



Application of Response Surface Methodology for Optimization of Phenol Removal from a Simulated Wastewater Using Rotating Tubular Packed Bed Electrochemical Reactor



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Abstract

Phenol removal from simulated wastewater by indirect electrochemical oxidation was investigated using a rotating tubular packed bed electrochemical reactor. Effects of operating parameters like current density (3-15 mA/cm²), rotation speed (100-500 rpm), initial phenol concentration (20-100 ppm), and pH (3-9) were investigated. Optimization of the process parameters was carried out by adopting response surface methodology (RSM) combined with Box-Behnken Design (BBD) where COD removal efficiency (RE %) was selected as a response function. The results indicated that initial phenol concentration has the main effect on the COD removal efficiency followed by current density then pH and rotation speed. The results of regression analysis revealed that the experimental data could be fitted to a second-order polynomial model with a value of determination coefficient (R²) equal to 98.38%. The optimum conditions of the process parameters based on RSM method were an initial phenol concentration of 41 ppm, current density of (9.3 mA/cm²), rotation speed of 367 rpm and pH = 3 where COD removal efficiency of (99.83%) was accomplished after 60 min of electrochemical oxidation process in which current efficiency of (9.87%) was observed and energy consumption of (179.86 KWh/Kg COD) was required.

Keywords: Three-dimensional electrodes, Rotating cylinder electrode, Woven screens, phenol removal, Response surface methodology

1. Introduction

Phenol and phenolic compounds are recognized as priority contaminants by the US Environmental Protection Agency (EPA), therefore effluents containing such compounds should be removed or degraded before discharging to environment. Stringent US (EPA) guidelines claim lowering phenol concentration in the polluted effluents to be lower than 1 mg/l [1]. Wastewaters containing phenolic compounds cannot be treated by biological process because of their ability to resist most common microorganisms [2]. During water treatment, phenolic compounds could be reacted with chlorine leading to generation of chlorophenols which are carcinogenic. Furthermore, they are poisonous even in their existence at little concentration and could cause taste and odor of fish. Therefore, the treatment of such organic pollutants is essential for environmental protection.

Phenol and its compounds appear in the effluents of many industries such as coal conversion plants, coal tar distillation, oil refineries, petrochemicals, polymeric resins, pharmaceuticals, pesticides, rubber reclamation, explosives, and textile industries. There are numerous conventional available methods to treat wastewaters involving phenols such as adsorption by activated carbon [3], adsorption by carbon nanotubes [4], chemical oxidation [5], solvent extraction [6], biodegradation [7], advanced oxidation processes [8], and oxidation in supercritical water [9]. However, these methods have essential disadvantages of being unfeasible from economical point view, degradation mechanism complexity, many operational problems, and inability to complete removal of phenol and its compounds [10]. Electrochemical oxidation is considered as a favourable

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Receive Date: 28 November 2020, Revise Date: 21 April 2020, Accept Date: 14 May 2020

DOI: 10.21608/EJCHEM.2020.26727.2547

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method that can be used for contaminants destruction [11]. It has been proved to be an efficient low cost, ease of control on the process parameters and the increase of its efficiency due to the using of modern designs of electrochemical reactors [12, 13]. At the electrochemical oxidation process, two routes were used to destroy the pollutants either by direct or indirect anodic oxidation methods. In the direct anodic oxidation route, contaminants are firstly adsorbed on the anodic surface then incinerated by direct transfer of electrons via anodic reaction. In the indirect oxidation route, strong oxidants such as hypochlorite/ chlorine, hydrogen peroxide, and ozone are produced electrochemically then reacted with the pollutants (organic compounds) in the solution [14]. Generally, chloride has been used in the indirect oxidation as a source of strong oxidant because chloride salts are usually existed in the polluted effluents [15]. Moreover, the activity of chlorine in degradation of dyes has been investigated extensively [16]. In the indirect oxidation process under acidic media, chlorine is more stable as oxidant agent since the ionization constant of hypochlorous acid is 2.95×10^{-8} ($pK_a = 7.53$), while Hypochlorite ion is the predominate as oxidant agent in alkaline media [17]. In the phenol electrochemical oxidation method, various electrode materials have been used such as Platinum (Pt), Nickel (Ni), Graphite, Ti/RuO₂, Ti/IrO₂, Ti/PbO₂, Ti/SnO₂-Sb, and boron-doped diamond (BDD). Previous works reported the Platinum as anodic material is more efficient in degradation of organic wastes, but its stability in saline medium is a point to be kept in mind as well as its high cost [18]. When nickel is used as anode, the efficiency of anodic oxidation is reduced due to formation of organic polymer matrix on its surface as a results of electro coagulation of the metal [19]. Ti/RuO₂ and Ti/IrO₂ are not very active for phenols oxidation as mentioned by previous studies because of the highly interaction of hydroxyl radical (OH•) with the anodic surface leading to transfer of oxygen from OH• at the electrode surface and creating higher oxidation state oxide [20]. SnO₂-Sb has short service life as well as deactivation problems [21]. Using PbO₂ as anode material could be led to further contamination of the wastewater with lead [22]. In spite of the high anodic stability of BDD as well as its wide potential window for discharging of water, it's using as anode for wastewater treatment is still limited due to its high cost [23]. In view of all aspects abovementioned, this research concerns with the using of indirect oxidation process via generating electrochemically an active chlorine to oxidize phenol using graphite anode. The choice of graphite as anode material is based on its low cost and availability as well as the good results obtained in our previous work on the treatment of petroleum refinery wastewater via indirect oxidation process with a graphite anode where a total removal of chemical oxygen demand (COD) has been achieved at lower energy consumption [24]. In our previous work [25], a rotating tubular packed bed electrochemical reactor have been used for copper removal from a simulated wastewater. This new electrochemical reactor design is composed from hallow cylinder fixed bed cathode rotated between two anodes

