

Treatment of Direct Red 23 in Recirculating Semi-Pilot System by O₃/UV Process: Operational Parameters Effect and Central Composite Design Modeling

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ABSTRACT: *The treatment of C.I. Direct Red 23 (DR23) solution has been investigated by the ozonation under UV irradiation (O₃/UV) in a recirculating semi-pilot mode. Decolorization efficiency (DE%) of DR23 was compared using the O₃ and O₃/UV processes, which were 74.9% and 92.7% after 30-min treatment of the dye (100 mg/dm³), respectively. Then, the effect of experimental parameters on the O₃/UV process including initial dye concentration, ozone mass flow rate, and initial pH was studied. The obtained results revealed that the decolorization efficiency increased by enhancing of ozone amount and decreasing the DR23 concentration; the decolorization process was performed efficiently at the basic condition (pH= 10) due to the production of extra hydroxyl radicals. The pseudo-first-order kinetic was observed for the dye decolorization. Electrical energy per order decreases using the O₃/UV process at the desired pH 10 indicating an adequate synergistic effect of the photolysis and ozonation. Eventually, the Central Composite Design (CCD) approach was properly applied for the prediction of the DE% with appropriate performance (R² = 98.52%) and optimization of the process.*

KEYWORDS: *Ozonation; UV irradiation; Azo dye; Decolorization; Central composite design.*

INTRODUCTION

Water stress is becoming a serious global threat, especially in developing countries, owing to the limited secure water sources. All industries consume water for various applications like processing, heating, cooling, washing, etc., and convert it to industrial wastewater; these effluents must be treated before their discharge to the environment to prevent their unfavorable effects

on the ecosystem and reduce water stress. Hence, the treatment of polluted waters is significant from an environmental viewpoint to prevent a wide variety of risks. Dyes are applied extensively in various industries including textile, paper, leather, cosmetics, and food; for instance, azo dyes, which have a refractory aromatic structure with at least one -N=N- bond are discharged

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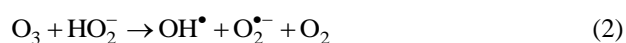
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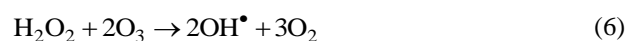
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in considerable amounts (up to 20%) into the effluents of the textile industry during their manufacturing and textile finishing. These dyes and their destruction by-products are toxic and carcinogenic. Moreover, textile industry wastewaters are deeply colored and have a remarkable Chemical Oxygen Demand (COD) [1, 2]. They are usually resistant to conventional biological treatments and physicochemical treatment processes including coagulation and adsorption, solely transferring the organic pollutants to other wastes, thereby making their disposal necessary. Consequently, it is essential to develop efficient water treatment methods for the elimination of such pollutants to prevent their hazardous accumulation in the aquatic environment, as it may, for instance, lead to advanced oxidation processes (AOPs) [3].

AOPs such as photoelectrocatalysis, electro-Fenton processes Fenton, and photocatalysis, not only decolorize but also mineralize various dyes unselectively with no or low secondary wastes by the generation of Reactive Oxygen Species (ROS) particularly hydroxyl radicals (OH^\bullet) [4, 5]. Among the AOPs as green treatment technologies, ozonation has been widely applied for the degradation of water contaminants due to its appropriate oxidation potential ($E_0 = 2.07 \text{ V}$). In situ generation of oxidants like the O_3 prevents risky storage and transportation of the oxidants like the hydrogen peroxide in the AOPs. The degradation of organic pollutants is explained by the O_3 electrophilic reaction with them in acidic conditions or by its decomposition to the OH^\bullet radicals in basic mediums (Eqs. 1 and 2). However, it has been found that contaminant degradation may not be obtained properly by merely using the O_3 treatment method [6, 7].



