Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

A novel Tubular Electrochemical Reactor with a Spiral Design of Anode for Treatment of Petroleum Refinery Wastewater

Ghazi Faisal Naser, [a]* Thamer J. Mohammed,[b] , Ali H. Abbar,[c]
[a] *Chemical Engineering Department - College of Engineering– Al Muthanna University –Iraq*
[b]*Chemical Engineering Department, Faculty of Engineering, University of Technology, Iraq*
[c]*Department of Biochemical Engineering, Al-Khwarizmi College of Engineering, University of Baghdad, Baghdad, Iraq*

Abstract

The use of a tubular electrochemical reactor (TER) with a novel design for batch recycle electrochemical treatment of petroleum refinery effluent was investigated. The reactor is composed from a cylindrical stainless steel cathode and a spiral porous graphite anode at its center. The impact of process factors like: NaCl addition ,current density, flow rate, and pH on the chemical oxygen demand elimination efficiency was studied using response surface methodology based on (BBD). For estimating the interaction between the response (RE %) and its independent factors, a quadratic model equation was developed. The quadratic model's accuracy was supported by its significant R^2 value (92.61 %). The optimization study illustrated that NaCl addition was the most effective factor on RE% followed by current density confirming that the oxidation process is governed by indirect electrochemical oxidation rout. Results also showed that the flow rate plays an important influence in maximizing the RE% with a new correlation. The optimal working conditions were a current density (26 mA/cm^2), pH (10), NaCl addition (1.899 g/l) and flow rate (4L/min.), resulting in a (COD)elimination efficiency of 85.12% with specific energy exhaustion of 116.17kWh/kg COD.

Keywords: COD removal, Electrooxidation, Tubular Electrochemical Reactor, Spiral anode, Petroleum refinery wastewater.

1. Introduction

Wastewaters generated by petroleum refineries considers as a major reference of the contamination of environment due to their high COD and salinity. As a result of the numerous toxic organic compounds present in these effluents, they must be treated carefully before being discharged into receiving areas **[1]**. Refineries often produce hazardous wastewater with minimum (COD, phenol, benzene , heavy metals)levels of (300,20,1,0.1) mg/L respectively and maximum levels of the same elements of (600,200,100,100) mg/L respectively **[2]**. Physicochemical procedures such as separation of (oil–water), coagulation and biological processing, are used to treat refineries effluents **[3]**. Recently, electrochemical treatment methods of wastewaters from petroleum refineries consider as attractive and environmentally friendly processes that can be performed in industrial areas under ambient temperature and pressure. Besides these methods offer many typical benefits such as versatility, environmental compatibility and energy efficiency **[4]**. In compare to traditional techniques, electrochemical oxidation, one of the electrochemical treatment methods, has received greater attention in recent years as an efficient treating wastewater technique. All reactions of electrochemical technique that occur during electrochemical oxidation are complicated and difficult to recognize, in addition the electrochemical removal methods of organic

*Corresponding author e-mail: ghazi_faisal@mu.edu.iq.; (Ghazi Faisal Naser).
Receive Date: 04 March 2022, Revise Date: 24 March 2022, Accept Date: 24 April 2022.
DOI: 10.21608/ejchem.2022.125257.5574

contaminants are complex in nature due to their reactions interactions **[5]**. To recover organic pollutants from wastewater, direct and indirect electrochemical techniques are commonly utilized. In indirect electrochemical oxidation, the addition of NaCl allows for an excess of chlorine gas to be discharged, resulting in irreversible hydrolysis and ionization processes. Consequently, $Cl2$ gas is released on the anode (reaction -1-) and rapidly reacts with the solution at the anode, followed by hydrolysis (reaction -2-) and ionization (reaction -3-), resulting in HOCl, a strong oxidant capable of oxidizing organic contaminants in wastewater **[6]**.

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (3)$$

In the electrochemical treatment of wastewaters, multiple configurations of electrochemical reactors were used. Stack cells, parallel plate reactors, flow cells with mesh anodes, rotational disc reactors, tubular electrochemical reactors (TERs), and three-dimensional electrodes are among them **[7]**. In an electrochemical process, designing and selecting an appropriate electrochemical reactor is important, as the reactor shape affects mass transfer inside the reactor, as well as the reactor's efficiency and process yield **[8, 9]**.

The tubular electrochemical reactor (TER) has been utilized by multiple researchers to treat many forms of organic wastewater using electrochemical-oxidation techniques, such as [Cr(VI)] from wastewater. **[10, 11]**, petroleum refinery waste-water **[12,13]**, textile wastewater [14], phenol removal from wastewater **[15,16]**, also pharmaceutical effluents**[17]**, in addition paint wastewater **[18]**. Most of these tubular electrochemical reactors consist of concentric cylindrical cathode and anode except Martínez-Delgadillo et al., **[10]** who used a tubular electrochemical reactor consisted of a cathode represented by central polished carbon steel rod and anode represented by spiral wire of the same material served for removing Cr(VI) from wastewaters. They concluded that for low intake velocities, reactor dispersion is strongly dependence influenced by inlet position and using spiral wire anode gives better reduction in the dispersion leading to lower residence time within the reactor. In further research the same authors used the same reactor and found that the best performance comes from an electrochemical reactor with a tangential intake. in comparison with central and lateral inlets **[11]**.

In this work, for the first time a new design of TER based on using a central spiral rode anode surrounded by hallow cylindrical cathode was utilized for treatment of petroleum refinery wastewater. Beside the material of electrodes was made from porous graphite that have high surface area in comparison with solid graphite material **[19]**.

Scare literatures on using TER for treatment effluents from petroleum refinery plants for example Skban Ibrahim et al.**[12]** investigated an electro-oxidation method to eliminate total petroleum hydrocarbon (TPH) of petroleum refinery effluents in addition ,elimination of chemical oxygen demand (COD) using a tubular electrochemical reactor with batch recycle mode of operation. They employed a tubular electrochemical reactor with a (stainless-steel) cathode and a (ruthenium oxide coated titanium) anode with 60% perforation. This sort of electrochemical reactor was able to reduce COD by about 85% while also completely removing all petroleum hydrocarbons. It is worthy to investigate the new proposed design of TER for removal of COD from locally wastewater produced from Al-Muthanna petroleum refinery _Iraq.

The purpose of this research is to analyses the activity of a novel tubular electrochemical reactor with a spiral design of anode in removal of COD from waste water. The influences of various operating parameters like NaCl addition , flow rate, pH, and current density were discussed using response surface methodology (RSM).

