ability to attack contaminants and convert them into water and carbon dioxide [13]. Unlike other advanced oxidation methods that generate hydroxyl radicals via chemical reaction (Fenton process) or photochemical reactions (photo-Fenton process), anodic oxidation does not involve using or storage of dangerous chemicals and has the ability to easily scale-up as well as reduce in labor cost and can be automated [14].

Two routes can be perused for the oxidation of contaminants by anodic oxidation, which are the direct and indirect routes. In the first (direct) route, the contaminants are first adsorbed onto the surface of anode then subjected to direct oxidation by electrons. In this case, the type of anodic material plays an essential role in the rate of oxidation of these pollutants [15]. Different kinds of anodic materials were utilized in the direct oxidation process and their oxidation strength has been investigated in the oxidation of various pollutants such as phenol [15]. They are Lead Dioxide (PbO_2), dimensionally stable anode (DSA), SnO_2-doped, and Boron-Doped Diamond (BDD). Among these, BDD is the best due to its high stability, chemical resistance, wide window for water oxidation, ability to generate weakly adsorbed hydroxyl radicals leading to an efficient oxidation process, and the ability of using it for long time to overcome the highly production cost of it [13,14].

In the second (indirect) route, many other oxidizing agents such as hypochlorite/chlorine, ozone, and hydrogen peroxide are indirectly generated at the anode, which attack the pollutants in the solution and convert them into less harmful compounds, carbon dioxide, and water [16,17]. In most wastewater, chloride ions are present and used in indirect oxidation to generate hypochlorite species by chemical reaction between chlorine gas generated from chloride ions and water [17]. In addition, many research papers have mentioned the activity of chlorine to degrade by indirect oxidation many contaminants such as dyes and complex organic materials [19]. Moreover, the addition of chloride ions leads to an increase in conductivity, thus reducing energy consumption during oxidation and increasing current efficiency [20].

In the present work, the organic Content as COD in wastewater produced from Al-Dewaniya petroleum refinery plant was reduced via indirect anodic oxidation process using a batch tubular electrochemical reactor consisted of concentric electrodes made from graphite where the impact of various variables including pH, current density, and addition of NaCl on the COD removal efficiency was investigated. The configuration of concentric electrodes used in the present work gives better distribution of current and potential along the two electrodes.

2. Experimental work

Twenty liters of wastewater generated from Al-Muthana petroleum refinery were taken from the reservoir prior to the biological unit in this plant and kept at temperature of 4 ºC until use. Table 1 displays the properties of this wastewater.

Table 1. Properties of Al-Muthana petroleum wastewater

Parameter	COD (ppm)	Conductivity (µS/cm)	pH	Turbidity NTU	T.D.S (ppm)	Cl^- (ppm)	SO_4^{-2} (ppm)
Value	800	3320	7.8	5.9	1325	456	534

A batch tubular electrochemical oxidation cell composed from a one-liter Pyrex beaker in which hollow cylinder graphite cathode with dimensions (80 mm inside diameter, 100 mm outside diameter, and 100 mm length) was inserted. A cover made of Perspex with dimensions (130 mm outside diameter and a thickness of 10 mm) was put on the beaker and has a central hole to fix the anode which is graphite rode with dimensions as 18mm in diameter and 90 mm in length. Also, it has two holes to insert probes of pH and conductivity -meters. The gap between electrodes was fixed at 30 mm. Glavanostaic operation at constant current was used in which the current was supplied via a digital power supply, Type (UTP3315TFL-II, China). Firstly, 790 ml of wastewater was put into the beaker and then stirred at a speed of 100 rpm via a magnetic hotplate stirrer for a period of time (ten minutes) then its pH was regulated utilizing (1M) HCl or(1M) NaOH for the value according to run condition and finally cathode was inserted and the cover was assembled with beaker. All experiments were performed at 25 ºC (room temperature). Fig.1 displays the configuration of the electrooxidation system.

