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# Employing Fenton-like process for the remediation of petrochemical wastewater through Box–Behnken design method

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ABSTRACT

In this study, the wastewater of special economic zone petrochemical plant in Iran was re-mediated through Fenton-like method using $FeCl_3$ and hydrogen peroxide. The Box-Behnken design was employed to decrease the amounts of experiments and to perform the statistical exploration of the results. The purpose of this project was to decrease the chemical oxygen demand (COD) of petrochemical wastewater and optimize the COD removal. The effects of operating parameters such as pH, hydrogen peroxide and Iron (III) ion concentration were inspected. The optimal conditions predicted by the model were as the following: $[Fe^{3+}]$ = 1.76 mM, pH at 5.63, and $[H_2O_2]$ = 17.86 mM. The maximum efficiency in the removal of COD by the experiment and model were 72.06% and 74.9%, respectively. Furthermore, other pollutant characteristics including total organic carbon (TOC), biological oxygen demand (BOD), and total dissolved solids (TDS) were decreased considerably.

*Keywords:* Special economic zone petrochemical; Fenton-like process; Advanced oxidation process; COD removal; Box-Behnken design

## 1. Introduction

Nowadays, due to the severe rules, standards, and environmental distresses, a broad area of research has been concentrated on promoting present water treatment methods and developing more economical approaches that can efficiently re-mediate poisonous and resistant organic pollutants from wastewater. The classical wastewater treatment methods involve conventional physical, chemical and biological methods; however each of them has some limitations such as working costs, secondary contamination, and lengthy treatment times. Therefore, using new techniques minus these deficiencies is essential. Advanced oxidation processes (AOPs) create robust oxidizing groups like hydroxyl radicals, which can be extensively applied to remove organic impurities that are problematic to remove over biological approaches [1–2].

Various AOPs are used for the remediation of wastewater containing organic pollutants. For example, heterogeneous photo-catalytic reaction over $TiO_2$ [3,4], ozonation [5,6], UV/$H_2O_2$ [7], photo-Fenton, and Fenton methods [8] have been used for this purpose.

While the Fenton method has been explored and used widely in wastewater treatment, but it has some difficulties such as great working cost, narrow optimum pH range, great volume of the iron slurry formed, and problems with recovering of the homogeneous catalyst ($Fe^{2+}$) [9]. The $Fe^{3+}$ salt which is used in Fenton-like process is of lower cost compared to $Fe^{2+}$. Thus Fenton-like process has been considered in some researches. In order to overcome these deficiencies, considerable attention has been devoted to upgrade the Fenton procedure. Pliego et al. suggested various approaches which can increase the efficiency of

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Fenton-like process such as radiation, heterogeneous catalysts, and electro chemistry [10]. Using Fenton like process for the remediation of petroleum refinery wastewater was inspected by Basheer Hasan et al. [11].

Other kinds of homogeneous and heterogeneous catalysts were employed as Fenton-like system to exchange $Fe^{2+}$, involving $Fe^{3+}$ [12], $Cu^{2+}/Cu^{+}$ [13], schorl [14], and nano zero-valent iron [15].

The major distinction between the homogeneous and heterogeneous Fenton-like methods includes the various sites that the catalytic reactions happen. In the homogeneous method, the reactions take place in the entire liquid phase, but in the heterogeneous ones, the catalytic route occurs on the surface of the catalyst. One of the critical issues in the heterogeneous method is the adsorption and diffusion of $H_2O_2$ and other reagents into the catalyst surface [16,17].

There are several statistical soft wares to design the experiments and statistically analyze the results such as Design Expert, Minitab and R software [18–20]. However, in this research, the Box-Behnken response surface methodology was applied to design the experiments. The results were statistically analyzed using Design Expert software (version 11).

In our previous work, the wastewater of oil refinery was treated by photo Fenton method [21]. However, in this study, the wastewater obtained from one of the units in Special Economic Zone petrochemical Company in Iran, was treated by Fenton-like procedure. It comprises a blend of aromatic and aliphatic hydrocarbons with varied portions. The effect of different variables such as pH, Ferric ion and hydrogen peroxide concentrations on COD reduction was investigated.

## 2. Materials and methods

### 2.1. Materials

The wastewater samples were provided through one of the subset companies of Special Economic Zone petrochemical in Iran and conveyed to laboratory and kept at 4°C. Chemical reactants used for the catalytic experiments were iron (III) chloride, $FeCl_3$ (30% (w/w) as a source of iron (III) ions), hydrogen peroxide solution (30% w/w), which were both obtained from Merck Company. $MnO_2$ (≥ 99%), hydrochloric acid (37%), and caustic soda (>97%) were supplied by Sigma-Aldrich Company.