2. Experimental

2.1. Material and Apparatus

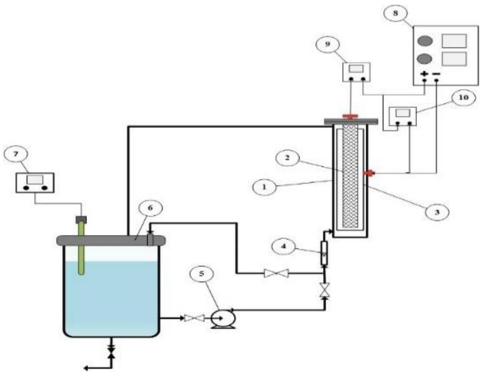
A quantity of 120 liters of wastewater have been collected from Al-Muthanna petroleum refinery discharge point then kept at temperature of (4 ºC) until use. **Table 1** displays the properties of the wastewater collected from Al-Muthanna petroleum refinery. The conductivity of raw water is 4.25 m.s./cm which is within the acceptable interval for generating low cell potential **[20]** hence no further addition of supporting electrolyte like Na_2SO_4 is required. The electrochemical system is shown schematically in **figure (1 - a)**. It consists of a tubular electro-chemical cell, 5liters capacity Perspex reservoirs for the wastewater, a recirculation pumps(GRANDFAR :

X15GR-10), a flow meter with a flow range from 0.5 to 7 L/min, for controlling the electrolyte flow rate. This arrangement enables the recirculation of wastewater through the electrochemical reactor in a batch recycle mode.

Table 1: Wastewater properties of Al-Muthanna petroleum refinery.

Parameter	value
COD (mg/l)	504
pH	7.2
TDS (mg/l)	3580
Cl^- (mg/l)	1560
$SO4^{-2}$ (mg/l)	445
Turbidity NTU	110
Conductivity (mS/cm)	4.25

The tubular electrochemical reactor as shown in **figure (1 – b)** was composed of cell body and cover both of them made from Teflon. The cell body has inside diameter of 100 mm and outside diameter of 110 mm with a length of 140 mm. It was closed from the bottom and provided with inlet portion having a diameter of 10mm which located on the lateral side of the body near the bottom. At the upper, the body cell was joined with a flange having inside diameter of 100 mm and outside diameter of 150mm with a thickness of 10mm provided with four holes 5mm for fixing the body with the cover. An outlet portion having a diameter of 10mm was located on the lateral side below the flange of the cell body. The cover has outside diameter of150 mm and thickness of 10 mm provided with a hole for joining anode and four holes 5mm for fixing cover with cell body via four bolts and nuts. A system based on concentric electrodes arrangement was constructed in the present work. The cathode was a tubular 316 stainless steel with dimensions of 99 mm outer diameter, 100 mm length, and 3 mm thickness. It was fixed inside the cell body via bolt and nut located at the center of its length. A spiral porous graphite rode was used as a new design of anode. It was purchased from Tokai Carbon Co., Ltd. with a porosity of 20-26% and BET surface area of 22.751 m²/g **[21]**. It has outside diameter of 60 mm and a length of 125mm. it was drilled along its length in spiral fashion with cavity of 5mm length and 5mm width. This design makes the electrolyte to flow along the lateral surface of the anode in a spiral movement.



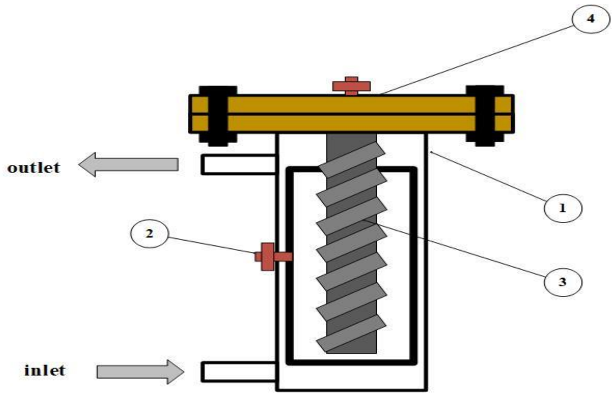
(a)

(b)

Figure 1: (a) The electrochemical system's diagram.(1) cell body, (2) anode,(3) cathode , (4)flow meter, (5) pump,(6)reservoir,(7) pH-meter,(8)power supply,(9) Ammeter,(10) voltmeter **(b)** The photographic electrochemical cell's diagram

The distance between both (anode and cathode) was fixed at 15 mm throughout the experiment. The schematic illustration of a tubular electrochemical reactor is shown in **Figure (2)**. During each run, a digital power supply with range (0–30 Volt), (0 – 5 Amp.) Type (UNI - T, UTP1305) was utilized to supply constant current. To obtain the required combining conditions, a 3 L solution was mixed with a magnetic stirrer at rotation value (500 rpm) for each experiment, then the required amount of NaCl (if needed) was added followed by pH adjustment using either 1M HCl or 1M NaOH with continuing the mixing at the same rotation speed then finally putting the solution in the reservoir and circulating it at constant flow rate. The adjusting of pH was performed by using a digital pH meter (HM Digital Inc.PH-200). All of the tests were conducted at a fixed temperature of 25 ±2 ºC.

(a)



(b)

Figure 2 : (a) A spiral porous graphite rode was used as anode **(b)**The electrochemical cell's diagram, (1) cell body, (2) cathode, (3) anode, (4) cell cover

Based on eq.4, the removal efficiency of COD was evaluated **[21]:**

$$RE\ \% = (COD_i - COD_f)\ /\ COD_i \qquad (4)$$

COD_i indicates the initial COD (mg /l) , COD_f indicates the final COD (mg /l) and R E % denotes for the removal efficiency of COD.

The energy consumption for a kilogram of COD that needs to be digested acts the amount of energy consumed in the process. Eq. 5 can be used to evaluate SEC in (kWh/kgCOD) **[21]**:

$$SEC= (E.I.t * 1000)\ /\ (COD_i - COD_f)\ V \qquad (5)$$

Where SEC refers to the specific energy consumption (kWh/kgCOD), E: acts voltage of cell (Volt), t: acts the time (hr.), I: acts the current (Amp.), V: acts the effluent volume (L), and COD_f and COD_i acts the final and initial chemical oxygen demand (mg/l) respectively.

