RESEARCH ARTICLE

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An Investigation of p-Nitro Cresol Removal from Aqueous Environment by Fenton Process in a Batch Reactor

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A-B-S-T-R-A-C-T

Background & Aims of the Study: One of the most carcinogenic and toxic pollutants is p-Nitro Cresol. In this study, the degradation and mineralization of p-Nitro Cresol in aqueous solution were investigated by Fenton process in a batch reactor.

Materials & Methods: This study is an experimental research on a laboratory scale. The study executed on synthetic wastewater having p-Nitro Cresol. The impact of operational factors such as pH, initial concentration of hydrogen peroxide and Ferrous ions was also investigated. The Box–Behnken design (BBD) of experiments and the response surface methodology (RSM) were employed to study the effects of three independent variables in the response function to acquire the optimal conditions.

Results: The ANOVA (analysis of variance) tests were executed to conclude the importance of the effects of independent variables on the response function. The ANOVA displayed a high determination coefficient value (R^2=92.88, R^2_{adj}=96.85 and R^2_{pred}=82.06) and satisfactory prediction second-order regression model. Different amounts of variables were optimized for the removal of p-Nitro Cresol in Fenton process. The optimum conditions predicted by the model were as follows: the (Fe^{2+})=0.77 mM, pH at 2.95, and (H_2O_2)=19.8 mM.

Conclusions: The results exhibited that at the predicted optimum conditions and after 45 min of reaction, the removal of p-Nitro Cresol and Chemical oxygen demand (COD) were 97.4 and 48.0%, respectively. The Fenton process was powerful in the removal of p-Nitro Cresol, but it can remove the COD to some extent

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Background

Pollution of water in the environment by toxic organic pollutants such as pesticides has become a global distress for water quality and as a basis of serious hazards for humans and animals. The Cresols denote groups of chemical phenolic compounds used widely in resin industrialized, herbicide such as dinitro-o-cresol, pharmaceuticals and surfactants. Wastewater from these industries along with petrochemicals hold a high concentration of Cresol derivatives. These pollutants retain an important hazard to the environment, as they are poisonous and recalcitrant in nature (1).

p-Nitro Cresol is a phenolic compound, wildly employed in the petrochemical, chemical and pharmaceutical businesses. It has been also listed as one of the important pollutants by the US-EPA (2).

There are three classical methods for the treatment of wastewater such as physical, chemical and biological methods. The classical systems have great operational costs, secondary pollution and a longer reaction time, so, using new methods without these problems are desirable. Advanced oxidation processes (AOPs) have been explored as successful approaches to treat environmental pollutants in water (3–4). Among these processes, Fenton treatment has been broadly used to degrade environmental pollutants (5), particularly in wastewater.

Different AOPs have been applied for the degradation of aromatic pollutants in aqueous phase. For instance, heterogeneous photo catalysis, Sonocatalysis, Ozonation (6–9), UV/H_2O_2 (10), Fenton and photo-Fenton processes (11–12) have been employed. The Fenton method is a good choice because it needs slight energy and low cost of chemicals (13). The Fenton technique generates hydroxyl radicals (OH•) proficiently based on the reaction between Fe (II) and H_2O_2 (Eqs.1, 2).

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \quad (1)$$
$$H_2O_2 + Fe^{3+} \rightarrow HOO^{\bullet} + H^{+} + Fe^{2+} \quad (2)$$

Also, Fe (III) can interrelate with the unused hydrogen peroxide, giving back Fe (II) (Eq. 2) (14).

Aims of the study:

The main purpose of this project is to use a Box-Behnken design of experiment for the optimization of operational factors such as pH, initial concentration of hydrogen peroxide and Ferrous ions on degradation of p-Nitro Cresol in Fenton process.

Materials & Methods

Materials

p-Nitro Cresol was acquired from the Merck Company of Germany and used without further purification. Distilled water was used in all of the experiments. Ferrous Sulfate hepta hydrate ($FeSO_4.7H_2O$) as the source of Fe (II), hydrogen peroxide solution (30% w/w), H_2SO_4 and NaOH are all supplied from Merck.

