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Degradation of Maxilon Blue GRL Dye Using Subcritical Water and Ultrasonic Assisted Oxidation Methods

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Abstract

This study was performed to investigate the degradation of Maxilon Blue GRL (MBG) which is widely used as a textile dye. MBG causes major trouble to human and other livings health due to exists in textile wastewaters. Using reliable methods such as subcritical water oxidation (SWO) and ultrasonic assisted oxidation (UAO) methods for cleaning the textile wastewater is of great importance. In this context, Subcritical water oxidation and ultrasonic assisted oxidation methods were applied using homemade stainless steel reactor system and Ultrasound system for degradation of MBG in aqueous solution. TOC removal was measured to determine the efficiency of the process. Experimental variables were evaluated by Response Surface Method (RSM) and optimum parameters and theoretical equations were proposed. ANOVA results of SWO experiments showed that utilized design was expressed by quadratic model. The properties of this model were presented by ANOVA terms. Maximum TOC removal rates obtained by using SWO and UAO were 89.44 % and 24.85 %, respectively. Obtained findings indicated the applicability of the performed methods in the treatment of wastewaters containing MBG by degradation.

1. INTRODUCTION

On a global scale, 100,000 various dyes, which are mostly used in the paper, textile and other industries, are commercially fabricated [1-3]. Especially, textile industry uses approximately half of the dye and organic pigment produced world-wide [4]. According to researches, the demand for these products passes over 30 million tons [5,6]. Unfortunately, the textile industry consumes excessive amounts of water, where 200 L of water are required to produce 1 kg of textile dye [7]. Therefore, large amounts of wastewater which contain remarkable amounts of non-fixed dyes alkalis, organic and inorganic salts, acids and heavy metals by textile industry occurs during this process [1,8]. The widespread disposal of the textile wastewater to the environment has been caused to serious contamination problems in many countries [9]. Although many traditional methods have been used to dispute the contamination of water sources, these processes can produce degradation products and toxic metabolites [10-13]. Thus, lots of adverse effects such as toxicity, mutagenicity and carcinogenicity can threat animal and human health and cause long-term health problems [14-16]. Another important problem caused by the textile wastewater is their existence that cause absorption and reflection of sunlight in the water. Reducing the absorption of light that is important for photosynthetic activities of the algae may cause many serious problems in the aquatic environment [17].

Textile industry uses many kinds of synthetic dyes. These dyes are complex aromatic structures that are physicochemically, thermally and optically stable [3,18]. Generally, dyes are classified by the chemical structures of their specific chromophoric groups. Azo dyes, involving Maxilon Blue GRL, have one or

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more nitrogen to nitrogen double bonds [–N=N–) and constitute a significant portion of dyes that are used in the textile industry [19,20].

Considering the damages of textile wastewater on human health, it has become an important topic to clean the textile wastewater before discharging of it to the environment. Many conventional methods such as flocculation, Fenton oxidation, membrane filtration, adsorption, phytoremediation, bioremediation, photochemical, ion exchange, electrochemical oxidation, electrolytic precipitation, and ozonation have been used for the treatment of wastewater [21,22]. However, more appropriate and environmentally friendly treatment technologies have been researched for reclaiming the textile wastewater [23].

Recently, advanced oxidation processes (AOP) have been used as treatment process of textile wastewater. AOPs are effective oxidation processes in which hydroxyl radicals are produced in the reaction medium. These hydroxyl radicals can effectively oxidize organic and inorganic compounds subjected in the process [22]. On the other hand, subcritical water oxidation (SWO), which is a member of AOP can be used for degradation of dyes in the textile wastewater. SWO can be used with or without oxidants such as hydrogen peroxide and oxygen which are used as the main source of hydroxyl radicals [17,23]. In addition, SWO carried out in subcritical water medium which is environmentally friendly solvent where water is heated between 373 and 647 K and pressurized high enough to keep it in the liquid state [17,24,25].