2.2. Design of experiments

The response surface methodology (RSM) is a combination of mathematical approaches for optimizing the operational conditions of the response that is influenced by various operating variables of the process. In this work, three levels and four factors Box–Behnken design as one of the best design used in RSM was assumed as an experimental design to satisfy and examine the process variables that affected on the COD removal. Four process parameters involving ((X1)current density), ((X2)pH), ((X3)NaCl addition), and ((X4) flow rate) were considered as experiment factors in the BBD while RE% was possessed as a response. The process factors scales were coded as (-1) for low level, (0) for middle point and (1) for high level **[22]**. **Table 2** shows the process elements with their levels. The selection of levels of these variables was based on previous studies **[13, 20, 21].**For obtaining the appropriate quadratic model with the acceptable statistical conditions, Box–Behnken offers the designs that required though using a set of the selected runs for a three-level factorial. The following equation can be used to estimate the number of runs (N) required to complete a Box–Behnken design. **[22]**:

$$N=2k(k - 1)+cp \qquad (6)$$

where k: denotes the number of variables and cp: denotes the central point's repeated number. Based on eq. 6, (27) runs were achieved for estimating the influence of the process factors on the RE%. **Table3** shows the BBD that has been suggested for this study. Depending on BBD, a 2^{nd}. order polynomial model can be used, with the following equation describing how the interaction terms fit with the experimental results. **[22]**:

$$Y= a_o+\sum a_i x_i+\sum a_{ii}\, x_i^2+\sum a_{ij}\, x_i\, x_j \qquad (7)$$

Which Y acts the response (RE), (i) and (j) denotes the index numbers for patterns, a_o: intercept term, x_1 , x_2 … x_k are the process factors. a_i : the 1st.order main effect, a_{ii} : the 2nd. order main effect and a_{ij} acts the influence of interaction. The regression coefficient (R_2) was evaluated after the inferential analysis to ensure that the model fit was appropriate.

Table 2: Refinery wastewater treatment process variables and their values

Process variables	range		
Codes :	Low(−1)	Middle(0)	High (+1)
(X1): Current density (mA/cm^2)	4	15	26
(X2): pH	3	6.5	10
(X3): NaCl (g/l)	0	1	2
(X4): flow rate (L/min.)	1	2.5	4

Table 3: Experimental design by Box-Behnken

Run	Blocks	Codes				Real values			
		x_1	x_2	x_3	x_4	Current density (mA/cm^2)X1	pH X2	NaCl addition (g/l) X3	flow rate (l/min) X4
1	1	-1	-1	0	0	4	3	1	2.5
2	1	1	-1	0	0	26	3	1	2.5
3	1	-1	1	0	0	4	10	1	2.5
4	1	1	1	0	0	26	10	1	2.5
5	1	0	0	-1	-1	15	6.5	0	1
6	1	0	0	1	-1	15	6.5	2	1
7	1	0	0	-1	1	15	6.5	0	4
8	1	0	0	1	1	15	6.5	2	4
9	1	-1	0	0	-1	4	6.5	1	1
10	1	1	0	0	-1	26	6.5	1	1
11	1	-1	0	0	1	4	6.5	1	4
12	1	1	0	0	1	26	6.5	1	4
13	1	0	-1	-1	0	15	3	0	2.5
14	1	0	1	-1	0	15	10	0	2.5
15	1	0	-1	1	0	15	3	2	2.5
16	1	0	1	1	0	15	10	2	2.5
17	1	-1	0	-1	0	4	6.5	0	2.5
18	1	1	0	-1	0	26	6.5	0	2.5
19	1	-1	0	1	0	4	6.5	2	2.5
20	1	1	0	1	0	26	6.5	2	2.5
21	1	0	-1	0	-1	15	3	1	1
22	1	0	1	0	-1	15	10	1	1
23	1	0	-1	0	1	15	3	1	4
24	1	0	1	0	1	15	10	1	4
25	1	0	0	0	0	15	6.5	1	2.5
26	1	0	0	0	0	15	6.5	1	2.5
27	1	0	0	0	0	15	6.5	1	2.5

3. Results and Discussion

3.1. Statistical analysis

As a first step the time of electrolysis for achieving all the experiments of BBD was determined by performing an experiment based on the following conditions: current density= 26mA/cm^2, pH=6.5, NaCl addition=1 g/l, Flow rate= 4l/min. The results are illustrated in **Table 4**.the selection of these values are based on previous studies in this topic. It was observed that electrolysis time of 180 is sufficient to adopted in the experimental design because it gives a RE%= 74.2% high than 70%. Using electrolysis time higher than this value may results in obtaining approximated values of RE% in all runs of the experimental design which in turn could be effected on the evaluating the interaction effect of each parameters.

Table 4: COD variation with time

COD(ppm)	Time (min.)
520	0
440	30
392	60
325	90
250	120
173	150
134	180
110	210
100	240

Twenty seven runs were carried out at various sets to study the common influences of the process parameters on a removal efficiency. **Table 5** shows the practical results of removal percentage that gained at 180 min as well as the predicted values based on the model equation. Specific energy consumption (SEC) is also outlined in the table. It was observed that RE% is in the range of 25-76%. The specific energy consumption is in the range of 7.51-231.82Kwh/kg COD. The difference among the centered points in the design is less than 2% confirming good reproducibility of results. By using Minitab-17 Software, Based on the analyzing the results of RE%, As indicated in Eq.8 below, a quadratic model in species of real values of system factors was developed, which connects RE% with process factors:

$$RE\% = 3.4 + 1.614\, X_1 + 5.39\, X_2 + 20.68\, X_3 - 8.81\, X_4 - 0.0237\,(X_1)^2 - 0.308\,(X_2)^2 - 5.64\,(X_3)^2 + 1.955\,(X_4)^2 - 0.0403\, X_1X_2 - 0.257\, X_1{*}X_3 + 0.147\, X_1{*}X_4 + 0.636\, X_2{*}X_3 + 0.190\, X_2{*}X_4 + 0.27\, X_3{*}X_4 \quad (8)$$

Where X1, X2, X3, X4 acts process variables while X1X2, X1X3, X1X4, X2X3, X2X4and X3X4 acts the interaction influence among these variables$(X1)^2$, $(X2)^2$, $(X3)^2$, and $(X4)^2$represent a measure of the fundamental influence of these factors. Synergistic and antagonistic impacts are shown by (+,-) signs in front of the variables and their interaction terms, respectively **[23]**.

Table 6 explains the (ANOVA) data of the response model in which: DF symbolize (degree of freedom), SeqSS symbolize (sum of the square), Adj. SS symbolize (adjusted sum of the square), Adj. MS symbolize (adjusted mean of the square), and Contr. % perform (contribution for each factor). Fishers :(F-test) and (P-test) were used to check the capacity of the model where high value of Fisher means that maximum limits of diversity may be fitted by using the equation of regression. The(P-value) utilized to determine whether F has a high value that is reasonable to distinguish the statistical importance of model. 95% of the changeable of the model could be discussed when its (P-value) < 5% **[24]**. According to findings of (Table 6), the quadratic model is essential with F-value of 10.3 and confidence level above 95 % (P-value equal to 0.0001). The lack of fit test may be utilized to see if the chosen model is acceptable for describing the data or if a more extensive model is required **[25]**. The (P-value) for lack of fit in the current work equal to 0.152, which is larger than (0.05), demonstrating that was not statically important when compared to the pure error **[25]**. As a result, the model can acquire reasonable prediction matching to the response values. The R^2 and adj. R^2 values in this research were assessed to be 0.9242 and 0.8358, respectively, confirming the model-predicted and experimental values' consistency **[26]**.