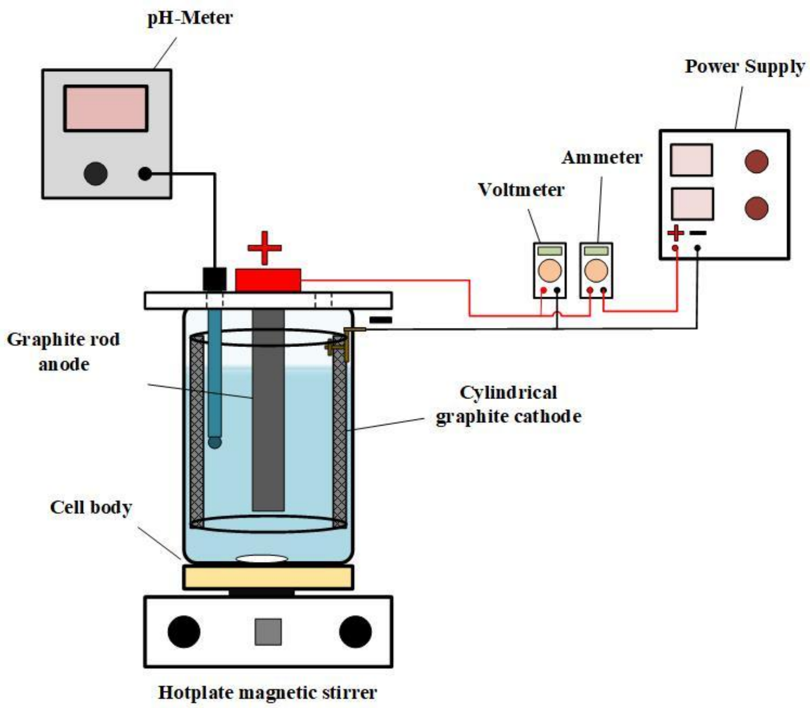

Fig. (1) The electrochemical apparatus

For detecting the pH of solution, a digital pH meter type- PH211, HNNA Instrument Inc, Romania was used while for measuring the TDS and conductivity of the solution performed using model COM-

100/HM digital meter, (Korea) was used. Every 10 min of treatment, samples were taken to analyze their COD value using thermos-reactor type-RD-125, Lovibond combined with spectrophotometer type-MD-200, Lovibond. Measuring the COD were achieved triply for each run and the average value was considered in this study.

The measurement of COD removal efficiency (RE%) was performed by Equation (1), [21]:

$$RE\% = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

To estimate the required energy consumption (EC) in unit (kWh/kg COD), Equation 2 was used [21]:

$$EC = \frac{U.I.t \times 1000}{(COD_i - COD_f)\,V} \qquad (2)$$

3. Results and discussion

3.1 Effect of current density

The decay of COD versus time for various values of current densities is displayed in Figure 2 using effluent with 1g/L NaCl and initial pH of 6. It was evident that an increase in the current density results in a decrease in the final COD value of wastewater. It has been cleared that the decomposition efficiency proceeds progressively like an almost exponential profile over time as the anodic oxidation proceeds. This demeanor can be explained as a gradual decrease in the concentration of organic pollutants during electrolysis coming from the generation of a high concentration of ClO^- which brings the oxidation process under the control of mass transfer in the bulk solution, in addition to a slight increase in the decomposition efficiency occurred at the final stage of oxidation due to the happen secondary reactions such as O_2 generation [22]. Similar exponential decay of COD was recognized by Souza and Ruotolo [13] in the treatment of petroleum refinery wastewater using BDD anode confirming the degradation process was under mass transfer process. The best current density in their work was 50mA/cm^2 which is higher than the value used in the present work because the high oxygen overvoltage of BDD in comparison with graphite. Santos et al. [25] found an exponential decay of COD but at low current density (10mA/cm^2) in case of using Ti/RuO_2 anode which has a lower oxygen overvoltage in comparison with BDD. Yun-Hai et al. [24] confirmed the exponential decay of COD in the treatment of oilefied produced wastewate using sno2 anode. However, using graphite in present work has the economic advantage as a good replacement of the expensive BDD.

Table 2 displays the COD removal efficiency at various current densities where a good COD removal of 84.25% was achieved at a current density of 8 mAcm^{-2} and electrolysis time of 120 min. No substantial increasing in COD removal higher than 8 mAcm^{-2} was observed. Besides, increasing the current density results of course in increasing the consumption of electricity energy. Utilizing higher current densities (>8mAcm^{-2}) lead an increase in the power consumption to be greater than 32.3Kwh/Kg COD. Therefore, selecting 8mAcm^{-2} is preferred for further study. The same trends regarding energy consumption were confirmed by previous works [13, 21- 25].

