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RESEARCH PAPER

COD Reduction in Petrochemical Wastewater Using the Solar Photo-Fenton Process

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Abstract

Water has been recognized as the most fundamental factor in organisms' lives and the most widely used element in industries, while currently, the world is dealing with water scarcity in many areas. This emphasizes the importance of preventing water contamination as well as returning contaminated water produced by industries to the production and consumption cycle. Yet, the need for environmental protection is a certain principle that is generalized in today's world. This necessity has become more important with the growth of industries and technologies and subsequent contamination. Advanced oxidation technology has been substantially developed in recent decades, becoming increasingly important in the treatment process of industrial wastewaters containing resistant organic materials that cannot be removed through conventional treatment methods to reduce water quality parameters. The present study has examined the chemical oxygen demand (COD) in the synthetic monoethyl amine wastewater prepared by the solar Photo-Fenton process. Principal effective parameters in the advanced oxidation technology, including the processing time, the concentration of hydrogen peroxide ion, the concentration of iron (II) ion, and pH, were investigated by the response surface methodology (RSM) through 30 random experiments using central composite design method (CCD) to optimize reaction conditions. The most sufficient operational conditions were achieved at pH=4, $[Fe^{2+}]$ =2 mM, $[H_2O_2]$ =20 mM, and t=90 min for the COD removal rate of 77.08%.

Keywords:
Central Composite Design,
COD Removal,
Experiment Design,
Solar Photo-Fenton Process,
Wastewater Treatment

Introduction

Today, the human has faced numerous and significant challenges in the field of water resources management and freshwater supply considering population growth and demographic changes, development of urbanization and industry, drinking water scarcity, and negative impacts of climate change [1]. Reuse and recovery of industrial wastewaters can effectively decrease the global concern on water scarcity [2].

As a widely used material, monoethanolamine (MEA) is an integral part of oil, gas, petrochemical, power plants, and cement. It is used mainly in gas refineries for the gas sweetening process as a carbon dioxide absorber from natural gas. Since these mentioned industries have been regarded as advanced industries of Iran and considering their essential need for monoethanolamine within their production processes, a large amount of industrial wastewater containing monoethanolamine would be produced. In this regard, environmental problems caused by these wastewaters would be concerned due to higher amounts of chemical oxygen demand (COD) in such wastewaters [3,4].

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Advanced oxidation processes (AOPs) are applied as a set of chemical treatment methods for the removal of problematic organic materials as well as for the destruction and decomposition of natural and synthetic chemicals from wastewaters threatening the environment and public health. The most significant advantage of this method is producing high-concentrated hydroxyl radicals (OH•) [5,6]. After fluorine, this radical is the most strong oxidizing agent capable of oxidizing most organic compounds completely to carbon dioxide, water, and inorganic acids [7].

Advanced oxidation processes are typically non-selective due to high oxidation reactions allowing simultaneous treatment of multiple contaminants. This radical non-selectively reacts with organic molecules fast and spontaneously with no need for other additives. This reaction rate is about 10^8-10^{10} $M^{-1}.s^{-1}$ [8,9] at the normal temperature and pressure [10].

In this method, hydroxyl radical is produced through the combination of oxidizing agents (O_3 and H_2O_2), radiation (ultraviolet or ultrasonic), and catalysts (such as Fe^{2+}). Employing ultraviolet radiation besides an appropriate oxidizing agent like H_2O_2 is a suitable way to remove organic contaminants resistant to biodegradation. The absorption of a photon by H_2O_2 separates it into two hydroxyl radicals. Hydrogen peroxide has been recognized as an excellent oxidizing agent due to unstable conditions, which easily lose additional atomic oxygen [11,12]. Iron ions are widely used catalysts for the oxidation of a difficult-to-remove class of contaminants associated with hydrogen peroxide. The Fenton process comprises all reactions represented in reactions 1 to 6 [13,14]. Ferric and ferrous ions, hydroxyl radical, and hydrogen peroxide produce hydroperoxyl radical through some other steps of the chemical reaction. The total removal of organic carbon needs a large amount of oxidizing agent or a long retention time [15].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \quad (1)$$
$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \quad (2)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (3)$$
$$OH\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (4)$$
$$Fe^{2+} + HO_2\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (5)$$
$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (6)$$

In 2015, Palaniandy et al. have examined the use of Fenton reagent and titanium dioxide simultaneously under sunlight for refinery's wastewaters leading to 62% COD removal as being close to estimated values. They introduced the solar Photo-Fenton process as an efficient method for petroleum wastewater treatment with no energy required [16].

Durán et al. have performed an investigation in 2015 on the effect of the solar Photo-Fenton process on wastewaters produced by beverage manufacturing plants. Water quality specifications represented 96.6% TOC removal, 99.8% BOD removal, 91% turbidity, and total COD removal and toxicity in the wastewater [17].