It is clear from **Table 6** that among every factors, NaCl addition (X3) was the most significance factor effect on RE% with a contribution percentage equal to 31.12%, which indicates the function of chloride ions on the decomposition of organic compound during the electro oxidation. With a percentage contribution (19.93%), the effect of current density (X1) is the second most important. Flow rate has a considerable effect on RE% with a percentage of contribution of 14.27%.This is an indication that flow rate has an important function in the process by increasing the mass transfer and lowering the thickness of the boundary layer along the surface of anode. Furthermore, the contribution of 2-way interaction impacts on the RE% about 2.17% which very small and could be ignored and all 2-way interactions being non-significant. The contributions of the quadratic influences on the RE% was about 12.25% which is significant.

Table 5: Results of experimental of BBD to remove COD

Run	blocks	X_1	X_2	X_3	X4	R E% Actual	R E% predicted	S E C (kWh/kg COD)
1	1	4	3	1	2.5	25.00	32.088	16.46
2	1	26	3	1	2.5	45.00	51.753	160.04
3	1	4	10	1	2.5	53.00	48.405	7.51
4	1	26	10	1	2.5	66.80	61.870	80.09
5	1	15	6.5	0	1.0	34.50	36.970	125.68
6	1	15	6.5	2	1.0	60.00	56.870	51.37
7	1	15	6.5	0	4.0	44.90	50.188	110.24
8	1	15	6.5	2	4.0	72.00	71.688	56.88
9	1	4	6.5	1	1.0	44.00	43.838	14.12
10	1	26	6.5	1	1.0	55.29	55.548	90.54
11	1	4	6.5	1	4.0	55.00	53.002	8.32
12	1	26	6.5	1	4.0	76.00	74.422	92.69
13	1	15	3	0	2.5	37.70	31.022	109.59
14	1	15	10	0	2.5	41.00	39.788	106.15
15	1	15	3	2	2.5	47.80	47.272	82.69
16	1	15	10	2	2.5	60.00	64.938	74.29
17	1	4	6.5	0	2.5	25.10	25.209	30.99
18	1	26	6.5	0	2.5	47.40	47.424	231.82
19	1	4	6.5	2	2.5	52.00	51.559	11.53
20	1	26	6.5	2	2.5	63.00	62.474	170.31
21	1	15	3	1	1.0	46.00	43.174	95.83
22	1	15	10	1	1.0	51.00	54.390	71.99
23	1	15	3	1	4.0	59.00	55.192	50.26
24	1	15	10	1	4.0	68.00	70.409	53.61
25	1	15	6.5	1	2.5	55.20	55.167	64.08
26	1	15	6.5	1	2.5	53.40	55.167	63.7
27	1	15	6.5	1	2.5	57.10	55.167	65.6

Table 6: ANOVA for COD elimination

Source	**DF**	**Seq. S S**	**Cr.** (%)	**Adj SS**	**Adj MS**	**F − Value**	**P − Value**
Model	14	3817.69	92.42	3817.69	272.69	10.3	0.0001
Linear	4	322.25	78.01	3222.25	805.56	30.89	0.0001
X1	1	823.20	19.93%	823.20	823.20	31.56	0.0001
X2	1	524.04	12.69%	524.04	524.04	20.09	0.001
X3	1	1285.47	31.12%	1285.47	1285.47	49.29	0.0001
X4	1	589.54	14.27%	589.54	589.54	22.60	0.0001
Square	4	505.90	12.25%	505.90	126.47	4.85	0.015
X1*X1	1	23.08	0.56%	43.73	43.73	1.68	0.220
X2*X2	1	76.84	1.86%	75.99	75.99	2.91	0.114
X3*X3	1	302.76	7.33%	169.48	169.48	6.50	0.026
X4*X4	1	103.21	2.50%	103.21	103.21	3.96	0.070
2-Way Interaction	6	89.55	2.17%	89.55	14.92	0.57	0.746
X1*X2	1	9.61	0.23%	9.61	9.61	0.37	0.555
X1*X3	1	31.92	0.77%	31.92	31.92	1.22	0.290
X1*X4	1	23.57	0.57%	23.57	23.57	0.90	0.361
X2*X3	1	19.80	0.48%	19.80	19.80	0.76	0.401
X2 * X4	1	4.00	0.10%	4.00	4.00	0.15	0.702
X3 * X4	1	0.64	0.02%	0.64	0.64	0.02	0.878
Error	12	312.97	7.58	312.97	26.08		
Lack-of-fit	10	302.81	7.33	302.81	30.28	5.96	0.152
Pure error	2	10.17	0.25	10.17	5.08		
Total	26	4130.67	100				
Summary Model	S	R^2	R^2 (adj.)	PRESS			
	5.107	92.42	83.58	1767.04			

3.2. Influence of process factors on the COD elimination efficiency

Graphical presentation of quadratic model depended on R.S.M was employed to knowledge effect of process variables and their combination on the removal efficiency. **Figures (3 a, b)** demonstrate the total impacts of (current density) and (NaCl addition) on the RE% whith pH=6.5 and flow rate equal to 2.5 L / min. **Figure (3 - a)** denotes response surface while **figure (3 - b)** presents the equivalent contour plot. From **figure (3-a)**, It is obvious that there has been an increase in current density causes an increasing RE% over the whole range of NaCl addition. For example, with no addition of NaCl, increasing of current density from 4 to 26mA/cm^2 results in increasing RE% from 25.10% to 47.40% (**Table 5**, exp.17 and 18).Same behavior with less increasing was observed at NaCl addition of 2 g/l (**Table 5**, exp.19 and 20). The most significant parameter in electrochemistry is the applied current density, which governs electron transport and the production of reactive oxidants **[27, 28]**, and so directly effects pollutant removal rates. Such major affecting function of current densities through the elimination of contaminants from different wastewater in numerous studies **[29, 30].**

Effect of NaCl addition is more pronounced than current density, for example at 4 mA/cm^2 of current density, increasing the addition of NaCl from 0 to 4 g/l results in increasing RE% from 25.1 to 52% (**Table 5**, exp.17 and 19).Same behavior was observed at higher current density. Literature surveys shown that addition of NaCl has different effects on the oxidation process. It enhances the degradation efficiency as well as shorten the reaction time because of the reaction between the produced (chlorine / hypochlorite) and the (organic molecule). Also it increases the conductivity of mixture leading to less power consumption **[31-34]**.

Depending on results of contour plot, it is obviuos that R.E% ≥60 % might be gained within a small region in which NaCl addition is (1-2 g /l) and current density is within 15-26 mA/cm^2.

