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Optimization of TNT Wastewater Treatment by Combination of Coagulation and Fenton Processes Using RSM Methodology

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Keywords

TNT,
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ANOVA.

Abstract

In this study, the treatment of trinitrotoluene (TNT) wastewater has been studied by using combination of coagulation and Fenton process and modeled by RSM (response surface methodology). At first, coagulation used as the pretreatment process. In this process, PACl was implemented. In the Fenton process, the produced hydroxyl radical has caused the destruction in the molecular structure by attacking to TN compounds. RSM method has been used for the design of the experiments and modeling TNT removal efficiency. Some parameters have been selected as effective parameters on Fenton process, including PH, hydrogen peroxide (H_2O_2), ferrous sulfate, reaction time and temperature. In addition, analysis of variance (ANOVA) was conducted to assess the model and determine the affecting factors which have a greater contribution to the response parameters.

1. Introduction

TNT is known as one of the most important explosives [1]. It is widely used for military and nonmilitary purposes in the world, and the presence of this substance in soil and under groundwater is remarkably increasing [2]. TNT and its accessory products are very toxic so, that they can cause some diseases, including sort of cancers, anemia, liver disorder, inflammation of the skin and the reduction of the immune system. Therefore, TNT has been introduced as a serious pollutant by US EPA (US environmental protection agency). TNT, due to its chemical structure (Figure 1), is stable in the environment and also it preserves its properties for the soil and aqueous solution [3].

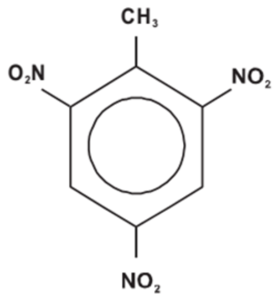

Figure 1. TNT (2,4,6-trinitrotoluene)

For TNT treatment, different methods have investigated such as biological methods [4], adsorption [5], O3/H2O2 [6], photocatalytic oxidation [7], wet air oxidation [8] and Fenton [9]. The biological treatment is an inefficient method because of the attack of nitro compounds to the enzymes [10]. In addition, the results of other studies have shown that the conventional chemical methods are also inefficient. This is because of their high resistance to nitro groups [9]. To further remove the TNT components, the advanced treatment methods are needed. Recently, advanced oxidation process such as Fenton, with the use of oxidants such as hydrogen peroxide with the addition of metal catalysis, produce hydroxyl free radicals, which they can oxidize the late biodegradable compounds in TNT and change them to a harmless substance such as CO2, H_2O and mineral salt [11].

Fenton process is widely used due to its simple technology and also its lower operating costs compared to other advanced oxidation processes [12]. Fenton process is defined based on electron transfer between H_2O_2 and a metal ion (generally iron ions) which serves as homogeneous catalytic [13]. According to Barb et al. [14] mechanism, in an acidic environment, the mechanism of redox Fenton process (due to hydrogen peroxide reaction with ferrous ion or ferrous) is as follows

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$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}O_2H + H^+ \quad (2)$$
$${}^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}O_2H + H_2O \quad (3)$$
$${}^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (4)$$
$$Fe^{3+} + {}^{\bullet}O_2H \rightarrow Fe^{2+} + O_2H^+ \quad (5)$$
$$Fe^{2+} + {}^{\bullet}O_2H + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$
$${}^{\bullet}O_2H + {}^{\bullet}O_2H \rightarrow H_2O_2 + O_2 \quad (7)$$

According to the investigations, Fenton process efficiency depends on some variables such as PH, temperature, H_2O_2, the catalyst concentration and time [15]. However, the price of chemical materials used in this method is expensive. To reduce the amount of chemicals material in Fenton process, pretreatment process such as coagulation can be implemented. Determination of the optimal amount of affecting parameters to Fenton is necessary for the further decreases in the costs and the amount of consumer chemicals and also for achieving the high efficiency. Recently the statistical methods of design of experiments (DOE) such as RSM replaced with the "one factor at a time" method because by using DOE, we can consider the effects of parameters and their interaction. This method is very time-consuming and costly [16]. Several investigations have been carried out on the TNT wastewater treatment by Fenton [17, 18], but none of these studies have provided a solution to reduce the disadvantages of Fenton. Thus in this study, the effect of combination of coagulation and Fenton on TNT removal was investigated by using RSM experimental design until to detect the optimal value and the impact of the effective parameters of the system.

