IJPAS | INTERNATIONAL JOURNAL PURE AND APPLIED SCIENCES
ISSN: 2149-0910
Vol. 10(1); 290-302 (2024)
DOI: 10.29132/ijpas.1485873

Research Article

Subcritical Water Oxidation of Diethyl Phthalate Using H_2O_2 and $K_2S_2O_8$ as Oxidizing Agents: Application of Box-Behnken Design

Özkan GÖRMEZ*, Ahmet Murat GİZİR

Received: 17.05.2024
Accepted: 27.06.2024

[1] Mersin University, Faculty of Science, Department of Chemistry, Mersin, Türkiye; ozkan.grmz@gmail.com; agizir@mersin.edu.tr
* Corresponding author

Abstract: Phthalates are known for their harmful effects on human health, including being carcinogenic, toxic, and causing endocrine disruption. Therefore, removing phthalates from aquatic environments is an important issue for researchers. This study aims to compare the efficiency of hydrogen peroxide (HP) and potassium persulfate (PS) oxidants in degrading diethyl phthalate using the oxidant-assisted subcritical water oxidation method. Additionally, the study statistically examines the effect of operational parameters (temperature, oxidant concentration, and treatment time) on diethyl phthalate degradation using the Box-Behnken design. Results indicated that temperature was the primary parameter affecting diethyl phthalate degradation, with both oxidants fitting a quadratic model. The highest total organic carbon (TOC) removal rate (100%) was achieved when potassium persulfate was used as the oxidant in the oxidation experiments. When hydrogen peroxide was used as the oxidant, the maximum TOC removal efficiency was determined to be 87%.

Keywords: Advanced Oxidation Processes; Subcritical water oxidation; Response Surface Methodology; Box-Behnken Design; Endocrine disrupting chemicals

Oksitleyici Ajan Olarak H_2O_2 ve $K_2S_2O_8$ Kullanılarak Dietil Ftalatin Subkritik Su Oksidasyonu: Box-Behnken Tasarımının Uygulanması

Özet: Ftalatlar insan sağlığı üzerine kanserojen, toksik ve endokrin bozucu gibi zararlı etkileriyle bilinmektedir. Bu nedenle ftalatların sucul ortamlardan uzaklaştırılması araştırmacılar için önemli bir konudur. Bu çalışma, oksidant destekli subkritik su oksidasyon yöntemini kullanarak, dietil ftalatın parçalanmasında hidrojen peroksit (HP) ve potasyum persülfat (PS) oksidanlarının etkinliğini karşılaştırmayı amaçlamaktadır. Buna ek olarak çalışma, Box-Behnken tasarımını kullanarak operasyonel parametrelerin (sıcaklık, oksidan konsantrasyonu ve işlem süresi) dietil ftalat bozunması üzerindeki etkisini istatiksel olarak da incelimektedir. Ayrıca çalışma, Box-Behnken tasarımını kullanarak operasyonel parametrelerin (sıcaklık, oksidan konsantrasyonu ve işlem süresi) dietil ftalat bozunması üzerindeki etkisini istatistiksel olarak da incelemektedir. Elde edilen sonuçlar, dietil ftalat bozunmasını etkileyen birincil parametrenin sıcaklığın olduğunu ve her iki oksidant için ikinci dereceden bir modele uyduğunu gösterdi. Oksidasyon deneylerinde en yüksek toplam organik karbon (TOC) giderim oranı (%100) potasyum persülfat kullanıldığında elde edilmiştir. Hidrojen peroksit kullanıldığında ise maksimum TOC giderim veriminin %87 olduğu belirlendi.

Anahtar Kelimeler: İleri oksidasyon teknikleri; subkritik su oksidasyonu; cevap yüzey Metodu; Box-Behnken dizaynı; endokrin bozucu kimyasallar

1. Introduction

Phthalates/phthalate esters (PAEs) are common plasticizers used to increase the flexibility and durability of polymer-based materials. It is used extensively in many different fields, especially in the production of PVC products, toys, synthetic fibers, paint pigments, insect repellent, medical products and cosmetics [1,2]. It is known that the annual consumption of phthalates, which has been used in many industries since the 1920s, is over 1 million tons only in China, and approximately 90% of this is in the PVC sector [3]. PAEs, are widely used due to their low cost production and versatile chemical properties, are generally connected to the product structure by weak van der Waals forces or hydrogen bonds, so they are easily separated from the products and quickly transported to the environment. As a result, they spread easily to the environment and pollute the water, soil and air [2,3]. Phthalates, which are on the list of carcinogenic and endocrine disrupting chemicals, have many toxic and mutagenic effects, as well as negative effects on the reproductive systems of humans and animals [4,5]. Phthalates have been shown to be distributed in surface waters and river bottoms at various concentrations (ng/L to mg/L). Therefore, phthalate members such as dimethyl phthalate, diethyl phthalate, dibutyl phthalate etc. have been classified as priority pollutants by organizations such as the China National Environmental Monitoring Center, the US EPA and the EU [1,6]. It is an important issue to remove both the wastewater and natural water resources contaminated with these chemicals, which pose such serious dangers to the environment and human health.

