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Research Article / Araştırma Makalesi

COLOR AND COD REMOVALS BY PHOTOCATALYTIC DEGRADATION: AN EXPERIMENTAL DESIGN APPROACH AND COST ANALYSIS

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ABSTRACT

Removal efficiencies of color and chemical oxygen demand (COD) after TiO_2-mediated photocatalytic degradation process of synthetic wastewaters prepared using Methylene Blue as a fairly toxic textile dye were quantified in the present study. For this purpose, effects of lamp type, initial dye concentration (mg/L), catalyst dose (g/L), reaction time (min), aeration (mL/min), temperature (^oC), and initial pH were considered using design of experiments (DOEs). Plackett-Burman Design and Fractional Factorial Design were set to screen for the most influential explanatory variables. Box-Behnken Design and Central Composite Design as optimization designs were used in the optimization of the significant predictors detected. 3-D response surface plots and ANOVA results demonstrated that ultraviolet-C yielded the highest removal efficiencies of color and COD, with a significant interaction effect of aeration by catalyst dose on the removal efficiencies.
Keywords: Photocatalytic degradation, methylene blue, design of experiments.

1. INTRODUCTION

The use of dyes is so widespread in many types of industries, in particular, in textile sector that techniques concerning waste reduction, recycling, reuse and recovery have gained great significance to deal with increasingly growing rates and amounts of waste generation[1-3]. Reactive azo dyes are among the types most commonly used in textile industry[4-6]. Discharge of wastewaters contaminated with reactive azo dyes without treatment, and even effluent wastewaters after treatment pose a significant health risks to both humans and the ecosystems[7]. Azo dyes and their reaction yields such as aromatic amine were reported to have carcinogenic impacts on the environment[8].

Main conventional processes of wastewater treatment include adsorption, flocculation, settling, and filtering[9]. However, Fenton, ultrasound, photocatalytic degradation, and ozonation known as advanced oxidation processes have been recently on demand owing to their enhanced treatment ability to achieve higher removal efficiencies in a shorter period of time [10-12]. Photocatalytic degradation (PD) increases the presence of OH^- radicals in the recipient environment of wastewater, thus accelerating the breakdown of complex and aromatic organic pollutants. This process consists of the following three separate or con current mechanisms: (1) electron detachment, (2) O_2 release, and (3) H^+ detachment[13-15].

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Recently, the focus has been on the integration of experimental design, optimization and modeling of operational variables. Designs of experiment (DOEs) such as Box-Behnken (BBD), central composite (CCD), fractional factorial (FFD), Plackett-Burman (PBD) and Taguchi Orthogonal Array (TOA) designs have been utilized by public and private R&D institutions in order to minimize experimental runs and errors as well as maximize information derived from experimental data. There exist limited studies in related literature about comparative evaluations of DOEs in terms of their efficacy and cost which may provide better leverage points in the selection of the best-fit DOE to elucidate interaction effects and optimize operational parameters in a cost-effective way[16-20].

In light of the above considerations, the objective of the present study was to optimize titanium dioxide (TiO_2)-mediated photocatalytic removal efficiency of color and chemical oxygen demand (COD) in aquatic solutions with methylene blue (MB), a highly toxic dye used in textile, based on the integration of four DOEs for screening and optimization of significant operational variables and theirs costs, and empirical models of the best-fit multiple non-linear regressions (MNLR).

2. MATERIALS AND METHODS

2.1. Dye solutions

Methylene blue dye (MB, C.I. 52015) used in the experiments was purchased at a purity level of 99% from Polar Lab (Adana, Turkey). Prior to its use in the experiments, it was not subjected to purification, and stock solutions prepared adding 1.0 g MB to 1000 mL distilled water were utilized in the experiments upon their required dilutions.

2.2. Photocatalytic reactor

The experiments were carried out using a photocatalytic reactor system custom-designed by the authors (Figure 1) which consists of a vertically located and jacketed stainless steel container of cylindrical shape with 1.25 L volume capacity. Light sources used included ultraviolet A (UVA) and C (UVC), and visible light [9]. A heated magnetic stirrer was situated underneath the reactor, and air pump was also used for aeration.

Figure 1. Photocatalytic reactor system.

Initial dye concentration (IDC, mg/L), cata lyst dose (CD, g/L), aeration rate (AR, mL/min), reaction time (RT, min), temperature (T, °C), and initial pH were used as the continuous explanatory variables, while light type (LT) was used as the categorical predictor in the quantification and optimization of their influences on the photocatalytic removal of color and COD.