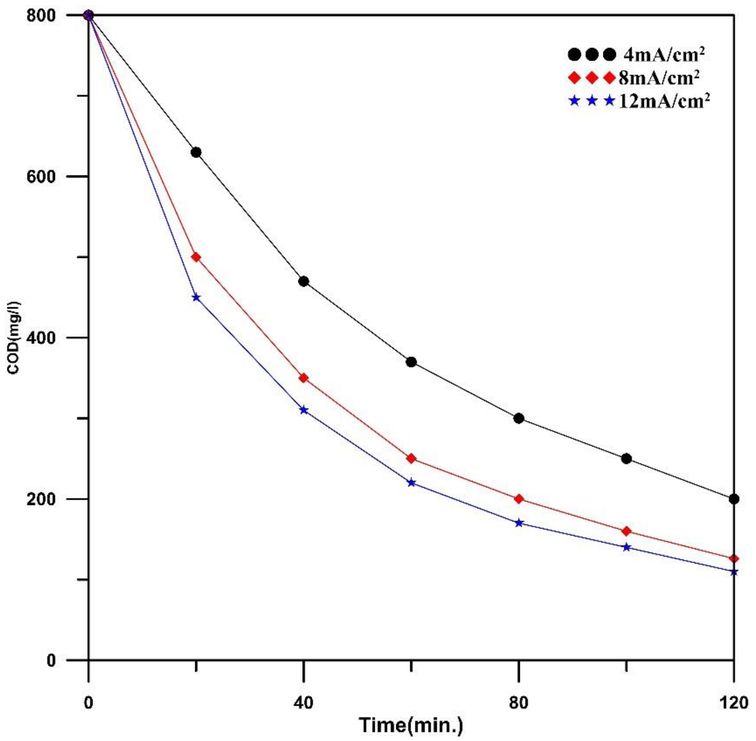

Fig. (2) The influence of current density on COD removal at pH=6, 1g/L NaCl, 25°C.

Table 2. The influence of current density on COD removal

Current density (mA/cm^2)	**RE%**	**EC (kWh/kg COD)**
4	75	10.5
8	84.25	32.3
12	86.25	44.6

3.2 Effect of pH

Figure 6 shows the decay of COD over time at various pH using the effluent with 1 g/L NaCl and operating at a current density of 8 mA^{-2}. The results show that starting with a lower initial pH can lead to a higher removal efficiency with a lower final value of COD. This behavior was clearly observed in Table 3 where a significant effect of pH was observed on COD removal. The maximum value of COD removal efficiency occurred when the pH value was equal to or less than 6. A similar trend was confirmed by Fil et al [26] in their work for treating wastewater from pistachio processing industry via indirect anodic oxidation utilizing a graphite anode where obtaining higher removal efficiency for COD occurred only in acidic solution in the presence of NaCl. Ibrahim et al. [23] demonstrated that neutral conditions lead to higher removal of COD compared to alkaline media. This behavior can be elucidated by the fact that the presence of chlorine ions in the oxidation process can lead to formation of hypochlorous as a stronger oxidizing agent in the acidic solution compared to the hypochlorite that is generated in the basic solution, hence anodic oxidation in general results in a better removal of COD in acidic or neutral conditions than in basic conditions. Previous studies confirmed that active chlorine exists as hypochlorite under alkaline conditions, which is a less powerful oxidizing agent against organic species compared to hypochlorous acid, which is the main species present at pH close to 3 [21,26,27].

However, to safely discharge the effluent, it is recommended to use a pH value close to neutral conditions and then a pH of 6 was considered for further study.

