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OPTIMIZATION OF THE ELECTRO-FENTON PROCESS FOR COD REDUCTION FROM REFINERY WASTEWATER

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Abstract

This study shows the results of the experimental investigation of refinery wastewater treatment by the electro-Fenton process. The experiments were designed using Taguchi design approach with an orthogonal array (OA) of L_{16} runs. Four process variables (current density (CD), temperature (T), Fe^{2+} concentration (Fe^{2+}), and time (t)) at four different levels were considered for the present design. Regression analysis was performed to predict a correlation for the response function (chemical oxygen demand (COD) reduction efficiency) of the treatment process by the electro-Fenton technique. Analysis of variance (ANOVA) was carried out to verify the significant variables that control COD reduction. Moreover, a linear model analysis was implemented for the signal to noise (S/N) ratios with "larger the better" and for means. Based on S/N ratios and means responses, the operating conditions for optimum COD reduction were: CD = 8 mA/cm^2, T = 60°C, Fe^{2+} = 0.4 mM, and t = 6 h, at which 87.35% of COD was reduced. ANOVA shows that the operating temperature had the most significant impact on COD reduction efficiency. The R-square value for the predicted COD reduction correlation was 90.00%. Considering ranks based on delta statistics, the relative magnitude of effects of the process variables were: T, Fe^{2+}, t, and CD.

Key words: COD reduction, electro-Fenton, refinery wastewater, Taguchi method

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1. Introduction

Petroleum refinery effluents (PREs) are highly polluted wastewater; typically, it contains high levels of harmful aromatic and aliphatic contaminants, to a great extent, as same as its concentrations in crude oil (Alkmim et al., 2017; El-Naas et al., 2014; Mohammad et al., 2019). Large volumes of PREs are generated because of high water consumption in the refining process (Abbas A.S. et al., 2016; Coelho et al., 2006). Refinery wastewater are characterized by its priority pollutants because of its toxic and harmful effects on the environment and human beings, and phenols are one of the main important of these contaminants (Abdelwahab et al., 2009).

Even though the recent strict global adjustments and rules to control pollution are highly considered, the need for efficient water treatment technologies becomes essential (Britto-Costa and Ruotolo, 2012). There are many researches on treatment technologies of wastewater, namely: coagulation-flocculation (Ammar and Akbar, 2018; Li et al., 2018; Salehin et al., 2016), adsorption (El-Naas et al., 2010, 2017), membrane (Allami et al., 2018) and electrochemical. Electrochemical treatment processes offer several distinct benefits such as environmentally appropriate, flexibility, energy efficiency, safety, selectivity, proper to automation, and economic (Brillas et al., 2009; Salman et al., 2018).

The electro-Fenton process is one of the most popular electrochemical oxidation processes that is adeptly used to degrade persistent organic molecules in wastewater (Brillas et al., 2009). The power of the electro-Fenton process comes from hydroxyl free radicals ($^{\bullet}OH$) that are generated from the incentive decomposition of hydrogen peroxide (H_2O_2) in the

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presence of an iron salt (Fe^{2+}) in an acidic medium (Moreira et al., 2017). In the electro-Fenton process, Fe^{2+} and H_2O_2 can be generated promptly in the solution. H_2O_2 is produced from the reduction of dissolved oxygen at the cathode (Eq. 1), while Fe^{2+} is generated from reduced ferric cations (Fe^{3+}) as in Eq. (2) or from a sacrificial iron anode (Eq. 3) (Yan et al., 2014).

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

$$Fe^{(3+)} + e^- \rightarrow Fe^{(2+)} \quad (2)$$

$$Fe \rightarrow Fe^{(2-)} + e^- \quad (3)$$

Eq. (4) displays the production of $^{\bullet}OH$ from the reaction of H_2O_2 with Fe^{2+} (Pimentel, 2010). $^{\bullet}OH$ produced from Eq. (4) initialize the devastating oxidation of the organic contaminants (RH) and make highly active organic free radicals ($R^{\bullet}$) (Eq. 5), which are undergone to further oxidation reactions and transformed to more stable products by Fe^{3+} and Fe^{2+}, O_2, $^{\bullet}OH$, and H_2O_2 (Umar et al., 2010).

