

Treatment of Synthetic Wastewater Containing Diethyl Phthalate through Photo-Fenton Method by Box-Behnken Design

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Background & Aims of the Study: Diethyl phthalate (DEP) cannot be proficiently degraded by ultraviolet (UV) radiation and hydrogen peroxide (H₂O₂) oxidation separately; however, the photo-Fenton method is verified to be operative and can completely degrade this pollutant. Currently, advanced oxidation methods have been growing to be employed for the remediation of industrial wastewater. In the present study, the photo-Fenton process investigated the degradation and mineralization of the aqueous solution containing DEP.

Materials and Methods: Synthesized wastewater was used in this study. In addition, the effects of operative factors, such as the initial concentrations of H₂O₂, ferrous ion, and DEP, have been studied. The response surface methodology and Box-Behnken design of experiments were applied to examine the effects of three sovereign variables on the response functions to obtain the optimum circumstances.

Results: The analysis of variance was carried out to determine the importance of the effects of independent variables on the response function. Various amounts of variables were optimized for the removal of DEP. At optimum conditions (i.e., H₂O₂ concentration of 400 mg/l, ferrous concentration of 75 mg/l, and DEP concentration of 50 mg/l) and 60 min following the reaction, the rates of degradation efficiency for DEP and chemical oxygen demand (COD) were 100% and 85.3%, respectively.

Conclusion: According to the obtained results, the suggested quadratic model showed good correctness. The statistical analysis of the model indicated that the model was satisfactory to predict the performance of the processes. The obtained findings demonstrated that the photo-Fenton processes can be used for the complete and partial removal of DEP and COD from wastewater, respectively. The benefits of the photo-Fenton process were less sludge formation, fewer chemicals, and time obligation but at the cost of consumed power. The power consumption can be reduced by employing sunlight instead of artificial UV light to a larger amount. The photo-Fenton procedure was influential in the degradation of DEP and can considerably decrease COD.

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Background

Today, water is likely to be the chief reason

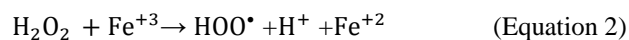
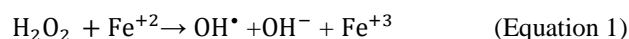
for the upcoming fights worldwide; accordingly, in the following century, freshwater capitals are similarly valued as oil wells. Therefore, human life is in danger due to the limited number

of freshwater resources. Approximately, 2.1 billion of the inhabitants around the world have no access to harmless drinking water, and nearly 80% of infectious diseases in the Third World countries originate from drinking dirty water (1–3).

Diethyl phthalate (DEP) is one of the most commonly known phthalates with great water solubility and short-chain in various environmental samples comprising drinking water, surface water, and seawater. As DEP is problematic for photo-chemically and biologically degradation (4), there is a robust essential to look for operative treatment methods for such contaminants; as a result, water reuse and treatment are very significant issues.

Conventional remediation techniques were reported with high operational charges, long reaction times, and secondary contamination. Therefore, it is essential to examine the application of novel approaches lacking the aforementioned difficulties. Advanced oxidation processes (AOPs) generate hydroxyl radicals as robust oxidizing species. The hydroxyl radicals can be extensively employed for the removal of organic contaminants that cannot be treated by biological treatment methods (5).

Various AOPs were applied to degrade organic contamination in the water phase. For instance, heterogeneous photocatalysis, ozonation (6–9), ultraviolet (UV)/H₂O₂ (10), photo-Fenton, and Fenton methods (11–14) have been applied for this subject. The photo-Fenton and Fenton methods are good options due to the need for low-cost chemicals and low energy (e.g., hydrogen peroxide and iron salts) (15–16). It is clear that the Fenton technique generates hydroxyl radicals well originated from the reaction between H₂O₂ and Fe (II).



Furthermore, Fe (III) can react with the

leftover H₂O₂, giving back Fe (II) (Equation 2) (13). In the photo-Fenton method, the reduction of ferric to ferrous ions is improved through the production of further OH[•] radicals leading to an increase in the oxidation of pollutants. The AOPs are recognized as effective techniques for the removal of pollutants from industrial wastewaters. The aforementioned techniques were used in some studies for wastewater treatment (17).