(external graphite cylinder and internal graphite solid bar). This configuration gives excellent turbulence for the electrolyte mounted between the electrodes leading to higher mass transfer rate toward the surface of the electrode in comparison with traditional rotating cylinder electrodes. Besides using woven screens as a fixed bed cathode give further turbulence action to the solution. Hence the main object of the present work is to study the removal of phenol using rotating tubular packed bed electrochemical reactor.

In previous studies related to electrochemical wastewater treatment, a traditional one-factor-at-a-time approach (OFAT) has been used frequently. This method changes only one factor at a time while keeping others constant. However, the factors interactions cannot be specified via OFAT experiments. Designed experiment technique considers as the more efficient method that takes into account the impact of two or more parameters on a response as well as their interactions. The designed experiment claims fewer resources (runs, time, and materials) to get the required results. Besides, by using designed experiment method, the evaluation of the effects of each parameter will be more precise [26]. Response surface methodology (RSM), as a designed experiment technique, is the major subject in the statistical design of experiments. It was used extensively at different industrial processes related to wastewater treatment like adsorption [27], chlorine disinfection [28], electrocoagulation [29], Fenton-related process [30], modified Fenton process [31], and electrochemical oxidation of textile dye wastewater [32]. RSM is a collection of mathematical and statistical approaches that have been used successfully in modelling and analysing of different problems in which different parameters effect on the response of interest were studied. The relative effect of different affecting variables on a response is the target of RSM in which the best operating conditions are obtained by optimizing this response [33]. Hence, the second aim of the present research is to optimize process factors like current density, initial phenol concentration, rotation, and pH to get higher phenol removal rate. Box-Behnken design (BBD) of the response surface methodology was used as an optimization approach where no previous works have been achieved on the optimization of phenol removal using tubular packed bed woven screens electrode

2. Experimental work

The experimental runs were performed in a 0.5 L Perspex-cylindrical electrolytic cell. The cathode was a rotating tubular packed bed electrode constructed from 316 stainless steel woven screens wrapped around stainless hallow cylinder acting as a current feeder. The hallow cylinder current feeder was opened at the bottom and closed at the upper. It was perforated with a total of (15) holes with diameter (6 mm) distributed uniformly on the lateral surface of the cylinder. The cathode feeder has outer diameter (35 mm), inner diameter (28 mm) with total length (60 mm). The lower part of this feeder is jointed with a Teflon sleeve has diameter (30 mm) and thickness of (6 mm), while the upper part is jointed with a Teflon sleeve has diameter (30 mm) and thickness of

(8 mm) in order to fix the wrapped woven screens sheets on the current feeder. The stainless steel woven screens used in the present work have mesh no. 30 wire /inch with porosity of 0.7146 and a specific surface area of 38.06 cm^{-1} [24]. The cathode current feeder was attached to the shaft of a variable speed motor via a stainless steel rod (7 mm diameter and 100 mm length) fixed on the cathode feeder. The cathode has a lateral surface area (45 mm diameter and 53 mm long). Graphite cylinder having dimensions (90 mm inside diameter, 5 mm thickness, and 66 mm long) was utilized as outside anode (working electrode) while central graphite rod having dimensions (60 mm length and 20 mm diameter) was used as inside anode. For ensuring a uniform primary current distribution, the three electrodes (cathode, outer anode and inside anode) were concentric in the cell body. The schematic diagram of the electrochemical system is shown in Figure 1.