$$Fe^{(2+)} + H_2O_2 \rightarrow Fe^{(3+)} + {}^{\bullet}OH + OH^- \quad (4)$$

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \rightarrow \text{further oxidation} \quad (5)$$

Many parameters have a great impact on the degradation efficiency of the organic pollutants presented in wastewaters by the electro-Fenton oxidation process (Gökkuş et al., 2017), namely pH, initial wastewater concentration, Fe^{2+} concentration, applied current density, operating temperature, electrode material, and reaction time. The traditional way to verify the effect of a set of parameters on the efficiency, varying one variable at a time and holding the others fixed, does not give satisfying results over a wide range of settings. It takes a long time and high cost before the optimized level of operation is included. Therefore, a design of parameters is essential for experimental work with several inputs. Taguchi's parameter design is frequently and efficiently applied in industry, but it also can be used for scientific research (Jamaludin et al., 2016). The target of Taguchi design consists in making a robust process/or product versus noise parameters (ungovernable or expensive to control factors) by finding out the ideal set of process parameters that optimize the performance (Das et al., 2014).

The present study aims to analyze the effects of the control variables on the COD reduction in wastewater by the electro-Fenton process and identify the ideal set of the variables that maximize the efficiency. Four control factors including temperature (*T*), current density (*CD*), Fe^{2+} concentration (Fe^{2+}), and time (*t*) were selected for our study.

2. Experimental

2.1. Design of experiments

Taguchi experimental design based on the orthogonal array (OA) technique allows examining the effect of several inputs on the response characteristic together with a minimum number of runs (Dean and Unal, 1991). The effect of four process parameters: temperature (30-60°C), current density (2-8mAcm^{-2}), Fe^{2+} concentration (0.05-0.4 mM), and time (1-6 h) were considered. Each of the four control parameters is checked on four levels, as shown in Table 1.

Table 1. Control parameters and their levels

Control parameter	*Levels*			
Temperature, °C	30	40	50	60
Current density, mAcm^{-2}	2	4	6	8
Fe^{2+} concentration, mM	0.05	0.1	0.2	0.4
Time, h	1.5	3	4.5	6

Table 2 shows the layout of L_{16} (4^4) OA used in this study. The notation 4^4 stands for that there were 4 variables and each of them was examined on 4 different levels. Taguchi parameter design was explained to identify the best control parameters levels that gives the optimum output characteristic by performing a linear model analysis for signal-to-noise ratios (S/N) and means and analysis of variance (ANOVA) to find out the statistical significance of each parameter on the output. Moreover, the parameters effects are graphically examined.

Table 2. Layout of L_{16} (4^4) OA

No.	*T, °C*	*Fe^{2+}, mM*	*CD, mAcm^{-2}*	*t, h*
1	30	0.05	2	1.5
2	30	0.1	4	3
3	30	0.2	6	4.5
4	30	0.4	8	6
5	40	0.1	2	4.5
6	40	0.05	4	6
7	40	0.4	6	1.5
8	40	0.2	8	3
9	50	0.2	2	4.5
10	50	0.4	4	6
11	50	0.05	6	1.5
12	50	0.1	8	3
13	60	0.4	2	6
14	60	0.2	4	4.5
15	60	0.1	6	3
16	60	0.05	8	1.5

Regression analysis was also used to bring out a mathematical relation between predictors (process parameters) and the response (percentage of reduced COD). Minitab 19 software (Minitab Inc, 2010) was used to develop the experimental design of Taguchi and to perform the analysis.

2.2. Electro-Fenton oxidation experiments

Degradation of refinery wastewater (COD = 1124 mg/L, TDS = 970 mg/L and pH= 7.4) by the electro-Fenton process was performed in an open, undivided cell with a working volume of 0.5 liter. The anode was MnO_2-graphite electrode (1.5 cm diameter and 6 cm length) prepared in previous work (Abbas Z.I. and Abbas A.S., 2019), while the cathode was a hollow cylindrical graphite electrode (10 cm outside diameter, 8 cm inside diameter and 15 cm length). The anode was fixed at the center of the cathode and rotated at 200 rpm by electrical gearbox (Heidolph Standard, Dual-Range Mixer, with LED 115 VAC). Before electrolysis, compressed air (Resun ACO-001) with a flow rate of 1 L/min was bubbled into the solution for 20 minutes and remained for the whole time of operation for all experiments to ensure O_2 saturation in the electrolysis media. A required catalytic amount (0.05, 0.1, 0.2, and 0.4 mM) of $FeSO_4 \cdot 7H_2O$ (BDH) was added, and the current was remained constant at certain values (2, 4, 6, and 8 mA cm^{-2}).