2. Materials and Methods

Under the temperature of 25 ºC, the synthesized TNT was added in a certain amount of purified water, in order to the obtained Wastewater was used for analyzing the effect of Fenton process on the efficiency of the TNT removal.

2.1. Materials

In this study, polyaluminium chloride (PACl) used in the coagulation process as the pretreatment process. Also, iron sulfate ($FeSO_4.7H_2O$, Merck) was used in Fenton process as a source of iron bivalent (Fe (II)) for reacting with hydrogen peroxide. For this purpose, a stock solution of iron sulfate and a stock solution of hydrogen peroxide was respectively prepared in a concentration of 50mM and 400mM. In order to set PH, we used one normal sodium hydroxide solution (Merck) and one normal sulfuric acid (Merck). All the stages of producing these sample were conducted in accordance with the standard method [19]. We used double-distilled water for dilution of all the solution.

2.2. TNT Analyze

The concentration of TNT residue in synthesized wastewater was measured by using a spectrophotometer. The measures are as follows: 2-5 ml of TNT sample was diluted with 10 ml distilled water, then 2 ml sulfuric acid 4%, 5ml Na_2SO_3 5%, 2ml Cetylpyridinium chloride 3% and 2ml diethyamino-2 33% were added to the solution, and the TNT concentration was measured at the wave length of 466nm which in it, the maximum wave length was observed [2]. For measuring, the set of PerkinElmer LAMBDA 750 was used.

2.3. Experimental Procedure

The experimental procedure is that 0.3 liters of a wastewater are placed in the one-liter reactor. The more volume of the reactor is to provide the essential space for the prevention of the overflow of the solution. The process was conducted at atmospheric pressure and at the temperature of 25oC. Since the initial pH of the wastewater was higher than 6 and the optimal environment of Fenton process is acidic, so the PH of samples in the range of 3 to 5 for evaluating the impact of PH on the removal efficiency became acidic by solution of sulfuric acid and then the solution was mixed at a speed of 250 rpm. After that the solution of iron Fe (II) was added to the wastewater in different doses and then mixed. After 5 minutes, the solution became a homogeneous solution, H2O2 solution was added in different amounts, at this time, Fenton reaction began. After 45 minutes, NaOH is added to the solution in order to the PH solution reach to the top of 8 and therefore Fenton reaction was completed. After this step, 0.5 ml poly was added to flocculation be done. Flocculation was carried out in ten minutes at the speed of 20 rpm to the flocs don't break up. These values were optimized before the test by using jar test device.

2.3. Design of Experiments

RSM method is used for the promotion, process optimization and examination of the relative importance of the effective factors even in the presence of complex interactions. The response surface methodology is a series of experimental, mathematical and statistical deduction method that is used as an inefficient statistical method for designing the experiments and the optimization of the process. By using this method, the number of experiments reduced whereas the overall cost reduced. RSM is also able to present a mathematical model of the polynomial and evaluate the main and the corresponding effects of various parameters. In general, the optimal values of the selected parameters obtained with the fewer errors. In this study in order to evaluate the effect and the optimization of the parameters, the CCD (Central Composite Design) method was used for the designing of the experiments. Among a variety of RSM methods, CCD, because of simplicity and high flexibility, is used more widely. The experiments were conducted by CCD method for five independent variables such as PH, the concentration of hydrogen peroxide, ferrous ion concentration, reaction time and the reaction temperature at three different levels of course with the help of software program such as design-expert V9.