Another salient oxidation method is ultrasonic assisted oxidation (UAO) method which is a member of AOPs, too. UAO is one of the recent degradation technologies utilized for treatment of the textile wastewater. However, only a few works related to oxidation of hazardous materials have been reported [22]. In this process, strong radicalic species such as $^{\bullet}OH$ and $H^{\bullet}$ are produced through activating H_2O_2 by ultrasonic waves [26,27,28]. UAO method generally requires lower treatment costs than other methods [22].

Response surface methodology (RSM) is an efficient statistical and mathematical experimental design technique. Being an economic and time-saving method, RSM which provides more information from a limited number of experiments. RSM is used to optimize experimental variables and evaluate the response through interactions between the variables. Box-Behnken Design (BBD) is one of the most efficient and commonly used statistical model of RSM design. BBD is used to optimize and examine the influence of independent variables on measured response [29,30,31].

In this study, degradation of Maxilion Blue GRL (MBG) dye was performed using SWO method and effectiveness of UAO method was also examined. Although, there is a lot of work related to textile dyes, a limited number of studies have been reported on MBG. MBG was selected as a model pollutant for contaminated textile wastewaters since MBG is widely used in textile industry in Turkey [18]. Hydrogen peroxide, which is an eco-friendly agent and degraded to H_2O and O_2 after treatment was used as the oxidant [1, 24]. In addition, RSM was used to optimize the degradation process.

2. MATERIALS AND METHODS

2.1. Materials

H_2O_2 and TOC Cell Test Kits were purchased from Merck (Germany). N_2 gas was supplied by Linde gas (Turkey). Ultra-pure water was prepared using Millipore Milli-Q Advantage A10, Maxilon Blue GRL dye was used to prepare the dye solution.

2.2. Experimental procedure

Degradation experiments of MBG were carried out under treatment conditions which are shown in Table 2 in the case of SWO. All SWO experiments were done using a home-made system containing degradation reactor which was used in our previous work [32]. The reactor was filled with 150 ml of 100 ppm MBG dye solution. Pressure was fixed at 30 bar supplied by N_2. All runs were done in triplicate at different temperatures, treatment times and oxidant concentrations. Table 1 demonstrates all parameters and their conditions.

In the case of UAO, Bandelin GM 3200 ultrasonic homogenizer along with KE-76 ultrasound probe was used. 150 ml of 25 ppm of MBG dye solution was added into the beaker and determined amount of H_2O_2 was added on it. Then, the probe of the ultrasonic system was immersed in to the solution. Degradation of the MBG was performed under atmospheric pressure applying various amplitude value of the ultrasonic system and treatment times.

2.3. Analysis Methods

All fractions were collected at the end of the treatment time designated according to Table 2 and TOC analysis was done using TOC cell kit and Merck Nova 30 A spectroquant photometer. Experimental TOC removal rates of MBG were calculated according to the equation indicated in our previous work [32].

2.4. Response surface modelling

Response surface methodology (RSM) is a useful statistical tool for evaluating the performance of a system through designing experiments and assessing the relationship between independent variables [33,34]. Box-Behnken Design (BBD), which is one of the RSM design methods, was used to optimize the degradation process and determine the relationship between the experimental variables and evaluating the response over all experimental variables.

The effectiveness of each variable that has a critical role on the efficiency of the process was investigated at three levels (-1, 0 and +1). x_1, x_2 and x_3 symbolize temperature (K), ratio of H_2O_2 concentration/dye concentration and treatment time (min), respectively. Y (response), was symbolize the percentage of the dependent variable (TOC removal). Table 1 indicates the experimental design. The results were evaluated using Design Expert 9.0.6.2 version and the theoretical equation model for the degradation of MBG was proposed [35].

Table 1. *Experimental design of the independent variables employing in the RSM.*

Independent Variables	Factors	Ranges and Levels		
		-1	0	1
Temperature (K)	x_1	373	423	473
Oxidant/Dye ratio	x_2	10	15	20
Treatment time (min)	x_3	20	40	60

15 experiments were performed using H_2O_2 for degradation of MBG, in randomized order as shown in Table 2. The convenience of the performed model was determined using analysis of variance (ANOVA). The proposed quadratic model was expressed by the R^2, R^2_{adj} and evaluated by means of Fisher's 'F' test and *P*-value.