Experiments were monitored by the DC power supply (UNI-T: UTP3315TF-L) potentiostat/galvanostat that assured the application of different currents. The operating temperature was measured by a mercury thermometer and set to the desired values (30, 40, 50, and 60°C ±1°C) by using hotplate magnetic stirrer (Stuart CB126). The initial pH of solutions was adjusted in a range of 2.8 to 3.0 by the addition of 1 M H_2SO_4 (Thomas Baker). This pH range was chosen to optimize the H_2O_2 production in a medium saturated with dissolved O_2 (Pimentel, 2010). The pH was measured by a pH meter (Basic20) and calibrated with three standard buffers at pH values of 4, 7 and 9. The ionic strength of the solution was maintained constant by adding 50 mM Na_2SO_3 to improve the conductivity. Samples were withdrawn before and after electrolysis, and COD analysis was performed to estimate the degradation efficiency in terms of reduced COD percent. Fig. 1 shows a schematic diagram of the experimental setup.

2.3. Test method: COD analysis

The efficiency of the electro-Fenton process was determined by testing COD of wastewater before and after electrolysis. Collected samples were digested with an oxidizing agent ($K_2Cr_2O_7$) for 120 min at 150°C in (Lovibond COD reactor RD 125).

Digested samples were cooled down to room temperature and further being analyzed in a photometer (MD 200 COD VARIO Photometer).

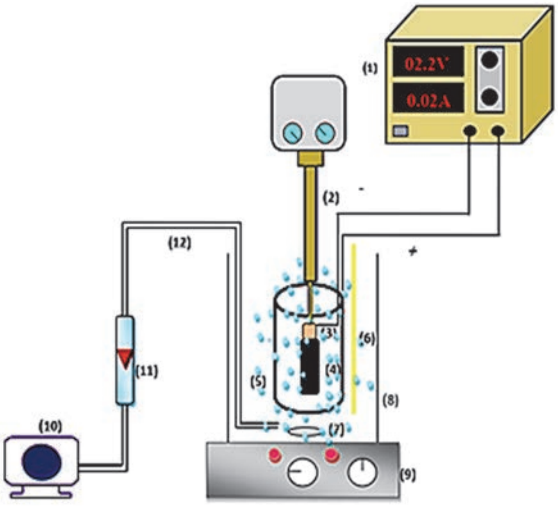

Fig. 1. Schematic diagram of the electro-Fenton oxidation experiments, (1) power supply, (2) electrical gearbox, (3) brass ring, (4) MnO_2 anode electrode, (5) graphite cathode, (6) thermometer, (7) magnetic bar, (8) beaker, (9) hot-plate magnetic stirrer, (10) air pump, (11) flow meter, (12) rubber tube

The *COD reduction* from the treated solution by the electro-Fenton process was evaluated using Eq. (6).

$$\text{COD Reduction (\%)} = \frac{COD_{\circ} - COD_t}{COD_{\circ}}(100) \tag{6}$$

where $COD_{\circ}$ is the initial value of *COD* concentration (in mg/L) at zero time, while COD_t is the value of COD concentration (in mg/L) after *t* time electrolysis.

3. Results and discussion

3.1. Taguchi design analysis for COD reduction

The sets of the process variables in the $L_{16}(4^4)$ standard OA obtained from Taguchi design were implemented and the quality characteristic of the process at each set was evaluated. COD reduction of organics is the quality characteristic of the electro-Fenton process and it was estimated from Eq. (6) and recorded in Table 3.

Taguchi method anticipates the signal to noise (S/N) ratios to recognize control parameters levels that minimize the variance of the response induced by noise factors. The S/N ratio is the desired output value (mean of the output) to the undesired value (standard deviation of the output), the noise is the undesired value. There are three types of S/N ratios: the larger the better (LTB), the nominal the better (NTB), and the smaller the better (STB). The choice of S/N type depends on the experimental goal and on the desired quality characteristic of the process. To maximize the COD reduction efficiency, the larger the better (LTB) S/N ratio type was chosen (Eq. 7). The standard formula for evaluating this response is:

$$\left(\frac{S}{N}\right)_i = -10\log\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_{ij}^2} \quad (7)$$

where Y_{ij} is the measured value of the process response for i^{th} trail and j^{th} run, while n is the number of duplications (Chaulia and Das, 2008). In general, for any *S/N* ratio formula, the highest *S/N* ratio represents the best results (Nandhini et al., 2014).

