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Treatment of petroleum refinery wastewater by electrochemical oxidation using graphite anodes

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ABSTRACT

An electrochemical oxidation method was performed in a batch electrochemical reactor using graphite anodes for treating an effluent obtained from Al-Diwaniyah petroleum refinery plant. The effective f process parameters like current density (4-20m Acm^{-2}), pH (3-9), and NaCl concentration (0-3 g/l) on the COD and phenol removal efficiency have been investigated. The results reveal that the best conditions were current density 12 mA cm^{-2}, pH 7, NaCl concentration 2 gl^{-1} at a treatment time of 60 minutes. Under best conditions of COD removal efficiency 100% and phenol removal efficiency 99.12% were obtained at current efficiency 33.5% and power consumption 59.9 kWh/kg COD. The anodic oxidation was proven to be efficient for treatment Al-Diwaniyah petroleum refinery effluent to get effluent with features in agreement with the standard limits for discharge to the environment at a lower cost.

1. Introduction

The petroleum refinery industry converts crude oil into its major fractions that can be additionally handled through a series of physical, thermal, and chemical conversion and separation steps into valuable petroleum products such as gasoline, kerosene, Liquefied Petroleum Gas (LPG), fuel oil, diesel fuels, waxes, and lubrication oils [1]. For the purpose of manufacturing the above mentioned products, huge quantities of water are used in refinery processes, especially for distillation, hydro-treating, thermal cracking and catalytic cracking, desalting and cooling systems. Petroleum refining process generates wastewater of about 1.6 times the volume of the processed crude oil. The characteristics of petroleum refinery effluents are usually influenced by the production mode, plant configuration and types of oil [2]. Generally, the petroleum refinery effluents contain high concentrations of inorganic and organic compounds, chemical additives (surfactants and inhibitors of corrosion), suspended solids, chloride, oil, and grease which added to effluent during the operations of producing petroleum products [3]. This petroleum refinery effluent is usually rich in Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) which are responsible for damaging plants, sea, river as well as to surface and groundwater sources [4]. The polluted wastewater generated by refineries contains COD levels of approximately 300–600 mg/L but not limited ; benzene levels of 1–100 mg/L; phenol levels of 20–200 mg/L, heavy metals levels of (0.2–10 mg/L Pb and 0.1–100 mg/L Cr); and other pollutants. . However, concentration of phenol can alter based on the nature of the process [5]. The concentration of Phenol in the range 5–25 mg L^{-1} considers as a toxic material for humans and aquatic life ,therefore the highest allowable limits of phenol in petroleum refinery effluents should be in the range of 0.5 - 1.0 mg L^{-1} [6] . A maximum acceptable limit of <0.0005 mg L^{-1} for phenol in potable drinking water was assigned by the European Union (EU), in its 80/778/EC directive [7]. Direct discharging of these effluents could result in many environmental pollution issues. Approximately 80-90 percent of the water used in the petroleum refinery plants is discharged as wastewater, therefore applying of wastewater treatment is not only to avoid environmental pollution issues but also to reuse of the water again hence another economic benefit for oil refineries [8]. Methods used for the treatment of petroleum refinery effluent involve coagulation [9], chemical oxidation [10], advanced oxidation processes

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Nomenclature

COD	Chemical oxidation demand ((mg L^{-1})	*F*	Faraday's constant (96487 C/mol)
TDS	Total dissolved solid ((mg L^{-1})	*V*	Effluent volume (L)
BOD	Biological oxygen demand (mg L^{-1})	ΔC	COD Difference values (g/L)
DSA	Dimensionally stable anode	*I*	Current (A)
Cond	Conductivity (µS/cm)	*t*	Electrolysis time (s)
C_i	Initial concentration (mg L^{-1})	*EC*	Electrical energy consumption (kWh/kg)
C_f	Final concentration (mg L^{-1})	U	Applied cell voltage (Volt)
RE	Removal efficiency (%)	COD_i	Initial chemical oxygen demand (mg L^{-1})
CE	Current efficiency (%)	COD_f	Final chemical oxygen demand (mg L^{-1})