### 2.2. Experimental setup and procedure

The tests were performed in a one-liter glass photo reactor. The reactor was prepared with a sampling port (Fig. 1). In this study the UV lamp was switched off along all experiments. The reactor had a water casing with an exterior flow, adjusted by a thermostat to regulate the temperature at 25°C. The thermo bath, from Korean Company (BW 20G) was utilized for temperature control of the reaction medium. The solution was mixed by a stirrer to prevent the settling of Ferric ions and keeping the solution to be homogenized in the reactor. A pH meter, PT-10P Sartorius Instrument, from Germany Company was applied to regulate the primary pH of the wastewater. To control the amounts of

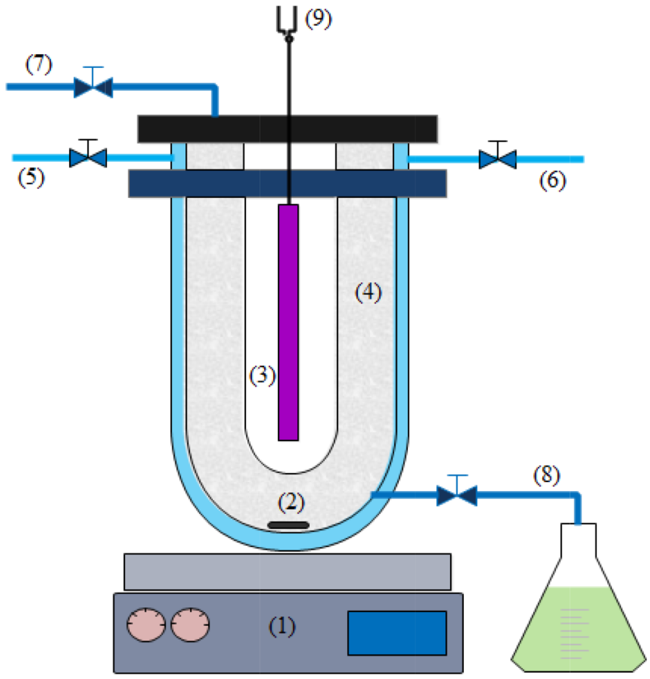


Fig. 1. Graphical diagram of the experimental reactor system: (1) Magnetic stirrer, (2) Magnetic stirrer bar, (3) UV lamp (it was switched off in this work), (4) Glass reactor, (5) Cooling water supply, (6) Cooling water return, (7) wastewater inlet, (8) Treated wastewater, (9) Electrical connection.

COD removal, the samples were analyzed by a spectrophotometer (DR 5000, Hach, Jenway, USA) at 600 nm and the COD was monitored using standard methods reported in the literature [22].

About 1000 ml of the industrial wastewater was tested for each run. Before each test, some impurities were removed by sedimentation and filter paper to avoid the reactor from clogging. Table 1 shows the characteristics of wastewater, containing TDS, TOC, BOD, COD, pH, and conductivity. The reaction time was lasted for 70 min in all runs. The $BOD_5$ to COD ratio in the original wastewater was about 0.33 (Table 1) which implies that biological process is inappropriate for treatment of such a wastewater sample. The COD removal percent was calculated by the following equation:

Table 1
The wastewater properties in special economic zone petrochemical company

| Property | Unit | Results | |
|---|---|---|---|
| | | Before treatment | After treatment |
| TDS | ppm | 1100 | 250 |
| TOC | ppm | 630 | 200 |
| $BOD_5$ | ppm | 700 | 300 |
| COD | ppm | 2100 | 585 |
| pH | – | 9 | 6.0 |
| Conductivity | µS/cm | 800 | 350 |

$$\text{COD Removal efficiency}(\%) = \left(\frac{COD_0 - COD_t}{COD_0}\right) \times 100 \quad (1)$$

where $COD_0$ and $COD_t$ denote $COD$ values before treatment and treatment at any time $t$, respectively. The remaining amounts of hydrogen peroxide in the samples, was removed by $MnO_2$ powder to avoid interfering with COD analysis. The samples were sieved to separate $MnO_2$ precipitates [23].

### 2.3. Experimental design and statistical analysis

The Box-Behnken experimental design approach was employed to optimize the percentage of COD removal from the typical industrial wastewater. The influence of hydrogen peroxide dosage ($C_{HP}$), the concentration of Ferric ion ($C_F$), and acidity ($pH$) on the COD removal were explored. The input variables ($C_{HP}$, $C_F$, and $pH$), and their values were presented in Table 2.