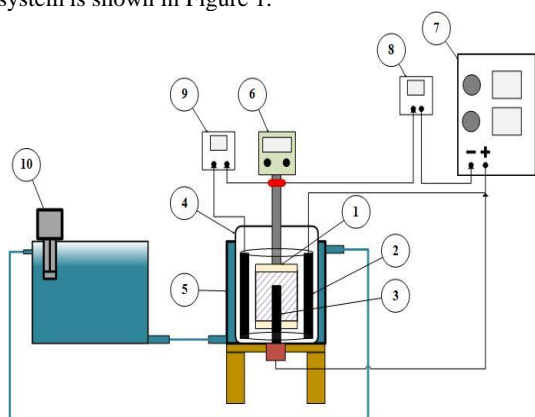


Fig. 1: The schematic diagram of the electrochemical system: 1) cathode, 2) outside anode, 3) inside anode, 4) cell body, 5) jacket, 6) electrical motor, 7) power supply, 8) Ammeter, 9) voltmeter, 10) water bath circulator

Sodium sulfate (Na_2SO_4) was used as a supporting electrolyte and phenol as organic pollutant system. NaCl was used at concentration 1 g/L [24]. All chemicals were of reagent grade. Doubly distilled water was used for preparing electrolytic solutions containing phenol dissolved in $0.5 \text{ M Na}_2\text{SO}_4$ and 0.017 M NaCl at concentrations (20, 60, 100 ppm). The final pH of electrolytic solutions was regulated by addition (1M) H_2SO_4 or (1M) NaOH . All runs were proceeded at a fixed temperature of $25 \pm 1^\circ\text{C}$. Phenol degradation rate was studied and expressed as COD depletion. The concentration of COD in solution was specified by taken a sample of effluent (2ml), digested with $\text{K}_2\text{Cr}_2\text{O}_7$ (oxidizing agent) 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 spectrophotometer (MD200, Lovibond). The COD values corresponding to phenol concentration of 20, 60, and 100 ppm were 39.9, 158.53, and 275.23 ppm respectively.

The COD removal efficiency can be evaluated based on eq.1 [34]

$$RE\% = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (1)$$

Where RE% stands for the removal efficiency, COD_i represents the initial COD (mg L^{-1}), and COD_f is the final COD (mg L^{-1})

The current efficiency in any electrooxidation process refers to the fraction of the total current which is passed for target reaction. It has been computed 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 determined from eq.2 [35]:

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

where F represents the constant of Faraday (96,487 C/mol), V stands for the effluent volume in (L), ΔC represents the difference in the COD values in (g/L), I is the current in (A), 8 represents a unit consistency dimensional factor, it's the equivalent mass of oxygen {32g of O_2 /4mol of electrons} (g/mol), and t stands for the time of electrolysis (s)

The electrical energy consumption (EC) in any anodic oxidation represents the amount of the consumed energy in the process for a kilogram of COD that requires digesting. EC in (kWh/kg) may be acquired with the use of eq. 3 [36]:

$$EC = \frac{E.I.t \times 1000}{(COD_i - COD_f)V} \quad (3)$$

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

2.2 Design of experiments

The relationship between a process response and its variables can be determined by applying a collection of statistical and mathematical methods adopted by RSM [37]. In this work, 3-level 4-factor Box–Behnken experimental design was implemented to verification and check the variables that influenced on the phenol removal from simulated wastewater. Initial phenol concentration (X1) Current density (X2), rotation speed (X3), and pH value (X4) were taken as the process parameters, while the COD removal efficiency was taken as a response. The scales of process variables were coded as -1 (low level), 0 (middle or central point) and 1 (high level) [38]. Table 1 illustrates the process variables with their chosen levels. Box–Behnken improves designs to get the suitable quadratic model with the required statistical properties by using only a part of the runs needed for a 3-level factorial. The number of runs (N) needed for performing of Box–Behnken design can be determined by the following equation [39]:

$$N = 2k(k-1) + cp \quad (4)$$

Where k represents number of process variables and cp is the reiterated number of the central point.

In this research, twenty seven runs as BBD array designated by the software of Minitab-17 program were conducted for evaluating the impacts of process parameters on the removal efficiency of COD. Table 2 illustrates the BBD proposed for the present research. The selected **Table 1**

values of current density in the present is based on the total immersed anodic surface area (186.92 cm²) of the two graphite.

Process variables with their level for removal of phenol

Process parameters	range in BBD		
Coded levels	Low(-1)	Middle(0)	High (+1)
X1-Initial Phenol concentration (ppm)	20	60	100
X2- Current density (mA/cm ²)	3	9	15
X3-Rotation speed(rpm)	100	300	500
X4-pH	3	6	9

Table 2

Box- Behnken experimental design

Run	Bk.	Coded value				Real value			
		x ₁	x ₂	x ₃	x ₄	Concentration (ppm) X1	Current density (mA/cm ²) X2	Rotation (rpm) X3	pH X4
1	1	-1	1	0	0	20	15	300	6
2	1	-1	0	0	1	20	9	300	9
3	1	0	-1	-1	0	60	3	100	6
4	1	1	0	1	0	100	9	500	6
5	1	0	-1	1	0	60	3	500	6
6	1	1	1	0	0	100	15	300	6
7	1	1	0	-1	0	100	9	100	6
8	1	0	1	1	0	60	15	500	6
9	1	0	-1	0	-1	60	3	300	3
10	1	0	0	-1	-1	60	9	100	3
11	1	-1	0	0	-1	20	9	300	3
12	1	0	0	1	1	60	9	500	9
13	1	0	0	0	0	60	9	300	6
14	1	-1	0	-1	0	20	9	100	6
15	1	0	1	0	1	60	15	300	9
16	1	0	0	0	0	60	9	300	6
17	1	1	0	0	-1	100	9	300	3
18	1	-1	-1	0	0	20	3	300	6
19	1	0	1	0	-1	60	15	300	3
20	1	0	-1	0	1	60	3	300	9
21	1	0	0	1	-1	60	9	500	3
22	1	-1	0	1	0	20	9	500	6
23	1	1	-1	0	0	100	3	300	6
24	1	0	0	0	0	60	9	300	6
25	1	0	0	-1	1	60	9	100	9
26	1	1	0	0	1	100	9	300	9
27	1	0	1	-1	0	60	15	100	6