Figures (4 a,b) demonstrates the combined influences of flow rate and current density on the RE% at pH value equal to (6.5) and sodium chloride addition of (1 g/l). **Figure (4 - a)** acts the plot of response surface, so **Figure (4 - b)** shows the plot of equivalent contour. **Figure (4-a)** shows clearly RE% increases with increasing current density over the whole range of flow rate. The most significant point in this figure is the role of flow rate on the RE%. It was observed that increasing flow rate from 1 to 2.5 L/min has no significant effect on RE% however beyond 2.5L/min, there is a drastic increase in the RE% to reach76% at higher current density of 26mA/cm^2 (**Table 5**, exp.12). This phenomena demonstrates the significant role of the new design of anode where the spiral movement of electrolyte on the surface of anode results in more turbulence effect as the flow rate increases leading to high amount of chlorine gas to dissolve and react with water. Furthermore, increasing the flow rate reduces energy consumption and improves the mass transfer coefficient. A linear relation between RE% and flow rate was observed by Skban Ibrahim et al.**[35]** using TER with two smooth cylindrical electrodes. Adopting the new design of anode offers a nonlinear correlation between flow rate and RE%.

Depending on contour plot results, it is evident that RE% ≥70 % might be be achieved within a small region in which flow rate is within (3.8-4L/min) and current density is within 18-26 mA/cm^2.

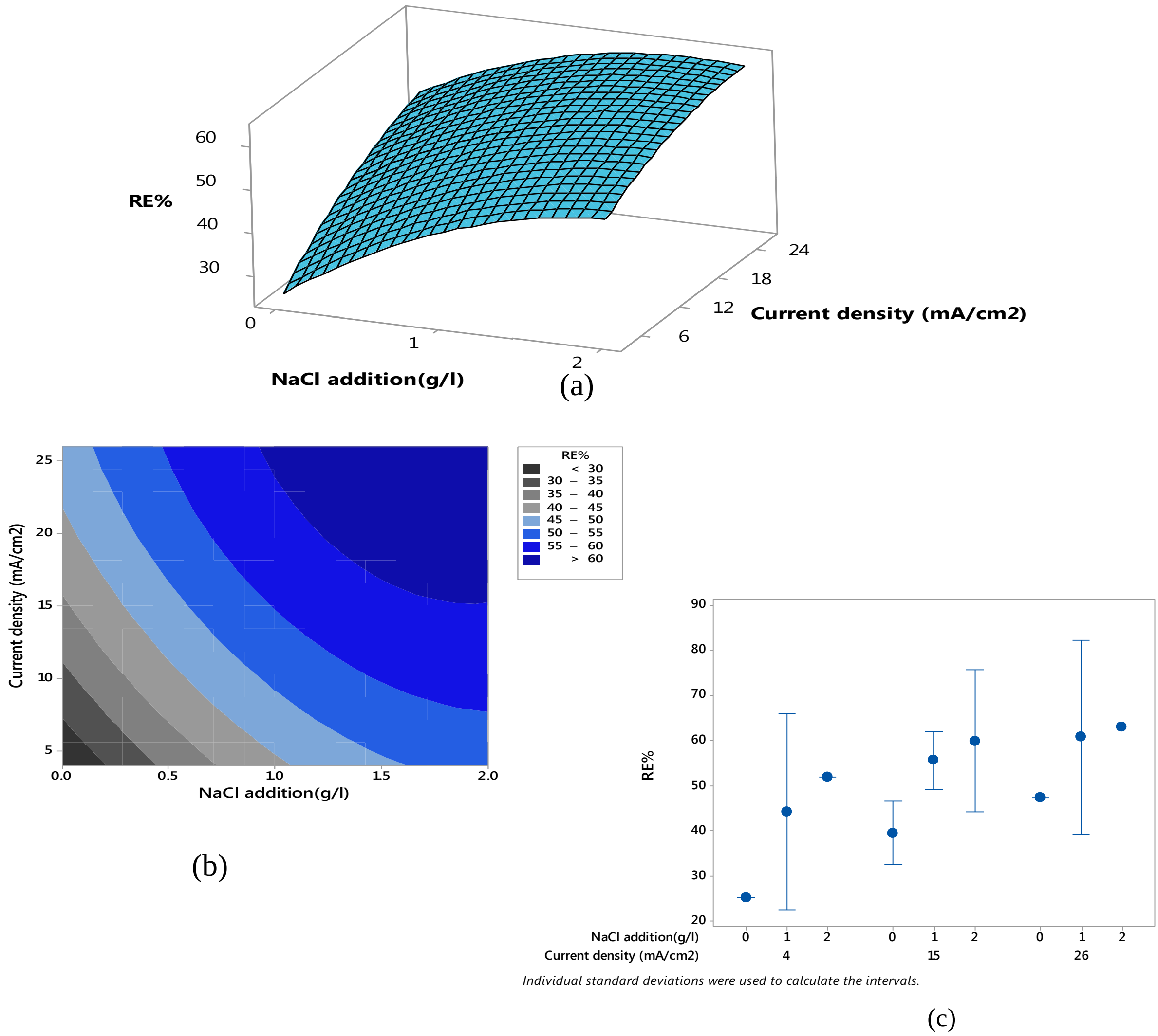
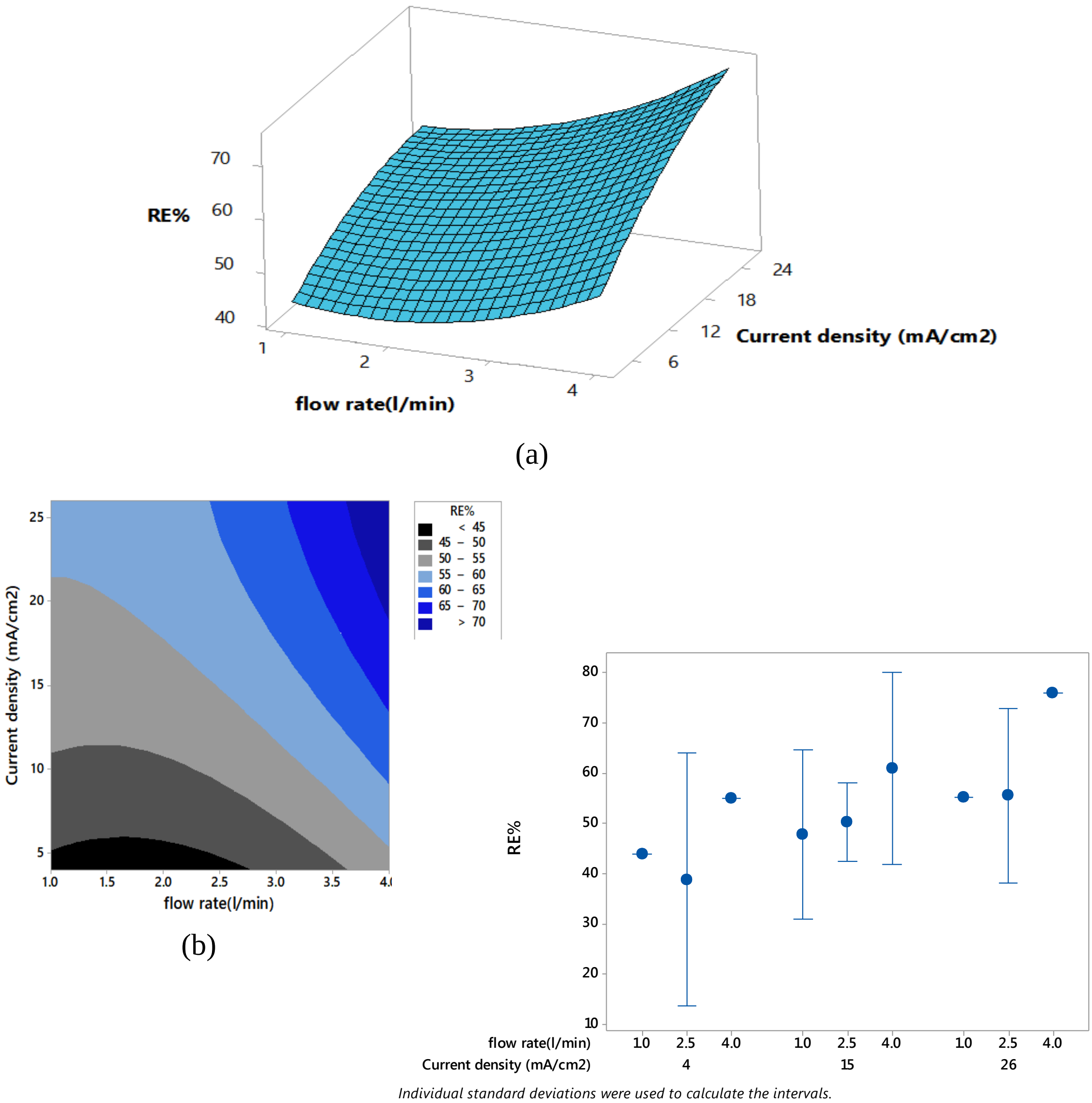