The effect of the independent variables including PH(X_1), the concentration of hydrogen peroxide [H_2O_2] (X_2), the concentration of ferrous ion [Fe (II)] (X_3), reaction time (X_4) and temperature (X_5) have been investigated at three different levels. The actual and encoded values high (+1), average (0), low (-1) of the mentioned variables, are shown in table 1. High and low levels of H_2O_2, Fe (II), PH, time reaction and temperature were determined according to the researches conducted before.

Table 1. The actual and encoded values

Parameters	Codes	Levels		
		+1	0	-1
pH	X_1	3	4	5
[H_2O_2]	X_2	3	5	7
[Fe(II)]	X_3	1	2	3
Time(min)	X_4	15	30	45
Temperature(°C)	X_5	20	30	40

Table 2 shows the arrangement of the experiments a based on CCD method. After doing experiments, the removal efficiency of TNT was calculated by using Eq. (8) and these values were considered as a response function.

$$\% \text{ REMOVAL}=1-\frac{C_0}{C_1}\times 100 \tag{8}$$

In above equation, C_0 and C_1 are the initial concentration of TNT and its final concentration after Fenton process, respectively.

3.1. Coagulation Pretreatment

To pretreatment of TNT coagulation process was used. To evaluate the performance of coagulant, the effect of concentration in initial pH of wastewater was investigated. Accordingly, at concentration of 200 ppm the removal efficiency reached to 18%.

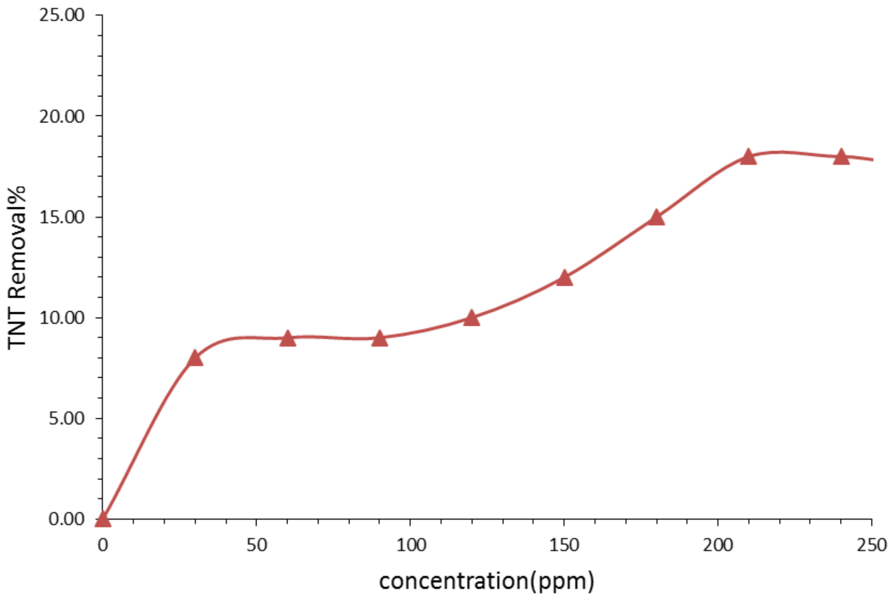


Figure 1. TNT removal efficiency

3.1. Fenton Process Optimization

In CCD method, analyzing the main and the mutual effects of the factors on TNT removal efficiency and analyzing the experimental results, a polynomial model is defined. In most cases, a quadratic equation is used for analyzing the results. The initial proposed and default model in the form of full quadratic model by considering all terms is as follows [20]

$$Y=\beta_0+\sum_{i=1}^{k}\beta_i x_i+\sum_{i=1}^{K}\beta_{ii}x_{ii}^{2}+\sum_{i=1}^{k}\sum_{i=j=1}^{K}\beta_{ij}x_i x_j+\varepsilon_0 \tag{9}$$

where Y is a response variable, *K* is the number of the independent variables, β_0 is a constant coefficient, β_i is the liner effects, β_{ii} is the square effects, β_{ij} is the mutual effects. x_i and x_j represent the level of the independent parameters in an encoded way and ε_0 is a random error [20].