The obvious superiority of the solar Photo-Fenton process relative to the ozone-based process was also confirmed by Guzmán et al. (2016) by comparing the effects of both approaches on the COD and DOC removal in citrus wastewaters. However, they measured the cost of 13.8 Euros per cubic meter of wastewater for using sunlight [18].

The present study sought to investigate the performance of the Photo-Fenton process in the presence of the sun's ultraviolet radiation instead of using the UV lamp on the removal of chemical oxygen demand and total organic carbon produced by monoethanolamine present in the wastewater of gas refinery containing monoethyl amine. In this respect, a multi-variate experiment was conducted based on the response surface methodology to determine optimal values of experimental variables for the chemical oxygen demand removal. Moreover, the effect of hydrogen peroxide and iron ion concentrations, the processing time, and pH were examined while controlling the amount of chemical oxygen demand and total organic carbon.

Material and methods

Material

The synthetic wastewater containing 800 ppm monoethyl amine was examined in this study. Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) as a source of Fe^{2+}, hydrogen peroxide solution (30% w/w), and MnO_2 were prepared from Merck, Germany. All experiments have conducted using double distilled water.

Experiment procedures

Herein, experiments were conducted in an open pipe reactor made of PVC pipe with four liters' capacity. The reactor was placed in an open space under direct sunlight to take advantage of a natural source of ultraviolet radiation. The solution was circulated within the reactor using a small pump for homogenizing the mixture and preventing the sedimentation of iron ions. Desired amounts of bivalent iron salt and hydrogen peroxide were injected into the reaction vessel through two separate syringes. Fig. 1 depicts a schematic setup used in this study. After performing experiments, samples' COD value was measured using a spectrophotometer (DR 5000, Hach, Jenway, USA) at 600 nm.

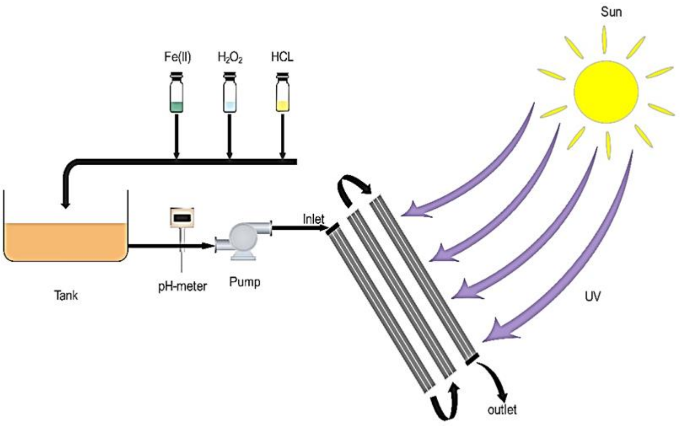

Fig. 1. Schematic of the device prepared for the experiments

Each experiment has employed two liters of synthetic monoethyl amine wastewater. Different concentrations of H_2O_2, Fe^{2+}, process time, and pH were examined, and the chemical oxygen demand was measured using standard methods [19]. The following equation determines the COD removal rate:

$$\text{COD removal } \% = \frac{[COD]_0 - [COD]}{[COD]_0} \times 100 \quad (7)$$

$[COD]_0$ is the COD value at the beginning of the reaction (for the synthetic wastewater), and $[COD]$ is for the COD value at the reaction time. Due to the interference of H_2O_2 with the COD test, the remaining amount of hydrogen peroxide in samples was removed using MnO_2 powder, and samples were then filtered to separate MnO_2 powders [20].

Experiment design

Response surface methodology is a set of statistical and mathematical methods used for the analysis of experimental results and the development, advancement, and optimization of processes. In this regard, the intended surface is usually affected by various input variables. This dependence on inputs can be represented as an equation to optimize the respective response.

Considering the benefits of a nonlinear second-degree equation as well as available operational information, this model was chosen to investigate the effect of input variables on output variables during the transesterification process. This second-degree polynomial model can be considered as below:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_{ij} \tag{8}$$

where Y is the response, X_i and X_j are independent variables, and β_i, β_{ii}, and β_{ij} stand for coefficients of linear, second-degree, and interaction terms, respectively.

The proposed models were examined for responses using Analysis of Variance (ANOVA), and regression coefficients were estimated for linear, interaction, and second-degree terms, and the quality of fitting equations of the models was represented using the convergence coefficient R^2. Moreover, R_{adj}^2 is an adjusted coefficient of R^2, that can be used to measure the model precision. This coefficient has not increased by increasing model factors while decreases when adding unnecessary factors to the model. The significance and effectiveness of model factors were statistically analyzed using p-value and F-value. Thus, the p-value must be first determined to be compared with 0.05 so that if it was lower than 0.05, the model would be significant. The F-value is calculated as follows [21]:

$$F - \text{value} = \frac{\left(\frac{\text{SS}}{DF}\right)_{reg.}}{\left(\frac{\text{SS}}{DF}\right)_{res.}} \tag{9}$$

where SS and DF are the sum of squares and degrees of freedom, respectively. Subscripts $reg.$ and $res.$ represent regression and residual, respectively.