Figure 3: The influence of current density and NaCl addition on the removal efficiency:(a)Plot of response surface, (b) contour plot, (c) Interval plot (holding: pH=6.5 and flow rate= 2.5 l/min)



(c)

Figure 4: the influence of current density and flow rate on the efficiency of (COD) elimination:(a) Plot of Response surface, (b) plot of contour (c) Interval plot (holding: pH =6.5,NaCl =1g/l)

Figures (5- a,b) demonstrates the influences of current density and pH on the elimination efficiency at constant flow rate 2.5L/min. and NaCl addition of 1 g/l. **Figure (5-a)** denotes the plot of response surface while **figure (5- b)** demonstrates the plot of equivalent contour. **Figure (5-a)** displays that RE% increases with increasing current density at the whole range of pH. Meanwhile, the opposite effect was observed by pH , where increasing pH from 4 to 7 leads to a drastic increase in RE% while beyond 7 the RE% is slightly increased. Similar behavior was noticed by Skban Ibrahim et al. **[32]** for processing of petroleum refinery effluent in batch recycle mode of operation using TER with two cylindrical electrodes.

According to the plot of contour results, it is obvious that RE% ≥60 % could be achieved within a limited region in which pH is within (6-10) and current density is within 18-26 mA/cm^2.

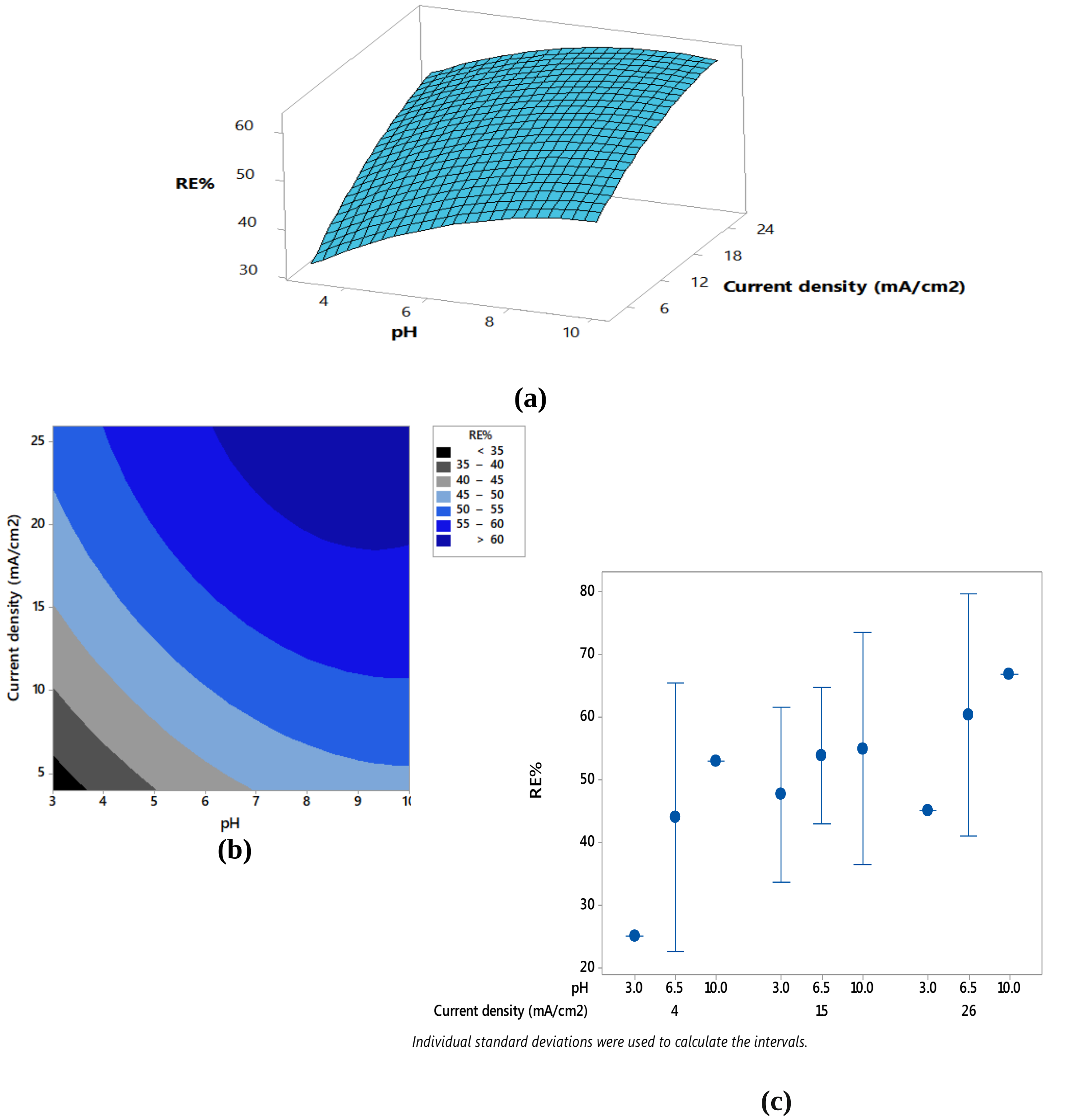


Figure 5: The impact of current density and pH on the efficiency of COD elimination: (a)Plot of Response surface, (b) Plot of contour , (c) Interval plot (holding: flow rate 2.5 l/min, NaCl=1g/l)