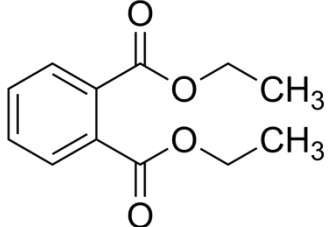
In a study carried out by Huang et al., the Fenton, photo-Fenton, and electro-Fenton processes were compared regarding the degradation of Remazol Black B dye (18). In the aforementioned comparative study, the organic wastewater was converted into inorganic substance, and the rates of removal efficiency were 70% and 93% in the Fenton and electro-Fenton processes, respectively. This result was responsible for decreasing iron ions in the cathode.

The photo-Fenton was reported with the efficacy of higher than 98% based on the recovery of iron ions. The results showed that organic contaminants, such as formic acid, which cannot be removed using the Fenton technique, could be completely and quickly destroyed by the photo-Fenton method (18). In the current study, the synthetic wastewater containing DEP was remediated through the Photo Fenton method. The effects of various factors, including the concentrations of hydrogen peroxide, DEP, and ferrous, on DEP removal were investigated using the Box-Behnken design (BBD).

Materials & Methods

The FeSO₄·7H₂O, DEP (99.5%), and hydrogen peroxide solution (30% w/w) were supplied from Merck Company. Manganese oxide (MnO₂) (≥99%) was provided by Sigma-Aldrich Company, and distilled water was used in all the experiments. The properties of DEP

Table 1) Chemical structure and maximum absorption of diethyl phthalate

Pollutant	Molecular structure	λ_{\max} , nm	M_w (g mol ⁻¹)
Diethyl phthalate		230	222.24

are presented in Table 1.

Experimental Setup and Analytical Procedure

The experiments were carried out in a glass photoreactor with 1-liter capacity and prepared using a sampling system (Figure 1). The source of (UV-C) light was a 15W Philips vertically placed at the center of the reactor. The reactor was prepared by a water jacket with an exterior flow controlled by a thermostat for adjusting and maintaining the temperature at 25°C. A water bath (BW-20G, Jeio Tech Co., Daejon, Korea) was employed to control the temperature at 25°C.

The solution was stirred to be homogenized and avoid the precipitation of iron ions in the reactor. A pH meter (PT-10P Sartorius

Instruments, Germany) was utilized for the measurement of the primary pH of the solution fixed at 3. The samples were transferred to a spectrophotometer (DR 5000, Hach, Jenway, USA) at 600 nm, and the chemical oxygen demand (COD) was measured using the standard methods (19).

About 1000 ml of synthetic wastewater was used in each test. The concentrations of ferrous ions, hydrogen peroxide, and DEP were the intended parameters, and the goal was to decrease the DEP concentration and COD amounts in synthetic wastewater. In all runs, the reaction time was reported as 30 min. The rates of DEP and COD removal were calculated using equations 3 and 4 as follows:

$$\text{Removal of DEP (\%)} = \left(\frac{DEP_0 - DEP_t}{DEP_0} \right) \times 100 \quad (\text{Equation 3})$$

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

where DEP_0 and $[COD]_0$ are the concentration of the DEP and amount of COD at the initiation of the reaction, and DEP_t and $[COD]$ are the concentration of the DEP and amount of COD at time t , respectively. The remaining hydrogen peroxide in the samples was eliminated through the MnO_2 powder to prevent from interfering with the COD test. Then, MnO_2 powders were separated using a filter (20).