3. RESULTS AND DISCUSSION

3.1. Optimization of degradation of MBG using SWO

Table 2. *BBD with actual/coded values and experimental TOC removal results.*

Run no.	x_1:T (K)	x_2:C (Oxidant/Dye ratio)	x_3: t (min)	*Y*: Response (TOC Removal, %)
1	473 (+1)	10 (0)	40 (-1)	69.8
2	373 (-1)	20 (+1)	40 (-1)	72.29
3	373 (-1)	15 (-1)	60 (+1)	89.44
4	423 (0)	15 (-1)	40 (-1)	78.07
5	373 (-1)	15 (-1)	20 (0)	79.55
6	423 (0)	15 (-1)	40 (-1)	81.49
7	423 (0)	10 (0)	20 (0)	58.75
8	473 (+1)	20 (+1)	40 (-1)	65.05
9	423 (0)	15 (-1)	40 (-1)	77.7
10	423 (0)	20 (+1)	60 (+1)	65.7
11	473 (+1)	15 (-1)	60 (+1)	68.8
12	423 (0)	20 (+1)	20 (0)	61.64
13	473 (+1)	15 (-1)	20 (0)	64.05
14	423 (0)	10 (0)	60 (+1)	59.9
15	373 (-1)	10 (0)	40 (-1)	78.07

Table 2 displays the experimental conditions for 15 runs and their results. It is clear from Table 2 that the highest and the lowest TOC removal percentages were obtained at run 3 and run 7 as 89.44 % and 58.75 %, respectively.

Table 3. *ANOVA results of obtained quadratic model.*

Source	Sum of squares	Degrees of freedom	Mean square	F Value	*p*-value prob > F
Model	1027.56	9	114.17	4.79	0.0497
x_1	333.47	1	333.47	13.98	0.0134
x_2	0.42	1	0.42	0.018	0.8992
x_3	49.25	1	49.25	2.07	0.2102
x_1x_2	0.27	1	0.27	0.011	0.9201
x_1x_3	6.60	1	6.60	0.28	0.6212
x_2x_3	2.12	1	2.12	0.089	0.7777
x_1^2	35.24	1	35.24	1.48	0.2784
x_2^2	436.54	1	436.54	18.31	0.0079
x_3^2	166.53	1	166.53	6.98	0.0458
Residual	119.22	5	23.84	-	-
Pure Error	8.73	2	4.37	-	-
Cor Total	1146.78	14	-	-	-

R^2 = 0.8960, R^2_{adj} = 0.7089, Adequate precision = 6.928

Table 3 shows ANOVA results for the obtained model. The model F-value was calculated as 4.79. This value implies the significance of the model. There is only a 4.97 % chance that an F-value of this order could occur due to noise according to data given in Table 2. R^2 and R^2_{adj} values were determined as 0.8960 and 0.7089 respectively, in case of using H_2O_2. Adequate precision, which is a measure of the signal-to-noise ratio and compares the range of the predicted values at the design points to the average prediction error was calculated as 6.928 where the value greater than 4 is desirable Therefore, this value indicates that the model can be employed to navigate the design space [36].

The theoretical model is given in Equation 1 in terms of coded factors. This equation is useful for making predictions for the efficiency of the degradation for given levels of each factor. Examining the term of the above mentioned equation, it can be said that term x_3 is the most effective variable in the process followed by x_1^2 and x_2x_3.

$$Y_1 = +79.09 - 6.46x_1 - 0.23x_2 + 2.48x_3 + 0.26x_1x_2 - 1.29x_1x_3 + 0.73x_2x_3 + 3.09x_1^2 - 10.87x_2^2 - 6.72x_3^2 \quad \text{(eq. 1)}$$

(Y_1= TOC removal, %)