The principal factors were selected considering optimization performed in previous studies. These parameters and their values are represented in Table 1. In this regard, pH (1, 2, 3, 4, and 5), the concentration of Fe^{2+} (1, 2, 3, 4, and 5 mM), the concentration of H_2O_2 (5, 20, 35, 50, and 65 mM), and the process time (60, 90, 120, 150, and 180 min) were considered for the experiment.

Table 1. Operational parameters and levels

Factor	**Unit**	**Symbol**	**Levels**				
			-2	**-1**	**0**	**+1**	**+2**
Acidity	-	pH	1	2	3	4	5
Ferrous concentration	mM	$[Fe^{2+}]$	1	2	3	4	5
Hydrogen peroxide concentration	mM	$[H_2O_2]$	5	20	35	50	65
Time	min	t	60	90	120	150	180

Among all response surface methodology (RSM) techniques, the central composite design method is the most widely used design for modeling the second-order response surface. The structure of these designs is based on full factorial designs or partial/fractional factorial designs associated with duplication at the central point and an axial point. Ordinarily, the whole experiment is divided into two main groups in this type of design. The first group consists of experiments for the central and factorial part, and the second group is subjected to the central and axial part experiments. The central part experiments are repeated in both groups representing two major results, comprising the criterion for measuring the net error value and stabilizing the difference of predicted responses. Hence, this difference can be stabilized by 3 to 5 repetitions at the central point if the value was equal to 1 [21]. Experiment design comprised 30 experiments proposed by the Design-Expert 7.0.0 Trial software, and all experiments were conducted randomly to minimize experimental errors (Table 2).

Table2. CCD table along with the independent variables and the COD removal

	Manipulated variables				**Response**
No.	**pH, -**	**$[Fe^{2+}]$, mM**	**$[H_2O_2]$, mM**	**t, min**	**COD removal %**
1	3	5	35	120	51.36
2	3	3	35	120	32.56
3	4	4	20	150	39.39
4	3	3	35	120	30.82
5	4	2	50	90	54.80
6	3	3	35	120	34.26
7	3	3	35	120	37.70
8	3	3	35	120	29.12
9	3	3	35	180	29.12
10	3	3	65	120	52.75
11	1	3	35	120	29.12
12	5	3	35	120	61.68
13	3	3	35	120	32.56
14	3	3	35	60	39.39
15	2	2	50	150	46.22
16	2	2	20	90	37.70
17	2	2	20	150	49.67
18	4	4	20	90	54.80
19	2	4	20	90	10.32
20	2	4	20	150	17.15
21	3	1	35	120	53.26
22	4	4	50	90	58.24
23	2	2	50	90	32.56
24	4	2	20	90	77.09
25	4	2	20	150	70.21
26	4	2	50	150	8.58
27	2	4	50	90	61.99
28	4	4	50	150	42.84
29	3	3	5	120	58.24
30	2	4	50	150	65.07

Results and Discussion

Analysis of Variance for the response

Table 2 summarizes the results of the experiment design for COD removal. A model was then achieved by analyzing experiment results precisely. The quality of this mathematical model was confirmed by the coefficient of determination (R^2) and the adjusted coefficient of determination (R^2) as being 93.61% and 89.71%, respectively. Fig. 2 illustrates the precision of the predicted model, in which predicted and experimental COD values have been compared with each other. As can be observed, there has been relatively suitable compliance between experimental data and predicted results. Thus, the COD removal rate has been expressed using a second-degree polynomial equation with the help of the error least squares method:

$$COD_{rem.} = 25.905 + 43.335pH - 57.967[Fe^{2+}] - 1.371[H_2O_2] + 0.852t - 0.700pH.[H_2O_2] - 0.249pH.t + 0.829[Fe^{2+}].[H_2O_2] - 0.006[H_2O_2].t + 2.883pH^2 + 4.610[Fe^{2+}]^2 + 0.024[H_2O_2]^2 \quad (10)$$

where pH represents the amount of acidity, $[Fe^{2+}]$ and $[H_2O_2]$ are concentrations of iron and hydrogen peroxide in mM, and t stands for the retention time in min.