Statistical analysis and experimental design

The experimental design was used for the optimization of the DEP removal efficiency in

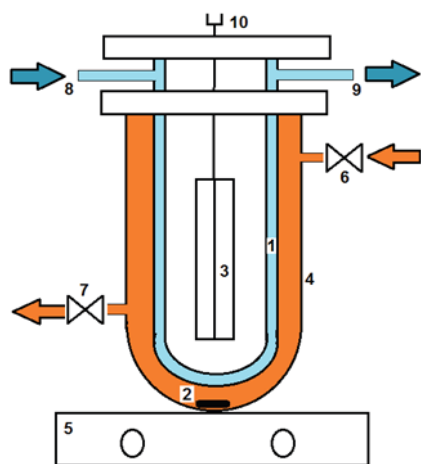


Figure 1) Schematic diagram of used laboratory reactor; (1) cooling water jacket; (2) magnetic stirrer bar; (3) ultraviolet lamp; (4) glass reactor; (5) magnetic stirrers; (6) input wastewater; (7) output wastewater; (8) cooling water input; (9) cooling water output; (10) electric connection

Table 2) Experimental levels and ranges of independent variables

Variable	Unit	Symbol	Dimension and level		
			Low (-1)	Middle (0)	High (+1)
Diethyl phthalate concentration	mg/l	C_{DEP}	50	100	150
Ferrous Concentration	mg/l	$C_{Ferrous}$	25	50	75
Hydrogen peroxide Concentration	mg/l	C_{HP}	100	250	400

a scientific way. The effects of ferrous concentration (C_F), hydrogen peroxide concentration (C_{HP}), and DEP dosage (C_{DEP}) were investigated on DEP removal efficiency. Table 2 tabulates the input variables (i. e., C_{HP} , C_F , and C_{DEP}) with their values and dimensions.

The BBD experiment requires a low number of tests (15 tests for three variables) (21). Due to the design of the experiments, the resulting model ($Res.$), as a polynomial equation of independent variables, was presented for the response variable as follows:

$$Res. = b_0 + \sum b_i x_i + \sum \sum b_{ij} x_i x_j + \sum \sum b_{ii} x_i^2 + \varepsilon \quad (\text{Equation 5})$$

where ε is the remainder of the equation; b_0 is a constant number; b_{ij} is a linear interaction among the input variables of x_i and x_j ($i = 1, 2$ and $j = 1, 2, 3$); b_i is the slope of the variable; b_{ii} is the second order of the input variable x_i ($i = 1, 2, 3$).

Results

The analysis of variance (ANOVA) was employed to investigate the importance of operating variables in the polynomial equation (Equation 4) (22). In the ANOVA, the p -value of 0.05 was statistically significant. The p -values of less than 0.0500 showed the importance of model terms. The values higher than 0.1000 indicated no significance regarding the model terms. The statistical significance of the second-order models was introduced by F -value. The p -value will be much lower once the estimated F -value is higher than the F -value in the Table indicating the significance of the

statistical model. The F -value was calculated by dividing the mean squares of regression, namely square, linear, and interaction, by the mean squares of residual as follows (23):

$$F - \text{value} = \frac{MS_{Reg.}}{MS_{Res.}} = \frac{SS_{Reg.}/DF_{Reg.}}{SS_{Res.}/DF_{Res.}} \quad (\text{Equation 6})$$

where the number of terms minus 1 represents the regression degree of freedom ($DF_{Reg.}$), and the total degrees of freedom minus the regression degree of freedom equals the residual degree of freedom ($DF_{Res.}$) (23). About 15 tests (i.e., 2 replicates at the central point and 13 runs) were included in the design of the experiments. The rates of DEP removal are presented in Table 3. The tests were randomly carried out to decrease the experimental errors.

Analysis of response variance and design of experiments

In the photo-Fenton method, the optimum conditions in the removal of DEP were obtained, and the impacts of three independent variables, including H_2O_2 , Fe^{2+} , and DEP concentrations, on the removal of DEP were studied using the BBD. The experimental results of the removal of DEP were presented in Table 3. By the adoption of the least-squares error procedure, the quadratic relationship was obtained for the determination of the response regarding the three independent variables as follows:

$$DEP \text{ Removal } \% = 55.8 + 0.062C_{DEP} + 0.261C_{Ferrous} + 0.1121C_{H_2O_2} - 0.002093C_{DEP}^2 + 0.00035C_{Ferrous}^2 - 0.000122C_{H_2O_2}^2 - 0.00132C_{DEP}C_{Ferrous} + 0.00043C_{DEP}C_{H_2O_2} - 0.000020C_{H_2O_2}C_{Ferrous} \quad (\text{Equation 7})$$