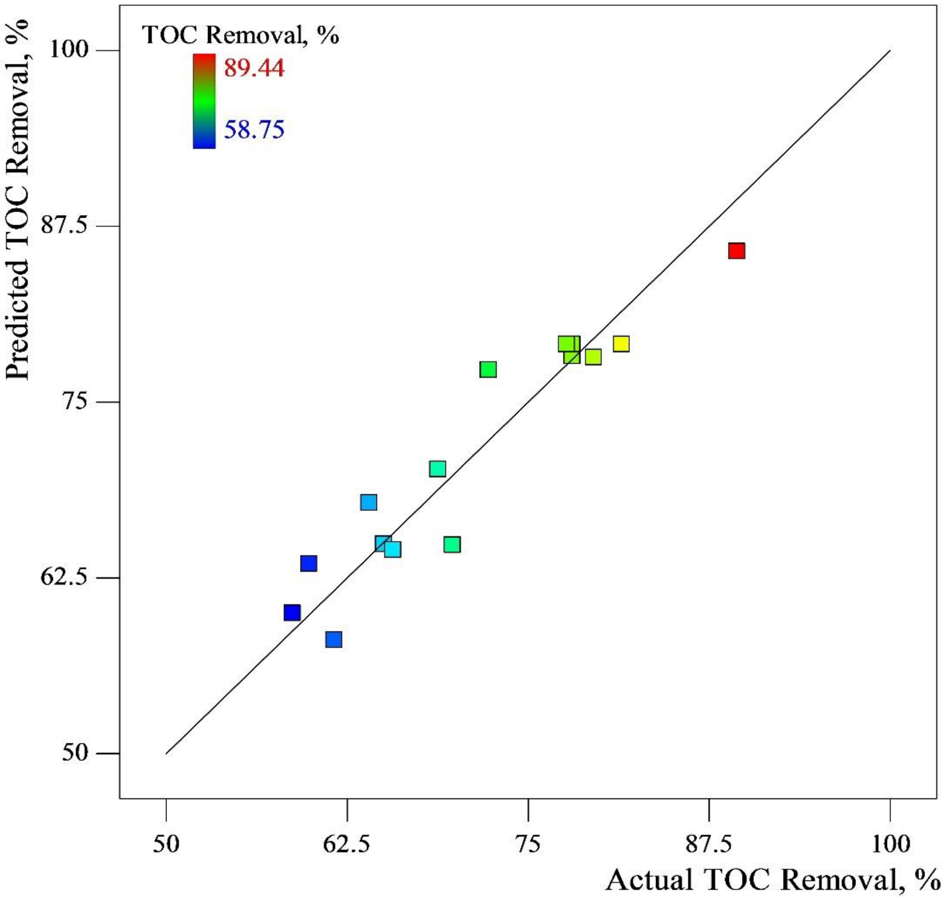

Figure 1. *Graph of the predicted response values versus the actual response values of TOC removal of MBG.*

Predicted TOC removal versus the actual TOC removal of MBG was presented in Figure 1. It is clearly shown from Figure 1 that all points distributed around the diagonal lines are predicted well by the employed model. This correlation is supported by the R^2 and R^2_{adj} values mentioned above.