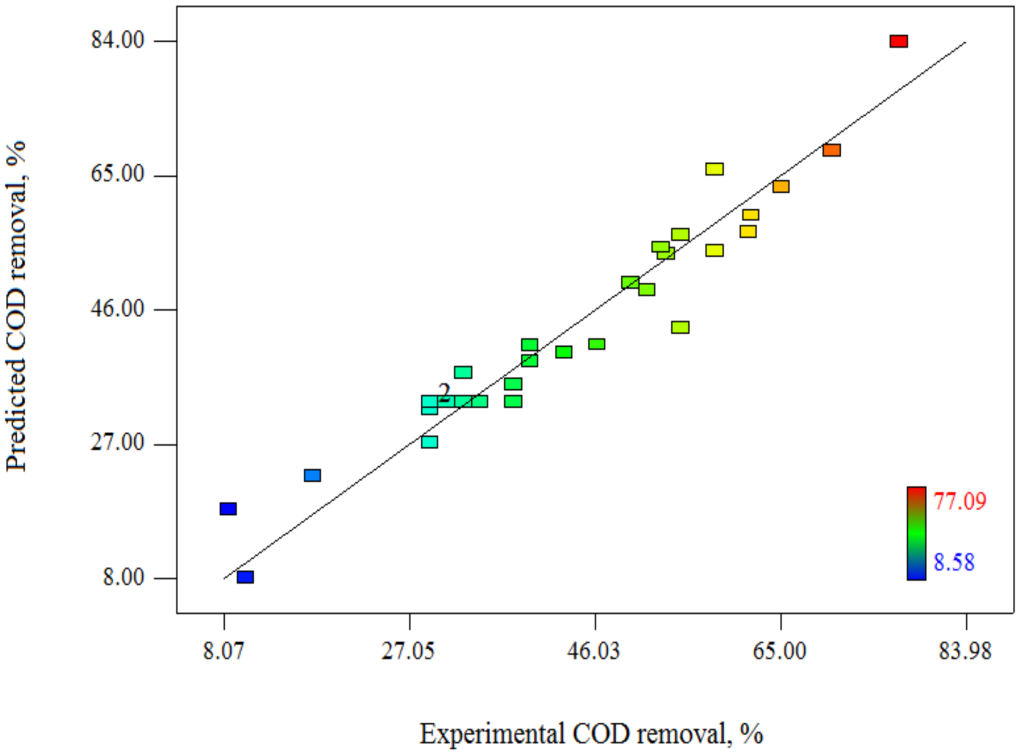

Fig. 2. Comparison of experimental and predicted values for COD removal

Table 3 demonstrates the ANOVA results for the proposed COD removal rate model. The total and model degrees of freedom and error residual were 29, 11, and 18, respectively. Based on the results provided in this table, the F-value of the model is large, and the proposed model is statistically significant. Moreover, the p-value for the model lack-of-fit has been 0.0529, which was larger than 0.05 representing insignificant lack-of-fit.

Table 3. Analysis of variance (ANOVA) for COD removal model

Source	SS	DF	MS	F-Value	p-Value Prob>F	Level of Significance
Model	7767.58	11	706.14	23.98	<0.0001	significant
pH	942.38	1	942.38	32.00	<0.0001	significant
$[Fe^{2+}]$	39.60	1	39.60	1.34	0.2613	not significant
$[H_2O_2]$	0.37	1	0.37	0.013	0.9117	not significant
t	197.86	1	197.86	6.72	0.184	not significant
$pH.[H_2O_2]$	1764.63	1	1764.63	59.92	<0.0001	significant
$pH.t$	891.77	1	891.77	30.28	<0.0001	significant
$[Fe^{2+}].[H_2O_2]$	2474.81	1	2474.81	84.03	<0.0001	significant
$[H_2O_2].t$	107.07	1	107.07	3.64	0.0726	non significant
UV^2	232.72	1	232.72	7.90	0.0116	significant
$[Fe^{2+}]^2$	595.17	1	595.17	20.21	0.0003	significant
$[H_2O_2]^2$	818.51	1	818.51	27.79	<0.0001	significant
Residual	530.10	18	29.45			
Lack of Fit	486.39	13	37.41	4.28	0.0592	not significant
Pure Error	43.71	5	8.74			
Cor Total	8297.68	29				

According to the proposed model calculation (Eq. 10), terms with p-values less than 0.05 have been more important in the regression model. Considering Table 3, the linear term of pH, second-degree terms of pH^2 and $[Fe^{2+}]^2$, and interaction terms of $pH.[H_2O_2]$, $pH.t$, $[Fe^{2+}].[H_2O_2]$, $[H_2O_2].t$ are significant for the COD removal model.

Effects of operational and optimization parameters

As mentioned earlier, the effects of pH with values of 1, 2, 3, 4, and 5, the concentration of Fe^{2+} with values of 1, 2, 3, 4, and 5 mM, the concentration of H_2O_2 with values of 1, 2, 3, 4, and 5 mM, and process time with values of 60, 90, 120, 150, and 180 min were examined on the COD removal rate of the synthetic monoethyl amine wastewater. As specified in Table 3, interaction terms of $pH.[H_2O_2]$, $pH.t$, $[Fe^{2+}].[H_2O_2]$, $[H_2O_2].t$ were significant in the COD removal from the intended wastewater. Figs. 3 to 6 represent the interplay of these variables on the COD removal.