Table 3 presents the Taguchi parameters design with the experimentally obtained responses (COD reduction) and *S/N* ratios.

3.2. Linear model analysis

The linear model analysis provides coefficients for each parameter measured at (No. of levels minus 1) p-values, t-values. These outcomes are necessary to examine the statistical significance of each parameter to the response and the order of effectiveness of each factor on the process response.

3.2.1. Linear model analysis for means and S/N ratios

The order of the coefficients by absolute value signifies the relative strength of the relationship between process response (reduced COD) and process parameters (T, CD, Fe^{2+}, and t). Each coefficient describes the size and direction of the relationship between the response and the parameter. Tables 4 and 5 show the estimated model coefficients (Coeff.) for *S/N* ratios and means at no of levels-1.

Linear model analysis by Taguchi experimental design for COD degradation is carried out with a 'larger the better' approach for the *S/N* ratios (Eq. 7). *S/N* ratios against T, CD, Fe, and t gave details of the main effects plot for *S/N* ratios as in Fig. 2, which displays the main effects plot for *S/N* ratios in the assessment of COD reduction. Maximum COD reduction achieved at a parameter level that possesses the highest value for the *S/N* ratio.

The combination of (T = 60°C, CD= 8 mAcm^{-2}, Fe^{2+} = 0.4mM, and t = 6 h) parameters gave the highest COD reduction of 87.35%. Fig. 3 presents the main effects plot for means. Analysis for means showed that the values for means displayed the same order of significance of the process variables that noticed in the *S/N* ratios.

Table 3. Taguchi parameter design of $L_{16}(4^4)$ standard orthogonal array with responses and *S/N* ratios corresponding to each parameter sets

No.	***T, °C***	***Fe^{2+}, Mm***	***CD, mAcm^{-2}***	***t, h***	***Reduced COD, %***	***(S/N)***
1	30	0.05	2	1.5	24.47	30.046
2	30	0.1	4	3	32.96	30.361
3	30	0.2	6	4.5	38.41	31.689
4	30	0.4	8	6	53.79	34.614
5	40	0.1	2	4.5	49.17	33.833
6	40	0.05	4	6	52.32	34.374
7	40	0.4	6	1.5	59.77	35.530
8	40	0.2	8	3	52.73	34.441
9	50	0.2	2	4.5	57.74	35.825
10	50	0.4	4	6	46.91	36.312
11	50	0.05	6	1.5	47.13	35.354
12	50	0.1	8	3	41.36	34.277
13	60	0.4	2	6	69.39	36.826
14	60	0.2	4	4.5	61.97	35.844
15	60	0.1	6	3	66.96	36.516
16	60	0.05	8	1.5	66.23	36.422

Table 4. Estimated model coefficients for *S/N* ratios

Term	***Coeff.***	****SE Coeff.***	***t-value***	***p-value***
Constant	34.5164	0.1420	243.051	0.000
temp 30	-2.8391	0.2460	-11.542	0.001
temp 40	0.0281	0.2460	0.114	0.916
temp 50	0.9254	0.2460	3.762	0.033
CD 2	-0.3836	0.2460	-1.560	0.217
CD 4	-0.2939	0.2460	-1.195	0.318
CD 6	0.2558	0.2460	1.040	0.375
Fe 0.05	-0.4677	0.2460	-1.902	0.153
Fe 0.10	-0.7696	0.2460	-3.129	0.052
Fe 0.20	-0.0668	0.2460	-0.271	0.804
time 1.5	-0.5924	0.2460	-2.408	0.095
time 3.0	-0.2710	0.2460	-1.102	0.351
time 4.5	0.0475	0.2460	0.193	0.859