Table 3) Design of experiment for three independent variables and their responses

Run no.	Manipulated variables			Responses (%)
	C_{DEP}	$C_{Ferrous}$	C_{HP}	
1	100	75	400	92.0
2	100	50	250	79.4
3	100	25	100	61.3
4	50	50	400	97.1
5	100	25	400	86.6
6	50	50	100	73.0
7	100	50	250	79.1
8	150	75	250	60.0
9	100	75	100	67.0
10	50	75	250	98.8
11	150	50	400	76.0
12	150	50	100	39.0
13	150	25	250	53.0
14	100	50	250	79.3
15	50	25	250	85.2

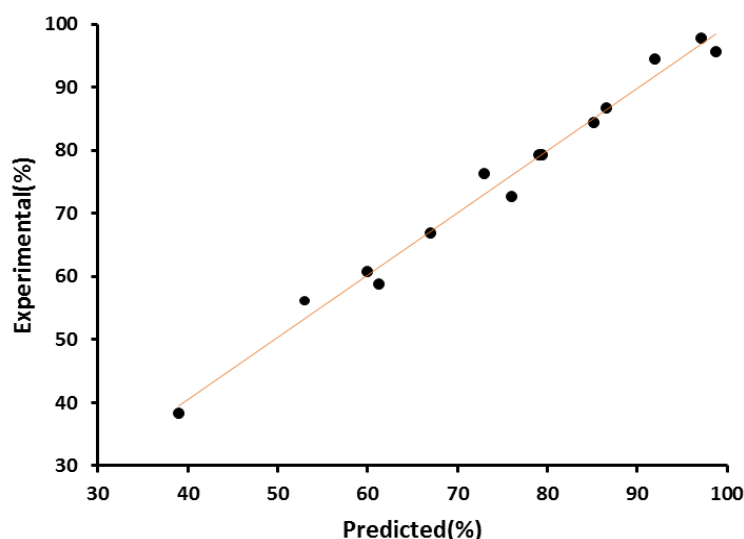


Figure 2) Comparison of predicted and experimental values

The predicted values of the quadratic model in comparison to the experimental values in terms of the DEP removal were illustrated in Figure 2. The predicted values in the removal of DEP were gained through equation 7.

Table 4 tabulates the results of the ANOVA regarding the evaluation of the DEP removal model. As shown in Table 4, the residual error and degree of freedom for the model are 5 and 9, respectively. The tabulated F -value and the calculated F -value were shown in Table 4. In

addition, the estimated F -value of the model was greater than the tabulated F -value; therefore, the p -value was very low ($p < 0.0001$), and the model was significant. The p -values of C_{HP} , C_F , and C_{DEP} , and their squares were less than 0.01 and considered statistically significant (24). However, the p -value of the binary interaction between the variables was higher than 0.05 indicating that the interaction of variables was non-significant. Furthermore, the lack of fit was reported with a p -value of higher

Table 4) Results of analysis of variance for introduced model in removal of diethyl phthalate

Source	DF	Adj SS	Adj MS	F-value	P-value
Model	9	3841.07	426.79	37.11	0.00
Linear	3	3664.51	1221.50	106.20	0.00
C_{DEP}	1	1987.65	1987.65	172.81	0.00
$C_{Ferrous}$	1	125.61	125.61	10.92	0.021
$C_{H_2O_2}$	1	1551.24	1551.24	134.87	0.000
Square	3	124.05	41.35	3.60	0.101
C_{DEP}^2	1	101.12	101.12	8.79	0.031
$C_{Ferrous}^2$	1	0.17	0.17	0.02	0.907
$C_{H_2O_2}^2$	1	28.09	28.09	2.44	0.179
Two-way interaction	3	52.52	17.51	1.52	0.317
$C_{DEP} \cdot C_{Ferrous}$	1	10.89	10.89	0.95	0.375
$C_{DEP} \cdot C_{H_2O_2}$	1	41.60	41.60	3.62	0.116
$C_{Ferrous} \cdot C_{H_2O_2}$	1	0.02	0.02	0.00	0.966
Error	5	57.51	11.50		
Lack of fit	3	57.46	19.15	820.89	0.001
Pure error	2	0.05	0.02		
Total	14	3898.58			

Model summary

S	R ²	R _{adj} ²	R _{pred} ²
3.39144	98.52%	95.87%	76.41%

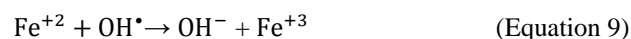
than 0.05, signifying the model's mismatch.