Coupling ozonation with ultraviolet irradiation (O_3/UV) is more efficient than the O_3 process for the treatment of diverse organic pollutants in the aquatic environment. The UV irradiation provides enough energy to dissociate chemical bonds (Eq. 3); as a consequence, the produced hydrogen peroxide from the O_3 in water (Eq. 4) can absorb UV light or react with ozone to generate OH^\bullet radicals (Eqs. 5 and 6). The generated OH^\bullet radicals have a higher oxidation potential ($E_0 = 2.8 \text{ V}$) than the O_3 molecules [8-10].



A semi-batch reactor permits partial reactants addition as process time proceeds; moreover, it is more suitable in liquid phase reactions. The degradation efficiency of a pollutant in treatment processes increased with time and more passage of the solution through the semi-batch reactors. In addition, the contaminated solution is illuminated efficiently by the UV light in the semi-batch systems. Eventually, the obtained data can be applied to design a continuous flow system [11, 12].

The water treatment by the AOPs is quite intricate because a treatment process is influenced by several operational parameters; hence, it is difficult to model the process based on intrinsic reactions. Central Composite Design (CCD) as one of the response surface methods is properly utilized in science and engineering as a promising method due to its simplicity of modeling and prediction. The CCD requires a reasonable number of runs to model the response, which is influenced by the experimental variables; thus, less time and cost are needed. The CCD method is also properly applied to obtain the optimized experimental parameters for the water treatment processes to achieve the desired response value [13].

The aim of this study was to evaluate the DR23 decolorization as a model azo dye by the O_3 and O_3/UV processes in a recirculating semi-pilot system. Then, the effect of some operational variables including the initial DR23 concentration, process time, ozone mass flow rate, and initial pH on the dye degradation efficiency was investigated by the O_3/UV process. Finally, the CCD model was developed to predict the decolorization efficiency (DE%) and also to define the operational conditions in order to achieve the desired degradation of dye.

EXPERIMENTAL SECTION

Materials

The model di-azo dye (Fig.1), Direct Red 23, was provided by Shimi Boyakhsaz Company, Iran (Molecular formula= $\text{C}_{35}\text{H}_{25}\text{N}_7\text{Na}_2\text{O}_{10}\text{S}_2$, Color index number= 61570, $\lambda_{\text{max}} = 500 \text{ nm}$ and $M_w = 813.72 \text{ g/mol}$). This dye and its

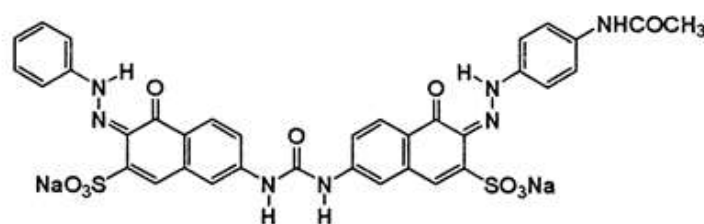


Fig. 1: Chemical structure of Direct Red 23.

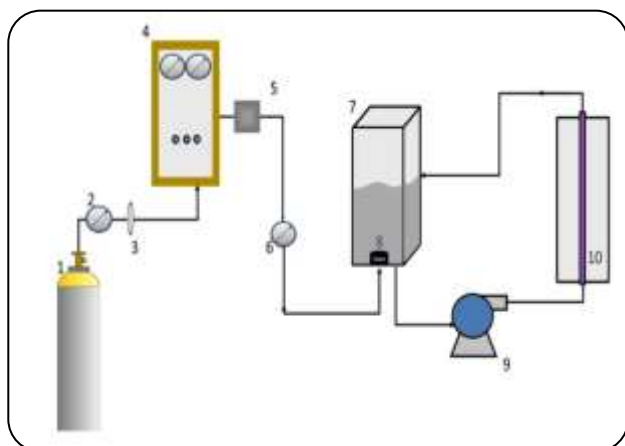


Fig. 2: Schematic of the recirculating semi-pilot reactor. (1) oxygen gas (2) pressure regulator (3) oxygen flow meter (4) ozone generator (5) ozone analyzer (6) pressure gauge (7) diffuser (8) tank (9) recirculation pump (10) UV-C lamp.

decolorization by-products such as aromatic amines can menace the environment seriously owing to their carcinogenic effects [14]. Sodium hydroxide (99%) and sulfuric acid (98%) were supplied from Merck (Germany). Distilled water was used in the experiments.