According to Eq. (9), the quadratic polynomial model was obtained for the estimation of the interaction between the independent parameters and determining the TNT removal efficiency.

Table 2. Experimental results

EX.NO	pH	H_2O_2(mM)	Fe^{2+}(mM)	Time(min)	Temperature(°C)	TNT Removal%
1	4	5	2	30	30	81.68
2	5	7	3	15	20	76.26
3	3	5	2	30	30	82.25
4	4	5	2	30	30	80.73
5	3	3	3	45	40	62.92

6	4	5	2	30	40	72.25
7	3	7	3	45	20	54.00
8	5	7	1	15	40	41.00
9	4	5	2	30	30	86.14
10	4	7	2	30	30	82.16
11	4	5	2	30	30	77.69
12	4	5	2	30	30	80.35
13	3	7	3	15	40	66.50
14	5	3	3	15	40	41.35
15	4	5	2	45	30	83.68
16	4	5	1	30	30	60.95
17	4	5	3	30	30	69.35
18	5	5	2	30	30	58.52
19	3	3	1	15	20	71.35
20	4	5	2	30	20	82.16
21	3	7	1	45	40	68.52
22	4	5	2	15	30	85.95
23	5	3	3	45	20	44.35
24	5	7	1	45	20	32.54
25	4	3	2	30	30	53.28
26	5	3	1	45	40	24.63

3.2. ANOVA Analysis

Eq. (10) was obtained after the removal of the inefficient terms. The additional terms were identified by statistical analysis ANOVA and were removed from the final model. In addition to the determination of the relative importance of various parameters, the variance analysis used for the estimation of the error variation. The significance of this model was evaluated by the regression number, lack-of-fit, F-test and the P-values. The results of the statistical analysis for TNT removal efficiency illustrated in Table 3.

$$\begin{aligned}\text{TNTRemoval\%} &= 79.31 - 11.87X_1 + 14.44X_2 + 4.2X_3 - 1.13X_4 - 4.96X_5 - 1.53X_1X_2 + 11.75X_1X_3 + 1.98X_1X_4 + 7.16X_1X_5 - \\ &5.85X_2X_3 - 10.94X_2X_4 - 1.88X_2X_5 + 0.85X_3X_4 + 7.05X_3X_5 + 8.71X_4X_5 - 7.67X_1^2 - 10.33X_2^2 - 12.9X_3^2 + 6.76X_4^2 - 0.85X_5^2\end{aligned} \tag{10}$$

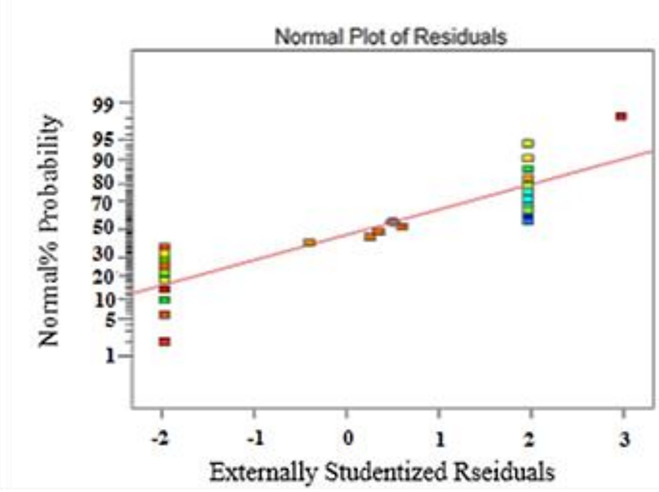
Table 3. ANOVA for response quadratic model