A second order polynomial model can be adopted based on BBD where fitting the interaction terms with the

experimental data can be described by the following equation [40]:

$$Y = a_0 + \sum a_i x_i + \sum a_{ii} x_i^2 + \sum a_{ij} x_i x_j \quad (5)$$

Where Y represents the response (RE%), i and j are the index numbers for independent variables, a_0 is intercept term, $x_1, x_2 \dots x_k$ are the process variables (independent variables) in coded form. a_i is the first-order (linear) main effect, a_{ii} second-order main effect and a_{ij} is the interaction effect. Analysis of variance was performed then the regression coefficient (R^2) was estimated to confirm the goodness of model fit.

3. Results and discussion

3.1 Statistical analysis

Optimization and investigation the combined effects of process parameters on the COD removal efficiency were

Run Order	Blocks	Conc. (ppm)	Current density (mA/cm ²)	Rotation (rpm)	pH	RE%		E (Volt)	CE (%)	EC (kWh/kg COD)
						Actual	Predict			
1	1	20	15	300	6	100	99.469	4.80	2.01	802.01
2	1	20	9	300	9	94	95.325	5.15	3.14	549.19
3	1	60	3	100	6	66.9	70.875	3.37	26.29	42.95
4	1	100	9	500	6	72	71.406	5.60	16.60	113.04
5	1	60	3	500	6	80.5	79.858	3.30	32.07	34.48
6	1	100	15	300	6	82.3	83.477	5.80	11.38	170.71
7	1	100	9	100	6	61.9	62.673	4.40	0.14	103.31
8	1	60	15	500	6	100	97.158	6.32	7.95	266.21
9	1	60	3	300	3	92.6	91.898	3.20	36.89	29.07
10	1	60	9	100	3	96.9	92.619	4.50	12.87	117.18
11	1	20	9	300	3	100	102.725	5.48	3.34	549.37
12	1	60	9	500	9	79.1	83.277	4.30	10.50	136.17
13	1	60	9	300	6	97.5	97.500	4.55	12.95	117.75
14	1	20	9	100	6	96	95.565	4.25	3.21	443.86
15	1	60	15	300	9	99.8	99.473	5.65	7.95	238.10
16	1	60	9	300	6	97.5	97.500	4.67	12.95	120.86
17	1	100	9	300	3	80.7	80.508	4.30	18.60	77.48
18	1	20	3	300	6	92	90.719	3.61	9.22	130.79
19	1	60	15	300	3	100	100.748	6.22	7.97	261.57
20	1	60	3	300	9	66.9	65.123	6.10	26.65	76.70
21	1	60	9	500	3	99.9	101.602	5.65	13.26	142.70
22	1	20	9	500	6	98	96.198	5.70	3.28	584.62
23	1	100	3	300	6	48.6	49.027	3.00	33.61	29.92
24	1	60	9	300	6	97.5	97.500	4.87	12.95	126.00
25	1	60	9	100	9	84.7	82.894	4.95	11.25	147.43
26	1	100	9	300	9	61.45	59.858	4.70	14.16	111.16
27	1	60	15	100	6	95	96.775	6.65	7.57	294.40

achieved by performing the twenty seven statistically designed batch runs for various combinations of these parameters. Table 3 displays results of present work including COD removal efficiency (RE %), energy consumption (EC), and current efficiency (CE %) that obtained at electrolysis time of 60 min. It was observed that the removal efficiency of COD was in the range of 48.6 -100%, while the current efficiency in the range (0.14 -36.89%). The values of energy consumption was ranged between 29.07 and 802.01 Kwh/kg COD.

Table 3

Experimental results of BBD for phenol removal

Minitab-17 software was used to analyse results of the removal efficiency of COD where an experimental relationship between removal efficiency of COD and

process parameters was obtained and formulated by a quadratic model of the removal efficiency of COD (RE) in term of coded units of process variables:

$$\begin{aligned} \text{RE}\% = & 72.1 + 0.296 X_1 + 1.636 X_2 + 0.1132 X_3 \\ & + 0.05 X_4 - 0.006729 X_1^2 - 0.1683 X_2^2 - 0.000132 X_3^2 - \\ & 0.237 X_4^2 + 0.02677 X_1 X_2 + 0.000253 X_1 X_3 - \\ & 0.0276 X_1 X_4 - 0.00179 X_2 X_3 + 0.3542 X_2 X_4 - \\ & 0.00358 X_3 X_4 \end{aligned} \quad (6)$$

Where RE% is the response, i.e. COD removal efficiency, and X₁, X₂, X₃ and X₄ are initial phenol concentration, current density, rotation speed and initial pH respectively. Whereas the parameters X₁X₂, X₁X₃, X₁X₄, X₂X₃, X₂X₄, X₃X₄ represent the interaction effect of all the parameters of the model. X₁², X₂², X₃² and X₄² represent the double interactions effect of main parameters (initial phenol concentration, current density, rotation speed, and pH).