Photo reactor

The experiments were made in a glass cylindrical batch photo reactor with 1 liter of capacity. The light source was a mercury lamp, Philips 15 W (UV-C), which was immersed perpendicularly in the center of the reactor. The system was prepared with a sampling system. The reactor was equipped with a jacket of water and external circulating flow through a thermostat for regulating temperature fixed at 25 °C. The solution in the reactor was mixed well by stirrer. A pH meter, PT-10P Sartorius Instrument from Germany Company was employed to regulate the initial pH of the solution. Water bath, BW 20G model from Korean company was used for fixing temperature at 25 °C in all tests. The degradation of p-Nitro Cresol was calculated with high performance liquid chromatography (HPLC) from Knauer, Germany. A reverse phase column with 150 mm in length and 4.6 mm in diameter was filled with 3 µm Separon C_{18}. The Isocratic method was used with a solvent mixture of 30% deionized water and 70% of methanol with a flow rate of 1 ml. min–1.

General procedure

In each test, about 1000 ml of synthesized wastewater holding p-Nitro Cresol was used. Altered concentrations of Fe^{2+}, H_2O_2 and pH were used for optimization in Fenton process. An aqueous solution containing 10% of sodium sulphite was used to quench the reactions. The samples were taken and calculated by UV/Vis spectrophotometer and confirmed by high performance liquid chromatography (HPLC). The COD was measured based on standard methods (15). The removal percent for the p-Nitro Cresol and COD were achieved as in Eqs. (3) and (4):

$$\text{Removal of } p\text{−}Nitro\ Cresol\ (\%) = \left(\frac{[C]_0-[C]}{[C]_0}\right) \times 100 \quad (3)$$

$$\text{Removal of } COD\,(\%) = \left(\frac{[COD]_0-[COD]}{[COD]_0}\right) \times 100 \quad (4)$$

Where $(C)_0$ and $(COD)_0$ are the concentration of p-Nitro Cresol and amount of COD at the start of the treatment and (C) and (COD) are the concentration of p-Nitro Cresol and amount of COD at time t, in that order.

Results

The experimental design method was used and the percentage of the degradation of the p-Nitro Cresol was selected as responses to consider the optimum conditions. The BBD was employed with three independent variables involving the concentration of Ferrous ion (CF), hydrogen peroxide (CHP) and pH. The input variables and their levels in the experiment were presented in Table 1. In all runs, the time of reaction was 45 min.

Table1)The range and levels of the variables.

Factors	Symbol	Range and levels		
		-1	**0**	**+1**
Ferrous, mM	C_F	0.3	0.6	0.90
Hydrogen peroxide, mM	C_{HP}	8	16	24
pH	pH	2	3	4

Data analysis

The Box-Behnken experimental designs requests less runs rather than all other RSM designs (16). The following model was fitted to the response variable (Y) in the form of a polynomial equation (Eq. 5):

$$Y = b_0 + \sum b_i x_i + \sum\sum b_{ij} x_i x_j + \sum\sum b_{ii} x_i^2 + \varepsilon \qquad (5)$$

Where b_0 is a constant, ε is the residual term, b_{ij} is the linear interaction effect between the input variables, x_i and x_j (i=1,2 and 3; j=1,2 and 3), $b_i$is the slope of the variable, b_{ii} is the second order of input variable (x_i). The ANOVA was employed to explore the significance of each term in the polynomial equation (17). The MINITAB 17 was used to determine the coefficients of Eq. (5) with RSM. The experimental design involved 15 tests and the natural values of these factors for the removal of p-Nitro Cresol are presented in Table 2.

Table 2) Experimental design for three independent variables and the response.