3.3. Confirmation test and the optimization

The purpose of any optimization process is to achieve higher value of the response. As a result, RE% was choosed as the maximum, with a weight of 1.0. Minitab-17 Software's response optimizer was used to obtain optimization. Results of optimization are explained in (**Table7**) with the optimal desirability function DF of (1).

Table 8 displays two experiments were performed based on the optimized factors for confirming the optimization values. Chemical Oxygen Demand elimination efficiency (average value) of 83.175 percent was achieved after 180 minutes of electrolysis, which is consistent with the range of the best value obtained from best results (**Table 7**). Thus, BBD with DF may be utilized as efficient way for optimizing RE% by EO process using TER with spiral porous graphite anode. **Table 9** compares the properties of treated effluent based on the new TER concept to the properties of wastewater that has not been treated. It was obvious that treated wastewater has improved properties by RE% of 85.12% and final COD value of 75 ppm lower than the allowable limits for discharging effluents to the river achieving more than 97% removal of turbidity.

Table 7: The best values of process factors for improving COD removal efficiency

Response	goal	lower	target	upper	weight	importance
R E (%)	maximum	25	76	76	1	1
Solution: Parameters			**Results**			

Current density (mA/cm2)	pH	NaCl Conc. (g / l)	Flow rate (L/ min.)	R E (%) Fit	D_F	S E Fit	(95%) CI	(95%) PI
26	10	1.899	4	81.2744	1.0	7.40	(65.15, 97.40)	(61.68, 100.87)

Table 8: The optimum COD elimination efficiency was already established

Run	Current density (mA/cm2)	pH	NaCl (g/l)	Flow rate l/min.	E (Volt)	COD (ppm) Initial	COD (ppm) Final	R E (%)		EC (Kwh/kg COD)
1	26	10	1.899	4	11.1	504	75	85.12	83.175	116.17
2	26	10	1.899	4	10.67	533	100	81.23		110.64

Table 9: Properties of treated effluent versus the wastewater effluent

Effluent \ parameter	COD (ppm)	Turbidity (NTU)	$SO4^{-2}$ (mg/l)	Cl^- (mg/l)
Raw effluent	504	110	445	1560
Treated effluent	75	3	300	500

4. Conclusions

The electrochemical processing of petroleum refinery wastewater collected from Al-Muthanna refinery in a batch recycle mode utilizing a tubular reactor made of a stainless steel cylinder cathode with a spiral porous graphite anode at the center was examined. Optimization the influences of process variables namely NaCl addition, current density, flow rate and pH on the removing of COD using RSM were discussed. Results showed that the best conditions were current density equal to 26 mA/cm^2, NaCl concentration equal to 1.899g/l, pH of 10, and flow rate equal to 4L/min, in which efficiency of COD elimination of 85.12% , with specific energy consumption of 116.17 KWh /Kg COD were achieved. Besides, results showed that sodium chloride addition has the major impact on RE% followed by current density confirming that the indirect electrooxidation process is the dominant route in the present work. Besides, effect of flow rate is vital where higher removal of COD occurred at high flow rate due to the turbulence promotion action of the new design of the anode. It’s worthwhile to investigate the performance of such new design for the process of electrocoagulation in treatment of petroleum refinery wastewaters.

5. Conflicts of interest

“There are no conflicts to declare”.

6. Formatting of funding sources

Self

7. Acknowledgment

The authors are grateful for the supportive and technical help provided by the Al-Muthanna petroleum refinery staff in completing this study.

8. References

[1] A. Alva-Arg´aez, A.C. Kokossis and R. Smith. The design of water-using systems in petroleum refining using a water-pinch decomposition. *Chem. Eng. J.* ,**128** ,33–46(2007).

[2] WBG (World Bank Group), 1999. Pollution Prevention and Abatement Handbook: Toward Cleaner Production, Washington, D.C., USA.

[3] P. Stepnowski, E.M. Siedlecka, P. Behrend and B. Jastorff.Enhanced photo-degradation of contaminants in petroleum refinery wastewater .*Water Research*, **36** (9),2167-2172(2002).

[4] K. Rajeshwar, J.G. Ibanez, 1997. Environmental electrochemistry: fundamentals and applications in pollution abatement, Academic Press, San Diego, California, USA.

[5] A.G. Vlyssides, C.J. Israilides, M. Loizidou, G. Karvouni and V. Mourafetti. Electrochemical treatment of vinasse frombeet molasses.*Water Science and Technology*, **36**(2-3),271–278(1997).

[6] S.H. Lin, C.T. Shyu and M.C. Sun.Saline wastewater treatment by electrochemical method. *Water Research*, **32** (4) ,1059–1066(1998).

[7] Ibrahim, Dhorgham Skban; Veerabahu, C.; Palani, R.; Devi, Seethala; Balasubramanian, N. .Flow dynamics and mass transfer studies in a tubular electrochemical reactor with a mesh electrode, *Computers & Fluids*, **73**,97–103(2013).doi:10.1016/j.compfluid.2012.12.001

[8] Saravanathamizhan R, Paranthaman R and Balasubramanian N. Tanks in series model for continuous stirred tank electrochemical reactor. *Ind. Eng. Chem. Res.*,**47**(9),2976–2984(2008).

[9] Saravanathamizhan R, Paranthaman R, Balasubramanian N and Ahmed Basha C. Residence time distribution in continuous stirred tank electrochemical reactor.*Chemical Engineering Journal*,**142**(2),209–216(2008).