Eq.(6) shows how COD removal efficiency is influenced by the individual variables (linear and quadratic) or double interactions. Values of positive coefficients revealed that COD removal efficiency increased with the increasing of the related factors of these coefficients within the tested range while values of negative coefficients revealed the opposite effect. As can be seen all parameters (phenol concentration, current density, rotation speed and pH) were found to have positive effects on COD removal efficiency. The results showed that effects of interactions are significant with a total contribution of (19.46%) from the model. It means that these parameters are interrelated in their effects during the process. The predicted values of the COD removal efficiency estimated from Eq.6 are also

inserted in Table 3. BBD adequacy was identified by using analysis of variance (ANOVA). To test hypotheses on the parameters of the model, ANOVA divides the total variation in a set of data into individual parts supplemented with specific sources of variation [41]. The adequacy of the model in ANOVA analysis is recognized based on Fisher F-test and P-test. Most of the variation in the response can be illustrated by the regression equation if the value of Fisher becomes higher. P-value is utilized for evaluating whether F is large enough to signalize statistical significance. (90)% of the variability of the model could be clarified when a P-value lower than (0.05) [38]. Table 4 illustrates ANOVA for the response surface model. In this table, degree of freedom (DOF), percentage of contribution (Cr. %) for each parameter, sum of the square (SeqSS), adjusted sum of the square (Adj SS), adjusted mean of the square (Adj MS), P-value, and F-value were evaluated. F-value of (52.11) and P-value of (0.0001) were obtained which indicates that regression of model is highly significance. The multiple correlation coefficient of the model was 98.38% conforming the regression of mode is statistically significant and only (1.62) % is not confirmed by the model. The adjusted multiple correlation coefficient (adj. R² = 96.49%) was in compatible with the predicted multiple correlation coefficient (pred. R²=90.68%) in this model.

Table 4
Variance Analysis (ANOVA) for COD removal

Source	DOF	Seq SS	Cr.(%)	Adj SS	Adj MS	Fisher-Value	P-value
Model	14	5673.22	98.38	5673.22	405.23	52.11	0.0001
Linear	4	4551.11	78.92	4551.11	1137.78	146.30	0.0001
(X1)	1	2495.53	43.28	2495.53	2495.53	320.89	0.0001
(X2)	1	1399.68	24.27	1399.68	1399.68	179.98	0.0001
(X3)	1	65.80	1.14	65.80	65.80	8.46	0.013
(X4)	1	590.10	10.23	590.10	590.10	75.88	0.000
Square	4	697.16	12.09	697.16	174.29	22.41	0.000
X1*X1	1	434.61	7.54	618.25	618.25	79.50	0.000
X2*X2	1	113.43	1.97	195.89	195.89	25.19	0.000
X3*X3	1	124.94	2.17	148.29	148.29	19.07	0.001
X4*X4	1	24.18	0.42	24.18	24.18	3.11	0.103
2-Way Inter.	6	424.96	7.37	424.96	70.83	9.11	0.001
X1*X2	1	165.12	2.86	165.12	165.12	21.23	0.001
X1*X3	1	16.40	0.28	16.40	16.40	2.11	0.172
X1*X4	1	43.89	0.76	43.89	43.89	5.64	0.035
X2*X3	1	18.49	0.32	18.49	18.49	2.38	0.149
X2*X4	1	162.56	2.82	162.56	162.56	20.90	0.001
X3*X4	1	18.49	0.32	18.49	18.49	2.38	0.149
Error	12	93.32	1.62	93.32	7.78		
Lack-of-Fit	10	93.32	1.62	93.32	9.33		
Pure Error	2	0.00	0.00	0.00	0.00		
Total	26	5766.55	100.00				
Model summary		S	R-sq	R-sq(adj)	press	R-sq(pred.)	
		2.78870	98.38%	96.49%	537.536	90.68%	

Results of ANOVA showed that percent of contribution of phenol concentration is (43.28 %) which means that phenol concentration has the main effect on the COD removal efficiency. While current density has the second effect with a contribution of (24.27 %) followed by pH (10.23%) then rotation speed (1.14 %). It is clear that rotation speed in the present work has the minor effect which means that the system is not under mass transfer conditions it may be under bulk reaction control (reaction of chlorine with water). The main percent of contribution in the model is taken by linear term (78.92%) followed by the square term with percent of contribution 12.09% then 2-way interaction with percent of contribution 7.37 %. The results assured that phenol concentration and current density are the most significant factors in degradation of phenol by indirect oxidation.