Note: SE Coeff. is the standard error of a model's coefficients*

Table 5. Estimated model coefficients for means

Term	*Coeff.*	**SE Coeff.*	*t-value*	*p-value*
Constant	54.5655	0.6321	86.319	0.000
temp 30	-15.3275	1.0949	-13.999	0.001
temp 40	-1.0684	1.0949	-0.976	0.401
temp 50	4.8220	1.0949	4.404	0.022
CD 2	-1.5178	1.0949	-1.386	0.260
CD 4	-1.4015	1.0949	-1.280	0.291
CD 6	1.3625	1.0949	1.244	0.302
Fe 0.05	-2.3366	1.0949	-2.134	0.123
Fe 0.10	-4.3576	1.0949	-3.980	0.028
Fe 0.20	-0.8290	1.0949	-0.757	0.504
time 1.5	-3.2474	1.0949	-2.966	0.059
time 3.0	-1.1515	1.0949	-1.052	0.370
time 4.5	0.2370	1.0949	0.216	0.843

*Note: *SE Coeff. is the standard error of model's coefficients*

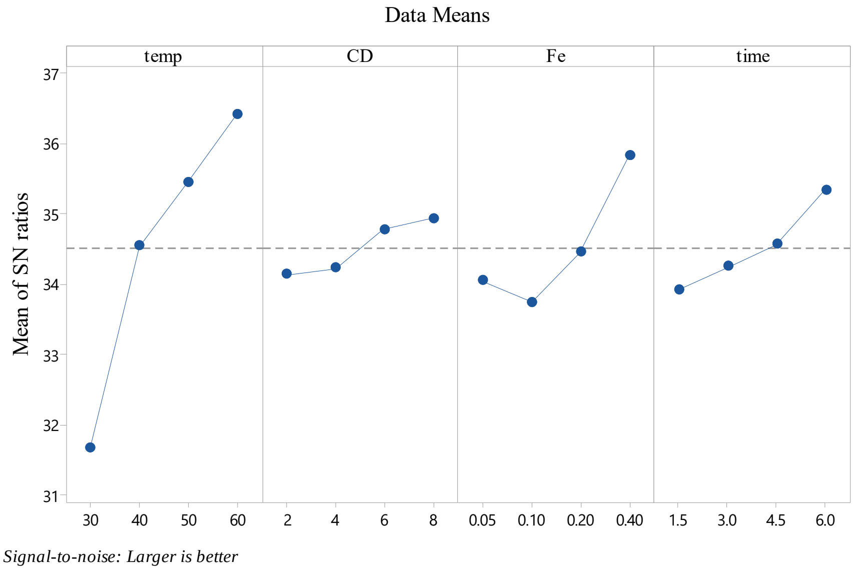

Fig. 2. Main effects plot for S/N ratios

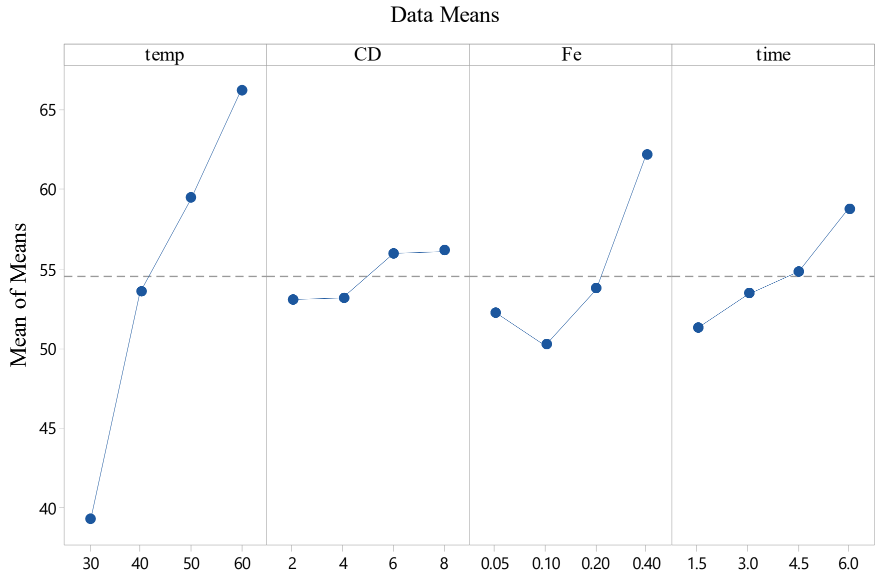

Fig. 3. Main effects plot for means

3.2.2. Analysis of variance for means and S/N ratio

Analysis of variance (ANOVA) was evaluated for *S/N* ratios and means for the process quality characteristic under study. The sequential sum of squares (Seq SS) and an adjusted sum of squares (Adj SS) in the ANOVA table showed the relative importance of each parameter. The main outcomes of an ANOVA study record the sources of variation, degrees of freedom for each source, a total sum of squares, and mean squares. Moreover, f-statistics and p-values obtained from ANOVA study, are used to determine whether the parameters are statistically significant.