2.3. Spectrophotometric analysis

The maximum wavelength for MB was determined as 637 nm. Color (C_{RE}) and COD (COD_{RE}) removal efficiencies were based on spectrophotometric measurements at this wavelength, and Eq (1) or Eq (2), respectively, as follows:

$$C_{RE} = \frac{A_o - A_i}{A_o} \times 100 \quad (1)$$

$$COD_{RE} = \frac{COD_o - COD_i}{COD_o} \times 100 \quad (2)$$

where A_o and A_i refer to color values (IU) measured initially and at a time t, respectively. COD_o and COD_i refer to COD (mg/L) values measured initially and at a time t, respectively. Spectrophotometric analysis was carried out using a spectrophotometer (Hach DR 5000, France). For COD analysis, a Hach DRB 200 heater, and Hach LCI400 tube tests were used. COD measurements were made utilizing Hach LCI400 kits based on the following procedure adopted. Concurrently, 2 mL distilled water and 2 mL samples were inserted and mixed in the kits. At 150°C for 2 h, they were stored in Hach DRB 200 digester. Finally, they were cooled down gradually to 60°C, stirred once and left at room temperature. COD values were determined measuring the kits with high degree of clarity at room temperature. As a result of the characterization of stock solutions of effluents prepared under the experimental conditions stated in Section 2.1, initial (control) color and COD values were estimated at 1.359 IU and 135 mg/L O_2, respectively. Since initial dye concentrations specified in the DOEs were prepared through dilutions from the stock solutions, initial color and COD values were re-determined for each solution concentration obtained.

2.4. Cost analysis

In addition to the removal efficiencies, changes in the costs of photocatalytic removal were quantified in USD as a function of the related explanatory variables taken into account. The costs of color and COD removals were estimated using Eqs (3) and (4), respectively, thus:

$$C_{RE} = \Big\{\Big[\text{amount of catalyst (g)} \times \text{unit price of catalyst} \left(\frac{\$}{\text{g}}\right)\Big] + \Big[\text{amount of dye (g)} \times \text{unit price of dye} \left(\frac{\$}{\text{g}}\right)\Big] + \Big[\text{amount of electricity (kWh)} \times \text{unit price of electricity} \left(\frac{\$}{\text{kWh}}\right)\Big] + \Big[\text{amount of acid or base (g)} \times \text{unit price of acid or base} \left(\frac{\$}{\text{g}}\right)\Big] + \Big[\text{rate of aeration (mL/min)} \times \text{unit price of electricity for aeration} \left(\frac{\$}{\text{(mL/min)}}\right)\Big]\Big\} \quad (3)$$

$$COD_{RE} = \Big\{Eq(3) + \Big[\text{quantity of COD tests (piece)} \times \text{unit price of COD tests} \left(\frac{\$}{\text{piece}}\right)\Big]\Big\} \quad (4)$$

2.5. Designs of Experiment

The experiments for the color and COD removals consisted of the following two stages: (1) screening the seven explanatory variables for the most influential predictors, and (2) optimization of operational conditions of the predictors found significant. The screening stage was carried out using PBD and FFD. In the optimization stage, BBD and CCD were used considering two-way and three-way interactions, thus suggesting optimal operational conditions.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Screening by Plackett-Burman (PBD) and fractional factorial (FFD) designs

Our PBD and FFD results in Table 1 consistently showed that only IDC, CD, LT, and AR out of the seven predictors were significantly influential on the color and COD removals. Similarly, only RT, AT, and IDC were found to play a significant role in determining costs. PBD and FFD Pareto plots of standardized effects for the four response variables are presented in Figures 2 and 3, respectively.

As visualized by the PBD and FFD Pareto charts in Figures 2 and 3, LT, IDC, AR, and CD were found influential on color and COD removals, while RT, CD, and IDC significantly affected the costs of the removals according to the empirically generated threshold value of 2.78 and 2.31, respectively, based on the experimental data. The relative significance of the operational variables was also presented in Figures 1 and 2. These findings can be also considered a sensitivity analysis. Regardless of the screening DOE type, the same significant predictors were determined consistently. Also, it should be noted that only linear effects of the predictors were assessed in accordance with the screening DOEs.

Table 1. PBD and FFD schemes.