Run No.	Manipulated variables			Removal of	
	X_{C_F}	$X_{C_{HP}}$	X_{pH}	Exp.	Pred.
1	0.3	8	3	36.7	34.0000
2	0.9	8	3	50.0	51.0000
3	0.3	24	3	71.0	70.0000
4	0.9	24	3	92.0	94.7000
5	0.3	16	2	69.1	68.7250
6	0.9	16	2	87.3	83.2250
7	0.3	16	4	54.4	58.4750
8	0.9	16	4	85.3	85.6750
9	0.6	8	2	39.5	42.5750
10	0.6	24	2	84.5	85.8750
11	0.6	8	4	43.5	42.1250
12	0.6	24	4	81.6	78.5250
13	0.6	16	3	94.6	94.4667
14	0.6	16	3	94.1	94.4667
15	0.6	16	3	94.7	94.4667

Discussion

Central composite design model

The objective of this section was to determine the optimum condition for maximum removal of p-Nitro cresol in Fenton process. The stages of CCD were studied by many investigators (18–19). The 3-factors CCD matrix and experimental results achieved by the removal of the p-Nitro Cresol is presented in Table 2.

The correctness of the model are illustrated in Fig. 1, which compares the experimental values against the predicted responses of the model for the degradation of p-Nitro Cresol.

These results were exposed a good agreement between predicted and experimental values. It was observed that the predicted response from the model is in agreement with the experimental values.

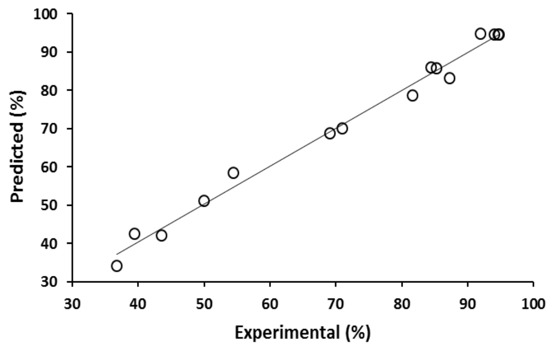

Figure 1) Comparing the experimental and predicted value for the removal of p-Nitro Cresol in Fenton process.

ANOVA tests for the removal of p-Nitro Cresol by Fenton process

In this study, by BBD and RSM, the effects of three independent variables on the response function were studied to obtain the optimal conditions. The mathematical relation between the response and three important variables can be appraised by a quadratic polynomial equation (20). The equation for the removal of the p-Nitro Cresol is presented in the following equation (Eqs. 6):

$$\text{Removal of p-NitroCresol(\%)} = -164.8 + 125.4\, X_{C_F} + 13.60\, X_{C_{HP}} + 56.9\, X_{C_{pH}} - 112.7X_{C_F}^2 - 0.3421X_{C_{HP}}^2 - 10.30X_{C_{PH}}^2 + 0.802X_{C_F}X_{C_{HP}} + 10.58X_{C_F}X_{C_{PH}} - 0.216\, X_{C_{HP}}X_{C_{PH}} \quad (6)$$

All of the obtained results from BBD, the observed values and predicted response values with residuals for all runs are presented in Table 3.

Table 3) ANOVA tests for quadratic models for the removal of p-Nitro Cresol by Fenton process.

Sources	DF	SS	MS	*F*-value	*P*-value
Fenton					
Model	9	6418.45	713.16	48.87	0.000
Linear	3	4075.91	1358.64	93.09	0.000
X_{C_F}	1	869.45	869.45	59.57	0.001
$X_{C_{HP}}$	1	3176.05	3176.05	217.62	0.000
$X_{C_{pH}}$	1	30.42	30.42	2.08	0.208
Square	3	2275.49	758.50	51.97	0.000
$X_{C_F}^2$	1	380.08	380.08	26.04	0.004
$X_{C_{HP}}^2$	1	1770.19	1770.19	121.29	0.000
$X_{C_{pH}}^2$	1	391.40	391.40	26.82	0.004
2-Way Interaction	3	67.05	22.35	1.53	0.315
$X_{C_F}X_{C_{HP}}$	1	14.82	14.82	1.02	0.360
$X_{C_F}X_{C_{pH}}$	1	40.32	40.32	2.76	0.157
$X_{C_{HP}}X_{C_{PH}}$	1	11.90	11.90	0.82	0.408
Error	5	72.97	14.59		
Lack – of – fit	3	72.76	24.25	234.73	0.004
Pure error	2	0.21	0.10		
Total	14	6491.42			
Model Summary	S	R^2	R_{adj}^2	R_{pred}^2	
	3.82025	98.88%	96.85%	82.06%	