Experimental setup and procedure

Fig. 2 illustrates the ozonation coupled with the UV irradiation semi-pilot system for the treatment of DR23 with considerable concentrations. The experimental set-up (with a workable capacity of 5 dm³) comprised a rectangular Plexiglas reactor. O₃ was produced by an ozone generator (Lab-802, 69 W, Ozomatic) and fed to the reactor from its bottom using a diffuser. The amount of ozone mass flow rate (1.5 -8.4 g/h) was adjusted by the oxygen flow regulation. The outlet of the reactor was pumped to a stainless steel photoreactor equipped with a UV-C lamp (TUV T8, 30 W, Germany). In each experiment, 5 dm³ of the DR23 with a known concentration (100-10000 mg/dm³),

pH (3-10), and other distinct operational parameters were recirculated in the system by the pump (16.8 W). The absorbance of DR23 was measured by a spectrophotometer (UV-2100, Unico, USA), and DE% was calculated by Eq. (7):

$$DE\% = \frac{A_0 - A_t}{A_0} \quad (7)$$

Where A_0 and A_t are the dye absorbance in the beginning and for each process time, respectively.

Experimental design

The CCD approach is the combination of mathematical and statistical methods for the prediction and optimization of a process [13]. In this research, the effect of three experimental variables including initial DR23 concentration (mg/dm³) (X_1), the ozone mass flow rate (g/h) (X_2), and the processing time (min) (X_3) on the DE% by the O₃/UV process was investigated. Minitab 16 Software was used to plan the experiments and analyze the experimental data; the extreme values of the independent variables were selected according to the preliminary experiments. Totally, 20 experiments with two repetitions were carried out at pH 10. The X_i independent variables were coded as x_i for the CCD modeling using Eq. (8):

$$X_i = \frac{X_i - X_0}{\delta X} \quad (8)$$

Where X_0 is the value of X_i at the center point and δX shows the step change. The experimental ranges and the levels of the operational variables are presented in Table 1.

RESULTS AND DISCUSSION

Control experiments and kinetic study

It should be noticed that the greatest degradation of DR23 was observed by the O₃/UV process, as compared to the O₃ or UV irradiation after 30 min of the process (Fig. 3).

Table 1: Experimental ranges and levels of the independent variables.

Independent variables	Ranges and levels				
	-1.68	-1	0	+1	+1.68
[DR23] ₀ (mg/l) (X ₁)	329.55	500	750	1000	1170.45
O ₃ (g/h) (X ₂)	1.63	3	5	7	8.36
Time(min) (X ₃)	9.77	20	35	50	60.23

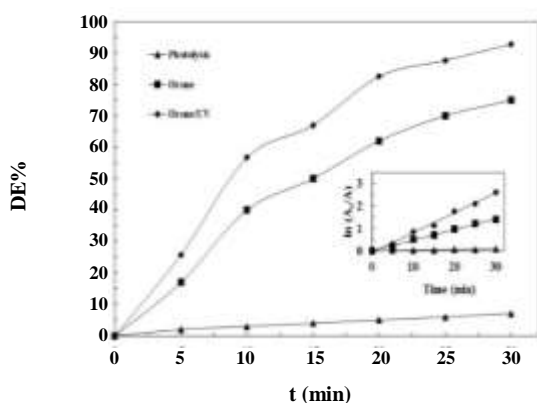


Fig. 3: Comparison of direct photolysis, ozone, and O₃/UV processes in degradation of DR23. The inset demonstrates mentioned processes obey pseudo-first-order kinetics. [DR23]₀ = 100 mg/dm³, ozone mass flow rate = 1.5 g/h and pH = 10.