[11], adsorption [12], biological approaches [13], membrane treatment [14], and electrochemical techniques [15, 16]. Generally, in most these methods, the approach is to transform of pollutants from one medium to another at low efficiency, besides, the choice of any method for treating the effluents of petroleum refinery depends on the composition of these effluents and the final purpose of effluents (discharge or reuse). Among them, electrochemical treatment methods have attracted attention due to the numerous advantages gained by these methods such as versatility, selectivity, and cost effectiveness [17]. Besides, electrochemical reactions are not depended on the properties of the wastewater and can use any value of current to be supplied to the electrochemical reactor [18]. One of the most important electrochemical methods is the anodic oxidation (also known as electrochemical incineration) which depends on generation of hydroxyl (strong oxidant) on the surface of an electroactive anode then these radicals attack the organic compounds existing in wastewaters and transform them to water and CO2 [19]. In contrast to chemical and advanced oxidation processes, like Fenton reaction which based on using iron ions and hydrogen peroxide as reagents in its chemical mechanism, as well as photo-Fenton process which used Fenton reagents with Ultra violet (UV) radiation to generate the hydroxyl radical, anodic oxidations do not need to use or stored of dangerous substances, in addition to easiness of scale-up. Other benefits involve low labour requirements since the processes are fairly simple and could be automatized. The method gives environmental advantages, as it uses electron as the main reagent [20]. During an anodic oxidation process, organic compounds can be incinerated by direct or indirect oxidation. In a direct process, the pollutants are first adsorbed on the surface of an anode and then undergo an oxidation reaction via transfer of electrons directly. In this case, the material of the electrode used for oxidation of organic compounds is the most important variables to be taken into account for obtaining high rates of electro-oxidation. The oxidation powers of many types of anodes like Boron-Doped Diamond (BDD), Dimensionally Stable Anode (DSA), lead dioxide (PbO2), and doped-SnO2 have been investigated for the direct oxidation of many organic substances such as phenol [21–24]. Among these electrodes, BDD is the best anodic material for degradation of organic compounds, because it has a wide potential window for discharging of water and its ability to generate weakly adsorbed hydroxyl radicals which giving rapid and efficient anodic oxidation [19]. Besides, BDD electrode has higher stability and chemical-resistant than other anodes which enables it to be used for a long time justifying its high cost. At the indirect processes, strong oxidants such as hypochlorite/chlorine, hydrogen peroxide, and ozone are generated by anodic oxidation then reacted with the organic compounds in the bulk solution [25, 26]. Chloride is particularly engaging for use in the indirect oxidation due to the presence of chloride salts in wastewaters [27]. Furthermore, previous works confirmed the role of active chlorine in the anodic oxidation of dyes and different organic substances [28]. Adding of chloride ions to the effluents was found by many researchers to be contributed in minimizing the energy consumption because of the enhancing in the current efficiency and oxidation kinetics as well as reducing of cell potential [29,30].

In the present work, indirect anodic oxidation process was used to remove Chemical Oxygen Demand (COD) and phenol from petroleum refinery wastewater resulted from Al-Diwaniyah petroleum refinery plant using a batch electrochemical reactor in which the effect of different parameters such as current density, pH, and NaCl concentration were investigated.

2- Experimental work

Petroleum refinery effluent samples were provided by Al-Diwaniyah petroleum refinery plant. Sample (20L) was collected from the feed tank to the biological treatment unit and stored in closed containers at temperature 4 ºC until use. Characterization of this sample is shown in table 1. Besides the properties of effluent taken from the settling tank of the final stage of the biological treatment that was measured by petroleum refinery plant administration with the permissible limit were mentioned in this table for comparison

Table 1. Characteristics of the effluents in Al-Diwaniyah petroleum refinery plant.

Test	feed tank sample	settling tank*	Permissible limit*
COD(mg/l)	160	65	100
pH	7.8	7.5	(6-9.5)
T.D.S	1710	1680	-----
Cl (mg/l)	931	119	100
SO_4(mg/l)	560	400	400
Turb.	5.17	6.44	41.3
Cond. (µS/cm)	3320	----	-----
Phenol(mg/l)	0.17	(0.01-0.05)	0.06

*provided by Al-Diwaniyah petroleum refinery plant administration

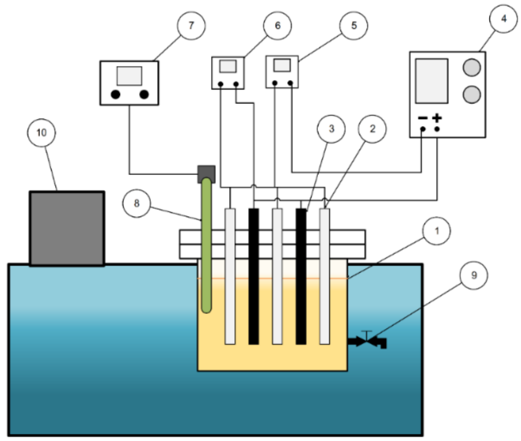

Figure 1. The electrochemical system: 1) cell body, 2) cathode (stainless steel), 3) Anode(graphite), 4)power supply, 5)Ammeter, 6)Voltmeter, 7)pH-meter, 8) pH-probe, 9) discharge valve, 10)water bath.