Advanced Oxidation Processes (AOPs), used in recent years, have become an important method used in the degradation of toxic and stable organic pollutants [7]. In this method, which is based on the production of radicals such as $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals nonselectively attack target organic molecules and mineralize them by breaking them into molecules such as CO_2 and H_2O [8]. One of the popular AOPs method used to degrade organic pollutants in water is subcritical water oxidation (SWO) process. The popularity of SWO in recent years is attributed to its applicability to wastewater containing a wide range of pollutants and its being an environmentally friendly process. The main advantage of this process is that the application of various conditions in which the pressure can be applied at values sufficient to keep water in the liquid phase while keeping the temperature between 373-647 K. Another advantage of the method is the availability of oxidants such as O_2, H_2O_2 (HP) and $K_2S_2O_8$ (PS) that will increase radical production [9-11].

While carrying out all these experimental studies, determining the effect of each experimental parameter on the result and the synergistic effects of the parameters requires very time-consuming and costly processes. Response surface methodology (RSM) is a highly effective statistical program used to determine the effects of these system variables and perform experimental modeling. Compared to traditional optimization methods, RSM provides more useful information with fewer experiments to determine the effects of variables on the system [12,13]. The Box-Behnken design (BBD) which is a member of RSM, is a free, spherical, rotational quadratic design consisting of the center point and midpoints of the edges of the cube. However, the BBD allows calculation of the response function at intermediate levels and, through careful design and analysis of experiments, allows prediction of system performance at any experimental point studied [14,15].

In the current study, the degradation of diethyl phthalate (DEP), which is a low molecular weight member of the phthalate family and poses serious risks to the environment and human health, was performed oxidant assisted subcritical water oxidation using HP or PS. During the SWO process, the oxidation efficiency of DEP was calculated by the total organic carbon (TOC) contents. Within the scope of the study, the effects of temperature (K), oxidant concentration (mM) and processing time (min) as system variables, on the oxidation efficiency of DEP were examined using RSM and BBD.

2. Materials and methods

2.1. Materials

Diethyl phthalate ($C_{12}H_{14}O_4$) was purchased from Sigma-Aldrich (USA). Potasium persulfate ($K_2S_2O_8$) and hydrogen peroxide (30% wt, H_2O_2) were obtained from Merck (Germany). Nitrogen gas (N_2) gas was supplied by Linde gas (Turkey). Ultra-pure water used in all stages of the study was prepared using Millipore Milli-Q Advantage A10.

2.2. Box-Behnken Design of Oxidant Assisted Subcritical Water Oxidation

Box-Behnken design (Design Expert V11, Germany) was used to reveal the effect of independent variables on the oxidation of DEF by oxidant assisted SWO process. The BBD experimental matrix has 3 levels (-1, 0, +1) and temperature (373-473 K), processing time (20-60 min) and oxidant concentration (20-50 mM) were applied as independent parameters. The experiments were carried out in three repetitions and the results were depicted in Table 1.

2.3. Subcritical Water Oxidation Process and Analysis

Oxidation experiments of diethyl phthalate were carried out using a fixed bed high pressure reactor made of stainless steel with a volume of 200 mL (hand-made). A 100 mg/L stock aqueous solution of DEP used in SWO process. In oxidation experiments, 150 mL of DEP solution placed in the steel reactor and a certain amount of oxidant was added to the solution in the reactor. The reactor was purged with N_2 gas to evacuate the remaining air. To ensure subcritical conditions, the reactor was pressurized with N_2 gas at 30 bar and the experiment was performed to the specified temperature and processing time. After the processing time for each experiment was completed, the reactor was rapidly cooled by immersion in an ice bath, degassed when it reached room temperature and a 20 mL sample was taken for analysis and stored at +4 ºC. Total Organic Carbon (TOC) measurements of samples were performed by a standard method using a TOC cell kit and Merck Nova 30 A spectroquant photometer [16].

3. Results and Discussion

3.1 The Evaluation of Box Behnken Design Results for the Oxidation of Diethyl Phthalate using Hydrogen Peroxide and Potasium Persulfate as Oxidants

The experimental TOC removal percentages of DEP obtained by BBD using HP and PS oxidants were shown in Table 1. As depicted from Table 1, the maximum TOC removal efficiency using HP was obtained as 84.01% after 40 min, at 373 K and 50 mM of HP, while the minimum TOC removal value was 43.71% after 40 min at 473 K and using 20 mM of HP. In case of using PS oxidant, the maximum 91.95% TOC removal was achieved at the end of the 60 min experimental period at 473 K and a concentration of 35 mM PS. Also, the minimum % TOC removal value was determined as 68.85% after 40 min at 373 K and using of 20 mM PS. The quadratic models were proposed for both oxidants. Table 1 also shows the TOC removal efficiencies predicted by the proposed models.