The DE% was calculated to be 92.7, 74.9 and 7.1%, respectively at the same operational conditions of [DR23]₀ = 100 mg/dm³, ozone mass flow rate = 1.5 g/h and pH = 10. Direct photolysis of DR23 by UV could degrade it by the cleavage of chemical bonds; however, it was not an effective method for the treatment. The maximum treatment of dye was owing to the high production of hydroxyl radicals and hence, more oxidative ability, according to the reactions, as explained in the introduction section (Eqs. 1-6) in the case of the O₃/UV process [15]. The generated ROS, particularly hydroxyl radicals, could degrade the DR23 and increase the DE%. Hence, the combined process was selected to perform the remained experiments.

All of the processes followed the pseudo-first-order kinetic, which was consistent with the other AOPs [16]. The decolorization rate constants (k_{dec}) for the DR23 degradation (the apparent pseudo-first-order rate constants) at pH 10 were evaluated from $\ln(A_0/A)$ versus process time (t) plots (the inset of Fig. 3), as given in Table 2. The lines with suitable correlation coefficients ($R^2 \geq 0.985$)

confirmed the proposed kinetic. To determine the synergistic effect of the photolysis and ozonation, Eq. (9) was applied, using the obtained k_{dec} values (Table 2); Eq. (9) demonstrates the k_{dec} for the UV, O₃, and UV/O₃ processes as the k_{UV} , k_{O_3} , k_{UV/O_3} respectively. The synergy% was calculated as 44%, which revealed that the combined process efficiency was 44% more than the sum of the UV and O₃ processes, which have been utilized individually.

$$\text{Synergy\%} = \frac{k_{UV/O_3} - (k_{UV} + k_{O_3})}{k_{UV/O_3}} \quad (9)$$

It should be mentioned that the dye photolysis by the UV remained constant at various pHs (Table 2); moreover, the k_{O_3} was estimated to be 0.0283 and 0.0411 min⁻¹ at the pH 3 and 7 for the treatment of 100 mg/dm³ dye at 1.5 g/h ozone mass flow rate of the ozone process, respectively. Then, the synergistic effect of the UV and ozone at pH 3 and 7 was calculated to be 3 and 10%, respectively (using the related k_{dec} data in Tables 2 and 3). Hence, the highest synergistic effect was observed at the basic medium (pH 10), where the indirect attack of OH[•] radicals could be responsible for the dye decolorization; moreover, the UV irradiation could break down the generated hydrogen peroxide to the OH[•] radicals at the basic condition better than the acidic one (Eq. (5)) [17].

Effect of operational variables on the O₃/UV process and electrical energy consumption

Chemical oxidation processes apply oxidizing compounds like the ozone coupled with the UV, producing powerful non-selective OH[•] radicals at high pHs. These radicals, owing to their high oxidation capability can efficiently break the conjugated double bonds of chromophores and functional groups like the aromatic rings. The production of small non-chromophoric compounds declines the color of the solutions. Hence,

Table 2: Decolorization constants and electrical energy per order of the applied processes for DR23 degradation.

Process	k_{dec} (1/min)	R^2	E_{EO} (kWh m^{-3} order $^{-1}$)
Direct photolysis	0.0023	0.988	156.27
Ozone	0.0474	0.996	13.90
Ozone/UV	0.0881	0.993	10.09

$[DR23]_0 = 100 \text{ mg/dm}^3$, ozone mass flow rate = 1.5 g/h and pH = 10

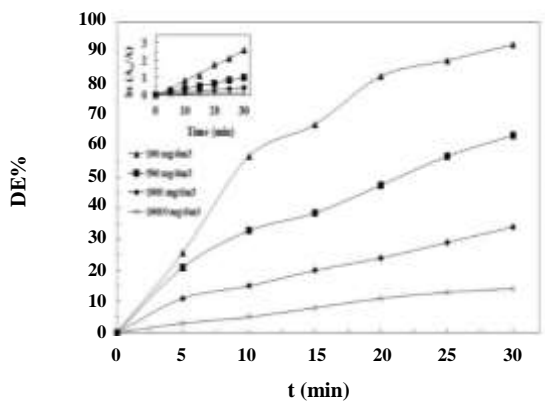


Fig. 4: Effect of initial DR23 concentration on DE% of O_3/UV process (ozone mass flow rate = 1.5 g/h and pH = 10). The inset plot was depicted according to the pseudo-first-order kinetics assumption.