Fig. 3 demonstrates the effect of pH and $[H_2O_2]$ in a contour 3D diagram on the COD removal rate from the intended wastewater. As can be seen at the least pH value (pH=2), the COD removal rate has increased by increasing the concentration of hydrogen peroxide from 20 mM to 50 mM. While a reverse trend was seen at higher pH values (pH=4) so that the COD removal rate was increased by decreasing the concentration of hydrogen peroxide from 50 mM to 20 mM. Meanwhile, there has been no considerable change in the COD removal rate by changing the concentration of hydrogen peroxide at medium pH values (i.e., pH=3). The highest COD removal rate was at pH=4 and $[H_2O_2] = 20\ mM$.

Fig. 4 represents the effect of pH and t in a contour 3D diagram on the COD removal rate from the intended wastewater. Herein, in lower pH values, the time had no remarkable effect on the COD removal rate of the wastewater (but a decreasing COD removal can be observed by increasing the reaction time). While at higher pH values (pH=4), the COD removal rate was increased by decreasing the time. As another outcome, the COD removal rate was increased by increasing pH within the least process time. In other words, the highest COD removal rate was achieved at pH=4 and t=90 min.

Fig. 5 illustrates the effect of $[H_2O_2]$ and $[Fe^{2+}]$ in a contour 3D diagram on the COD removal rate from the intended wastewater. The highest amount of COD removal was obtained at lower concentrations of hydrogen peroxide and iron (II) ion ($[H_2O_2] = 20mM$ and$[Fe^{2+}] = 2mM$). The COD removal rate was also considerable in higher concentrations of both ($[H_2O_2] = 50mM$ and$[Fe^{2+}] = 4mM$). According to this Figure, the COD removal rate was relatively low when the concentration of hydrogen peroxide was high, and the concentration of iron (II) ion was low, as well as when the concentration of hydrogen peroxide was low. The concentration of iron (II) ion was high. In conclusion, the interaction between $[H_2O_2].[Fe^{2+}]$ variables was positive (Eq. 10).