Table 1. *The experiments and predicted of TOC removal results were obtained using the Box-Behnken design*

Run	X_1 T (K)	X_2 t (min)	X_3 C_{ox} (mM)	TOC Removal (%) HP Exp.	HP Pred.	PS Exp.	PS Pred.
1	373 (-1)	40 (0)	50 (+1)	84.01	82.44	77.73	78.39
2	423 (0)	40 (0)	35 (0)	50.29	49.68	73.98	74.42
3	373 (-1)	20 (-1)	35 (0)	73.28	73.53	72.87	72.90
4	473 (+1)	60 (+1)	35 (0)	54.29	54.04	91.95	91.92
5	373 (-1)	60 (+1)	35 (0)	75.79	77.17	76.93	76.91
6	423 (0)	20 (-1)	50 (+1)	54.14	55.45	77.11	76.42
7	423 (0)	40 (0)	35 (0)	49.80	49.68	74.29	74.42
8	473 (+1)	20 (-1)	35 (0)	50.86	49.48	84.23	84.26
9	373 (-1)	40 (0)	20 (-1)	68.86	68.80	68.85	68.18
10	473 (+1)	40 (0)	50 (+1)	58.71	58.78	89.75	90.42
11	423 (0)	60 (+1)	20 (-1)	47.29	45.98	72.51	73.20
12	423 (0)	60 (+1)	50 (+1)	62.58	62.77	91.44	90.88
13	423 (0)	20 (-1)	20 (-1)	45.29	45.10	75.28	75.92
14	423 (0)	40 (0)	35 (0)	49.43	49.68	74.39	74.42
15	473 (+1)	40 (0)	20 (-1)	43.71	45.28	83.19	82.53
16	423 (0)	40 (0)	35 (0)	49.63	49.68	74.44	74.42
17	423 (0)	40 (0)	35 (0)	49.26	49.68	75.03	74.42

The compatibility of the quadratic model for the subcritical water oxidation of DEP was statistically evaluated with the analysis of variance (ANOVA). Table 2 shows the ANOVA results of the reduced quadratic models obtained using BBD.

The low *p*-values (< 0.0001) of the quadratic models and the *F*-values of 172.09 and 143.48 obtained for HP and PS oxidants, respectively, indicate that the experimental results are highly fitted with the proposed quadratic model. Terms with p-values lower than 0.05 have significant effects on the model. From Table 2, the high linear effects of the 3 independent variables (X_1, X_2, and X_3) can be seen in DEP oxidation with the SWO method for both oxidants. While only the quadratic effect of temperature (X_1^2) was high when HP oxidant was used, it can be seen from the small *p*-values and high *F*-values that quadratic effects are important in all three variables (X_1^2, X_2^2, and X_3^2) when PS oxidant is used. Among the interactive effect of the independent variables, the only important term belongs to between proceeding time and oxidant concentration (X_2X_3). In addition, the *p*-value of lack of fit for HP and PS expressed that only 0.68 and 3.19% error due to noise, respectively.

Table 2. *ANOVA results of the reduced quadratic models*

Source	HP Mean Square	HP *F*-value	HP *p*-value prob > *F*	PS Mean Square	PS *F*-value	PS *p*-value prob > *F*

Model	279.85	172.09	<0.0001	784.01	143.48	<0.0001
X_1	1113.21	684.53	<0.0001	347.77	509.14	<0.0001
X_2	33.54	20.62	0.0019	68.12	99.73	<0.0001
X_3	368.43	226.55	<0.0001	163.77	239.77	<0.0001
X_1X_2	0.21	0.13	0.7277	3.33	4.88	0.0582
X_2X_3	10.37	6.38	0.0355	73.10	107.02	<0.0001
X_1^2	677.54	416.63	<0.0001	65.15	95.38	<0.0001
X_2^2	5.94	3.65	0.0924	41.45	60.69	<0.0001
X_3^2	8.92	5.48	0.0473	9.76	14.28	0.0054
Residual	1.63			0.68		
Lack of Fit	3.10	19.72	0.0068	1.22	8.35	0.0319
Pure Error	0.16			0.15		

Table 3. *Regression and correlation analysis of quadratic models*

Model	**Standart deviation**	**Mean**	**C.V %**	**PRESS**	**R^2**	**R^2 adjusted**	**R^2 predicted**	**Adequate Precision**
HP	1.28	56.90	2.24	139.95	0.9942	0.9884	0.9378	40.20
PS	0.83	78.47	1.05	41.68	0.9931	0.9862	0.9472	38.51

With the help of the regression and correlation analysis results shown in Table 3, the reliability of the reduced quadratic models obtained with the BBD were evaluated for both oxidants. Adequate Precision values, which are an indicator of the usability of the model and must be greater than 4, were calculated as 40.20 and 38.51 for HP and PS, respectively. Adequate precision is a measure of the signal-to-noise ratio and compares the range of predicted values with the average prediction error at design points. While the correlation coefficient values of R^2, adjusted R^2 and predicted R^2 were calculated as 0.9942, 0.9884 and 0.9378 for HP, incase PS oxidant these correlation coefficients were 0.9931, 0.9862 and 0.9472, respectively. The difference between the adjusted R^2 and the predicted R^2 values for both quadratic models is less than 0.2, indicating the perfect agreement between the experimental values and the predicted values calculated with the help of the model. Also, the fit of the models was depicted in Fig. 1.