A rectangular perspex glass lab-scale batch electrochemical reactor was used for the anodic oxidation treatment experiments. It has inside dimensions (120 mm width x 120 mm length x 120 mm height) and active electrolyte volume of 1.25 L, provided with perspex cover of external dimensions (150 mm × 150 mm × 28 mm thickness). The cover contains slits for electrodes fixation and holes for inserting the probe of pH-meter and conductivity meter. A parallel plate configuration was adopted for the electrochemical reactor were three stainless steel plate cathodes (130 mm × 80 mm × 3 mm (thickness)) and two graphite anodes (130 mm × 80 mm × 3 mm (thickness)) were used. The distance between cathode and anode was fixed at15 mm. A digital direct current power supply (0–30 V, 0–5 A) Type (UNI-T, UTP3315PF) was used to provide constant current during each experiment. In each run, 1.25L solution was agitated using magnetic stirrer to achieve the proper mixing conditions then transfer to inside the cell. All the experiments were carried out at constant temperature 30 ºC using water bath (Memmert, type: WNB22, Germany). Fig.1 shows the schematic diagram of the electrochemical oxidation experimental setup supported by the required information. The electrolyte pH was measured using a digital pH meter (HNNA Instrument Inc.PH211, Romania) and the electrolyte acidity was adjusted by using HCl or NaOH for the appropriate experimental condition. Conductivity and TDS were measured by using (HM digital Inc. model COM-100, Korea). The samples were taken and analyzed to determine the COD and phenol concentration every 10 minutes of the electrolysis time.

The concentration of total organic compounds in the effluent is expressed in terms of Chemical Oxygen Demand (COD). Amount of COD in petroleum refinery effluents was measured by taken a sample (2ml) of effluent digested with an oxidizing agent ($K_2Cr_2O_7$) for 120 minutes at 150 °C in a COD thermos-reactor (RD125, Lovibond). The digested sample was cooled down to room temperature then analyzed in a spectrophotometer (MD200, Lovibond). Phenol was measured by using Method 8047 assigned by Hach Company/Hach Lange GmbH, USA [31]. Measuring of phenol concentration and COD were achieved three times and the average values were taken in this work.

The removal efficiency of COD and phenol were evaluated based on eq. (1), where C_i is the initial concentration (mg L^{-1}) and C_f is the final concentration (mg L^{-1}) [32]:

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

The current efficiency refers to the portion of the total current used for the specified reaction. It was calculated with the theoretical value that 1 molar electrons (96485 coulombs charge) would be transferred via oxidizing 8 g COD. Assuming all the COD removal was due to the electrochemical oxidation, then by counting the charges transferred and monitoring the COD removal in the solution, the Current Efficiency(CE%) could be estimated from equation [33]:

$$CE\% = \frac{F.V\,.\Delta C}{8I.t} \times 100 \qquad (2)$$

where F is Faraday's constant (96487 C/mol), V is the effluent volume in (L), ΔC is the difference in the COD values in (g/L), I is the current in (A), 8 is a dimensional factor for unit consistency, it is the oxygen equivalent mass {32 g of O_2 /4 mol of electrons} (g /mol), and t is the electrolysis time (s). The electrical energy consumption (EC) is the amount of energy consumed in the oxidation process for a kg of COD removed. EC in (kWh/kg) can be calculated by Eq. (3) [34]:

$$EC = \frac{U.I.t \times 1000}{(COD_i - COD_f)\,V} \qquad (3)$$

Where EC is the energy consumption (kWh/kg COD), U is the applied cell voltage (Volt),I is the current (A),t is the electrolysis time (h), COD_i and COD_f are the initial and final chemical oxygen demand (mg/l),and V is the effluent volume (L).