[10] S.A. Martínez-Delgadillo; H. Mollinedo-Ponce; V. Mendoza-Escamilla and C. Barrera-Díaz . Residence time distribution and back-mixing in a tubular electrochemical reactor operated with different inlet flow velocities, to remove Cr(VI) from wastewater. *Chemical Engineering Journal* ,**165**(3),776–783(2010). doi:10.1016/j.cej.2010.09.066

[11] S.A. Martínez-Delgadillo; H.R. Mollinedo P.; M.A. Gutiérrez; I.D. Barceló and J.M. Méndez . Performance of a tubular electrochemical reactor, operated with different inlets, to remove Cr(VI) from wastewater.*Computers and chemical Engineering*,**34**(4),491–499(2010). doi:10.1016/j.compchemeng.2009.05.016

[12] Martínez-Delgadillo SA, Morales-Mora MA and Barceló-Quintal ID. Electrocoagulation treatment to remove pollutants from petroleum refinery wastewater. *Sustain. Environ. Res*.,**20**(4),227–231(2010).

[13] Skban Ibrahim, D.; Seethala Devi, P.; Veerababhu, C.and Balasubramanian N. Treatment of Petroleum Effluent Using a Tubular Electrochemical Reactor. *Petroleum Science and Technology*,**32**(16),1932–1939(2014). doi:10.1080/10916466.2012.701693

[14] Körbahti BK, Tanyolaç A. Continuous electrochemical treatment of simulated industrial textile wastewater from industrial components in a tubular reactor. *Journal of Hazardous Materials*,**170**(2-3),771–778(2009).

[15] Körbahti BK, Tanyolaç A.. Modeling of a continuous electrochemical tubular reactor for phenol removal. *Chemical Engineering Communications*,**190**(5-8),749–762(2003).

[16] Körbahti BK, Tanyolaç A. Continuous electrochemical treatment of phenolic wastewater in a tubular reactor. *Water Research*,**37**(7),1505–1514(2003).

[17] Babu BR, Venkatesan P, Kanimozhi R and Ahmed Basha C. Removal of pharmaceuticals from wastewater by electrochemical oxidation using cylindrical flow reactor and optimization of treatment conditions. *Journal of Environmental Science and Health A* ,**44**(10),985–994(2009).

[18] Bahadir KK, Abdurrahman T. Electrochemical treatment of simulated industrial paint wastewater in a continuous tubular reactor . *Chemical Engineering Journal* , **148**(2-3),444–451(2009).

[19] Fahim, A., Abbar, A. Treatment of petroleum refinery wastewater by electro-Fenton process using porous graphite electrodes. *Egyptian Journal of Chemistry*, **63**(12),4805-4819(2020) doi: 10.21608/ejchem.2020.28148.2592

[20] 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**(3), 544–551(2013).

[21] Alkurdi, Sajjad S.; Abbar, Ali H. Removal of COD from Petroleum refinery Wastewater by Electro-Coagulation Process Using SS/Al electrodes. *IOP Conference Series: Materials Science and Engineering*, **870**, 012052(2020). doi:10.1088/1757-899X/870/1/012052

[22] Evans, M., 2003. Optimization of Manufacturing Processes: A Response Surface Approach. Carlton House Terrace, London.

[23] E. Ahmadi, B. Shokri, A. Mesdaghinia, R. Nabizadeh, M. Reza Khani, S. Yousefzadeh, M. Salehi and K. Yaghmaeian. Synergistic effects of α-Fe2O3-TiO2 and Na2S2O8 on the performance of a non-thermal plasma reactor as a novel catalytic oxidation process for dimethyl phthalate degradation. *Separation and Purification Technolology*, 250 ,117185(2020).

[24] Segurola, J., Allen, N. S., Edge, M., and Mc Mahon, A. Design of eutectic photoinitiator blends for UV/visible curable acrylated printing inks and coatings. *Progress in Organic Coatings*, **37**(1-2), 23–37(1999).

[25] Wu, J., Zhang, H., Oturan, N., Wang, Y., Chen, L. and Oturan, M. A. Application of response surface methodology to the removal of the antibiotic tetracycline by electrochemical process using carbon-felt cathode and DSA (Ti/RuO2–IrO2) anode. *Chemosphere*, **87** (6), 614–620(2012).

[26] Zhao, Q., Kennedy, J. F., Wang, X., Yuan, X., Zhao, B., Peng, Y., and Huang, Y. Optimization of ultrasonic circulating extraction of polysaccharides from Asparagus officinalis using response surface methodology. *International Journal of Biological Macromolecules*, **49**(2),181–187(2011).

[27] Khataee, A. R., Zarei, M., and Moradkhannejhad, L.Application of response surface methodology for optimization of azo dye removal by oxalate catalyzed photoelectro-Fenton process using carbon nanotube-PTFE cathode. *Desalination*, **258**(1–3), 112–119(2010).

[28] Molla Mahmoudi, M., Khaghani, R., Dargahi, A., and Monazami Tehrani, G. Electrochemical degradation of diazinon from aqueous media using graphite anode: Effect of parameters, mineralisation, reaction kinetic, degradation pathway and optimisation using central composite design. *International Journal of Environmental Analytical Chemistry*, 1–26(2020).

[29] Iranildes D. Santos , Marcia Dezotti , Achilles J.B. Dutra. Electrochemical treatment of effluents from petroleum industry using a Ti/RuO2 anode . *Chemical Engineering Journal*, **226** , 293–299(2013).

[30] Jawad, S., and Abbar, A. H. . Treatment of petroleum refinery wastewater by electrochemical oxidation using graphite anodes. *Al-Qadisiyah Journal for Engineering Sciences*, **12**(3),144-150(2019). https://doi.org/10.30772/qjes.v12i3.609

[31] Babu, B. R., Venkatesan, P., Kanimozhi, R., and Basha, C. A. . Removal of pharmaceuticals from wastewater by electrochemical oxidation using cylindrical flow reactor and optimization of treatment conditions. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, **44**(10), 985–994(2009).

[32] Hind M. Ibrahim; Rasha H. Salman. "Real wastewater Treatment by Electrocoagulation-Electro-oxidation Combined System: Optimization using Taguchi Approach". *Egyptian Journal of Chemistry*, **65**(3),135-145(2022).Doi:10.21608/ejchem.2021.88245.4247

[33] Ali H. Abbar and Sajjad S. Alkurdi .Performance Evaluation of a Combined Electrocoagulation– Electrooxidation Process for the Treatment of Petroleum Refinery Wastewater .*IOP Conf. Ser.: Mater. Sci. Eng.* ,1076 012027 (2021).

[34] José de Jesús Treviño-Reséndez, Alejandro Medel,YunnyMeas,Electrochemical technologies for treating petroleum industrywastewater,*Current Opinion in Electrochemistry*, **27**,100690(2021).

[35] D. Skban Ibrahim, P. Seethala Devi, C. Veerababhu and N. Balasubramanian. Treatment of Petroleum Effluent Using a Tubular Electrochemical Reactor. *Petroleum Science and Technology*,**32**(16),1932-1939(2014).DOI: 10.1080/10916466.2012.701693.