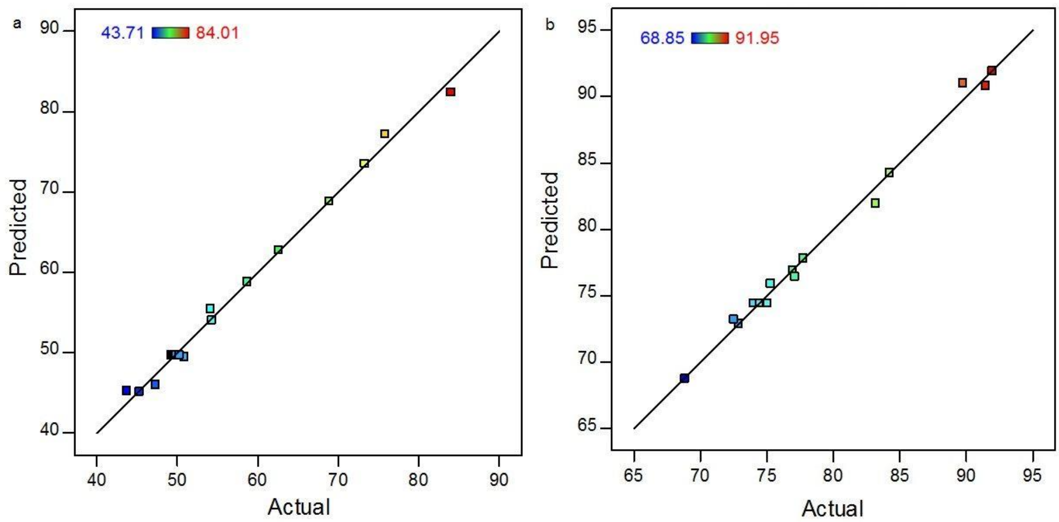

Figure 1. The actual values vs predicted values of the TOC removal efficiency of Diethyl phthalate using **a)** HP, and **b)** PS.

The quadratic polynomial equations derived by the RSM for the oxidation of diethyl phthalate with HP and PS were shown in Eqs. (3.1 and 3.2), respectively. With the help of these equations, the % TOC removal values can be calculated at any operating point at the intervals for the temperature (373-473 K), the experiment time (20-60 min), and the oxidant concentration (20-50 mM). ANOVA results give the effective terms on the model as discussed before. In addition, quadratic polynomial equations are useful in revealing which parameter affects the response in which direction [17,18]. For both oxidants, the most effective linear term in DEP oxidation was temperature. However, while the temperature (X_1) increase had a decreasing effect on TOC removal when using HP oxidant, it enhanced the oxidation efficiency performed in the case of PS oxidant. It seems that the parameter that has the least impact on the response among the independent variables is processing time (X_2). However, the interactive (synergetic) effect of processing time and oxidant concentration (X_2X_3) was positive on TOC removal efficiency.

$$\text{TOC Removal (\%)} = +49.68 - 11.80X_1 + 2.05X_2 + 6.79X_3 + 0.23X_1X_2 + 1.61X_2X_3 + 12.69X_1^2 + 1.19X_2^2 + 1.46\,X_3^2 \quad (3.1)$$

$$\text{\%TOC Removal } (Y) = +74.42 + 6.59X_1 + 2.92X_2 + 4.52X_3 + 0.91X_1X_2 + 4.27X_2X_3 + 3.93X_1^2 + 3.14X_2^2 + 1.52\,X_3^2 \quad (3.2)$$

In the SWO process where PS oxidant is used, the quadratic effect of all three independent variables is lower than the linear effects, also they were positive effects. However, it is seen that the quadratic effect of temperature was greater in the process using HP oxidant.

3.2 SWO Oxidation of Dietil Phthalate using Oxidants

The use of hydrogen persulfate in subcritical water oxidation supports the formation of various oxygenated reactive species (ROS), especially hydroxyl radicals with high oxidation potential (E^0= 2.8 V) due to Eqs. (3.3-3.7) [14,16].

$$H_2O_2 \xrightarrow{heat} 2\ {}^{\bullet}OH \quad (3.3)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (3.4)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow O_2^{\bullet -} + H^+ + H_2O \quad (3.5)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (3.6)$$

$${}^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (3.7)$$

The effect of each experimental variable on the oxidation of DEP can be examined in detail using 3D graphics obtained from the RSM using BBD. For the TOC removal efficiency of DEP, any of the parameters determined as the system variable which are temperature (X_1), processing time (X_2), and HP or PS concentration (X_3) can be kept constant and the dual effects of the independent variables can be discussed.