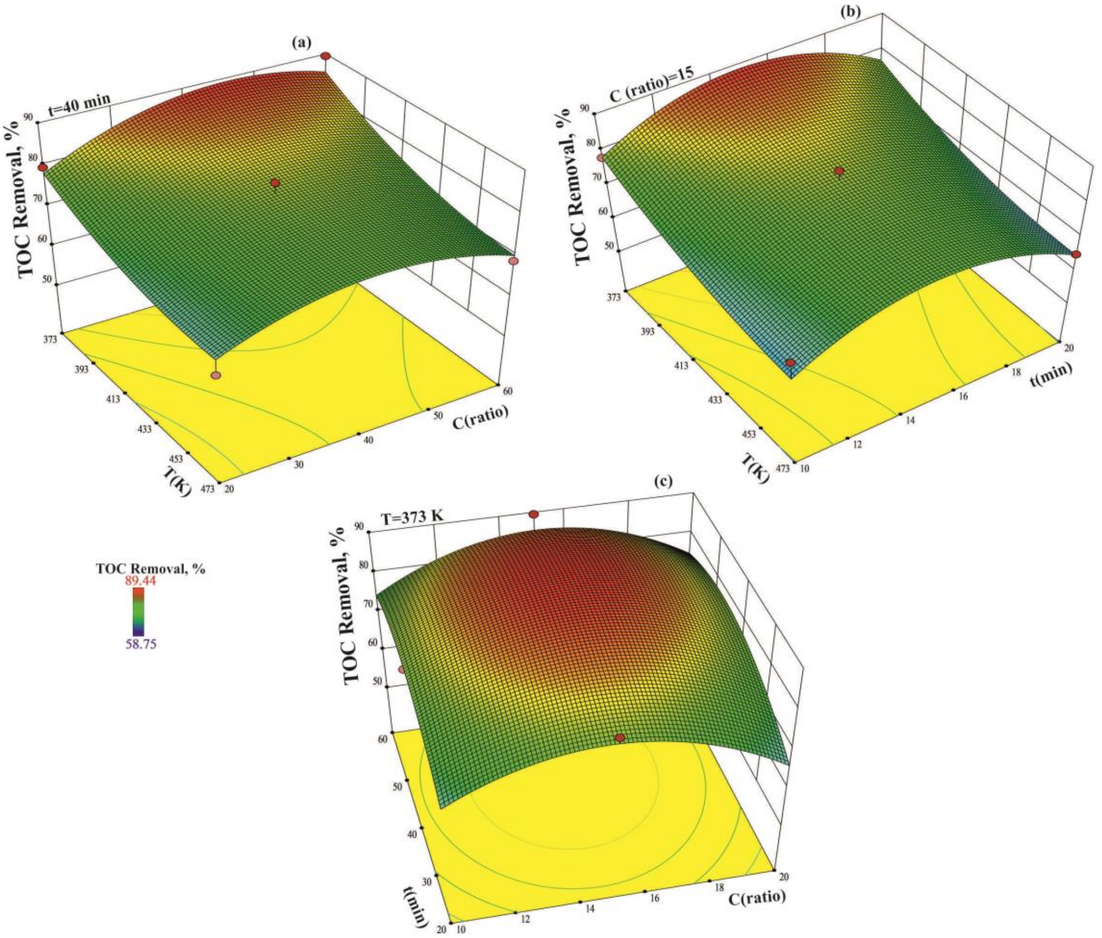

Figure 2. *3D plots of the relationship between experimental variables and response. (a) Effect of temperature (T) and ratio of H_2O_2 concentration/dye concentration (C) on TOC Removal of MBG using H_2O_2 at fixed t = 40 min. (b) Effect of temperature (T) and treatment time (t) on TOC Removal of MBG using H_2O_2 at fixed C = 15. (c) Effect of treatment time (t) and ratio of H_2O_2 concentration/dye concentration (C) on TOC Removal of MBG using H_2O_2 at fixed T = 373 K.*

Figure 2 displays the 3D plots of the effect and interaction of independent variables of temperature, the ratio of H_2O_2 concentration to dye concentration and treatment time on TOC removal of MBG using H_2O_2. It can be seen from figure 2 (a) that TOC removal percentages of MBG fairly depends on temperature and H_2O_2/dye concentration ratio. Lower levels of temperature along with medium levels of H_2O_2/dye concentration ratio enhanced the efficiency of the process that might be based on the formation of $^{\bullet}OH$ radicals which can easily attack the target compound [17,37].

Figure 2 (b) shows the combined effect of treatment time and temperature at a fixed H_2O_2/dye concentration ratio of 15. It is obvious that treatment time is a very effective on TOC removal rates. Beyond 30 minutes of treatment time, TOC removal rates enhanced due to presumptive formation of adequate free radicals in conditions of 373 K of temperature and fixed H_2O_2/dye concentration ratio of 15.