Exp design	Normal order	Exp order	CD	IDC	RT	T	pH	AR	LT
PBD	10	1	4	10	20	25	10	20	UVC
	4	2	4	10	60	45	6	20	UVA
	1	3	4	10	60	25	6	0	UVC
	5	4	4	50	20	45	10	0	UVC
	11	5	2	50	20	25	6	20	UVC
	2	6	4	50	20	45	6	0	UVA
	8	7	2	10	60	45	10	0	UVC
	3	8	2	50	60	25	10	0	UVA
	9	9	2	10	20	45	10	20	UVA
	7	10	2	50	60	45	6	20	UVC
	6	11	4	50	60	25	10	20	UVA
	12	12	2	10	20	25	6	0	UVA
FFD	16	1	4	50	60	45	10	20	UVC
	5	2	2	10	60	45	10	20	UVA
	11	3	2	50	60	25	10	0	UVC
	2	4	4	10	60	25	10	0	UVA
	9	5	2	10	20	45	10	0	UVC
	1	6	2	10	20	25	6	0	UVA
	3	7	2	50	60	45	6	0	UVA
	6	8	4	10	20	45	6	20	UVA
	10	9	4	10	60	45	6	0	UVC
	4	10	4	50	20	45	10	0	UVA
	8	11	4	50	60	25	6	20	UVA
	15	12	2	50	20	45	6	20	UVC
	14	13	4	10	20	25	10	20	UVC
	7	14	2	50	20	25	10	20	UVA
	13	15	2	10	60	25	6	20	UVC
	12	16	4	50	20	25	6	0	UVC

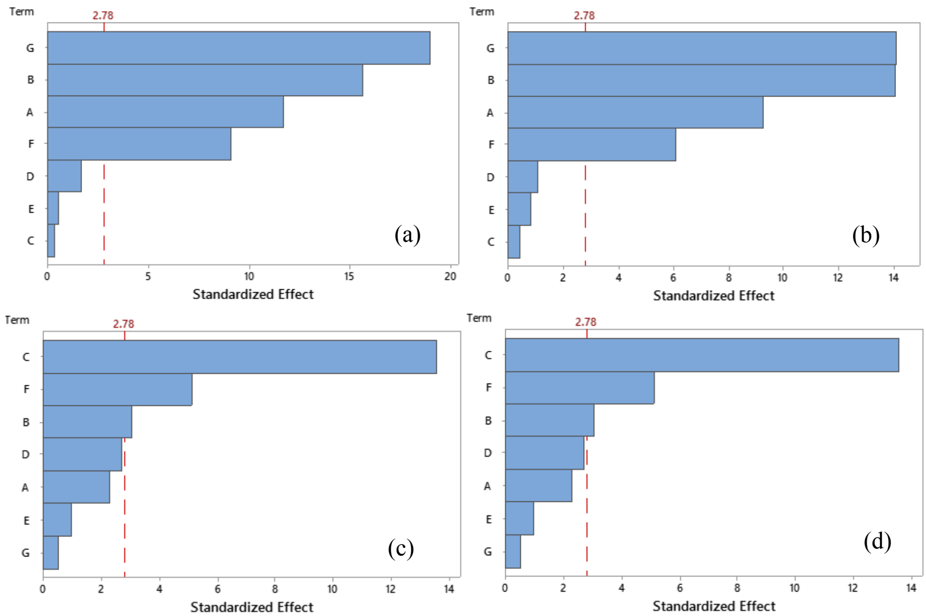

Figure 2. PBD Pareto charts of standardized effects on the four response variables of (a) color and (b) COD removals, and costs of (c) color and (d) COD removals as a function of CD (A), IDC (B), RT (C), T (D), pH (E) , AR (F), and LT (G).