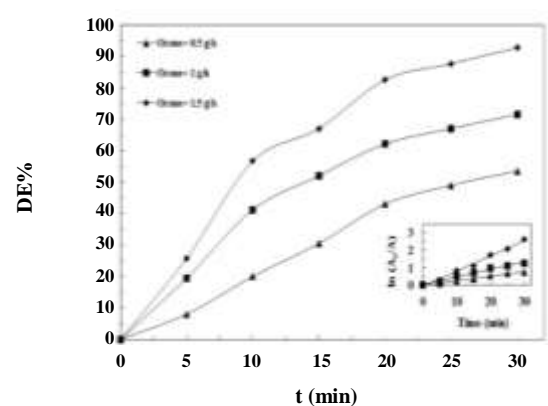


Fig. 5: Effect of ozone mass flow rate on DE% of O_3/UV process ($[DR23]_0 = 100 \text{ mg/dm}^3$ and pH = 10). The inset plot was depicted according to the pseudo-first-order kinetics assumption.

these processes are applicable for double-bonded dyes. The ozone can be applied in its gaseous form and as a consequence does not increase the volume of the solution, not leading to sludge generation [18]. The effect of the main operational variables including the initial DR23 concentration, the ozone mass flow rate, and pH on the dye decolorization was studied after 30 min of treatment. The degradation of the organic pollutants by the AOPs depends on their initial concentration. Thus, the runs were carried out at various concentrations of the dye. As can be seen from Fig. 4, when the dye concentration ranged from 100 to 10000 mg/dm^3 , the DE% declined from 92.7 to 14.1%. Under the same operating conditions of the O_3/UV process, a certain amount of hydroxyl radicals was generated. Hence, by increasing the DR23 molecules and their decolorization intermediates, the hydroxyl radicals could not be sufficient to oxidize them and consequently, the DE% decreased. Increasing the O_3 mass flow rate from 0.5 to 1.5 g/h enhanced the degradation of DR23 (Fig. 5). It could be related to the production of extra OH^\bullet radicals (Eqs. 1-6), which could oxidize the contaminants. The solution pH is a substantial control parameter for the O_3 including

processes. To determine the pH function, its value was altered from 3 to 10; the desired DE% was obtained at pH 10, while it declined at lower pHs (Fig. 6). The indirect attack of hydroxyl radicals to the DR23 at the basic pHs could be more efficient than the direct electrophilic attack of O_3 at the acidic pHs under the same operating conditions [10, 19]. In all runs, the decolorization rates obeyed the pseudo-first-order kinetic and the apparent pseudo-first-order rate constants (min^{-1}) were calculated by the slope of the inset plots of Figs 4-6, as presented in Table 3.

As electrical energy has a notable portion of the operational expenses in water treatment processes, electrical energy per order (E_{EO}) is a significant parameter for its assessment when the first-order kinetic is obtained. The E_{EO} is specified as the needed value of electrical energy (kWh) to degrade 90% of a pollutant per volume of solution (dm^3). The E_{EO} can be evaluated in a semi-batch set-up as follows [20, 21]:

$$E_{el} = \frac{38.4P_{el}}{Vk_{dec}} \quad (10)$$

Table 3: Decolorization rate constants and electrical energy per order of the O₃/UV process at various operational conditions.

[DR23] ₀ (mg/dm ³)	ozone mass flow rate (g/h)	pH	K _{UV/O₃} (1/min)	R ²	EEO (kWh/ m ³ order)
100	1.5	10	0.0881	0.993	10.09
500	1.5	10	0.0319	0.991	27.88
1000	1.5	10	0.0129	0.987	68.94
10000	1.5	10	0.0053	0.990	167.80
100	0.5	10	0.0273	0.990	32.58
100	1	10	0.0428	0.985	20.78
100	1.5	7	0.0480	0.985	18.53
100	1.5	3	0.0315	0.986	28.23