3. Results and discussion

3.1 Effect of current density

Figure 2 shows the abatement of COD with time at different current densities using effluent containing NaCl with a concentration of 2g/l and adjusted acidity initially at pH 7. It was clear that increasing current density leads to decrease the final COD value of the effluent. It was observed that the efficiency of degradation is higher at the initial stage of anodic oxidation; however, it then proceeded gradually as anodic oxidation continues. This behavior can be interpreted as the concentration of organic pollutants is high at the initial period of electrolysis so the electrochemical reaction is under current-limited control where nearly most the applied current is used to oxidize the organic compounds by the generated OCl^-. However, the concentration of organic pollutants is reduced gradually during the electrolysis leading to make the oxidation process under mass transport control, hence a slight increase in degradation efficiency is occurred due to the taken place of side reactions, such as oxygen evolution [35] .Table 2 shows the removal efficiency of COD at different current densities where complete removal of COD was obtained at current density equal or higher than $12mAcm^{-2}$ at electrolysis time of 60 min. The effect of current density on phenol removal efficiency is also reported in Table 2 where increasing current density results in increasing the removal efficiency of phenol. It is interesting to note that final phenol concentration is 0.0015 at current density of $12mAcm^{-2}$ which is lower than the permitted level and became lowest at higher current densities. An increase in current density would increase electricity consumption. Using current density higher than $12mAcm^{-2}$ resulted in increasing power consumption higher than (60Kwh/Kg COD) ,therefore it is the best to choose this current density for further investigation. Similar observations were found in previous studies [19, 34, 36, 37].

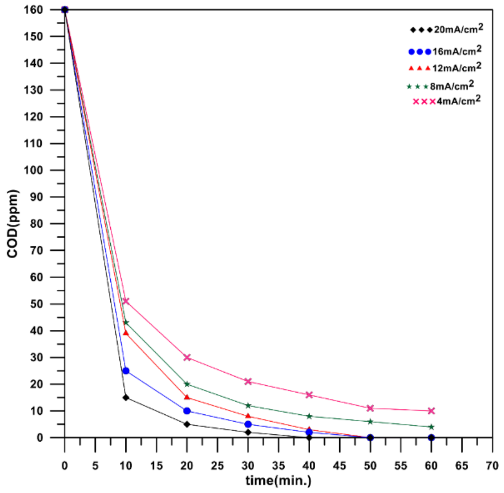

Figure 2. COD abatement with time at different current density. pH=7, [NaCl] = 2g/l, Temp. = 30◦C.

Figure 3 illustrates how the pH is affected by current density through the operation where pH decreased for the first 30 min then started to increase for further electrolysis time. Similar trend was observed by Souza and

Ruotolo [19] in the electrochemical treatment of an oil refinery effluent using boron-doped diamond anodes, where the pH started to decrease initially from a pH value of 9.5 then increased after (2 hrs.) of electrolysis time suggesting the responsibility of the intermediate compounds that generated during the electrolysis for the change in pH .

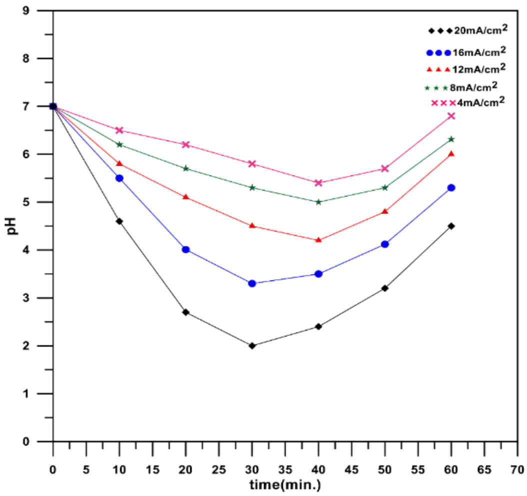

Figure 3 pH profile with time at different current density

3.2 Effect of NaCl concentration

Figure 4 displays the abatement of COD with time at different NaCl concentration using effluent with acidity adjusted initially to pH 7. It was clear that increasing NaCl concentration leads to a decrease in the final COD value of the effluent. Table 3 reveals this behavior where the effect of NaCl concentration on the removal efficiency of COD and phenol are reported. It can be seen that increasing of sodium chloride concentration from 0 to 3 g/L results in increasing of COD removal efficiency from 91.88 to 96.88% at abatement time of 30min, while a complete COD removal was obtained with and without addition of NaCl at various concentrations at abatement time of 60min. This is interesting results which confirm that chlorine ions which originally existing in the solution have the ability to degrade the pollutants even at low concentration. However, the final concertation of phenol is higher than 0.0015 at NaCl concentration lower than 2gl^{-1}. It is preferred to conduct further experiments at NaCl concentration of 2 g/L in which a complete removal of COD at the required level of phenol concentration discharge was achieved. Besides a negligible decrease in the energy consumption was observed at NaCl concentration higher than 2gl^{-1} also using higher concentration of NaCl may favor producing chlorinated organic compounds not destroyed by the anodic oxidation as proved by previous studies [38]. Similar trends were observed by Britto-Costa and Ruotolo [38] in the electrooxidation of phenol using BDD or DSA electrodes where COD removal increases with addition of NaCl. Souza and Ruotolo [19] studied the electrochemical oxidation of oil refinery effluent using boron-doped diamond anodes. They found that addition of 450 mg/l of NaCl gives higher removal of COD in comparison with no addition of NaCl. Ibrahim et al [34] investigated the electrochemical oxidation treatment of petroleum refinery effluent and found that increasing NaCl concentration gives higher abatement of COD using titanium anode. Figure 5 shows how the pH affected by NaCl concentration through the operation where pH is decreased for the first 30 min then started to increase for further electrolysis time. Santos et al. [37] found a similar trend in the treatment of an effluent from petroleum industry using Ti/RuO$_2$ anode where the pH decreases for time period shorter than 30min then start to increase after (30 min.) interpreting their results by the formation of low molecular weight of acid compounds like oxalic acid during the first period (30min.) then hypochlorite become the predominating species after that period.