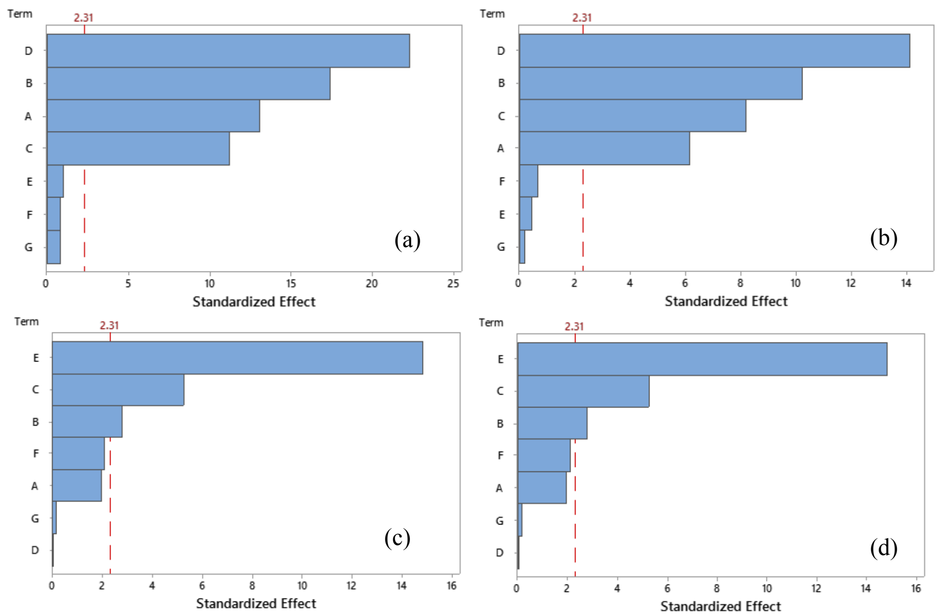

Figure 3. FFD Pareto charts of standardized effects on the four response variables of (a) color and (b) COD removals, and costs of (c) color and (d) COD removals as a function of CD (A), IDC (B), RT (C), LT (D), RT (E), T (F), and pH (G).

3.2. Optimization by Box-Behnken (BBD) and central composite (CCD) designs

Using IDC, LT, CD, and AR found significant as a result of the screening DOEs, the optimization DOEs of BBD and CCD were carried out using 51 experimental runs per each DOE. According to BBD, the interaction effects of CD by AR were found significant on the optimization of the color and COD removals and their costs (Figure 4).

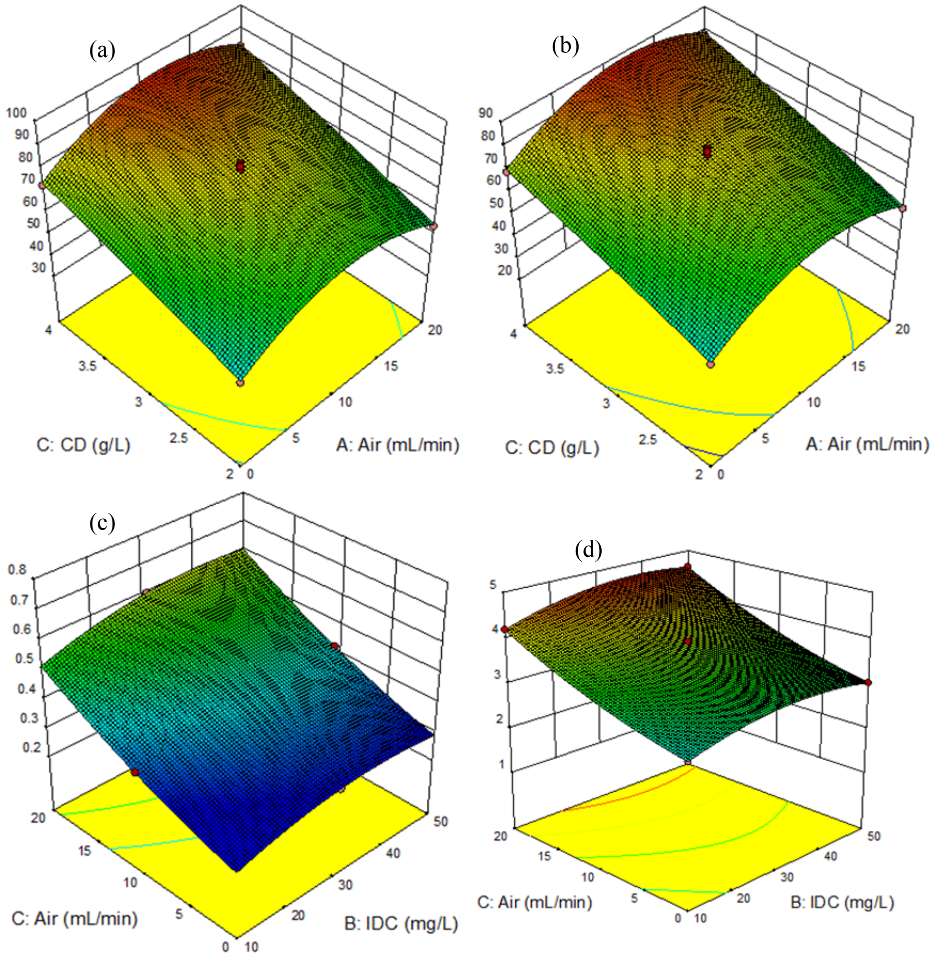

Figure 4. CD by AR (Air) and IDC by AR interaction effects on the four responses of (a) color and (b) COD removals and costs of (c) color and (d) COD removals according to BBD.