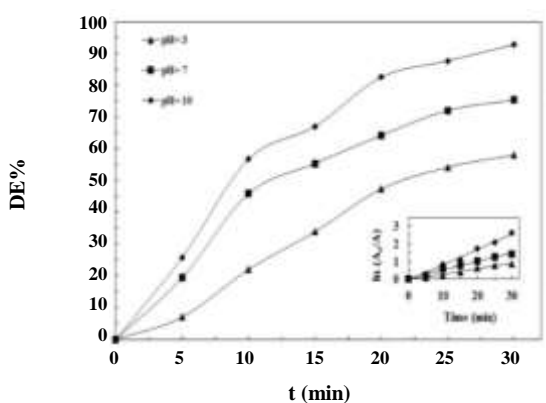


Fig. 6: Effect of pH on DE% of O₃/UV process (ozone mass flow rate = 1.5 g/h and [DR23]₀ = 100 mg/dm³) The inset plot was depicted according to the pseudo-first-order kinetics assumption.

Where P_{ej} is the sum of the input power (kW), V is the solution volume (L) and k_{dec} unit is min^{-1} . As all applied processes follow the pseudo-first-order kinetic, Eq. (10) could be used to determine the E_{EO} amounts, as given in Tables 2 and 3. It should be noticed that the input power of UV lamp, diaphragm pump, and ozone generator was 30, 16.8, and 69 W, respectively. Therefore, the total input power was defined for each process. The calculated results for the E_{EO} demonstrated not only the decrease in the consumed electricity by utilizing the O₃/UV process, in comparison with direct photolysis and ozone processes at the desired pH 10 (Table 1), but also showed that the same decolorization of the DR23 was carried out in less time. Furthermore, the operating parameters in the O₃/UV process had a remarkable influence on the E_{EO} (Table 3).

It is significant to note that E_{EO} was calculated to be 23.28 and 16.03 kWh/(m³.order) at pH 3 and 7 for treatment of 100 mg/dm³ dye at 1.5 g/h ozone mass flow rate by the ozone process, respectively. These amounts for the E_{EO} are higher than the related amounts at the same operational conditions using the O₃/UV process (Table 3), which are 28.23 and 18.53 kWh/(m³.order) at pH 3 and 7, respectively. Hence, the pH could have a significant function in the O₃/UV process; thus E_{EO} declined at the optimized pH. It should be mentioned that the synergistic effect of the photolysis and ozonation was observed at the various pHs; however, it decreased with the pH reduction.

CCD nonlinear model development and validation

Table 4 represents the operational conditions for each experiment and the observed experimental DE% as the dependent response variable. A nonlinear equation was obtained to correlate the decolorization efficiency and the independent experimental parameters.

$$DE\% = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1x_1 + b_{22}x_2x_2 + b_{33}x_3x_3 \quad (11)$$

By substituting the coefficient values in Eq. (12), which were calculated by the software, the CCD equation was developed as follows:

$$DE\% = 69.29 - 12.06x_1 - 14.69x_2 + 5.75x_3 + 1.11x_1x_1 + 0.71x_2x_2 - 3.36x_3x_3 + 3.91x_1x_2 + 1.46x_1x_3 + 0.28x_2x_3 \quad (12)$$

The experimental and calculated data, for DE% are given in Table 4. The correlation coefficient (R^2) was 98.52% demonstrating the proper capability of the CCD equation

Table 4: Matrix of central composite design for 3-factors the values of response (DE%).

Run Order	[DR23] (mg/L)	O ₃ (g/h)	Time	DE%		
				Experimental1	Experimental2	Predicted
1	-1.681	0	0	89.88	92.65	92.70
2	0	0	0	69.32	69.24	69.29
3	-1	1	1	97.99	96.88	95.15
4	0	1.681	0	93.99	95.56	96.01
5	0	0	0	69.22	69.23	69.29
6	1	-1	-1	31.84	28.64	30.16
7	0	0	0	69.00	69.14	69.29
8	0	0	0	69.56	69.77	69.29
9	-1	1	-1	86.30	84.77	86.02
10	0	0	1.681	64.44	64.36	69.44
11	0	1.681	0	43.33	45.65	46.60
12	-1	-1	1	76.49	74.99	73.02
13	1.681	0	0	48.12	52.36	52.15
14	1	1	-1	65.21	67.69	66.80
15	0	0	-1.681	50.5	53.11	50.11
16	-1	-1	-1	65.41	64.25	65.01
17	1	-1	1	47.45	46.29	44.02
18	0	0	0	69.45	69.55	69.29
19	0	0	0	69.45	69.66	69.29
20	1	1	1	85.65	83.01	81.78