Below, there is an explanation of each element listed in ANOVA Table:

- Source: refers to the source of variation which can be attributed to the factor, the interaction, or the error, while the total is a sum of all the sources.

- DOF: for each source in the ANOVA table, the degree of freedom is evaluated, and it is equal to the No. of parameters minus 1. Since the parameters are four, thus, the DOF is 3.

- SS: the sum of squares between groups (parameters) and the sum of squares within groups (error).

- MS: a mean square of each source is the quantity obtained from the division of the sum of squares on the degrees of freedom.

- F-value: it is calculated as (variance in the mean square between groups (MS)/mean of the within-group variance (error MS)); comparing the obtained F value with a critical one allows the determination of the statistical significance of each source; also, we can use p-value for this target.

- p-value: it is used to define the statistical significance of each factor; typically compared with a chosen alpha value.

Tables 6 and 7 show that the highest sum of squares (SS) value belonged to temperature 'T' and it had the greatest effect on the COD reduction. Based on p-values presented in tables below, the statistical significance of each variable is *T*, *Fe*, *t*, and *CD*. The variable *T* was the most significant, while the variable *CD* was the least significant in estimating COD reduction values and each variable possesses 3 DOF with 15 degrees of freedom for the full set of variables.

3.2.3. Response characteristic of means and S/N ratios

The responses for *S/N* ratios and means in Tables 8 and 9 present the average of the response characteristic for each parameter at each level and the ranks based on Delta statistics, which compare the relative magnitude of effects. The Delta statistic is the highest minus the lowest average for each factor. Ranks based on Delta values are as follows: rank 1 to the highest Delta value, rank 2 to the second-highest, and so on.

The *S/N* ratios and means of each level in the response Tables 8-9 are used to decide which level of each factor gives the best result. Based on the large the better, the results indicated that the best results are obtained at the fourth level of each parameter.

Table 6. ANOVA for *S/N* ratios

Source	*DOF*	*Seq SS*	*Adj SS*	*Adj MS*	*F*	*p*
T	3	49.8919	49.8919	16.6306	51.54	0.004
CD	3	1.9074	1.9074	0.6358	1.97	0.296
Fe	3	10.0641	10.0641	3.3547	10.40	0.043
t	3	4.3689	4.3689	1.4563	4.51	0.124
Residual Error	3	0.9680	0.9680	0.3227	---	---
Total	15	67.2004	---	---	---	---

Table 7. ANOVA for Means

Source	*DOF*	*Seq SS*	*Adj SS*	*Adj MS*	*F*	*p*
T	3	1573.13	1573.13	524.377	82.02	0.002
CD	3	34.19	34.19	11.397	1.78	0.323
Fe	3	326.93	326.93	108.978	17.05	0.022
t	3	116.99	116.99	38.998	6.10	0.086
Residual Error	3	19.18	19.18	6.394	---	---
Total	15	2070.43	----	----	----	---

Table 8. Response table for *S/N* Ratios *(Larger is better)*

Level	*T*	*CD*	*Fe*	*t*
1	31.68	34.13	34.05	33.92
2	34.54	34.22	33.75	34.25
3	35.44	34.77	34.45	34.56
4	36.40	34.94	35.82	35.33
Delta	4.72	0.81	2.07	1.41
Rank	1	4	2	3

Table 9. Response table for Means

Level	*T*	*CD*	*Fe*	*t*
1	39.24	53.05	52.23	51.32
2	53.50	53.16	50.21	53.41
3	59.39	55.93	53.74	54.80
4	66.14	56.12	62.09	58.73
Delta	26.90	3.07	11.88	7.41
Rank	1	4	2	3