Influence of operational variables

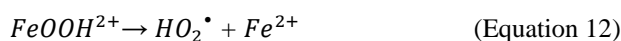
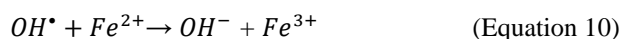
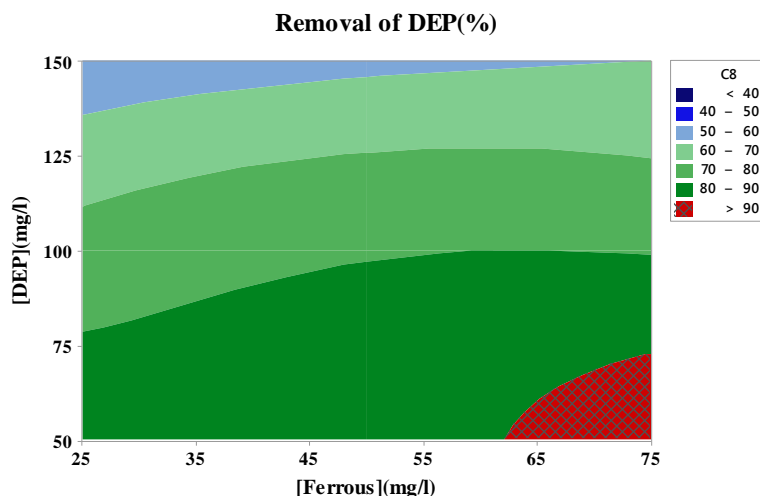
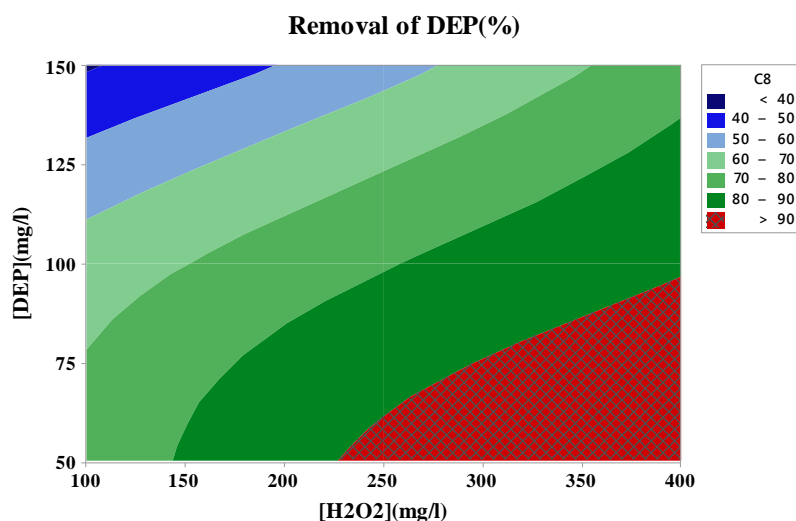
Figures 3-5 depict the effects of hydrogen peroxide (100, 250, and 400 mg/l), Fe²⁺ (25, 50, and 75 mg/l), and DEP (50, 100, and 150 mg/l) concentrations on the removal of DEP in synthetic wastewater. The aforementioned figures illustrated the three-dimensional (3D) plots of DEP removal based on these variables using equation 7. The 3D plot of the DEP removal according to hydrogen peroxide and DEP concentrations is depicted in Figure 3. In addition, the maximum percentage of DEP removal was obtained in low values of DEP and practically high values of hydrogen peroxide. In the photo-Fenton method, the DEP removal efficiency was enhanced with an excessive increase in H₂O₂ concentration.