The Box-Behnken experimental design needs a limited number of tests compared to the other response surface methodologies (RSM) [24]. The following model (Eq. (2)) was proposed for the response function ($Y$) as a polynomial equation of independent variables

$$Y = b_0 + \sum b_i x_i + \sum\sum b_{ij} x_i x_j + \sum\sum b_{ii} x_i^2 + \varepsilon \quad (2)$$

where ε is the residue of the equation, $b_O$ is a constant number, $b_i$ is the slope of the variable, $b_{ii}$ is the quadratic coefficient ($i$ = 1,2,3,), $b_{ij}$ is a linear relations between the input parameters of $x_i$ and $x_j$ ($i = 1,2$ and $j = 1,2,3$). Analysis of variance (ANOVA) was employed to investigate the importance of each parameter in Eq. (2) [25]. In the ANOVA, the level of importance or $p$-value was fixed at 0.05. The arithmetical importance of the second-order models was defined by $F$-value. When the calculated $F$-value is greater than the $F$-value in the table, the $p$-value will be much smaller; it designates the significance of the statistical model. The calculated $F$-value is obtained by dividing the mean squares of regression (including square, linear , and interaction) by the mean squares of residual as the following equation [26]:

$$F-\text{value} = \frac{MS_{Reg.}}{MS_{Res.}} = \frac{\frac{SS_{Reg.}}{DF_{Reg.}}}{\frac{SS_{Res.}}{DF_{Res.}}} \quad (3)$$

The residual degrees of freedom ($DF_{Res.}$) is the entire degrees of freedom minus the regression degree of freedom

Table 2
The range and levels of variables

| Variables | Symbol | Range and levels | | |
|---|---|---|---|---|
| | | –1 | 0 | +1 |
| Ferric (mM) | $C_F$ | 0.8 | 1.6 | 2.4 |
| Hydrogen peroxide (mM) | $C_{HP}$ | 8 | 16 | 24 |
| pH | pH | 3 | 6 | 9 |

and regression degree of freedom ($DF_{Reg}$) is the number of terms minus one [27]. The design involved 15 experiments (13 runs and 2 replicates at the central point); The COD removal percent as well as the value predicted by the model were presented at Table 3. In order to determine the contribution of each factor and interaction, the percent contribution was calculated using Eq. (4):

$$\text{Percent Contribution}(\%) = \frac{SS_F}{SS_T} \quad (4)$$

where $SS_F$ is the sum of squares of a factor and $SS_T$ is the total sum of squares of all variables.

## 3. Results and discussion

### 3.1. Modeling and optimization of COD removal in Fenton-like process

In this project, the influence of three independent variables on the response function was inspected using the BBD and RSM, to get the optimal conditions. The calculated relation between the response and three significant variables is considered by a quadratic polynomial equation. The relation for the degradation of COD is presented as the following equation:

$$\begin{aligned} \text{Removal of COD}(\%) &= -46.23333 + 39.51042X_{C_F} \\ &+ 2.09948X_{C_{HP}} + 23.04028X_{C_{pH}} - 10.89193X_{C_F}^2 \\ &- 0.062435X_{C_{HP}}^2 - 2.11065X_{C_{PH}}^2 - 0.078125X_{C_F}X_{C_{HP}} \\ &+ 0.020833X_{C_F}X_{C_{PH}} + 0.042708X_{C_{HP}}X_{C_{PH}} \end{aligned} \quad (5)$$

Table 3
Experimental design for three autonomous variables and their responses.

| Run No. | Manipulated variables | | | Removal of COD, % | |
|---|---|---|---|---|---|
| | $X_{C_{HP}}$ | $X_{C_F}$ | $X_{pH}$ | Exp. | Pred. |
| 1 | 8 | 2.4 | 6 | 60.9 | 61.76 |
| 2 | 16 | 1.6 | 6 | 71.4 | 71.27 |
| 3 | 8 | 1.6 | 9 | 40.5 | 40.68 |
| 4 | 16 | 2.4 | 3 | 53.5 | 52.79 |
| 5 | 24 | 1.6 | 9 | 46.3 | 46.45 |
| 6 | 24 | 0.8 | 6 | 60.7 | 59.84 |
| 7 | 8 | 0.8 | 6 | 56 | 55.11 |
| 8 | 24 | 1.6 | 3 | 54 | 53.83 |
| 9 | 16 | 1.6 | 6 | 70.3 | 71.27 |
| 10 | 16 | 2.4 | 9 | 44.5 | 43.46 |
| 11 | 16 | 1.6 | 6 | 72.1 | 71.27 |
| 12 | 8 | 1.6 | 3 | 52.3 | 52.15 |
| 13 | 16 | 0.8 | 3 | 46.2 | 47.24 |
| 14 | 16 | 0.8 | 9 | 37 | 37.71 |
| 15 | 24 | 2.4 | 6 | 63.6 | 64.49 |