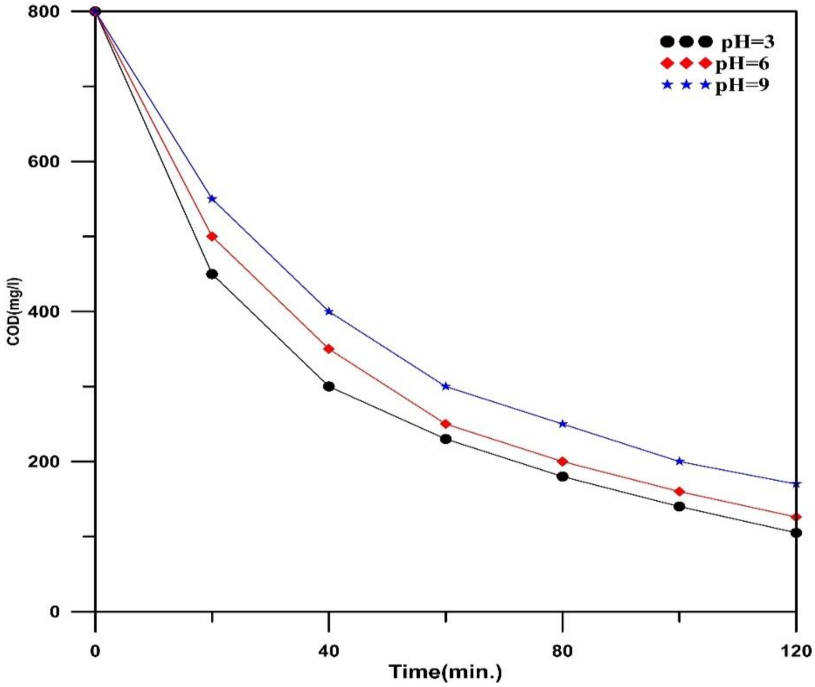

Fig. (3) The influence of pH on COD removal at 8 mAcm^{-2}, 1g/L NaCl, and 25°C.

Table 3. The influence of pH on COD removal

pH	RE%	EC (kWh/kg COD)
9	78.75	40.5
6	84.25	32.3
3	86.875	30

3.3 Effect of NaCl addition

The decay of COD verses time at different NaCl concentrations utilizing wastewater at a pH value of 6 and supplying a current density of 8 mA cm^{-2} is shown in Fig. 4. The results showed that increasing the addition of NaCl results in a decrease in the COD of the post-treatment wastewater. Table 4 also confirms this behavior. It was observed that increasing the NaCl concentration from 0 to 2 g/L leads to an increase in the removal efficiency of COD from 77.5 to 86.375% at the end of 120 minutes.

This result proved the ability of chlorine ions originally present in the wastewater to oxidize pollutants even at low concentrations. Besides energy consumption was slightly reduced as the concentration of NaCl goes beyond 1 g/L. Additionally using higher concentration of NaCl can lead to the generation of chlorinated organic compounds that are difficult to destroy by indirect anodic oxidation as observed in previous works [28].

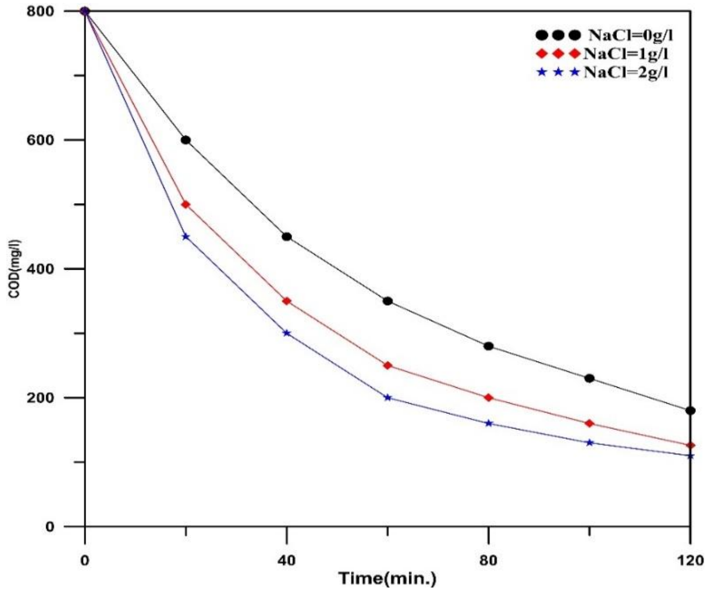

Fig. (4) The influence of NaCl addition on COD removal at 8mAcm^{-2}, pH=6, and 25°C.

Similar trends have been documented via Britto-Costa and Ruotolo [28] in their work for oxidation of phenol using a DSA or BDD electrode where the addition of NaCl increased COD. Souza and Rotolo [13] investigated the anodic oxidation of oil refinery wastewater using a BDD anode and discovered that the addition of 450 mg^{-1} NaCl led to a high removal of COD compared to without adding NaCl. Another study was conducted by Ibrahim et al. [23] for anodic oxidation treatment of effluents in oil refineries where the increase in NaCl concentration led to a better reduction in COD using a titanium anode. Nasser et al. [10] confirmed a similar trend in oil refinery wastewater treatment by anodic oxidation using a tubular electrochemical reactor with a spiral design of anode operating in a batch recycling system.