Different dosages of Fe²⁺ (range: 25-75

mg/l) were applied to reach the optimal concentration. As illustrated in Figure 4, it is clear that in the photo-Fenton process, the removal efficiency of DEP was enhanced with an increase in the dosage of ferrous ion according to the following equations:



In the photo-Fenton process, the production of hydroxyl radicals and removal of DEP were improved with an increase in the concentration of Fe²⁺ ions from 25 to 7 mg/l. Based on figures 3-5, the increase in the catalyst dosage was to some extent helpful. However, the catalyst could not be added without any limitations. High amounts of catalyst had a negative effect on DEP removal, since the scavenging outcomes might occur (Equations 10-12).



At the high catalyst amounts, the additional catalyst would consume the produced hydroxyl radical. Higher catalyst quantities would obviously upsurge the treatment cost.

Moreover, the excessive catalyst dosage would result in the production of high amounts of sludge, which would increase the need for the following sludge treatment.

The removal of DEP based on hydrogen peroxide and ferrous concentrations is depicted in Figure 4. At a pH of higher than 3, the main fraction of Fe (II) was precipitated as $Fe(OH)_3$, weakening the reaction between Fe^{2+} and H_2O_2 . In addition, in alkaline conditions, the removal

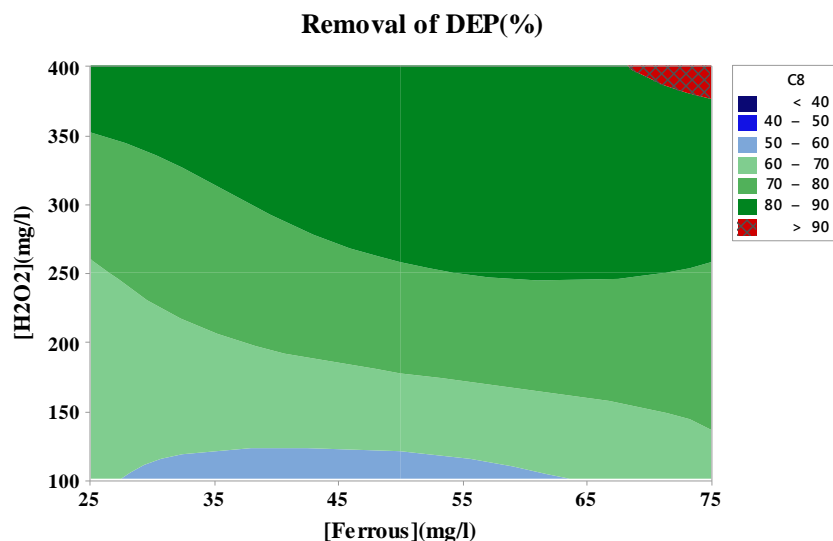


Figure 5) Contour plots of diethyl phthalate removal versus ferrous and hydrogen peroxide concentrations ($pH = 3$; $T = 25^{\circ}C$; $t = 60 \text{ min}$)

of DEP reduced because the H_2O_2 degrades faster into H_2O and O_2 . Therefore, based on the evidence and preliminary experiment in the present study, pH was fixed at 3 in all tests and was not optimized.

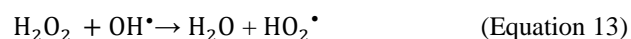
Optimization of working conditions

According to figures 3-5, it is obvious that the DEP removal efficiency is high at optimum circumstances. The amounts of different parameters were obtained for the optimization of the DEP removal using Design-Expert software (version 7.0.0). The optimum values and removal of DEP are presented in Table 5. It was certain that the maximum removal of DEP was achieved at a ferrous concentration of 75 mg/l, hydrogen peroxide concentration of

400 mg/l, and DEP concentration of 50 mg/l. The maximum predicted and experimental values in the removal of DEP by three replications were 103.49% and 100.0%, respectively.