Table 2. Effect of current density on COD and phenol removal efficiency

Current density mA/cm^2	Phenol conc. (mg/l) C_i	C_f	Phenol RE% at 60 min	COD Removal (%) at 30 min	at 60 min	CE (%)	EC (kWh/kg)
4	0.17	0.003	98.23	86.88	93.75	78.52	16.89
8	0.17	0.0016	99.05	92.50	97.50	40.20	41.15
12	0.17	0.0015	99.12	95.00	100	33.50	59.90
16	0.17	0.0005	99.70	96.88	100	25.13	87.14
20	0.17	0.0005	99.70	98.75	100	25.13	103.48

Table 3. Effect of NaCl concentration on COD and phenol removal efficiency

NaCl Conc. (g/l)	Initial Cond. µs/cm	Phenol conc.(mg/l) C_i	C_f	Phenol RE% at 60 min	COD Removal (%) at 30 min	at 60 min	CE (%)	EC (kWh/kg)
0	3320	0.17	0.002	98.82	91.88	100	26.8	93.33
1	4900	0.17	0.002	98.82	93.75	100	33.5	62.48
2	6510	0.17	0.0015	99.12	95.00	100	33.5	59.9
3	7900	0.17	0.0003	99.82	96.88	100	33.5	57

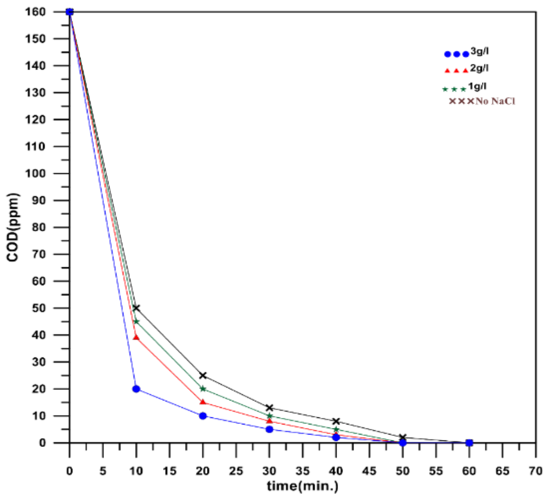

Figure 4. COD abatement with time at different NaCl concentrations. I=12mAcm^{-2}, pH=7, Temp. = 30◦C.