The importance of the coefficients is presented in Table 4. The Model F-value of 120.84 recommends that the model is important. There is just 0.01% chance that this large F-value could happen owing to noise. The P-values less than 0.0500 designate the significance of model terms. The amounts larger than 0.1000 indicate that the model terms are not significant. The linear terms; $C_{HP}$, $C_F$, $pH$, and their quadratic terms have a $p$-value of less than 0.01, therefore they are very significant. However, the term of the binary interaction between the variables has a $p$-value of higher than 0.05, which implies that the interaction of variables is insignificant. In order to improve the model, the insignificant terms were removed as shown in Table 5. Furthermore, percent contribution of each factor as calculated by Eq. (4) is provided in the table. The Pareto chart of the percent contribution of each effect is represented in Fig. 2.

As seen in Table 5 and Fig. 2, the highest contributions are devoted to the quadratic terms "$C^2$" and "$B^2$", respectively. The most effective linear factor on the response is pH which is followed by ferric concentration.

Table 4
ANOVA experiments for quadratic models in the reduction of COD by Fenton-like method

| Sources | DF | SS | MS | F-value | P-value |
|---|---|---|---|---|---|
| Model | 9 | 1736.67 | 192.96 | 120.84 | < 0.0001 |
| Linear | 3 | 269.25 | 269.25 | 168.62 | 0.0103 |
| $X_{C_{HP}}$ | 1 | 27.75 | 27.75 | 17.38 | 0.0087 |
| $X_{C_F}$ | 1 | 63.84 | 63.84 | 39.98 | 0.0015 |
| $X_{pH}$ | 1 | 177.66 | 177.66 | 111.26 | 0.0001 |
| Square | 3 | 1570.77 | 1570.77 | 983.64 | 0.0019 |
| $X_{C_F}^2$ | 1 | 179.42 | 179.42 | 112.36 | 0.0001 |
| $X_{C_{HP}}^2$ | 1 | 58.95 | 58.95 | 36.92 | 0.0017 |
| $X_{C_{pH}}^2$ | 1 | 1332.34 | 1332.34 | 834.36 | < 0.0001 |
| 2-Way interaction | 3 | 5.21 | 5.21 | 3.2624 | 1.5703 |
| $X_{C_F}X_{C_{HP}}$ | 1 | 1.0000 | 1.0000 | 0.6262 | 0.4646 |
| $X_{C_F}X_{PH}$ | 1 | 0.0100 | 0.0100 | 0.0063 | 0.9400 |
| $X_{C_{HP}}X_{C_{PH}}$ | 1 | 4.20 | 4.20 | 2.63 | 0.1657 |
| Lack of fit | 3 | 6.34 | 2.11 | 2.57 | 0.2928 |
| Pure error | 2 | 1.65 | 0.8233 | | |
| Total | 14 | 1744.66 | | | |
| Model Summary | S | $R^2$ | $R_{adj}^2$ | $R_{pred}^2$ | Adequate Precision |
| | | 0.9954 | 0.9872 | 0.9398 | 32.5209 |

The "Lack of Fit tests" matches residual error with "Pure Error" from replicated design points, If there is significant lack of fit, as depicted by a low probability value ("Prob > F"). As represented in the table, the lack of fit was not important compared to the pure error since its p-value (0.3296) was higher than 0.05, revealing that the model was suitable for predicting COD removal efficiencies within the mentioned ranges of the process factors.

The predicted $R^2$ of 0.9714 is in realistic agreement with the adjusted $R^2$ of 0.9868; i.e. the variance is less than 0.2. Adequate precision calculates the signal to noise ratio. A ratio superior than 4 is required. The ratio of 38.1864 specifies an appropriate signal. This model can be applied to route the design space.

The reduced quadratic equations for the degradation of COD based on the actual and coded factors are provided as follows:

$$\begin{aligned}&\text{Removal of COD}(\%) = -48.53333 + 38.38542X_{C_F}\\&+2.23073X_{C_{HP}} + 23.75694X_{C_{pH}} - 10.89193X_{C_F}^2\\&-0.062435X_{C_{HP}}^2 - 2.11065X_{C_{PH}}^2\end{aligned} \tag{6}$$

$$\begin{aligned}&\text{Removal of COD}(\%) = 71.27 + 1.86A + 2.82B\\&-4.71C - 4.00A^2 - 6.97B^2 - 19C^2\end{aligned} \tag{7}$$

The correctness of the model as illustrated in Fig. 3, compares the experimental values vs. the predicted responses by the model in the removal of COD. It was apparent that the predicted responses from the model are in agreement with the experimental data.