3.2 Effect of process variables on the COD removal efficiency

The interactive effect of the selected variables and their effect on the response was estimated via a graphical representation of statistical optimization using RSM. Figures (2-a, 2-b) show the effect of the initial phenol concentration on the removal efficiency of COD for various values of current density (3-15 mA/cm²) at constant rotation (300rpm) and pH (6). Figure 2-a represents the response surface plot while figure 2-b shows the corresponding contour plot. From surface plot, it was observed that, at current density (3 mA/cm²), a sharply decrease in COD removal efficiency occurs as the initial phenol concentration increased from 20 ppm to 100 ppm. However, this decreasing became more sluggish as the current density increased to 15 mA/cm². At phenol concentration of 20ppm, the results showed that removal efficiency of COD is linearly increasing with increasing of current density from 3 to 15 mA/cm². However, at high phenol concentration, this increasing in the removal efficiency of COD became more sluggish. The corresponding contour plot confirms that a maximum value of COD removal efficiency lies in a small area in which the current density ranged between 7.5-15 mA/cm² and phenol concentration between 20-60ppm.

The influence of pH value on the COD removal efficiency for different current density (3-15 mA/cm²) at constant rotation speed of 300 rpm and phenol concentration of 60 ppm is shown in Figures (3-a, 3-b). The response surface plot (Fig. 3-a) shows that COD removal efficiency is linearly increased with decreasing pH (became more acidity) at current density 3mA/cm². Nevertheless, at current density of 15 mA/cm², pH has no important effect on the COD removal efficiency. This is interpreted why the coefficient of pH in the model equation has a positive value with low value of the coefficient (0.05) in comparison with other factors. The reason for such behaviour may be increasing of current density would be led to increasing the rate of reaction the chlorine with water whatever the value of pH, however, at low current density, the reaction rate may govern by type of oxidant at that pH. Hence disinfection is increased at acidic condition because hypochlorous acid is a strong oxidizing agent and would be governed on the reaction [24].The corresponding contour plot (3-b) confirms that a maximum value of the removal efficiency of COD lies in a small area in which the current density ranged between 7.5-15 mA/cm² and pH 3-7.0.

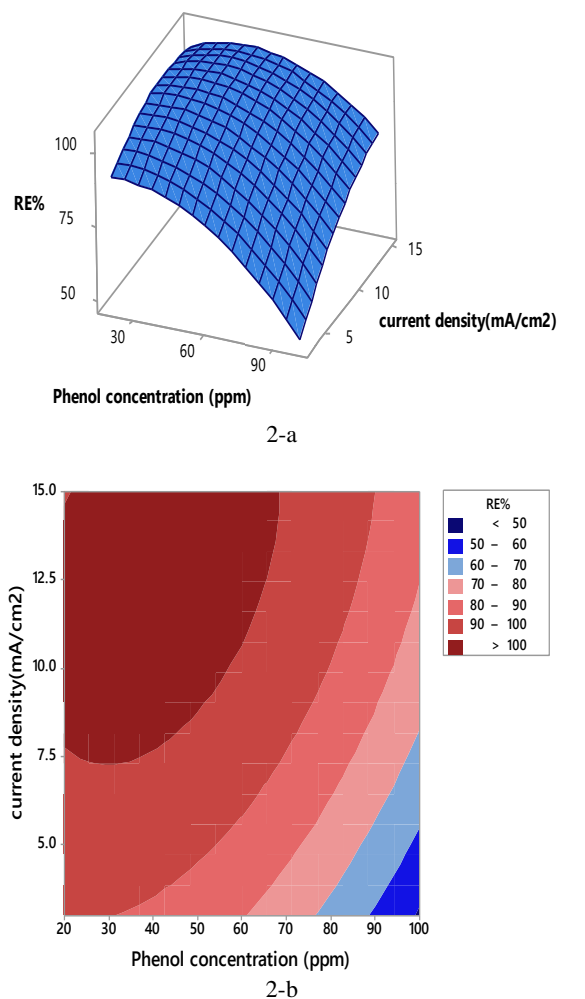
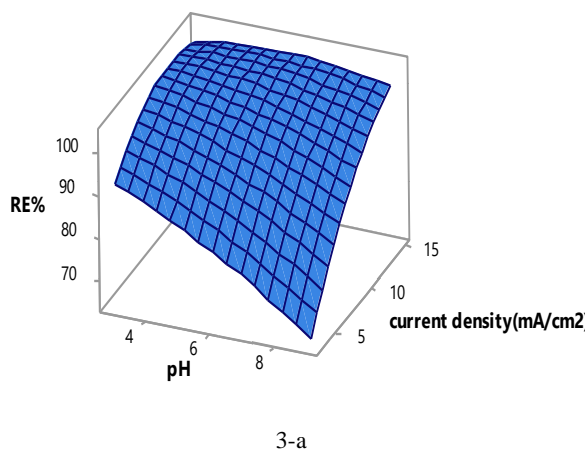