for predicting DE%. Furthermore, analysis of variance (ANOVA) is the other way to evaluate the significance of the CCD model. The ANOVA divides the variations of the obtained results into two categories, which are related to the model and experimental (residual) errors, respectively. F-value is described as the ratio of the mean squares of the model and residual errors; it shows if the variation from the model is significant or not, as compared to the residual error. If the F-value is higher than the tabulated value for a distinct freedom degree in the model at a significance level of α , the adequacy of the model is confirmed. The F-value was calculated as 222.17 in this study, which was considerably more than the tabulated F (2.21) at 95% significance, thereby confirming the CCD model accuracy. Eventually, the effect of each operational parameter on the DE% was calculated by Pareto analysis using Eq. (13):

$$P_i = \left(\frac{b_i^2}{\sum b_i^2} \right) \times 100 \quad (i \neq 0) \quad (13)$$

According to the coefficients (b_i) of the CCD model (Eqs. (11) and (12)), the ozone mass flow rate (50.80%), DR23 initial concentration (34.24%), and process time (7.78%) were the most effective parameters in the O₃/UV process. These findings were also confirmed by the obtained F-values for the ozone mass flow rate (1028.72), DR23 initial concentration (692.74), and process time (157.48) [22-24].

CCD plots and process optimization

The response surface and contour plots were plotted by applying the CCD model to show the influence of the independent parameters on the O₃/UV process.