### 3.2. The influence of operating variables

As stated earlier, this project explored the influences of hydrogen peroxide concentration (8, 16, and 24 mM), $Fe^{3+}$ concentration (0.8, 1.6, and 2.4 mM), and pH values (3, 6, and 9) on the COD removal efficiency in industrial wastewater. Figs. 4–5C display the three dimension (3D) plots of the COD removal (%) against these variables. These figures were plotted by Eq. (6).

#### 3.2.1. Effect of pH

In Fenton-like process, pH is a significant factor for operative wastewater treatment. Conversely, in the former studies the investigators always obtained dissimilar findings about the effect of pH in the homogeneous and heterogeneous Fenton-like method. Some discovered that acidic media was still the optimum pH, however others presented that the neutral or even alkaline pH led to the better proficiency.

According to the studies of Yang et al. and Xu et al. [28,29], it was clear that the organic pollutants can be treated more strongly in acidic condition than neutral pH, but Huang et al. and Feng et al. [30,31], had unlike results and the organic pollutants could be treated efficiently at near neutral (pH = 6.0) and even a little alkaline (pH = 9.0) conditions, when iron oxide/$SiO_2$ composite and pyrite were employed, respectively.

Other researchers [32–34] have described that in the homogeneous Fenton–like processes, the best pH range for

Table 5
ANOVA for the reduced quadratic model

| Source | Sum of Squares | df | Mean Square | F-value | p-value | Percent contribution (%) |
|---|---|---|---|---|---|---|
| Model | 1731.46 | 6 | 288.58 | 174.94 | < 0.0001 | Significant |
| A-$H_2O_2$ Conc. | 27.75 | 1 | 27.75 | 16.82 | 0.0034 | 1.51 |
| B-Ferric Conc. | 63.84 | 1 | 63.84 | 38.70 | 0.0003 | 3.48 |
| C-pH | 177.66 | 1 | 177.66 | 107.70 | < 0.0001 | 9.66 |
| $A^2$ | 58.95 | 1 | 58.95 | 35.74 | 0.0003 | 3.21 |
| $B^2$ | 179.42 | 1 | 179.42 | 108.77 | < 0.0001 | 9.76 |
| $C^2$ | 1332.34 | 1 | 1332.34 | 807.68 | < 0.0001 | 72.43 |
| Residual | 13.20 | 8 | 1.65 | – | – | 100.0 |
| Lack of fit | 11.55 | 6 | 1.92 | 2.34 | 0.3296 | Not significant |
| Pure error | 1.65 | 2 | 0.8233 | – | – | – |
| Corrected total | 1744.66 | 14 | | – | – | – |
| | Model summary | | | | | |
| $R^2$ | 0.9924 | | | | | |
| Adjusted $R^2$ | 0.9868 | | | | | |
| Predicted $R^2$ | 0.9714 | | | | | |
| Adequate precision | 38.1864 | | | | | |

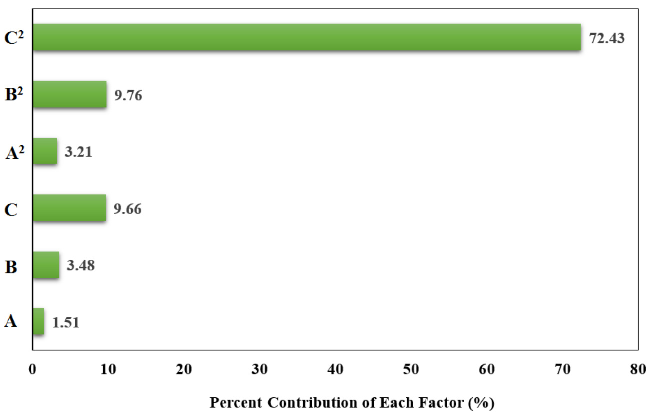


Fig. 2. Pareto chart of the percent contribution of each factor on COD removal (A = $H_2O_2$ concentration, B = ferric concentration, C = pH).

degradation of most organic pollutants were 2.5–3.0. These studies displayed that with a reduction in pH (<2.5), the scavenging effect of the hydroxyl radicals by $H^+$ becomes stronger [Eq. (8)].

$$\text{Removal of COD}(\%) = OH^{\bullet} + e^{-} + H^{+} \rightarrow H_2O \quad (8)$$

But the catalytic activity in the solution can be reduced by the hydrolysis and precipitation of $Fe^{3+}$ at pH > 3.0.