Fig.2. Response surface plot (a) and contour plot (b) for the impact of initial phenol concentration and current density on the efficiency of COD removal (RE%)(Hold values: rotation 300rpm,pH=6



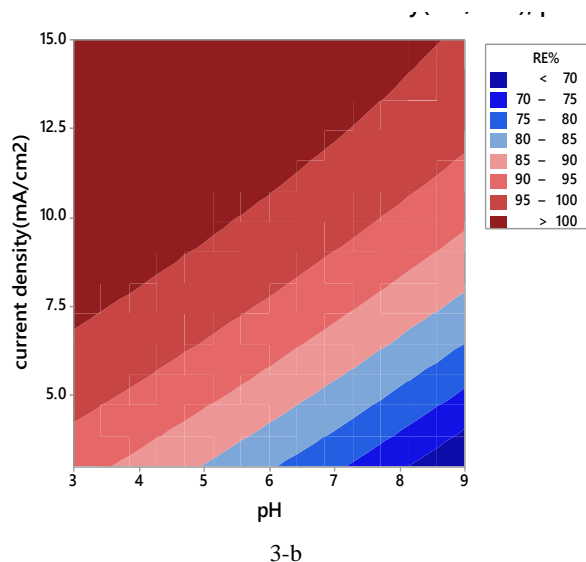


Fig. 3. Response surface plot (a) and contour plot (b) for the impact of pH and current density on the COD removal efficiency (RE%) (Hold values: rotation 300rpm, phenol concentration=60ppm)

Figures (4-a, 4-b) show the impact of rotation on the COD removal efficiency for various values of current density (3-15 mA/cm²) at constant phenol concentration of 60ppm and pH (6). Figure 4-a show that the COD removal efficiency is quickly increased with increasing of rotation speed at low value of current density up to 400rpm then slightly declined. However, this behavior became more sluggish as the current density reach to 15 mA/cm². The corresponding contour plot (4-b) confirms that a maximum value of the COD removal efficiency lies in a small area in which the current ranged between 11-15 mA/cm² and rotation speed range 200-400 rpm. Therefore, it can be seen that the RSM not only gives essential information on the interactions of parameters but also recognizes the feasible optimum values of the studied parameters.

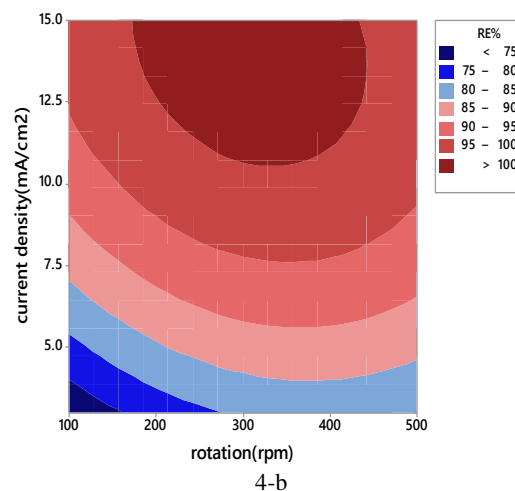
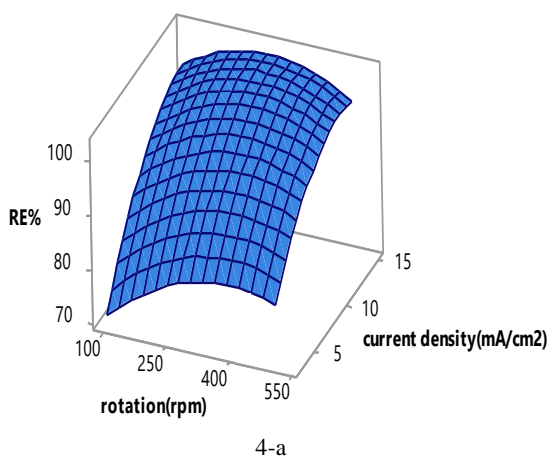


Fig. 4. Response surface plot (a) and contour plot (b) for the impact of rotation and current density on the COD removal efficiency (RE%) (Hold values: phenol concentration=60ppm, pH=6)

3.3 The optimization and confirmation test

Studying any electrochemical removal system claims optimizing of process parameters so as to minimize the losses in energy and consequently the losses in cost of treatment. For optimizing the system, criteria should be subjected to perform the desired objective by finding the specific point that make the function of desirability (D_F) to be maximum via regulating the weight or importance that may change the characteristics of the object. Five options of the variables of target fields were considered: none, maximize, minimize, objective and within the range. The desired objective was established as maximize for regarding to phenol removal. The independent parameters used in this research were recognized within the range of designed levels (current: 3-15 mA/cm², phenol concentration: 20-100 ppm, rotation: 100-500 rpm and pH: 3-9). The goal is designated as 'maximum' with respect of electrochemical removal of phenol with equivalent 'weight' 1.0. The upper limit value was allocated at 100% while the lower limit value of the COD removal efficiency was selected to be 48.6%. Under these settings and boundaries, optimization was performed with the desirability function of (1) leading to results shown in Table 5. As a confirmative step, duplicate experiments were achieved using based on the optimized parameters. The results display in Table 6. After 60 min of the electrolysis, removal efficiency of 99.83 % was achieved in pH=3 is in compactible with the range of the optimum value getting from optimization analysis with desirability function of (1) (Table 5). Therefore, adopting Box- Behnken design in combined with desirability function is successful and efficient in optimizing phenol removal using a tubular packed bed of woven screens rotating electrode.