Providing the oxidant/dye ratio above 12, elevated TOC removal rates were obtained from moderate to high levels of treatment time at the fixed temperature of 373 K. This fact proved that adequate treatment time and concentration of H_2O_2 is necessary to obtain high efficiency in the degradation process of MBG. In addition, TOC removal rates were obtained as 8.11 %, 9.0 % and 14.32 % in the 373 K, 423 K and 473 K respectively, without using any oxidants. These findings can prove the importance of the oxidant in the process.

When comparing our findings for MBG degradation by using subcritical water method to the results of Acid Red 274 degradation performed by Kayan and Gözmen, it can be said that our results are better [1].

In addition, our result is (89.44 %) noteworthy when taking into consideration the maximum TOC removal value (64 %) of Reactive Red 120 which performed by Daskalaki et al. [17].

Table 4. *Numerical optimization report of variables*

Number	x_1:T (K)	x_2:C (Oxidant/Dye ratio)	x_3:t (min)	*Y*:Response (TOC Removal, %)	Desirability
1	373.0	14.9	45.6	89.16	0.986
2	375.0	14.9	45.5	88.65	0.959
3	373.0	15.8	48.6	88.31	0.942
4	373.0	15.0	58.4	86.43	0.932
5	373.0	12.7	56.9	86.68	0.844
6	373.0	12.7	31.1	83.64	0.781
7	423.0	15.0	43.7	79.32	0.692
8	423.0	16.1	43.7	78.74	0.670
9	473.0	15.0	41.8	75.77	0.545
10	473.0	15.8	45.6	75.32	0.523

Optimization report, which presents the detailed of the views of optimisation outcomes, was given in Table 4. Numerical optimization is used to search the design space, performing the models created during analysis to find factor settings that meet the defined goals. It can optimize any combination of one or more goals. According to Table 4, the highest TOC removal can be selected with adjusting the desired desirability values. One can choose the desired goal for each factor and response from this table via setting variables to a maximum, a minimum, a target, within range or an exact value. The "importance" of each variable can be changed in relation to the other variables and desirability is kept at the highest value.

3.2. Degradation of MBG using UAO

Many tests were done with UAO method in the presence of various concentration of $K_2S_2O_8$ and H_2O_2 in the reaction medium for degradation of MBG. However, degradation percentage remained very limited in the case of $K_2S_2O_8$. Increasing the concentration of $K_2S_2O_8$ did not favor the degradation efficiency due to scavenging reaction between $^{\bullet}OH$ and $S_2O_8^{2-}$ [38]. Maximum TOC removal percentage of MBG was obtained as 24.85 % in the H_2O_2/dye concentration ratio of 10, amplitude of 80 %, fixed pH of 3, 333 K of temperature and in the initial MBG concentration of 25 ppm. In addition, additional experiments were performed to evaluate the effect of the frequency of ultrasonic system on the yield. It was obtained that frequency which is higher than % 80 did not increase the degradation efficiency. This phenomenon is based on the fact that active cavitation which provide the formation of $^{\bullet}OH$ radicals in H_2O_2 containing medium could not occur [38].

While Lin et al. obtained 83.5 % efficieny in the degradation of polycyclic aromatic hydrocarbons in textile dye sludge using Fenton process they reached only 45.5 % efficieny using ultrasound process [39]. Therefore, considering that the efficiency obtained with ultrasound method is limited, it can be seen that the value of 24.5 % obtained is very reasonable.

4. CONCLUSION

Environmentally friendly methods were used for the degradation of synthetically prepared MBG solution symbolizing textile dye wastewaters. Considerable TOC removal percentages were obtained for MBG using SWO based on the co-effect of subcritical water medium and effective oxidant, H_2O_2. 89.44 % of TOC removal rate was obtained as the utmost value in the case of SWO. In addition, RSM was used to evaluate TOC removal rates over experimental parameters and a theoretical equation of TOC removal for MBG was obtained. 24.85 % of TOC removal rate was obtained as maximum value in the case of UAO using H_2O_2. Although lower rates were obtained using UAO in comparing to SWO, UAO should not discredit due to being a safe and clean method. The effect of a catalyst in the UAO process should be evaluated for the degradation of MBG in further investigations.

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CONFLICT OF INTEREST
No conflict of interest was declared by the authors.

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