Fig 2a show the processing time and temperature effects on TOC removal efficiency by keeping the HP concentration at 50 mM. In the SWO process with HP as an oxidant, it is seen that DEP oxidation occurs more effectively at low temperatures. It can be said that the temperature increase contributes to the decomposition of HP into water and oxygen rather than the reactions that support the formation of radicals. After 60 min of processing, 87.02% TOC removal was achieved at 373 K, and this value decreased to 61.40% when the temperature was increased to 430 K. The increase in TOC removal to 63.89% by increasing the temperature to 473 K indicates that DEP oxidation increases as subcritical conditions are approached. Fig 2b illustrates the effect of HP concentration and time at 373 K on DEP oxidation. It is observed that processing time is not a very effective parameter at low HP concentrations, but when the HP concentration is above 40 mM, increasing time acts to increase DEP oxidation. The low TOC removal datas obtained when low HP concentration is applied reveals that the conversion efficiency of HP to hydroxyl radical has been low. For this reason, hydrogen peroxide concentrations may higher than the theoretically required amount increased the oxidation efficiency.

When the SWO results in which persulfate was used as oxidant were examined, higher DEP oxidation efficiencies were achieved compared to HP. The effect of temperature and time on TOC removal under conditions where the PS concentration was kept constant at 50 mM is given in Fig. 2c. After SWO performed for 20 min at 373 and 474 K temperatures, TOC removals were determined as 74.67 and 83.72%, respectively, and by increasing the time to 60 min, the change rate was determined as 13% and TOC removal reached 100% at 474 K. Thermal activation of persulfate allows the formation of the sulfate radical ($SO_4^{\bullet -}$) due to cleavage of the peroxide bond is given in Eq. (3.8) [19]. The sulfate radical has high oxidation potential (E^0= 2.5-3.1 V), similar to the hydroxyl radical. However, it also has advantages over the hydroxyl radical, such as being longer lasting, showing activity in a wide pH range, and being less affected by inorganic species that act as radical scavengers [20,21]. In fact, the formed sulfate radical reacts with water supports the formation of hydroxyl radical following Eq. (3.9).

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\bullet-} \quad (3.8)$$
$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \quad (3.9)$$

According to the SWO results performed at 464 K, it was determined that for effective DEP oxidation (> 81%), the PS concentration should be kept above 30 mM and the processing time should be kept above 40 min (Fig. 2d). When the time and PS concentration were increased to the highest level at the same temperature value, i.e. 60 min and 50 mM, 100% TOC removal was achieved.