Source	SS	DF	MS	F-Value	P-value
Model	7752.68	20	387.63	26.05	0.0009
pH(A)	281.56	1	281.56	18.92	0.0074
H_2O_2	417.03	1	417.03	28.03	0.0032
Fe^{2+}	35.28	1	35.28	2.37	0.1842
Time	2.58	1	2.58	0.17	0.6946
Temperature	49.10	1	49.10	3.30	0.1290
Residual	74.40	5	14.88		
Lack of Fit	36.57	1	36.57	3.87	0.1206
Pure Error	37.83	4	9.46		
Total	7827.08	25			

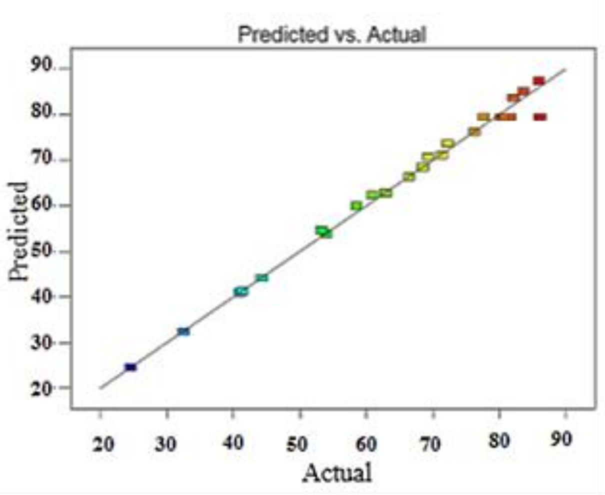
In Table 3, SS means the sum of the squares of each parameter in N level. DF refers to the degree of freedom and is equal to the number of levels minus one. Ms is a quality as the same as variance that means the average of the squares. This value is obtained by dividing the sum of the squadron the degree of the freedom. F is the ratio of the mean square to the means of the square error. P value represents the effect of each of the factor studied on response and the interaction between them. In order to identify the effect of the parameters or these available terms in the equation, we should refer to the P-value and F-value numbers. In general, the trace amounts of P-value ($p<0.05$), and the great amounts of F-value indicate that parameter has a significant effect on system. The results of the variance analysis show the meaningful effect of PH and the concentration of hydrogen peroxide on TNT removal efficiency. However, in this study PH were known as the most important factor in reducing TNT in Fenton process.

R2 coefficient represents the dispersion of the data and if this value is closer to 1, the computational models have greater consistency [21]. In this study, the correlation coefficient for TNT removal efficiency was equal to 99% that indicates the very top accuracy of this model in the response predication. R2 adjusted coefficient is 95%. This parameter usually represents the real value of correlation coefficient and preferred to R2.

The normal probability distribution of data and the comparison of the results of the model estimation and the actual results are represented in Figure 3. The probability graph in Figure 3(A) shows that the distribution of the residual values, that is the difference between the numerical prediction and experimental values, make a straight line and the remaining values scattered normally on both sides of the line. This graph shows that the experimental points reasonably have been aligned with the value predicted by the model. In Figure 3(B), the experimental values were compared with the predicted values for TNT removal efficiency that on the basis of this obtained results in this comparison, Figure 3(B) indicates a fairly acceptable level. All these results show an acceptable mathematical inter-partition of the procedure of the efficiency process by the model that the obtained model has a good ability for predicting the TNT removal efficiency.



A



B

Figure 2. The normal probability and regression graphs

Lack of fit is the main parameter for evaluating the predicted model. Accordingly, if the amount P-values of this parameter are greater than 0.05, shows the suitability of the obtained model. According to the Table 3, the P-value and F-value of the lack of fit parameter, are respectively 0.1206 and 3.87 that indicate a higher proportion of the computational model. Furthermore, the lower value of the coefficient of variation (CVTNT=5.83) show the high accuracies and reliability of these tests. AP (adequate precision) is a parameter signal ratio to noise (the ratio of the anticipated answer to its related error), that the value higher than 4 is known as a desirable value for AP [21, 22]. In this study, AP is equal to 18.11 that indicate this model is approved.