Table 4. The influence of NaCl addition on COD removal

NaCl addition ((g/L)	RE%	EC (kWh/kg COD)
0	77.5	39.8
1.0	84.25	32.3
2.0	86.375	29.6

4. Conclusions

The application of indirect anodic oxidation using graphite electrodes as a cheap material has been found to be an effective and environmentally friendly approach in treating effluent discharged from the Iraqi petroleum refining plant. An increase in efficiency of COD removal was observed with an increase in current density or NaCl addition. Whereas using any initial pH more than 7 results in decreasing the efficiency of COD removal. Current density has the greatest effect on COD removal efficiency compared to other variables. It is not preferable to increase the concentration of NaCl above 1 g/L because the TDS value exceeded the standard limits as observed experimentally. The best removal efficiency of 84.25% was achieved with a minimum energy consumption of 32.3 kWh/kg COD when operating at a current density of 8 mA cm^{-2} for an electrolysis time of 120 min after adjusting the pH of the wastewater to 6 and adding NaCl at a concentration of 1 g/L. Starting with a pH of 6 leads to an increase in the pH at the end of treatment to 6.8 as observed experimentally which is closer to the neutral value and thus safely discharging the post-treatment effluent into the environment

5. **Abbreviations and acronyms**

Symbol	Definition	unit
COD	Chemical Oxygen Demand	mg L^{-1}
BOD	Biological oxygen demand	mg L^{-1}
TDS	Total dissolved solid	mg L^{-1}
API	American petroleum institute	
RE	Removal efficiency	
C_i	Initial concentration	mg/l
C_f	Final concentration	mg/l
EC	Specific energy consumption	kWh/kg
U	cell voltage	volt
I	Current	Ampere
T	Electrolysis time	h
COD_i	initial chemical oxygen demand	mg/l
COD_f	final chemical oxygen demand	mg/l
V	volume of the effluent	L
BBO	Boron Doped Diamond	-
DSA	Dimensional Stable Anode	-

Acknowledgments
The authors thanks for the helpful and technical support made by Chemical Engineering Department staff / University of Al-Qadissiyah.

REFRENCES

1. IPIECA "International Petroleum Industry Environmental Conservation Association". Petroleum refining water/wastewater use and management. Operations Best Practice Series, London, UK.)2010(.
2. Diya'uddeen, B. H., Daud, W. M. A. W., & Aziz, A. A. Treatment technologies for petroleum refinery effluents: A review. *Process safety and environmental protection*, *89*(2), 95-105. (2011)

3. Coelho, A., Castro, A. V., Dezotti, M., & Sant'Anna Jr, G. L. "Treatment of petroleum refinery sourwater by advanced oxidation processes". *Journal of hazardous materials*, *137*(1), 178-184.. (2006)
4. El-Naas, M. H., Al-Zuhair, S., Al-Lobaney, A., & Makhlouf, S. "Assessment of electrocoagulation for the treatment of petroleum refinery wastewater". Journal of environmental management, 91(1), 180-185. (2009).
5. Abdelwahab, O., Amin, N. K., & El-Ashtoukhy, E. Z. "Electrochemical removal of phenol from oil refinery wastewater". Journal of hazardous materials, 163(2-3), 711-716. (2009).
6. Ma, F., Guo, J. B., Zhao, L. J., Chang, C. C., & Cui, D. "Application of bioaugmentation to improve the activated sludge system into the contact oxidation system treating petrochemical wastewater". Bioresource technology, 100(2), 597-602. (2009).
7. El-Naas, M. H., Al-Zuhair, S., & Alhaija, M. A. "Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon. Journal of hazardous materials", 173(1-3), 750-757. (2010).
8. Li, Y. S., Yan, L., Xiang, C. B., & Hong, L. J. "Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes". Desalination, 196(1-3), 76-83. (2006).
9. Najafinejad, M. S., Chianese, S., Fenti, A., Iovino, P., & Musmarra, D. "Application of Electrochemical Oxidation for Water and Wastewater Treatment" An Overview. Molecules, 28(10), 4208.; (2023).
10. Naser, G. F., Mohammed, T. J., & Abbar, A. H.; "A novel Tubular Electrochemical Reactor with a Spiral Design of Anode for Treatment of Petroleum Refinery Wastewater". Egyptian Journal of Chemistry, 66(1), 257-270.; (2023)
11. Zheng, Y., Wang, A., Lin, H., Fu, L., & Cai, W.; "A sensitive electrochemical sensor for direct phoxim detection based on an electrodeposited reduced graphene oxide–gold nanocomposite". RSC Advances, 5(20), 15425-15430.; (2015).
12. Lawan, M. S., Kumar, R., Rashid, J., & Barakat, M. A.; "Recent Advancement in the Treatment of Petroleum Refinery Wastewater"; (2023).
13. Souza, R. B. A., & Ruotolo, L. A. M.; "Electrochemical treatment of oil refinery effluent using boron-doped diamond anodes". Journal of Environmental Chemical Engineering, 1(3), 544-551; (2013).
14. Clematis, D., Delucchi, M., & Panizza, M.; "Electrochemical technologies for wastewater treatment at pilot plant scale". *Current Opinion in Electrochemistry*, 101172.; (2022).
15. Fu, R., Zhang, P. S., Jiang, Y. X., Sun, L., & Sun, X. H.; "Wastewater treatment by anodic oxidation in electrochemical advanced oxidation process", Advance in mechanism, direct and indirect oxidation detection methods. Chemosphere, 136993.; (2022).
16. Zhuo, Q., Lu, J., Niu, J., Crittenden, J. C., Yu, G., Wang, S., ... & Chen, Z.; "Electrocatalytic Oxidation Processes for Treatment of Halogenated Organic Pollutants in Aqueous Solution", A Critical Review. ACS ES&T Engineering, 2(10), 1756-1775.; (2022).
17. Abbar, A. H., Salman, R. H., & Abbas, A. S.; "Electrochemical incineration of oxalic acid at manganese dioxide rotating cylinder anode: role of operative parameters in the presence of NaCl". Journal of the Electrochemical Society, 163(13), E333.; (2016).