As presented in Fig. 5C, the best pH in this research was 7 due to maximum COD removal. This could be originated from the coagulation of ferric species, which can play a main role at neutral pH. These conclusions are in agreement with the findings of other researchers in homogeneous Fenton-like catalyst [35].

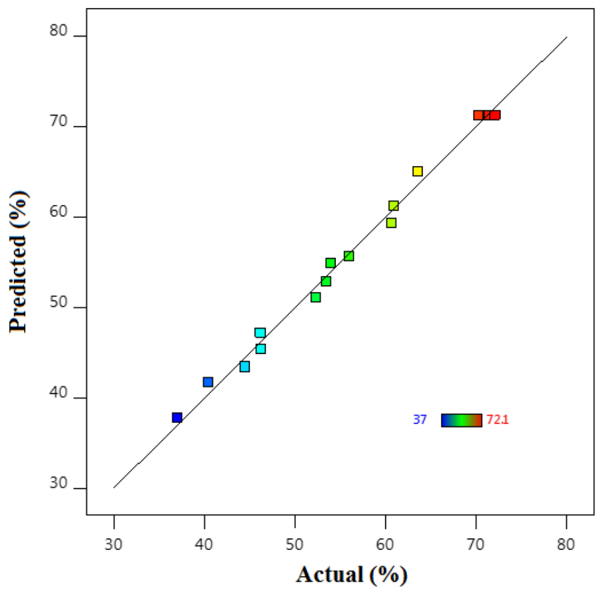


Fig. 3. Predicted vs. experimental values for the removal of COD in Fenton-like process.

At pH > 3, a major fraction of Fe(III) precipitates as $Fe(OH)_3$, diminishing the reaction between $Fe^{3+}$ and $H_2O_2$, and then the production of $Fe^{2+}$, but the coagulant effect of Ferric ion at neutral pH overcome this phenomenon. In alkaline condition (pH at 9) the removal of *COD* was decreased because the $H_2O_2$ degrades faster into $H_2O$ and $O_2$.

Based on the mentioned expressions, the study of the optimal pH range could be a difficult but important subject, which only can be obtained by experiment.

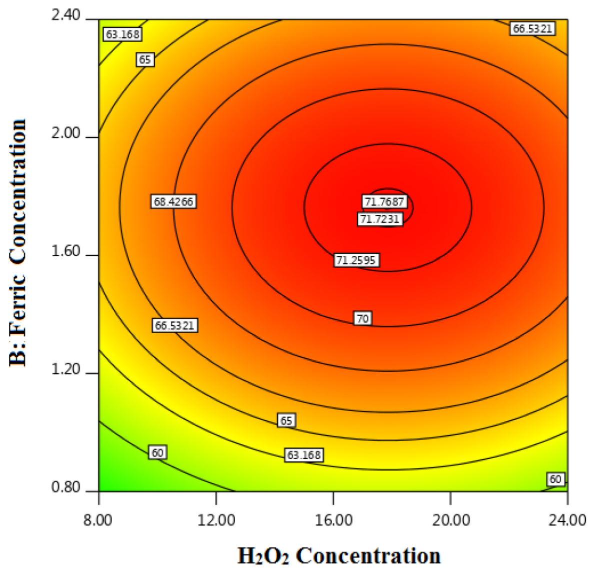


Fig. 4. Counter plot in the removal of COD against: the concentration of $H_2O_2$ ($X_{CHP}$) and ferric ions ($X_{CF}$).

### 3.2.2. *Effect of $H_2O_2$ concentration*

The concentration of $H_2O_2$, as the major source of hydroxyl radicals in the presence of catalyst, has a main role in the treatment of wastewater. The optimal concentration of $H_2O_2$ should be obtained by experiment. The treatment efficiency was reduced with a decrease in $H_2O_2$ dosage because the decomposition of $H_2O_2$ in the presence of catalyst to form hydroxyl radical was reduced. But, the excessive $H_2O_2$ quantity is not appropriate. Firstly, an excessive $H_2O_2$ dosage would enhance the treatment cost considerably when the capacity of wastewater is very high in an industrial scale. Secondly, extreme $H_2O_2$ dosage can interfere with the *COD* of the wastewater. The last and the most important issue is that the scavenger effect of $H_2O_2$ on hydroxyl radical [Eq. (9)] would be great when the $H_2O_2$ dosage is in excess [36,37].

$$\text{Removal of COD}(\%) = H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \qquad (9)$$

Therefore the $H_2O_2$ dosage should be in the optimal range and it was optimized in this process.

### 3.2.3. *Effect of catalyst dosage*

As can be seen from Figs. 4–5A, the rise in the catalyst amount is valuable to some extent. However, the catalyst cannot be used without any restriction. The extreme loading of catalyst has a negative influence on the removal of *COD*, because the scavenger effect may happen [Eqs. (10)–(12)].