3.3. The Effect of the Optimizing Parameter

Figure 4 shows the optimal points and the effect of the selected parameters on response function. These figures were created by using the computational models through the experimental points and the interpolation of the other points. According to the results of the independent and interactive effects of each parameters on TNT removal efficiency, the considered optimal levels of the factors are as follows: (a) PH=3, (b) [Fe(II)]=2 mM, (c) [H_2O_2]=7 mM, (d) time=15 min, (e) temperature=30 ^{o}C.

3.3.1. The Effect of PH

In order to evaluate the effects of PH in TNT removal, the samples which contained TNT were tested in three different PH levels, such as 3, 4, and 5. Generally, Fenton process in acidic aquatic has a sensible preference compered to alkaline aquatic. Figure 3 shows the synchronous effect of PH with other parameters for TNT removal efficiency. According to Figure 4, the independent changes of PH on removal efficiency, without considering the other variables, show that the maximum efficiency occurs at PH=3. According to the same researches, the maximum of TNT removal efficiency has been reported in PH=3 [23, 24]. At this PH, Fe(OH) is formed, that in comparison with Fe(II) is more active in Fenton process[25]. As can be seen, at PH higher than 3, the TNT removal efficiency decreases linearly to PH=4. This reduction of efficiency is due to iron sediment, whereas the amount of the free catalyst in solution reduces [26]. In addition, the hydroxyl radicals engaged by the H+ ions and so the efficiency of the advanced oxidation process reduced [27]. After PH=4, the trend is in decline with a constant slope.

3.3.2. The Effect of Iron Concentration and Hydrogen Peroxide

Figure 4(A) shows the three dimensional surface graph of the TNT removal efficiency for the hydrogen peroxide and PH. Accordingly, by increasing the concentration of H_2O_2 to 5 mM, the production of hydroxyl radicals is increased, whereas the process efficiency is obtained to 73.58%. Then, with increasing concentrations of up to 7mM, the changes are enhancing with a small slop, this because the hydrogen peroxide acts as a radical scavenger that by reaction with hydroxyl radical forms HO_2 (hydroproxyl radicals), so the number of hydroxyl radicals is reduced (Eq.(11)) [28].