Table 10. Coefficients

Term	*Coeff.*	*SE Coeff.*	*95% CI*	*t-Value*	*p-Value*	*VIF*
Constant	23.65	3.26	(16.56; 30.75)	7.26	0.000	
T*T	0.00925	0.00119	(0.00665; 0.01185)	7.75	0.000	1.35
T*t	0.0336	0.0134	(0.0045; 0.0627)	2.51	0.027	1.29
CD*Fe	5.72	1.28	(2.94; 8.50)	4.48	0.001	1.08

Table 11. Analysis of variance

Source	*DOF*	*Seq SS*	*Contribution*	*Adj SS*	*Adj MS*	*F-Value*	*p-Value*
Regression	3	1863.41	90.00%	1863.4	621.14	36.00	0.000
T*T	1	1428.40	68.99%	1036.4	1036.39	60.08	0.000
T*t	1	89.16	4.31%	109.1	109.12	6.32	0.027
CD*Fe	1	345.85	16.70%	345.9	345.85	20.05	0.001
Error	12	207.02	10.00%	207.0	17.25		
Total	15	2070.43	100.00%				

S	**R-sq*	*R-sq(adj)*	*PRESS*	***R-sq(pred)*
4.15351	90.00%	87.50%	400.929	80.64%

*Note: *R-sq: the correlation coefficient (R^2), **R-sq (pred.): the predicted correlation coefficient (pred. R^2)*

3.3. Regression analysis

Regression analysis implies modeling of a mathematical relationship between one or multiple continuous predictors (process variables) and one response (reduced COD). The obtained mathematical relationship is further applied to estimate new observation. The method of the least squares was used in the analysis to estimate the regression equation. The main outputs from regression analysis are regression equation, table of coefficients, and an ANOVA table, which explain the statistical significance, the size and the direction of the relationship between the variables and the process response.

The direction of the relationship between the variables and the response is denoted by the sign of each coefficient. Coefficients are those numbers in the regression model by which the variables (predictors) are multiplied and each one estimates the change in the mean response per unit change in a predictor while other predictors held constant. For each coefficient there is an estimated p-value which examines the null hypothesis, i.e., coefficients had none effect and are equal to zero. The regression equation for the reduced COD is given in Eq. (8).

$$COD\ reduction\ efficiency, \% = 23.65 + 0.00925 \cdot T^2 + 0.0036 \cdot T \cdot t + 5.72 \cdot CD \cdot Fe \quad (8)$$

The regression results from Table 10 indicated that all terms presented in the model are statistically significant because of their low p-values (< 0.05). Significant interaction terms (T^2, $T \times t$, and $CD \times Fe$) implies that the relation between a predictor (eg. T in $T \times t$) and the response depends on the other predictor in the term (in case, t). A goodness-of-fit test is an important implement to verify if the model provides enough fit to the data. The obtained model describes 90% (R^2) of the observed data and predicts new observations with a predicted R^2 (R-squared) of 80.64%.

Table 11 shows the ANOVA for reduced COD based on the regression correlation developed. Regression has the greatest impact on the model; it has the largest contribution (90%). The order of impact for the sources presented was: *Regression* > $T \times T$ > $T \times t$ > $CD \times Fe$ > *Error*, with a total DOF of 15. The residual plot used to determine the adequacy of the obtained model meet the assumption of the analysis (residuals are random and normally distributed). The various plots 'histogram of residuals', 'normal probability plot', 'residual fit' and 'residual order' (Minitab Inc., 2000) are shown in Fig. 4.

The Normal probability plot (Fig. 4a) shows that residuals are normally distributed. If the residuals are normally distributed, the points should generate a straight line. The normality assumption may be invalid since the points on the plot depart from a straight line. The normal probability plot of a dataset comprising less than fifty observations shows a curvature in tails even though the residuals are randomly distributed. Nonlinearity and a significant variance may be observed with a small number of observations, although the residuals are normally distributed.