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \qquad (10)$$

$$H_2O_2 + Fe^{3+} \rightarrow H^{+} + FeOOH^{2+} \qquad (11)$$

$$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \qquad (12)$$

In the high catalyst dosages, the hydroxyl radical generated would be spent by the extra catalyst. Higher cata-

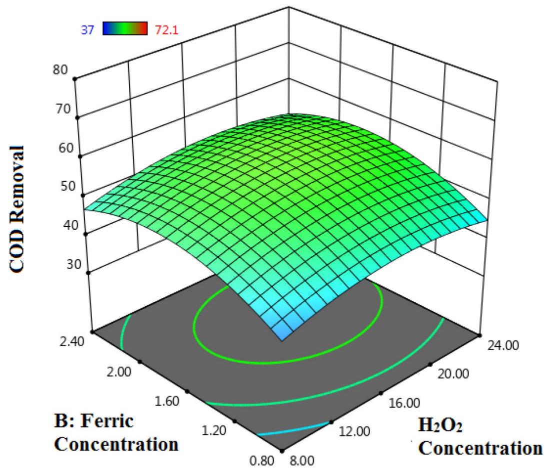


Fig. 5. (A) Surface plot in the removal of COD against: the ferric concentration ($X_F$) and the concentration of $H_2O_2$ ($X_{CHP}$) at pH = 3.

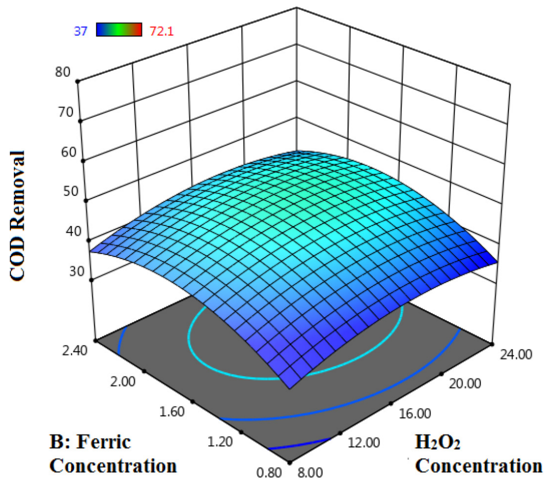


Fig. 5. (B) Surface of response for the removal efficiency of COD against: the ferric concentration ($X_F$) and the concentration of $H_2O_2$ ($X_{CHP}$) at pH = 9.

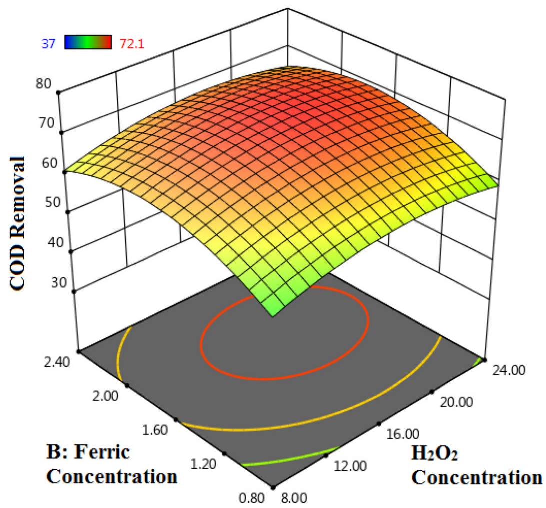


Fig. 5. (C) Surface of response in the removal efficiency of COD against: the dosage of ferric ions ($X_{CF}$) and concentration of $H_2O_2$ ($X_{CHP}$) at pH = 6.

lyst dosages would evidently enhance the treatment cost; the excessive catalyst concentration can lead to the production of a large amount of sludge, which would accelerate the need for the following sludge treatment. Moreover, it can raise the concentration of Iron in the wastewater to go beyond the discharge standard for the wastewater and further remediation is essential. The degradation efficiency and the remaining hydrogen peroxide concentration are affected by the initial concentration of the catalyst. The *COD* removal and decomposition of $H_2O_2$ were improved with an increase in the amount of ferric ion and then the residual concentration of $H_2O_2$ in the solution was reduced. The reaction of $H_2O_2$ with $Fe^{3+}$ leads to the formation of $Fe^{3+}$-peroxo complexes, and then their unimolecular decomposition into $Fe^{2+}$ and $HO_2^{\bullet}$ radicals indicates the kinetically restrictive step in the overall rate of $H_2O_2$ decomposition in homogeneous aqueous solution. The reaction of $Fe^{2+}$ with $H_2O_2$ is the sole source for hydroxyl radicals; so the concentration of $Fe^{2+}$ has an important role in the generation of hydroxyl radicals and subsequently on the depletion rates of pollutant molecule and $H_2O_2$.