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \tag{11}$$

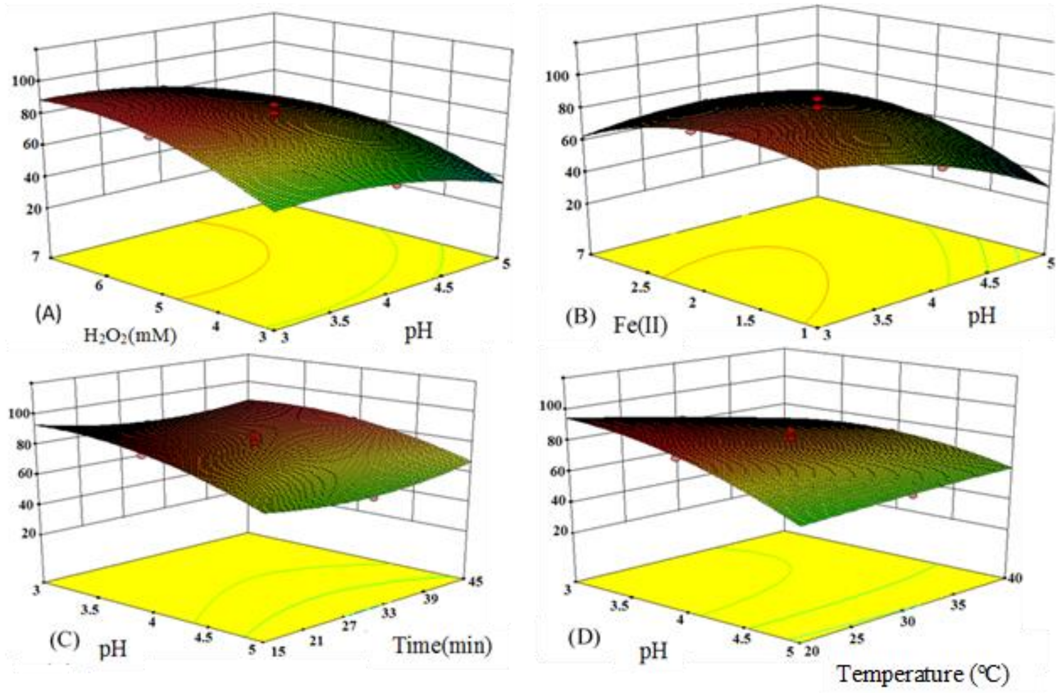


Figure 3. Three dimensional graphs of TNT removal efficiency

In general, by increasing catalyst concentration, the decomposition rate of the organic materials increased [29]. Additional, Fe (II) has a significant impact in transforming of TNT and other compounds, including nitroaromatic and nitramine to biodegradable products, whereas TNT changes into TAT (triaminotoluene), which TAT is extremely unstable [30], and decomposes under anaerobic biological treatment [31]. Due to the meaningful effects of linear and second degrees of iron (P<0.01), a curve can be expected in the form of three dimension. According to Figure 4(B), increasing the concentration of iron ions up to 2mM, increase TNT removal efficiency more than 80%. In this concentration, the production of hydroxyl radicals is at its highest level. According to Eq.(12), with an excessive increase optimum concentration, iron ions react with hydroxyl radicals that cause the reduction of hydroxyl radicals in the aquatic environment [32].

$$Fe^{2+} + {}^{\bullet}OH \rightarrow OH^{-} + Fe^{3+} \quad (12)$$

3.3.3. The Effect of Reaction Time

Figure 4(C) shows the effect of reaction time on TNT removal efficiency. Optimizing of time causes saving in the efficiency of the costs, money and energy consumption. In general, by increasing the reaction time, due to more exposure to hydrogen peroxide and iron ions, the productions of hydroxyl radicals is increased [34]. As can be seen, in the first time TNT removal rate is very low due to the decomposition of hydroxyl radical, and the changes take place by the constant slope. So it can be said that the optimization time of this process is 15 minutes.

3.3.4. The Effect of Temperature

The temperature by influencing on the reaction between hydrogen peroxide and iron has a significant impact on the decomposition of the organic materials. At the low temperatures, much time will be required for completing the reaction. However, by increasing temperature, removal efficiency increases, and it causes the reduction of the activated energy of TNT molecules, and demolition of TNT increases. Considering the reaction rate is directly related to temperature, and as shown in Figure 4(D) can be seen, at temperatures above 20°C, the amount of TNT removal efficiency gradually increased. According to Figure 4(D), it is clear that increasing the temperature from 30 to 40 °C, there haven't been any changes in the removal efficiency. The main reason is the decomposition of hydrogen peroxide to oxygen and water at high temperature [35]. Due to the cost related to energy consumption, the optimal temperature for wastewater treatment is recommended to be 30 °C.

3.4. Optimal Conditions

The obtained results show that there weren't any optimal values for Fenton process in any of designing experiments, so the final test was conducted under the condition (a) PH=3, (b) Fe=2mM, (c) $[H_2O_2]$=7mM, (d) time=15minutes, (e) temperature=30 °C. Based on results obtained under this condition, TNT removal efficiency was equal to 89.69% that shows the high efficiency of the Fenton process for removing TNT compounds.

4. Conclusions

In this study, the optimal operating conditions of coagulation and Fenton in order to achieve high efficiency removal of TNT and economic dosing chemicals were evaluated. Response surface methodology successfully used to optimize the important factors to TNT removal efficiency. In a result, the obtained model of removal of TNT have a suitable prediction. Based on the experimental results obtained, the combination of coagulation and Fenton was able to effectively reduce TNT under optimal conditions.

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