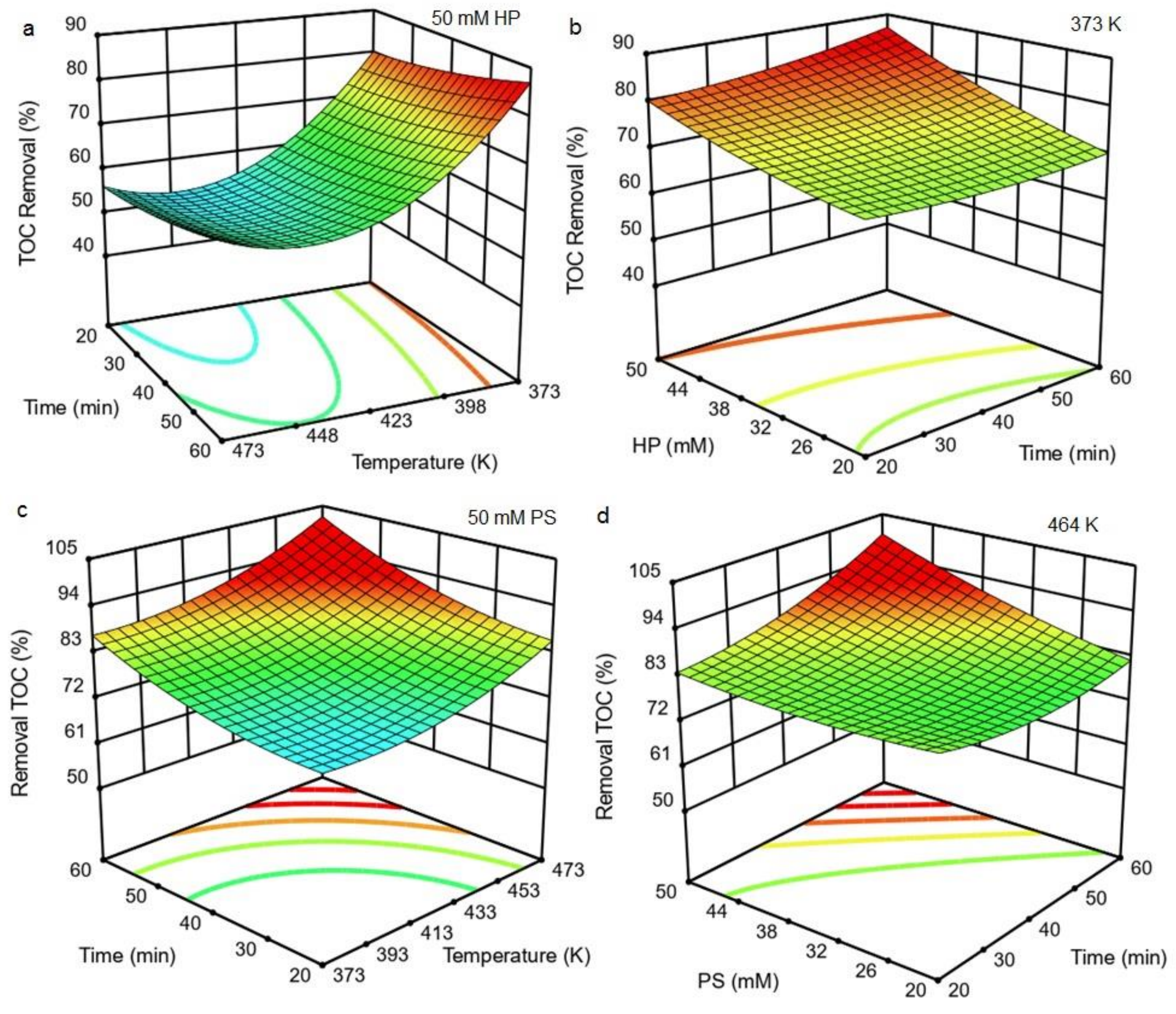

Figure 2. Effect of (a) temperature and time at 50 mM HP, (b) HP concentration and time at 373 K, (c) temperature and time at 50 mM PS, (d) HP concentration and time at 464 K on TOC removal of DEP.

In Table 4, the optimum conditions obtained statistically by the BBD and which can be used for the oxidation of diethyl phthalate with HP and PS are given. While obtaining these optimum conditions, experimental conditions were selected where the model could reach maximum TOC removal percentages. The important point is that the closer the acceptability value is to 1, the closer the results to be obtained from the system will be to the statistical data, that is, the correct results will be obtained. For example, if the researcher's goal is only to obtain the highest TOC removal % possible, they can achieve 87.0% TOC removal at the end of the 60 min experiment period by using 50 mM HP at 373 K temperature, as seen in Table 4. Additionally, if it is desired to obtain the highest possible % TOC removal for diethyl phthalate using PS, 100% TOC removal can be achieved at the end of the experiment period of 59 min by using 49.8 mM PS at 469 K temperature.

Table 4. *The Optimum conditions obtainable in the Response Surface Method for the oxidation of diethyl phthalate with HP and PS*

	HP					PS				
No	**T (K)**	**T (min)**	**C_{HP} (mM)**	**TOC Removal (%)**	**No**	**T (K)**	**T (min)**	**C_{PS} (mM)**	**TOC Removal (%)**	**Desirability**
1	373	60	50.0	87.0 ±1.3	1	469	59	49.8	100.1±0.8	1
2	373	60	49.9	86.9 ±1.3	2	469	60	49.3	100.2±0.8	1
3	373	60	49.1	86.4 ±1.3	3	472	58	49.3	100.3±0.8	1

The effects of each independent variable on the response under the conditions recommended as optimum for both oxidants are seen more clearly in Fig. 3. The main disadvantage of advanced oxidation methods is their application costs, because of this time, temperature and oxidant concentrations have been at average values in this study. However, it is possible to obtain more effective results at higher concentrations of both oxidants.