Discussion

The treatment proficiency reduced with a decline in H_2O_2 dosage because the breakdown of H_2O_2 decreased in the presence of a catalyst for the production of hydroxyl radicals. However, extreme H_2O_2 quantity was not appropriate. Firstly, an extreme H_2O_2 dosage highly increases the treatment cost. Furthermore, the scavenger effect of H_2O_2 on hydroxyl radical (Equation 13) is significant when the H_2O_2 dosage is in excess (25-26).



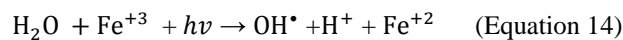
Therefore, the H_2O_2 dosage should be in the optimum range, and it was optimized. In the photo-Fenton process after 60 min of treatment, the removal of DEP was high that can be

Table 5) Optimal conditions in removal of diethyl phthalate ($T = 25^{\circ}C$; $t = 60 \text{ min}$)

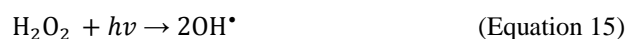
Parameter	Unit	Value
Hydrogen proxide concentration	mg/l	400
Ferrous ion concentration	mg/l	75
DEP concentration	mg/l	50
Predicted DEP removal	%	103.49
Experimental DEP removal	%	100

DEP: Diethyl phthalate

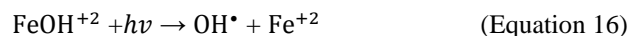
related to the extensive regeneration of all Fe^{3+} to Fe^{2+} improved by UV (Equation 14) (27).



The remaining ferrous ions were separated by changing the pH of the solution to the alkaline media at the end of the processes (28). At a high concentration of Fe (II), the initial generation rate of hydroxyl radicals, mostly formed by the cleavage of hydrogen peroxide, was very high. Accordingly, several hydroxyl radicals were consumed by the undesired reactions before they could be efficiently consumed for the degradation of DEP (Equation 15) (29).

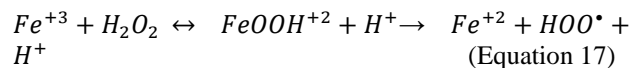


Additionally, the turbidity of solution can be changed to brown at high doses of ferrous ions, and subsequently, the absorption of the UV light reduced resulting in the recombination of OH^{\bullet} radicals (30). This result is in line with the findings of multiple studies (Equation 16) (31).



The results of the present study are consistent with the findings of a study carried out by Jafari Mansoorian H et al. (32) indicating that the removal efficiency decreased with increasing the concentration of DEP. Finally, it can be realized that the photo-Fenton process as the modified Fenton process is better than the Fenton process regarding the removal of pollutants from aqueous environments.

Based on equation 17, the Fe^{3+} was altered to Fe^{2+} , and the Fenton reaction was initiated for DEP removal. The renewal of the catalyst and production of extra hydroxyl radicals were obtained through the continuous irradiation of the Fe^{3+} solution. However, the reaction is terminated in case of the consumption of all the H_2O_2 by Fe^{2+} (33).



Conclusion

In the present study, the synthetic wastewater containing DEP was remediated by the photo-Fenton process, and the BBD was applied for designing the experiment. In addition, this study investigated the effects of H_2O_2 , Fe^{2+} , and DEP concentrations on DEP removal from synthetic wastewater. The results of the ANOVA showed that the operational variables were efficient in the removal of DEP. A quadratic model was introduced to assess the impacts of variables on the removal of DEP. At optimum conditions (i.e., hydrogen peroxide concentration of 400 mg/l, ferrous concentration of 75 mg/l, and DEP concentration of 50 mg/l) and after 30 min, the degradation rates of DEP and COD were reported as 100% and 85.3%, respectively.

Based on the obtained results, the offered quadratic model showed good correctness. The statistical analysis of the model indicated that the model was satisfactory to predict the performance of the processes. The obtained findings revealed that the photo-Fenton processes can be employed for the complete and partial removal of DEP and COD from wastewater, respectively. The benefits of the photo-Fenton process were less sludge formation, fewer chemicals, and time obligation but at the cost of consumed power. The power consumption can be reduced by employing sunlight instead of artificial UV light to a larger amount.

Footnotes

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Conflict of Interest

The authors declare that there is no conflict of interest.

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