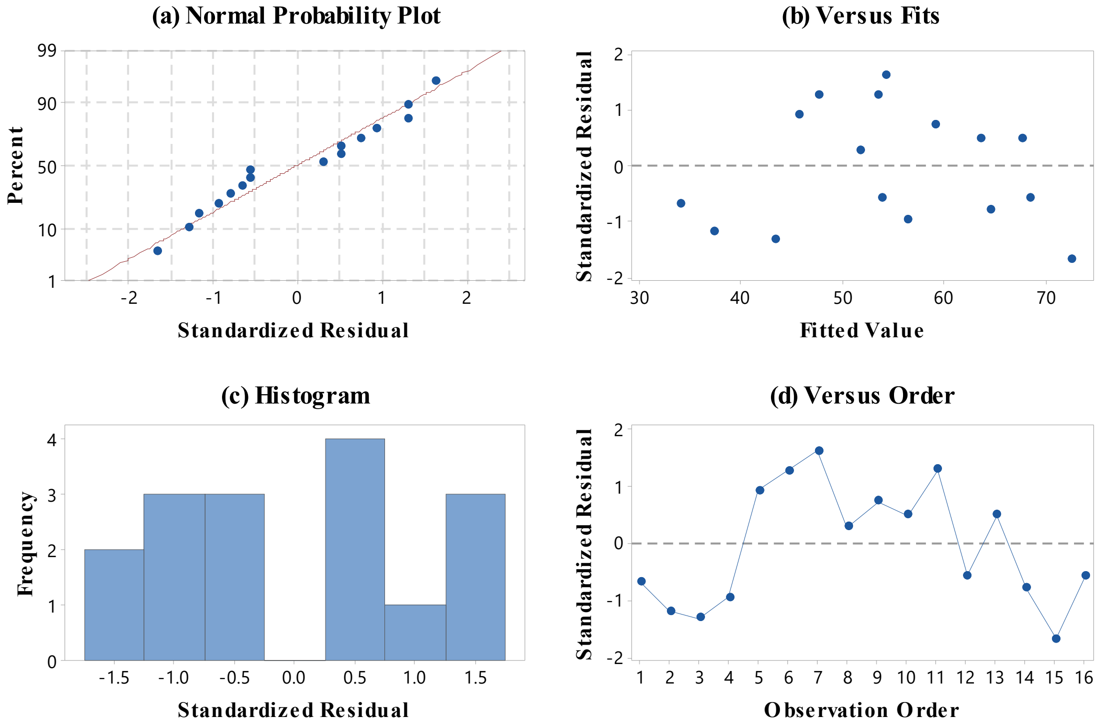

Fig. 4. Residual plots for COD reduction: (a) Normal probability plot, (b) Residual versus fit, (c) Residual versus order, (d) Residual versus order

In residuals versus fit (Fig. 4b), residuals lie in a random pattern around zero-line. In this plot, residuals must be randomly distributed around zero-line. An outlier may be recognized if a point located away from many points. Moreover, residuals should not exhibit any remarkable patterns. The following may refer to an error that is not random:

- An increasing or decreasing set of points.
- Domination of positive or negative residuals.
- Patterns, for example, decreasing residuals with decreasing fits.

Clusters around zero value occurred in the histogram (Fig. 4c) and that may indicate that the residuals are not normally distributed, but histogram pattern alone is not enough to make such a decision since the normal probability plot and residual versus fit indicated that residuals are normally distributed. The histogram plots should display a normal distribution of the observed response around a mean value equal to zero. Because the appearance of the histogram changes based on the number of intervals used to group the observations, the normal probability plot and goodness-of-fit tests are used to determine the normality of the residuals.

In residuals versus order (Fig. 4d), residuals are independent and have no detected manner. Plotting residuals versus the order of the collected data give an insight on whether the responses can be considered independent of each other. Independent residuals have no trend when displayed in time order. Ideally, residuals should fall randomly around centerline.

4. Conclusions

The effect of process variables on reduced COD in refinery wastewater by the electro-Fenton process was checked out using Taguchi experimental design. The experimental design was employed using the L_{16} OA technique. Four process variables on four levels, namely temperature, current density, Fe concentration and time, were selected to examine their effects on the output characteristic.

The optimum set of process variables was specified from a linear model analysis for *S/N* ratios and means. The ideal set was: temperature of 60 °C, the current density of 8 mAcm^{-2}, Fe concentration of 0.4mM, and the time of 6 h. Within the selected process variables, the temperature was determined to be the control variable that has a pronounced effect on the output characteristic, i.e. reduced COD. The optimum value of COD degradation efficiency from refinery wastewater by the electro-Fenton process for a 95% confidence interval (CI) was found to be 87.35% (± 3.5%).

The findings in this work are of great importance, which explains how each variable affects the reduction of COD from refinery wastewater by the applied electro-Fenton technique using MnO_2 anode, toward making process control having the desired variables settings.

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