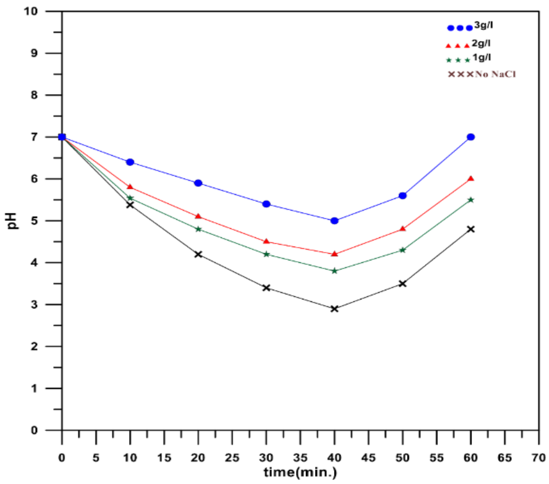

Figure 5 pH profile with time at different NaCl concentrations

3.3 Effect of pH

Figure 6 displays the abatement of COD with time at different pH using effluent containing NaCl at concentration of 2g/l. It was clear that decreasing pH leads to decrease the final COD value of the effluent. The effect of pH on the removal efficiency of COD and phenol was studied and shown in Table 4. It was observed that the initial pH has a substantial impact on the COD and phenol removal efficiency. The maximum removal efficiency of COD and phenol was occurred at pH equal or lower than 7. Similar observations were made by Fil *et al* [39] who studied the treatment of oistachio processing industry wastewater by anodic oxidation using graphite anode in the presence of NaCl where higher COD removal was observed at acidic solutions. Ibrahim *et al* [34] in their study found that neutral conditions give better results than alkaline medium with respect to COD removal. This behavior can be interpreted as the anodic oxidation generally gives better results in acidic or neutral conditions than the basic conditions when chlorine ions existing in the electrolytic process where formation hypochlorous which is a more powerful oxidant than hypochlorite has happened. Previous studies approved that at alkaline conditions the active chlorine exists in the form of hypochlorite which is a less strong oxidant towards organic species in regarding to hypochlorous acid that is the main species present at pH approached to 3 [39,40]. On the other hand, the final concentration of phenol is higher than 0.0015 as pH increased and became more alkaline.

The pH profile with time at different initial pH is illustrated in Figure 7 where the pH is decreased for the first 30 min then started to increase for further electrolysis time. Similar observations were found by previous works [19, 37]. Using an initial pH of 7 is recommended for the environment conditions since starting with pH=3 results in discharging effluent with pH lower than 6 as shown in Figure 7.

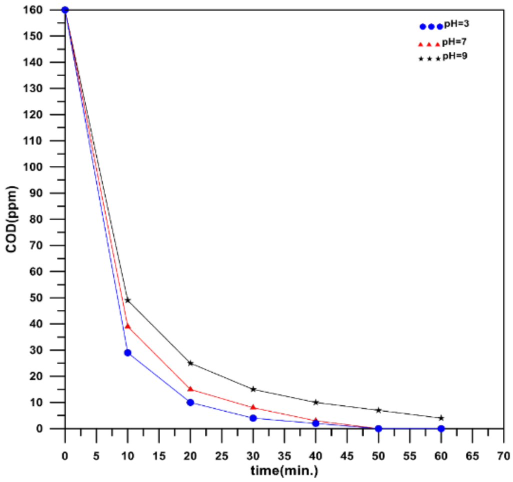

Figure 6. COD abatement with time at different pH. I=12mAcm^{-2}, [NaCl] = 2g/l, Temp. = 30◦C.

Table 4. Effect of pH on COD and phenol removal efficiency

pH	Phenol conc. (mg/l)		Phenol RE%	COD Removal (%)		CE (%)	EC (kWh/kg)
	C_i	C_f	at 60 min	at 30 min	At 60 min		
9	0.17	0.0025	98.53	90.63	97.5	27.22	72.03
7	0.17	0.0015	99.12	95	100	33.5	59.9
3	0.17	0.0013	99.23	97.5	100	33.5	56.61

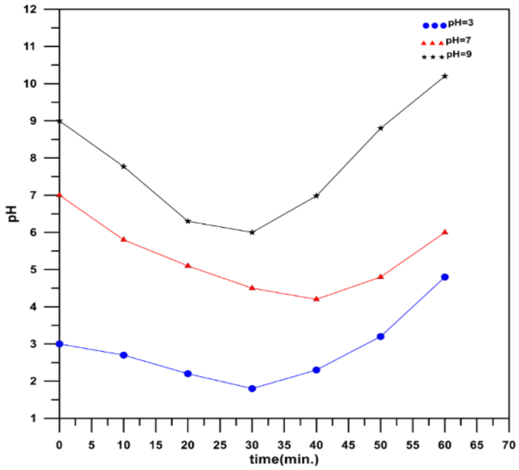

Figure 7 pH profile with time at different initial pH

4. Conclusions

Anodic oxidation using graphite anodes seems to be more efficient method for treatment of wastewater produced from Al-Diwaniyah petroleum refinery plant as confirmed by the present work. Increase in the current density, NaCl concentration resulted in an increase of COD and phenol removal efficiencies, while increasing the initial pH higher than 7 resulted in decreasing of COD and phenol removal efficiencies. Based on the results of this work, current density has a significant effect on the COD and phenol removal than the other variables.

By adjusting initial pH to a value of 7 , adding NaCl at concentration of 2g/l and applying current density of 12 mA cm^{-2} for an interval of time equal to 60 min, a complete removal of COD(100%) with phenol removal efficiency of 99.12% were achieved in which values of current efficiency(33.5%) and energy consumption(59.9kWh/kg) were observed. The energy consumption in the present work is relatively lower than that reported in previous works in the field of petroleum refinery effluent treatment using other anodes [19, 34, 37].