Based on CCD, the two-way IDC by AR interaction exerted a significant impact on the optimization of the responses (Figure 5). A total of eight best-fit MNLR models are presented in Table 2.

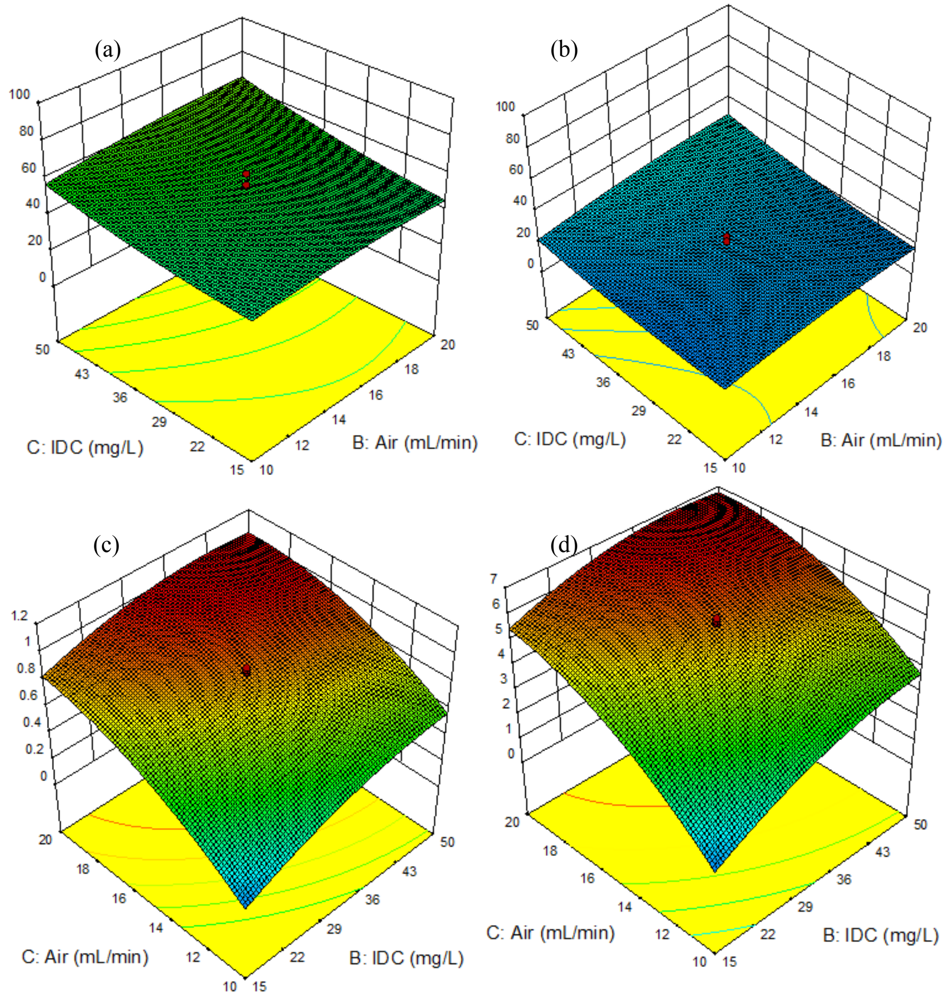

Figure 5. IDC by AR (Air) interaction effects on the four responses of (a) color and (b) COD removals and costs of (c) color and (d) COD removals according to BBD.

Based on BBD results, the most significant predictors were determined as the two-way interactions of CD by AR for color and COD removals and of IDC by AR for the costs. This finding was consistent with our CCD results. As can be seen in Figures 4 and 5, the increased CD and the decreased IDC led to an increase in both removals of color and COD, while the increased AR and IDC caused the increased costs. However, AR increased both color and COD removals in the range of 0 to 10 mL/min but decreased them in the range of 10 to 20 mL/min (Figures 4 and 5).

Table 2. The best-fit multiple non-linear regression (MNLR) models of TiO_2-mediated photocatalytic removals of color and COD, and their costs as derived from BBD and CCD.