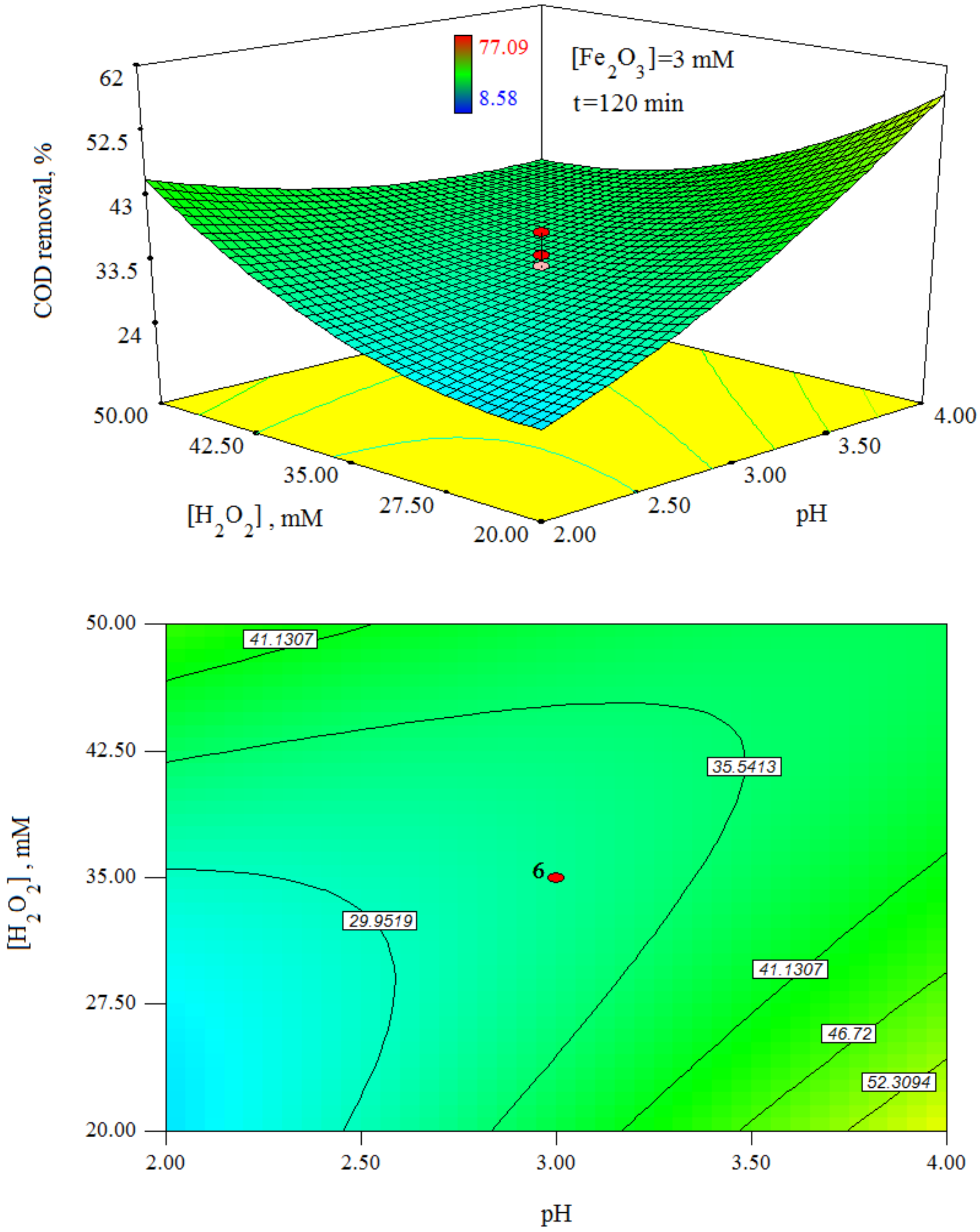

Fig. 3. 3D plots of COD removal based on acidity and the hydrogen peroxide concentration at constant conditions $(t = 120\ min, [Fe_2O_3] = 3mM)$

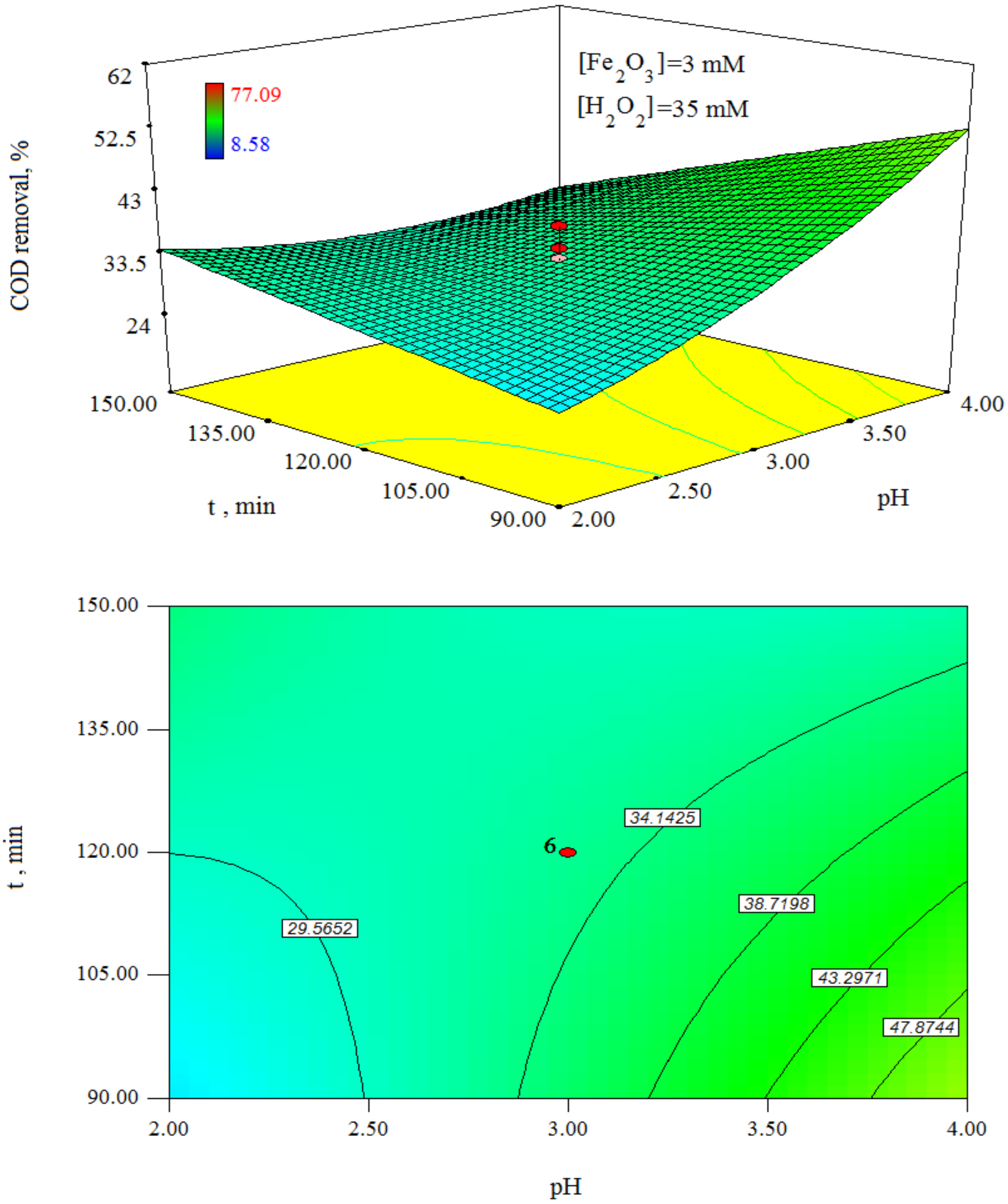

Fig. 4. 3D plots of COD removal based on acidity and time at constant conditions ($[H_2O_2] = 35mM, [Fe_2O_3] = 3mM$)

Fig. 6 shows the effect of $[H_2O_2]$ and t in a contour 3D diagram on the COD removal rate from the intended wastewater. As can be seen, the COD removal rate of the wastewater was decreased at all concentrations of hydrogen peroxide while increasing the processing time (from 90 to 150 min). A similar outcome was observed in Fig. 4 for the processing time. Diagrams of Fig. 6 also represent that the COD removal rate was higher in low or high values of the concentration of hydrogen peroxide rather than medium values. Therefore, the highest COD removal rate was achieved at t=90 min and $[H_2O_2] = 20mM$.