Different dosages of Fe^{2+} (from 0.3 to 0.9 mM) were used to reach its optimum concentration. As it can be seen from Fig. 2, the removal efficiency of p-Nitro Cresol was improved by an increase in the dosage of Ferrous ion based on the following equations (Eqs. 7,8).

$$H_2O_2 + Fe^{3+} \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \quad (7)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \quad (8)$$

The creation of hydroxyl radicals and consequently the removal of p-Nitro Cresol were enhanced by an increase in the concentration of Fe^{2+} ions from 0.3 to 0.6 mM.

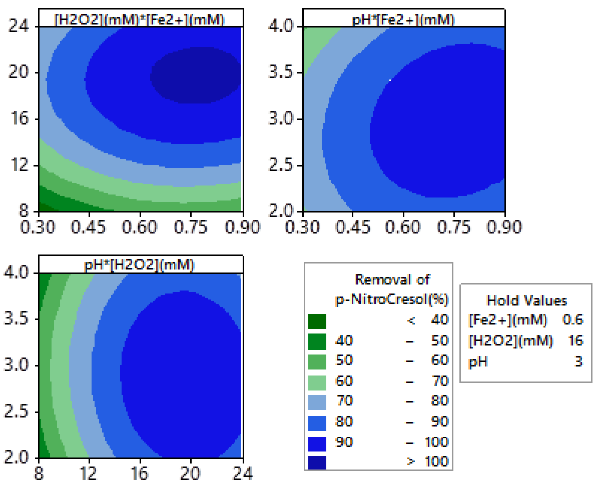

Figure 2) The contour plot of removal of p-Nitro Cresol in Fenton process based on (Fe^{2+}), (H_2O_2), and pH.

Effect of initial concentration of hydrogen peroxide

The removal of p-Nitro Cresol was increased by an increase in the concentration of H_2O_2 from 8 to 16 mM, because more OH• radicals were produced. But, by increasing in the dosages from 16 to 24 mM, the progress was not significant or even it was dropping. The hydrogen peroxide acts as free-radical scavenger at high concentrations, so, the degradation of p-Nitro Cresol was not significant (21). Besides, the auto decomposition of H_2O_2 to oxygen and water and the reaction of H_2O_2 with hydroxyl radicals instead of pollutant molecules was happened (22).

The optimal amounts of H_2O_2 proposed by Model was 19.8 mM for the removal of p-Nitro Cresol. Thus, H_2O_2 should be added at an optimum dosage. However, all of the added hydrogen peroxide was not consumed.

The model terms with a probability value larger than 0.05 was not significant. It was clear that the effect of 2-way interactions between variables was not important (23). The significance of the coefficients was presented in Table 3.

The total concentration of organics has been presented as COD values and it is essential to measure the COD after the degradation of the pollutants to verify the mineralization amount of the p-Nitro Cresol. Different initial concentration of p-Nitro Cresol had different COD, for example, about 180 mg/lit of COD was exerted from 0.65 mM or 100 mg/lit of p-Nitro Cresol.

The Fenton process can degrade p-Nitro Cresol efficiently, but pretty have difficulty with the removal of COD. The optimum conditions predicted by the model were as follows: the (Fe^{2+})=0.77 mM, pH at 2.95, and (H_2O_2)= 19.8 mM. Under the predicted optimum condition the removal efficiency of p-Nitro Cresol proposed by the software was 102.18%. The experiment was repeated once again at the predicted optimum condition and the removal of p-Nitro Cresol and COD was 97.4 and 48.0%, respectively.