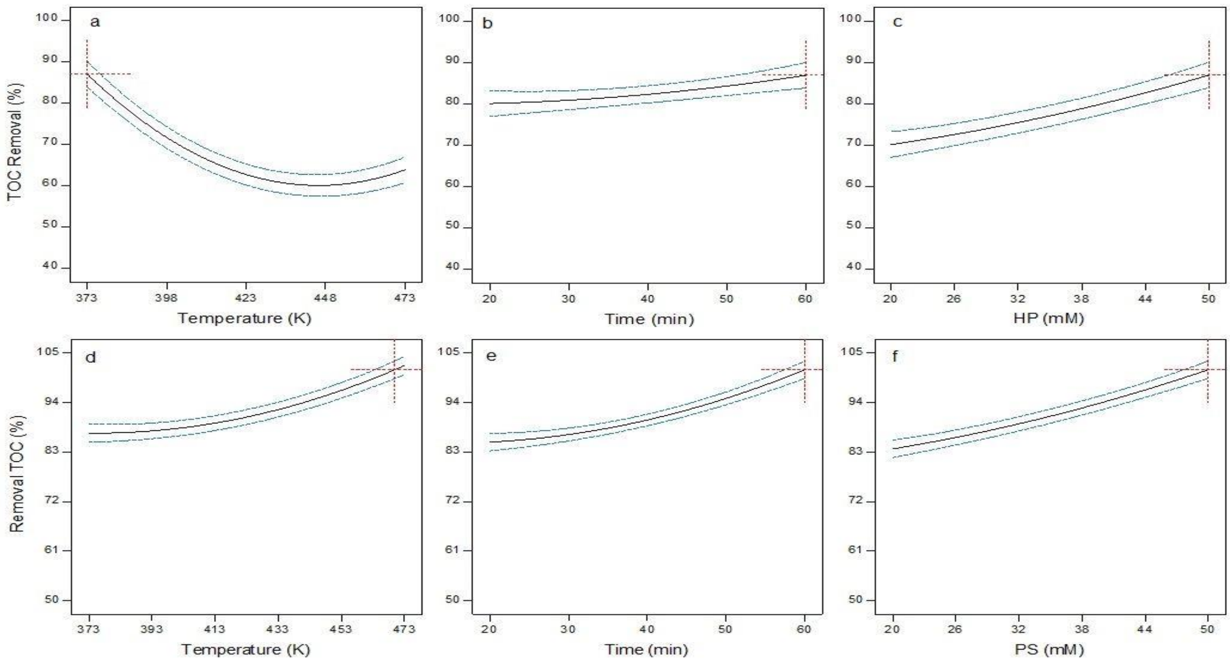

Figure 3. Effect of independent variables on the recommended optimum conditions for DEP oxidation

by (a-c) HP (373 K, 60 min, 50 mM HP) and (d-f) PS (470 K, 60 min, 50 mM PS) oxidant-assisted SWO method.

The quadratic models created by the Box-Behnken design (BBD) for the oxidation of diethyl phthalate using HP or PS as oxidants were validated by comparing the predicted TOC removal percent values with the experimental results obtained from random experimental points. Table 5 shows that the predicted values were in agreement with the experimental values, indicating that the models accurately represent the oxidation process for DEP using HP or PS oxidant.

Table 5. *The result of validation experiments for the oxidation of diethyl phthalate*

					TOC Removal (%)	
Oxidant	**Run**	**T (K)**	**t (min)**	**C_{ox} (mM)**	**Experimental**	**Predicted**
HP	1	398	45	40	66.09±1.09	61.87±1.27
	2	433	30	30	41.69±1.22	45.25±1.27
PS	1	373	60	50	87.23±1.04	87.53±0.82
	2	443	60	50	92.72±1.24	94.43±0.82

4. Conclusion

Phthalates are a class of chemicals known for their significant industrial use and their impact as endocrine disruptors. The release of wastewater containing phthalates into the environment poses a critical concern due to the potential negative consequences on both the environment and human health. Although there are a limited number of studies in the literature investigating phthalate degradation using advanced oxidation processes, no direct study using the subcritical water oxidation method has been found for diethyl phthalate. For this reason, the degradation of diethyl phthalate in aquatic environments by the subcritical water oxidation method carried out in this study, together with the high removal results obtained and the statistical evaluations and optimization of the method, is a guide for similar studies to be conducted in the future.

This study aimed to develop an effective method for treating wastewater containing diethyl phthalate using the oxidant-assisted subcritical water oxidation process. The researchers conducted detailed statistical evaluations of the oxidation process for diethyl phthalate, utilizing ANOVA tests with the Design Expert program. The results helped determine the optimum oxidation conditions for the treatment process. When hydrogen peroxide (HP) was used as the oxidant in the subcritical water oxidation (SWO) for diethyl phthalate, the maximum total organic carbon (TOC) removal was 87.0%. The optimum conditions were found to be a temperature of 323 K, a concentration of 50 mM HP, and a processing time of 60 minutes. It was observed that increasing the temperature was effective in reducing the oxidation of diethyl phthalate in the HP-supported SWO method.

On the other hand, higher oxidation values (100%) were achieved with potassium persulfate (PS) as the oxidant compared to HP. However, it was found that higher temperatures were required for the oxidation of diethyl phthalate in the PS-assisted SWO process. The optimal operating conditions for PS-assisted SWO were determined to be a temperature of 470 K, a concentration of 50 mM PS, and a processing time of 60 minutes.

Acknowledgements

I would like to thank Prof. Dr. Belgin GÖZMEN for their support. This work was supported by Mersin University Research Fund (Project No: BAP 2015-TP3-1072).

Author contributions

Özkan Görmez: Methodology, experimental studies, data evaluation, visualization, conceptualization, and writing-review editing. Ahmet Murat Gizir: Methodology, data evaluation, conceptualization, supervision, writing-review editing.

Data and code availability

All the data supporting this study's findings are available in this manuscript.

Declerations

Supplementary information Not applicable.

Ethical approval Not applicable.

Conflict of interest. The authors declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

ANOVA	Analysis of variance
AOPs	Advanced oxidation processes
BBD	Box-Behnken design
DEP	Diethyl phthalate
HP	Hydrogen peroxide
PAEs	Phthalates/phthalate esters
PS	Potassium persulfate
RSM	Response surface methodology
SWO	Subcritical water oxidation
TOC	Total Organic Carbon

References

[1] Wang Z., Shao Y., Gao N., Lu N., An N. (2018). Degradation of diethyl phthalate (DEP) by UV/persulfate: An experiment and simulation study of contributions by hydroxyl and sulfate radicals. *Chemosphere*, 193:602-610.