18. Palmas, S., Polcaro, A. M., Vacca, A., Mascia, M., & Ferrara, F. "Influence of the operating conditions on the electrochemical disinfection process of natural waters at BDD electrodes", Journal of Applied Electrochemistry, 37, 1357-1365. ;(2007).
19. Panizza, M., & Cerisola, G. "Electrocatalytic materials for the electrochemical oxidation of synthetic dyes". Applied Catalysis B: Environmental, 75(1-2), 95-101.; (2007).
20. Sandoval, M. A., Calzadilla, W., & Salazar, R.; "Influence of reactor design on the electrochemical oxidation and disinfection of wastewaters using boron-doped diamond electrodes". Current Opinion in Electrochemistry, 33, 100939.; (2022).
21. Sarhan Jawad, S., & H Abbar, A.; "Treatment of petroleum refinery wastewater by electrochemical oxidation using graphite anodes". *AL-Qadisiyah journal for engineering sciences*, *12*(3), 144-150.; (2019).
22. Panizza, M., Michaud, P. A., Cerisola, G., & Comninellis, C.; "Anodic oxidation of 2-naphthol at boron-doped diamond electrodes", Journal of Electroanalytical Chemistry, 507(1-2), 206-214. ;(2001).
23. Ibrahim, D. S., Devi, P. S., & Balasubramanian, N. ; "Electrochemical oxidation treatment of petroleum refinery effluent". Int. J. Sci. Eng. Res, 4(8), 1-5;(2013).
24. Yun-Hai, W., & Jun-Yao, K.; "Electrochemical Treatment of Oilfield Produced Wastewater on Ni-Sb-SnO2/Ti Electrodes", Journal of Advanced Oxidation Technologies, 16(2), 280-285.; (2013).
25. Santos, I. D., Dezotti, M., & Dutra, A. J.; "Electrochemical treatment of effluents from petroleum industry using a Ti/RuO2 anode", Chemical engineering journal, 226, 293-299.; (2013).
26. Fıl, B. A., Boncukcuoğlu, R., Yilmaz, A. E., & Bayar, S.; "Electro-oxidation of pistachio processing industry wastewater using graphite anode", *Clean–Soil, Air, Water*, *42*(9), 1232-1238.; (2014).
27. Scialdone, O., Randazzo, S., Galia, A., & Silvestri, G.; "Electrochemical oxidation of organics in water: role of operative parameters in the absence and in the presence of NaCl", Water research, 43(8), 2260-2272. ;(2009).
28. Britto-Costa, P. H., & Ruotolo, L. A. M. "Phenol removal from wastewaters by electrochemical oxidation using boron doped diamond (BDD) and Ti/Ti0. 7Ru0. 3O2 dsa® electrodes", Brazilian Journal of Chemical Engineering, 29, 763-773.; (2012).