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REFERENCES

[1] Y. Yavuz, A.S. Koparal, U.B. Ogutveren, Treatment of petroleum refinery wastewater by electrochemical methods, Desalination, 258 (2010) 201–205.
[2] A. Coelho, A. V. Castro, M. Dezotti, G. L.Sant'Anna, Treatment of petroleum refinery sourwater by advanced oxidation processes. *Journal of hazardous materials137* (1)*(*2006) 178- 184.
[3] A.M.Z. Ramalho, C.A. Martínez-Huitle, D.R. Silva, Application of electrochemical technology for removing petroleum hydrocarbons from produced water using a DSA-type anode at different flow rates, Fuel, 89 (2010) 531–534.
[4] Q.J. Rasheed, K. Pandian, K. Muthukumar , Treatment of petroleum refinery wastewater by ultrasound-dispersed nanoscale zero-valent iron particles. Ultrason Sonochem, 18(2011) 1138–1142.
[5] WBG (World Bank Group), Pollution Prevention and Abatement Handbook: Toward Cleaner Production, Washington, D.C., USA, 1999.
[6] Y. Han, X. Quan, S. Chen, H. Zhao, C. Cui, and Y. Zhao, Electrochemically enhanced adsorption of phenol on activated carbon fibers in basic aqueous solution, Journal of Colloid and Interface Science, 299(2)(2006)766–771.
[7] H. Jiang, Y. Fang, Y. Fu, and Q. X. Guo, Studies on the extraction of phenol in wastewater, Journal of Hazardous Materials, 101 (2) (2003)179–190.
[8] L.N. Mota, Development of a photochemistry reactor applicable in the treatment of phenolic wastewater present in the petroleum industry, Master's Thesis, Rio Grande do Norte Federal University, Brazil, 2005,ftp://ftp.ufrn.br/pub/biblioteca/ ext/bdtd/AndreLNM (in Portuguese).
[9] M.H. El-Naas, S. Al-Zuhair, A. Al-Lobaney and S. Makhlouf. Assessment of Electrocoagulation for the Treatment of Petroleum Refinery Wastewater. Journal of environmental management, 91 (2009) 180.
[10] O. Abdelwahab, N. Amin and E.Z. El-Ashtoukhy.Electrochemical removal of phenol from oil refinery wastewater, J. Hazard. Mater. , 163 (2009) 711.
[11] A. Coelho, A. V. Castro, M´arcia Dezotti, and G.L. Sant'Anna, Treatment of petroleum refinery sourwater by advanced oxidation processes‖, Journal of Hazardous Materials, B137 (2006)178–184.
[12] M.H. El-Naas, S. Al-Zuhair and M.A. Alhaija, J. Hazard. Mater.Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon.173 (2010) 750
[13] F. Ma, J.-b. Guo, L.-j. Zhao, C.-c. Chang and D. Cui. Application of bioaugmentation to improve the activated sludge system into the contact oxidation system treating petrochemical wastewater.Bioresource technology, 100 (2009) 597.
[14] Y.S. Li, L. Yan, C.B. Xiang and L.J. Hon. Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes. Desalination, 196 (2006) 76.
[15] Y. Yavuz and A.S. Koparal, J. Hazard. Mater. Electrochemical oxidation of phenol in a parallel plate reactor using ruthenium mixed metal oxide electrode ,136 (2006) 296.
[16] Y. Yavuz, A.S. Koparal and Ü.B. Öğütveren, Treatment of Petroleum Refinery Wastewater by Electrochemical methods. J. Environ. Eng. 134 (2008) 24.
[17] Y. Zheng, A. Wang, H. Lin, L. Fu and W. Cai. A sensitive electrochemical sensor for direct phoxim detection based on an electrodeposited reduced graphene oxide–gold nanocomposite. RSC Advances, 5 (2015) 15425.
[18] O. Abdelwahab, N.K. Amin, E-S.Z. El-Ashtoukhy, Electrochemical removal of phenol from oil refinery wastewater, Journal of Hazardous Materials, 163 (2009) 711–716.
[19] R.B.A. Souza, L.A.M. Ruotolo, Electrochemical treatment of oil refinery effluent using boron-doped diamond anodes, Journal of Environmental Chemical Engineering 1 (2013) 544–551.
[20] A. Anglada, A. Urtiaga, I. Ortiz, Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications, J. Chem. Technol. Biotechnol. 84 (2009) 1747–1755.
[21] J. Sun, H. Lu, H. Lin, L. Du, W. Huang, H. Li, Electrochemical oxidation of aqueous phenol at low concentration using Ti/BDD electrode, Sep. Purif. Technol. 88 (2012)116–120.
[22] E. Weiss, K. Groenen-Serrano, A. Savall, A comparison of electrochemical degradation of phenol on boron doped diamond and lead dioxide anodes, J. Appl. Electrochem. 38 (2008) 329–337.
[23] L.S. Andrade, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, J. Iniesta, V. Garcı´a-Garcia, V.Montiel, Degradation of phenol using Co- and Co,F-doped PbO2 anodes in electrochemical filter-press cells, J. Hazard. Mater. 153 (2008) 252–260.
[24] C. Borras, C. Berzoy, J. Mostany, J.C. Herrera, B.R. Scharifker, A comparison of the electrooxidation kinetics of p-methoxyphenol and p-nitrophenol on Sb-doped SnO2surfaces: concentration and temperature effects, Appl. Catal. B 72 (2007) 98–104.
[25] D. Rajkumar, J.G. Kim, Oxidation of various reactive dyes with in situ electro generated active chlorine for textile dyeing industry wastewater treatment, J. Hazard. Mater. 136 (2006) 203–212.
[26] A. H. Abbar, R. H. Salman, and A. S. Abbas, 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) (2016)E333-E340
[27] S. Palmas, A.M. Polcaro, A. Vacca, M. Mascia, F. Ferrara, Influence of the operating conditions on the electrochemical disinfection process of natural waters at BDD electrodes, J. Appl. Electrochem. , 37 (2007) 1357–1365.
[28] M. Panizza, G. Cerisola, Electrocatalytic materials for the electrochemical oxidation of synthetic dyes, Appl. Catal. , B 75 (2007) 95–101.
[29] I.D. Santos, J.C. Afonso, A.J.B. Dutra, Behavior of a Ti/RuO2 anode in concentrated chloride medium for phenol and their chlorinated intermediates electrooxidation, Sep. Purif. Technol., 76 (2010) 151–157.
[30] J.M. Aquino, M.A. Rodrigo, R.C. Rocha-Filho, C. Sa´ ez, P. Can˜izares, Influence of the supporting electrolyte on the electrolysis of dyes with conductive-diamond anodes, Chem. Eng. J., 184 (2012) 221–227.
[31] Hach Company ,Phenols test , Method 8047, https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=2ahUKEwj-15rdu8DjAhW-QEEAHfGbBL0QFjAAegQIBRAC&url=https%3A%2F%2Fwww.hach.com%2Fasset-get.download-