[2] Bensalah, N., Dbira, S., Bedoui, A. (2019). Mechanistic and kinetic studies of the degradation of diethyl phthalate (DEP) by homogeneous and heterogeneous Fenton oxidation. *Environmental Nanotechnology, Monitoring & Management*, 11:100224.

[3] Li, H., Miao, X., Zhang, J., Du, J., Xu, S., Tang, J., Zhang, Y. (2020). DFT studies on the reaction mechanism and kinetics of dibutyl phthalate initiated by hydroxyl and sulfate radicals: Prediction of the most reactive sites. *Chemical Engineering Journal*, 381:122680.

[4] Arrigo, F., Imppellitteri, F., Piccoione, G., Faggio, C. (2023). Phthalates and their effects on human health: Focus on erythrocytes and the reproductive system. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology*, 270:109645.

[5] Paluselli, A., Fauvelle, V., Galgani, F., Sempere, R. (2019). Phthalate Release from Plastic Fragments and Degradation in Seawater. *Environmental Science and Technology*, 53:166-175.

[6] Ghosh, S., Sahu, M. (2022). Phthalate pollution and remediation strategies: A review. *Journal of Hazardous Materials Advances*, 6:100065.

[7] Mahbub, P., Duke, M. (2023). Scalability of advanced oxidation processes (AOPs) in industrial applications: A review. *Journal of Environmental Management*, 345:118861.

[8] Dong, C., Fang, W., Yi, Q., Zhang, J. (2022). A comprehensive review on reactive oxygen species (ROS) in advanced oxidation processes (AOPs). *Chemosphere*, 308:136205.

[9] Hu, M., Chen, M., Li, Z., et al. (2024). Mechanism of catalytic subcritical water oxidation of m-nitroaniline and nitrogen conversion by $CuCo_2O_4$ catalyst. *Chemical Engineering Journal*, 490:151757.

[10] Yabalak, E., Ozay, Y., Dizge, N. (2021). Water recovery from textile bath wastewater using combined subcritical water oxidation and nanofiltration. *Journal of Cleaner Production*, 290:125207.

[11] Görmez, Ö., Akay, S., Gözmen, B., Kayan, B., Kalderis, D. (2022). Degradation of emerging contaminant coumarin based on anodic oxidation, electro-Fenton and subcritical water oxidation processes. *Environmental Research*, 208:112736.

[12] Aparna, Kumar, V., Nautiyal, R. (2024). Isolation and chemical characterization of lignocellulosic fiber from Pueraria montana using Box-Behnken design for weed management. *International Journal of Biological Macromolecules*, 268:131479.

[13] Sezer, M., Isgoren, M., Veli, S., Topkaya, E., Arslan, A. (2024). Removal of microplastics in food packaging industry wastewaters with electrocoagulation process: Optimization by Box-Behnken design. *Chemosphere*, 352:141314.

[14] Yabalak, E., Görmez, Ö., Gizir, A. M. (2018). Subcritical water oxidation of propham by H_2O_2 using response surface methodology (RSM). *Journal of Environmental Science and Health, Part B*. 53(5):334–339.

[15] Chaker, H., Ameur, N., Saidi-Bndahou, K., Djennas, M., Foumentin, S. (2021). Modeling and Box-Behnken design optimization of photocatalytic parameters for efficient removal of dye by lanthanum-doped mesoporous TiO_2. *Journal of Environmental Chemical Engineering*, 9:104584.

[16] Yabalak, E., Döndaş, H. A., Gizir, A.M. (2017). Subcritical water oxidation of 6-aminopenicillanic acid and cloxacillin using H_2O_2, $K_2S_2O_8$, and O_2. Journal of Environmental Science and Health, Part A, 52(3):210-220.

[17] Kayan, B., Akay, S., Kulaksız, E., Gözmen, B., Kalderis, D. (2017). Acid Red 1 and Acid Red 114 decolorization in H2O2 -modified subcritical water: process optimization and application on a textile wastewater. Desalination Water Treatment, 59:248-26.

[18] Görmez, Ö., Çalhan Doğan, S., Gözmen, B. (2022). Degradation of isoniazid by anodic oxidation and subcritical water oxidation methods: Application of Box-Behnken design. Journal of Environmental Science and Health, Part C, 40(1):1-26.

[19] Li, N., Wu, S., Dai, H., Cheng, Z., Peng, W., Yan, B., Chen, G., Wang, S., Duan, X. (2022). Thermal activation of persulfates for organic wastewater purification: Heating modes, mechanism and influencing factors. *Chemical Engineering Journal*, 450:137976.

[20] Ji, Y., Fan, Y., Liu, K., Kong, D., Lu, J. (2015). Thermo activated persulfate oxidation of antibiotic sulfamethoxazole and structurally related compounds. *Water Research*, 87:1-9.

[21] Luo, R., Wang, C., Yao, Y., Qi, J., Li, J. (2022). Insights into the relationship of reactive oxygen species and anions in persulfate-based advanced oxidation processes for saline organic wastewater treatment. *Environmental Science: Water Research and Technology*, 8:465-483.