Regarding Figs. 3 to 6 and Eq. 10, it is clear that the COD removal rate from the wastewater has had different optimal points. In other words, there have been several points where the COD removal rate can be significant. Optimization was conducted using the Design-Expert 7.0.0 Trial software. The highest COD removal efficiency can be obtained when pH = 4, $[Fe^{2+}]$=2 mM, $[H_2O_2]$=20 mM, and t=90 min. Under these conditions, the COD removal rate was 83.98% using the model (Eq.10). While the COD removal rate was 77.08% through experiments.

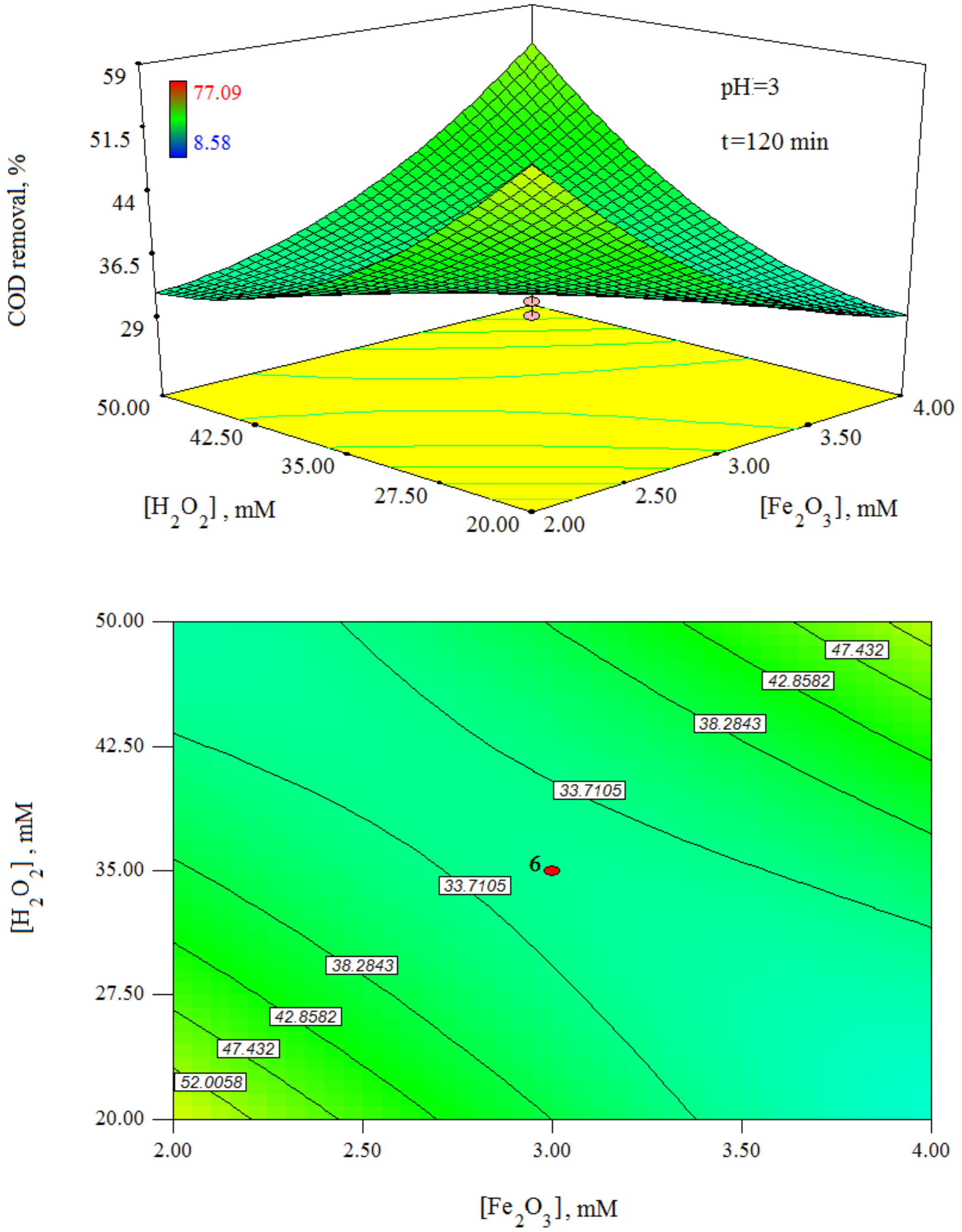

Fig. 5. 3D plots of COD removal based on the ferrous and hydrogen peroxide concentration at constant conditions ($pH = 3, t = 120\ min$)