en.jsa%3Fcode%3D55864&usg=AOvVaw1_zRXcmsLJbp_0Wlv5B5PB

[32] O. Abdelwahab, N. K. Amin, and E. S. Z. El-Ashtoukhy, “Electrochemical removal of phenol from oil refinery wastewater,” Journal of Hazardous Materials, 163(2-3) (2009) 711–716.

[33] Y.H. Wang, K.Y. Chan, S.A. Cheng, X.Y. Li, Electrolytic Generation of Ozone on Antimony- and Nickel-Doped Tin Oxide Electrode. J Electrochem Soc., 152(2005) D197-D200.

[34] D. S. Ibrahim, P. S. Devi, N. Balasubramanian, Electrochemical Oxidation Treatment of Petroleum Refinery Effluent, International Journal of Scientific & Engineering Research, 4(8) August 2013.

[35] M Panizza, P. A. Michaud, G. Cerisola, C. Comninellis, Anodic oxidation of 2-naphthol at boron-doped diamond electrodes. Journal of Electroanalytical Chemistry, 507(1, 2) (2001) 206–214.

[36] Y. H. Wang and J.Y. Kuang, Electrochemical Treatment of Oilfield Produced Wastewater on Ni-Sb-SnO2/Ti Electrodes, J. Adv. Oxid. Technol. , 16(2) (2013).

[37] I. D. Santos. M. Dezotti, A. J.B. Dutra, Electrochemical treatment of effluents from petroleum industry using a Ti/RuO2 anode, Chemical Engineering Journal, 226 (2013) 293–299.

[38] P.H. Britto-Costa and L.A.M. Ruotolo, Phenol removal from wastewaters by electrochemicaloxidation using boron doped diamond (BDD) and Ti/Ti0.7Ru0.3O2 DS Aelectrodes, Braz. J. Chem. Eng. , 29 (2012) 763–773

[39] B. A. Fıl ,R. Boncukcuoğlu, A. E. Yilmaz, S. Bayar, Electro-Oxidation of Pistachio Processing Industry Wastewater Using Graphite Anode. Clean – Soil, Air, Water, (2014) 1232–1238.

[40] O. Scialdone, S. Randazzo, A. Galia, G. Silvestri, Electrochemical oxidation of organics in water: Role of operative parameters in the absence and in the presence of NaCl, Water Res. , 43 (2009) 2260–2272.