Fig. 5 displays a 3D plot for the COD removal percent against hydrogen peroxide and Ferric concentration at pH of 3. The highest COD removal percent was achieved when employing the mean values for both variables (concentration of hydrogen peroxide and $Fe^{3+}$).

As shown in Figs. 4–5C, the COD removal percentage was the highest level in neutral pH. However, the COD removal in the average values of hydrogen peroxide concentration is somewhat higher than other values.

### 3.3. Optimization of operational variables and mineralization study

As displayed in Figs. 4–5C, it is apparent that the percentage of *COD* removal can be remarkable in optimum conditions. Employing Design Expert 11.0 software, the values of various variables were selected to optimize the removal of *COD*. These optimum amounts, together with the *COD* removal percent, are presented in Table 6. At these conditions, the maximum removal of *COD* via experiments and the value predicted by the model (Eq. (6)) were 72.06% and 74.9%, respectively. It should be noted that the experiments were performed with three replications.

In the removal of COD, the amounts of pH, TOC, BOD, TDS and electrical conductivity were measured at optimum conditions and the results are presented in Table 1. As it is identified, all of the contaminant factors were decreased considerably.

Table 6
Optimal coditions of variables and COD removal % (T = 25°C and *t* = 70 min)

| Parameters | Value |
|---|---|
| Hydrogen proxide concentration, mM | 17.86 |
| Ferric ion concentration, mM | 1.76 |
| pH | 5.63 |
| Predicted COD removal, % | 72.06 |
| Experimental COD removal, % | 74.9 |

The optimal conditions predicted by the model were as follows: the $[Fe^{3+}]$ = 1.76 mM, pH at 5.63, and $[H_2O_2]$ = 17.86 mM. Under the predicted optimum conditions the removal efficiency of *COD* suggested by the software was 72.06%. The predicted optimum conditions were examined and the removal of *COD* was 74.9 %. From Table 1 it is clear that after treatment the remaining *COD* (585 mg/l) is higher than the residual *TOC* (200 mg/l) which originated from oxidizable organic pollutants. The degradation and mineralization of wastewater were introduced as *COD* and TOC, respectively.

After the remediation of wastewater by Fenton like process, the carbon oxidation state (*COS*) and average oxidation state (*AOS*) were employed for biodegradability purpose. *COS* and *AOS* were estimated based on the following equations [38–40].

$$AOS = 4 - 1.5\frac{[COD]}{[TOC]} \tag{13}$$

$$COS = 4 - 1.5\frac{[COD]}{[TOC]} \tag{14}$$

where $[TOC]_0$ is related to the untreated wastewater feed. For carbon dioxide, *COS* or *AOS* is in the range of +4 as the most oxidized state of carbon, and for methane as the most reduced state of carbon it was –4. According to the presented data in Table 1, before the application of Fenton like process, both AOS and COS were –0.5, but after treatment these values were increased and the AOS and COS were +1.72 and +2.74, respectively.

These findings showed that the pollutants in the studied petrochemical wastewater were degraded to intermediate compounds. According to the change in the amounts of COS from negative to positive values, the biodegradability enhanced in some way. It can be confirmed that probably the composition of the produced intermediate is biocompatible and oxidized aliphatic pollutants. Therefore, it can be concluded that, the Fenton like process can be used as a pretreatment for biological process in the treatment of the studied real wastewater.

## 4. Conclusion

In this research, the wastewater of Special Economic Zone petrochemical company was treated through Fenton-like process. Box-Behnken method was used for experimental design and statistical analysis. The influence of $[H_2O_2]$, $[Fe^{3+}]$, and pH on the *COD* removal (%) in the petrochemical wastewater was explored. The results analyzed by ANOVA revealed that all operational factors were important and thus operative in *COD* removal. The reduced quadratic regression model equation was also advanced by seeing all the important factors affecting the *COD* removal to forecast the final response. The highest percentage in the removal of *COD* by the model was obtained at $[H_2O_2]$ =17.86 mM, $[Fe^{3+}]$ =1.76 mM, and pH = 5.63. The maximum removal of *COD* by the experiment and model were 72.06% and 74.9%, respectively. The results showed that the Fenton like process is a pretty cheap and effective approach for the treatment of the studied wastewater and based on mineralization studies, the Fenton like process can be used as a pretreatment for biological process in an industrial scale.

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