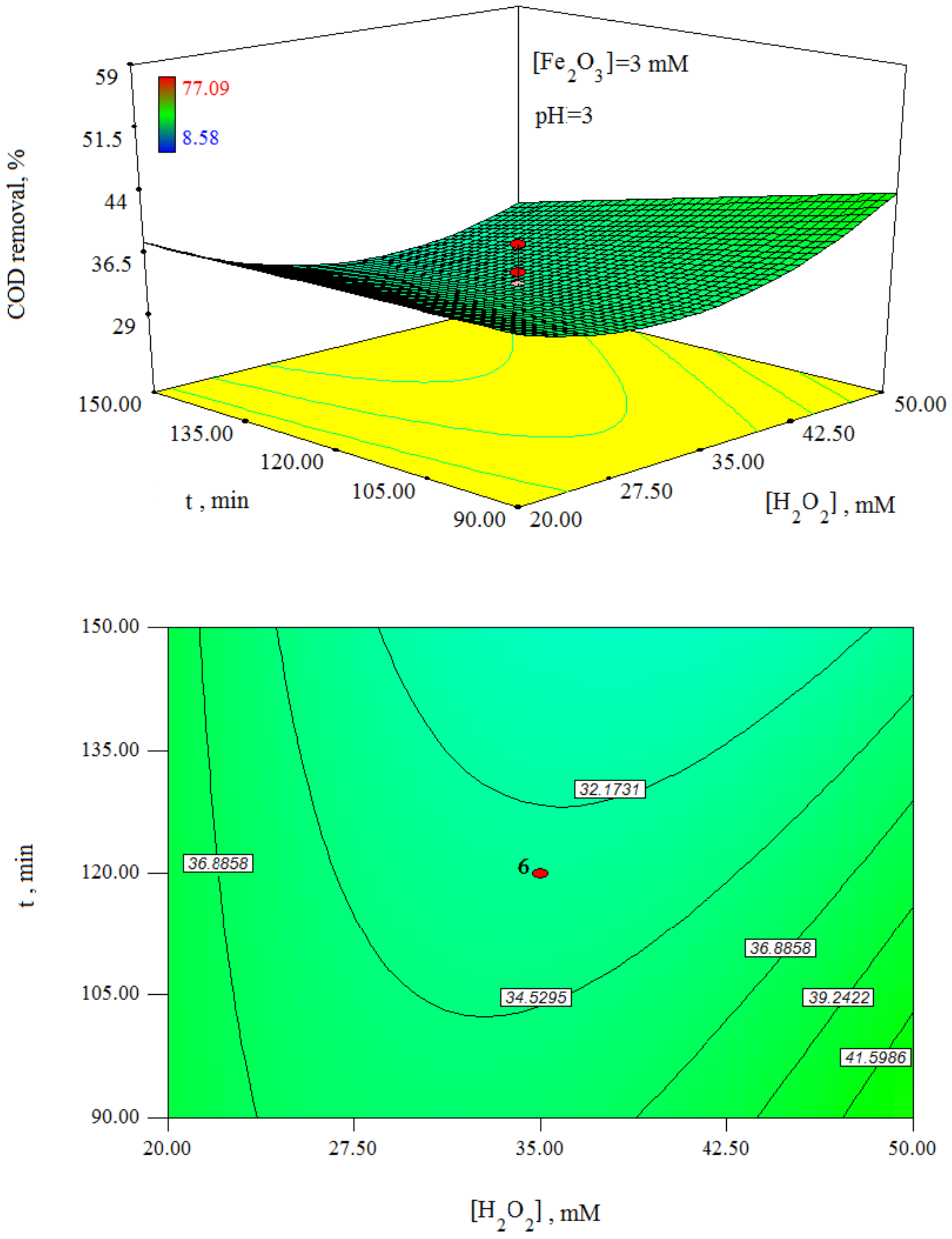

Fig. 6. 3D plots of COD removal based on the hydrogen peroxide concentration and time at constant conditions ($pH = 3, [Fe_2O_3] = 3mM$)

Conclusions

The present study sought to reduce the COD value of the synthetic monoethyl amine wastewater through the solar Photo-Fenton process using the central composite experimental design. In this regard, the effect of pH, the concentration of iron (II) ion, the concentration of hydrogen peroxide ion, and the processing time were investigated. Statistical analysis of the model confirmed that the model was satisfactory to predict COD removal. It was found that acidity was the main contributor to almost all impact categories. The removal efficiency of 77.08% was achieved by experiments under optimal operational conditions including pH=4, [Fe2+]=2 mM, [H2O2]=20 mM, and t=90 min. All in all, this work's results may be a useful tool for the industry since the effective treatment of wastewater is a major problem, and AOPs strongly required energy and chemical inputs. Therefore, the solar Photo-Fenton process could provide a clean energy source for AOPs energy requirement.

Acknowledgments

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