Table 5

Optimum values of the process factors that maximized COD removal efficiency.

Response	Goal	Lower	Target	Upper	Weight	Importance		
RE (%)	maximum	48.6	Maximum	100	1	1		
Solution: Parameters			Results					
Current density (mA/cm ²)	Rotation (rpm)	Conc. (ppm)	pH	RE (%) Fit	D _F	SE Fit	95% CI	95% PI
9.303	366.667	41.010	3	105.839	1	1.61	(102.32; 109.35)	(98.82; 112.86)

Table 6. Confirmative value of the optimum removal efficiency

Run	Current density (mA/cm ²)	Rotation (rpm)	Conc. (ppm)	pH	E (Volt)	COD (ppm)		RE % at 60 min		CE %	EC (Kwh/kg COD)
						Initial	final	actual	Average		
1	9.3	367	41	3	5.3	118	0.13	99.89	99.83	9.87	179.86
2	9.3	367	41	3	5.25	122	0.27	99.77			

3.4 Comparison with previous works

The optimum conditions revealed that the indirect anodic oxidation of phenol could be performed using rotating tubular packed bed electrochemical reactor with an initial phenol concentration (41 ppm) where COD removal efficiency of 99.83% resulted from decreasing COD from (118ppm) to (0.13ppm) could be achieved at the end of electrolysis time (60 min). In this case, an energy consumption of 179.86kWh/kg COD or 21.2 kWh/m³ is required to deliver current efficiency of 9.87%. In Table 7, we have made an extensive comparison between the present research with other related works for phenol degradation by indirect anodic oxidation process using various types of electrode under several conditions. It is

clear that results of present work give better COD removal efficiency at 60 min starting from a lower concentration of phenol (41ppm) when compared with previous works. This may be interpreted as that the high turbulence generated by rotating electrode led to dissolve more chlorine in water consequently more HOCl production hence more degradation of phenol. Current efficiency is within that reported by previous works. Energy consumption is lower than that reported by previous works[42],[43]

Table 7

Comparison of present work with Literature for indirect anodic oxidation of phenol using different electrodes under various conditions.

Electrode type	Phenol conc.(ppm)	pH	Current density	Time (min)	COD RE (%)	EC (Kwh/Kg COD)	CE (%)	Ref.
Graphite	100	12	10	300	63.5	-----	17	[44]
Ti/TiO ₂ -RuO ₂ -IrO ₂	100	9	7.2	20AhL ⁻¹	82.5	591.8	3.7	[42]
Ti/RuO ₂	100	7	10	60	99	77	10	[17]
Ti/PbO ₂	50	5.5	10	180	91	1196	3.05	[43]
Ti/PbO ₂ -Sn	500	5	10	6AhL ⁻¹	41.2	----	10.3	[45]
Ti/SnO ₂ -Sb ₂ O ₃ -Nb ₂ O ₅ /PbO ₂	500	7	20	120	69	-----	21	[46]
Ti/PbO ₂	250	2	20	300	78	----	10.3	[10]
Graphite	41	3	9.3	60	99.83	179.86	9.8	This work

4. Conclusions

It was established that phenol removal from a simulated wastewater effluent could be performed successfully in a rotating tubular packed bed electrochemical reactor. RSM by BBD shown to be a very valuable and accurate approach for optimizing the

electrochemical oxidation of phenol. High R² value for the regression model equation was revealed by ANOVA analysis confirming high degree of agreement between the the experimental data and quadratic model. The present results confirm that phenol concentration has the main impact on the COD removal efficiency approving that electro oxidation reaction is not under control of mass

transfer. The optimum values of the process parameters were initial phenol concentration of 41.0 ppm, current density of 9.3 mA/cm², rotation speed of 367 rpm, and pH 3. Under these conditions, it was possible to reduce COD from 118 ppm to 0.13ppm (RE=99.89%) in a matter of 60 min in a lower energy consumption of 179.86kWh/kg COD. these results confirm that the effect of promotion turbulence that generate during the rotation of cathode would be led to achieving high mass transfer rate toward the surface of anode.

5. Conflicts of interest

There are no conflicts to declare

6. Acknowledgment

Authors thanks the staff of Chemical Engineering Department, College of Engineering- University of Al-Qadisiyah for the helpful and technical assistance for supporting the research.

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