The contour and response surface plots for the removal of p-Nitro Cresol in Fenton process are presented in Figs. 2,3,4 and 5.

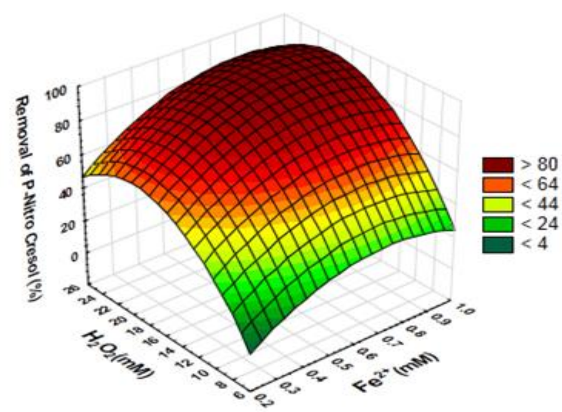

Figure 3) Surface of response for the removal efficiency of p-Nitro Cresol versus: the dosage of Frrous ions and H_2O_2.

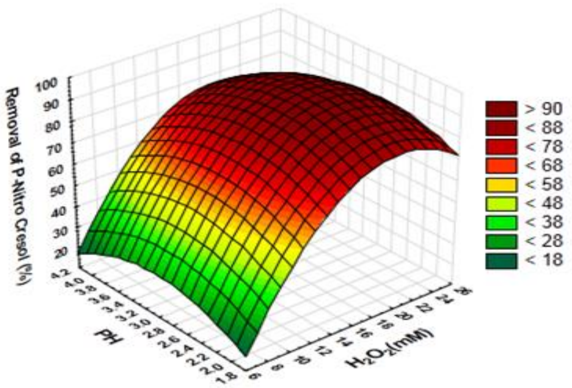

Figure 4) Surface of response for the removal efficiency of p-Nitro Cresol versus: the pH and the concentration of H_2O_2.

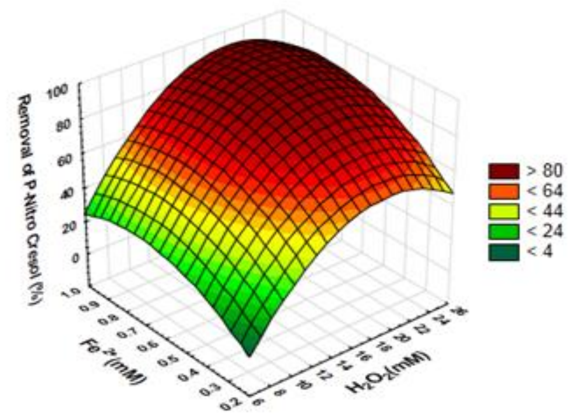

Figure 5) Surface of response for the removal efficiency of p-Nitro Cresol versus: the dosage of Frrous ions and H_2O_2.

Conclusion

In this study the Box-Behnken design of the experiment and RSM were employed for the removal of p-Nitro Cresol in aqueous environment by Fenton process.

The effect of initial concentrations of H_2O_2, Fe^{2+} and pH on the removal of p-Nitro Cresol has been studied. The ANOVA test was performed to determine the significance of independent variables on the response function. The optimum conditions predicted by the model were as follows: the (Fe^{2+})=0.77 mM, pH at 2.95, and (H_2O_2)= 19.8 mM.

Three-dimensional plots were used to study the parts of each factor, as well as their interactions on the removal of p-Nitro Cresol. The ANOVA test displayed a high determination coefficient value (R^2=92.88, R^2_{adj}=96.85 and R^2_{pred}=82.06) and satisfactory prediction second-order regression model. At the predicted optimum condition and after 45 min of reaction, the removal of p-Nitro Cresol and COD was 97.4 and 48.0%, respectively. The Fenton process can degrade p-Nitro Cresol proficiently, but pretty has difficulty with the removal of COD.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

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