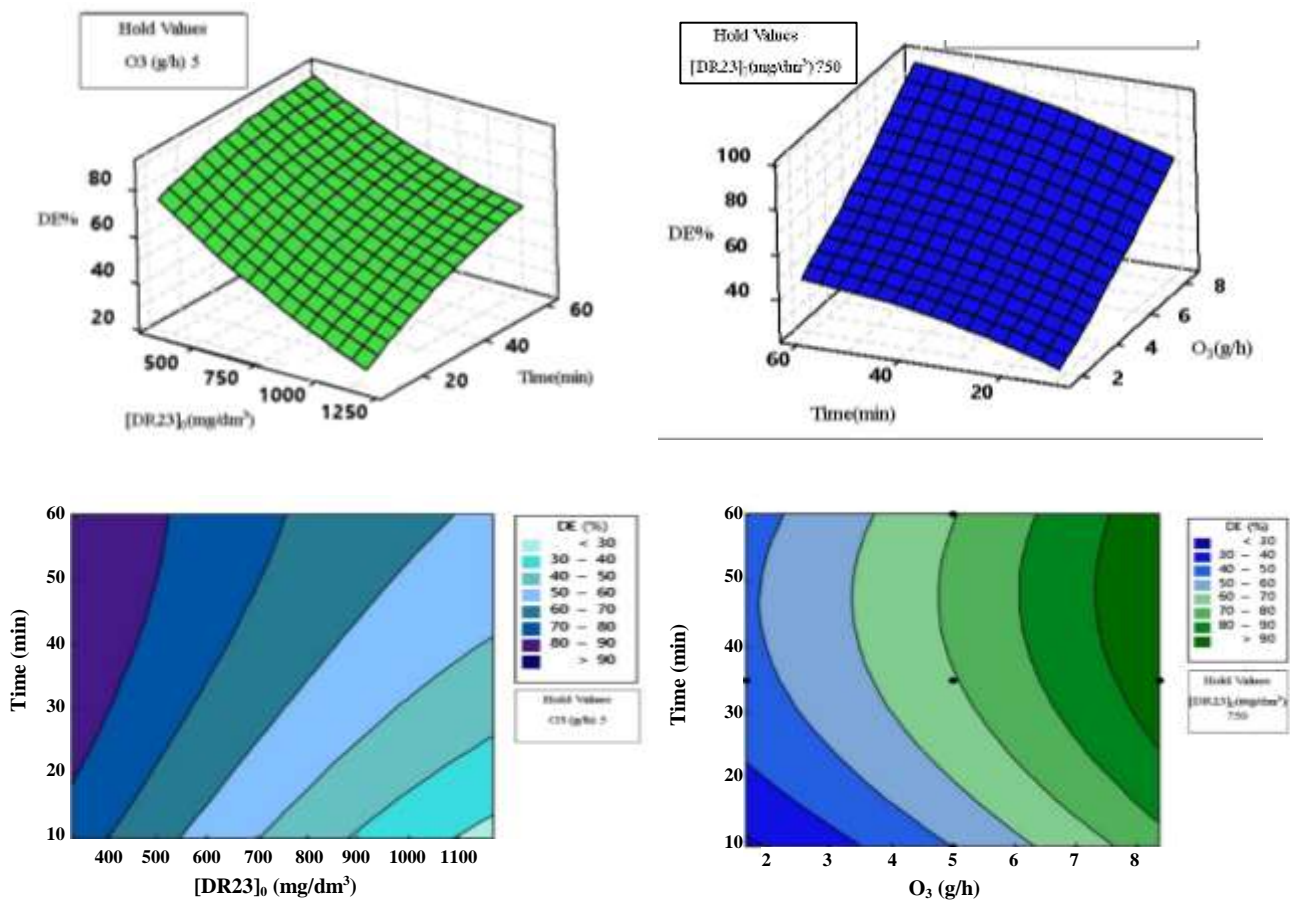


Fig.7. Response surface and contour plots for DR23 degradation: (a) Effects of ozone and time; (b) Effects of initial dye concentration and time.

Figs. 7a and b demonstrate the influence of the two independent parameters on the DE% within their experimental ranges while the other variable was kept unchanged. It can be observed from Fig. 7a that the enhancement in the initial DR23 concentration led to the decrease of DE% at the holding value of 5 g O₃/h during the 60-min treatment. It was due to the extra DR23 molecules and their decolorization by-products, which had to be degraded by the same concentration of hydroxyl radicals formed at identical operational conditions. Fig. 7b demonstrates the effect of the O₃ mass flow rate on the O₃/UV performance; the DE% increased as a result of the enhancement of O₃ amount with the holding value of 750 mg/dm³ DR23 during the 60-min treatment due to the extra hydroxyl radicals production. After the development of the nonlinear CCD model, it could be applied not only for the calculation of DE% in various experimental conditions but also for the definition of the optimized conditions related

to dye decolorization. One of the desired conditions for the approximately complete decolorization of DR23 is determined as the initial DR23 concentration of 330 mg/dm³, and the ozone 7 g/h after 35 min of treatment. The predicted DE% for these conditions was 99.50% and the experimental DE% was observed to be 99.14%, which revealed that the CCD model could properly specify and predict the DE% [25-29]. Moreover, the COD removal was obtained to be 62.5% at the same above-mentioned desired operational conditions based on the open reflux method [30].

CONCLUSIONS

The DR23 decolorization, as a model azo pollutant, was properly studied by applying the O₃/UV process in the recirculating semi-pilot reactor. After investigating the effect of the operational parameters on DE%, the nonlinear CCD model was obtained as a function of the initial DR23 concentration, the ozone mass flow

rate, and process time, for the optimization of the treatment process and the prediction of DE%. The obtained data revealed that the estimated values were consistent with the experimental data with $R^2 = 0.9852$; one of the desired conditions for the dye decolorization (99.50%) was predicted as $[DR23] = 330 \text{ mg/dm}^3$ and ozone mass flow rate $= 7 \text{ g/h}$ after 35 min of the process at the $\text{pH} = 10$, which was obtained to be 99.14% experimentally.

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