Response	Predictor	Color		COD	
		BBD	CCD	BBD	CCD
Removal	Intercept	66.98	42.18	63.63	34.65
	AR	3.35	-4.40	3.27	-4.41
	IDC	-2.61	2.54	-2.40	2.55
	CD	11.33	6.72	10.76	6.68
	LT[1]	-9.84	-13.57	-9.43	-13.62
	LT[2]	-2.56	2.95	-2.39	2.96
	AR*IDC	0.81	-3.86	0.59	-3.88
	AR*CD	0.84	-15.66	0.80	-15.60
	AR*LT[1]	-0.27	1.41	-0.088	1.48
	AR*LT[2]	-0.27	-0.26	-0.34	-0.28
	IDC*CD	-1.31	1.79	-1.24	1.72
	IDC*LT[1]	0.21	-0.37	0.37	-0.43
	IDC*LT[2]	0.21	0.031	0.12	0.050
	CD*LT[1]	-0.92	-2.37	-0.88	-2.39
	CD*LT[2]	-0.92	0.55	-0.88	0.39
	AR^2	-13.46	-2.28	-12.87	-2.27
	IDC^2	-3.23	-1.99	-3.15	-1.98
	CD^2	-0.71	2.54	-0.59	2.54
Cost	Intercept	0.58	0.86	3.76	5.66
	RT	0.10	0.041	0.65	0.27
	IDC	0.026	0.15	0.17	0.98
	AR	0.12	0.28	0.75	1.83
	RT*IDC	-0.010	-0.051	-0.083	-0.34
	RT*AR	-0.033	0.041	-0.21	0.27
	IDC*AR	0.0075	-0.049	0.035	-0.32
	RT^2	-0.056	-0.072	-0.36	-0.47
	IDC^2	-0.041	-0.086	-0.27	-0.56
	AR^2	0.027	-0.12	0.16	-0.82

LT was used as the categorical variable with the following three levels of LT[1]: Daylight, LT[2]: UVA, and LT[3]: UVC held as the reference level.

3.3. Optimization of operating conditions

The resultant optimal conditions obtained to maximize TiO_2-catalyzed photodegradation removals and to minimize their costs are provided in Table 3.

Table 3. Optimal operating conditions under TiO_2-catalyzed photodegradation of methylene blue.

DOE	AR	IDC	CD	LT	Color removal	COD removal	Desirability
BBD	11.60	11.04	4.00	UVC	93.62	89.05	0.99
CCD	20.00	10.00	2.00	UVC	89.33	81.98	0.87
	AR	IDC	RT		Cost	Cost	Desirability
BBD	0.80	12.25	21.24		0.26	1.70	1.00
CCD	10.00	15.03	20.00		0.05	0.35	0.98

It is an important requirement that color and COD removals are maximized, while their costs are minimized for practical purposes. Thus, our above findings included concurrently optimized operational conditions under which the maximum color removals were achieved with %93.6 (0.402 IU to 0.026 IU) for BBD and with %89.3 (0.402 IU to 0.043 IU) for CCD. Similarly, the maximum COD removals of %89.0 (15 to 1.65 mg/L O_2) and %81.9 (15 to 1.65 mg/L O_2) were accomplished under the same conditions, respectively. Considering these high removal values for the aquatic solutions, TiO_2-mediated photocatalytic degradation appears to be very promising for effluents that contains methylene blue.

4. CONCLUSION

For the first time, not only were the color and COD removals by the photocatalytic degradation optimized using the two screening and two optimization DOEs, but also their costs were integrated into the optimization in this study. The most influential predictors included LT, CD, AR, IDC for the color and COD removals and RT, AR, IDC for their costs. The maximum color and COD removals by TiO_2-mediated photocatalytic degradation were estimated at %93 and %89, respectively. These maximum values were achieved using the optimal operational conditions determined through the optimization DOEs thus: 11.6 mL/min AR, 11.04 mg/L IDC, 4 g/L CD, and UVC lamp type. The fact that the initial COD value of about 135 mg/L O_2 of the aquatic solution was reduced up to 14 mg/L O_2 in a time period of only 30 min points to a highly significant impact of TiO_2-based photocatalytic degradation on the improvement of effluent water quality for textile and similar industries. In the future studies, there remain to be explored uncertainty and sensitivity analyses of empirical modeling and optimization results based on Markov chain-Monte Carlo simulations.

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