Degradation of CTAB by UV/H$_2$O$_2$ AOP – Optimization of process parameters

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In the present study, the most popularly statistical tool, response surface methodology (RSM) has been used to optimize the important process parameters such as peroxide dose, initial concentration of cetyltrimethyl ammonium bromide (CTAB), pH and NO$_3^-$ concentration for degradation of CTAB from wastewater by UV/H$_2$O$_2$ advanced oxidation process (AOP). Experimental design and optimization of the degradation process were done by central composite design (CCD). Results revealed that increase in CTAB concentration and nitrate concentrations adversely affect the CS degradation. On the other hand, higher H$_2$O$_2$ concentration and pH showed an increase in fluence-based rate constant upto a maximum followed by decrease in degradation rate upon further increase in concentration of each factor. The maximum fluence-based rate constant (0.0044 cm^2 mJ^{-1}) for degradation of CTAB was obtained at optimized conditions of 100 mg L^{-1} of CTAB, 0.25 mM of nitrate concentration of NO$_3^-$ and 1 mol H$_2$O$_2$ per mol of CTAB at the solution pH of 7.

Keywords: UV-H$_2$O$_2$, CTAB, rate constant, response surface method, central composite design.

Introduction

The uses of surfactants in various industries are huge, ranging from recovery and purification of raw materials in petroleum and mining industries; quality enhancement of finished products like cosmetics, pharmaceuticals, food products and paints. Aprat from this it is widely used in domestic activities. Based on the charge of polar head group of surfactant molecules, these are of four types – anionic, cationic, nonionic and amphoreticor zwitterionic. In this present study, cetyltrimethyl ammonium bromide (CTAB) has been presented as cationic surfactants (CS). Generally, CS are utilized in biocides, processing additives, mining, hair conditioning, cosmetics, disinfection, anti-rust products etc. They have great toxicological effect on aquatic life and human health. Removal of CS is very difficult by using conventional treatment methods due to concerns of sludge disposal and toxicity of CS.

Advanced oxidation processes (AOPs) are being used for degradation of surfactants for last two decades. The degradation is done by generating powerful oxidant, hydroxyl radicals (HO$^\bullet$)[1]. HO$^\bullet$ reacts with electron rich organic compounds. O$_3$/UV, H$_2$O$_2$/UV[2], UV/TiO$_2$/H$_2$O$_2$[3] and photo-Fenton process[4] are generally used for the surfactant degradation. Among them, homogeneous UV-H$_2$O$_2$ AOP is widely used to completely mineralize the CS[5].

Different process variables such as H$_2$O$_2$ dose, pollutants concentration, pH, different interfering substances like nitrate concentration effect the degradation process. In conventional process, the effect of each parameter is studied independently, with other parameters keep constant. In this process, the influence of all parameters are not considered and the optimization of the factors will require a large number of experiments, more time and materials. However, response surface methodology (RSM) using central composite design (CCD) is used widely for optimization of wastewater treatment processes[6–8]. The goal of the present work is to optimize the influence of process parameters for degrada-

tion of synthetic wastewater containing CTAB by photochemical process (UV/H_2O_2) using above mentioned statistical tool.

Materials and methods

(A) Reagents:

Cetyltrimethyl ammonium bromide (CTAB), Orange II, chloroform and 30% hydrogen peroxide were used for experimental purpose. Other chemicals of high purity were used in this work. Synthetic CTAB wastewater and all other solutions were prepared using distilled water.

(B) UV reactor:

A batch type UV reactor (Manufacturer: M/s. Lab Tree, India) consists of eight low-pressure mercury lamps (emission peak centered at 254 nm) were used to perform all UV based experiments. The photon flux was determined to be $1.9(\pm0.1)\times10^{-4}$ Einstein/L-min and fluence of the system was calculated to be $113(\pm5.7)$ mJ/cm^2-min[9].

(C) Analytical method:

CTAB (0–12 mg L^{-1}) was determined using a simple spectrophotometric method[10]. Orange II (concentration: 0.4×10^{-3} *M*) was used as ion pairing agent of CTAB. CTAB solution of 4 mL was taken into a separating funnel (25-mL capacity). Then, 1 mL Orange II solution and 5 mL of chloroform were added to the CTAB solution. The mixture was shacked for a time period of 1 min and then aqueous chloroform layer was separated. The absorbance of the chloroform layer was measured at 485 nm wavelength. The absorbance and concentration were related as: Absorbance = $0.0348\times$concentration (mg L^{-1}) + 0.0007 with co-relation coefficient of $R^2 = 0.9996$

(D) Degradation of cationic surfactant bearing wastewater:

All photochemical experiments were carried batch wise and illuminated by UV lamp at regular time interval from 1 to 10 min. Samples were taken after every 1 min of irradiation. The percentage degradation of CTAB was calculated and the experimental data was analyzed by different kinetic models. In the present work, it was found that the degradation of CTAB followed pseudo-first order kinetic model, the linearized form of which is shown below[11]:

$$\ln \frac{[C]}{[C]_0} = -k'_{app} H' \qquad (1)$$

where, [C] = CTAB concentration at a time t; $[C]_0$ = CTAB concentration initially taken; k' = fluence based, pseudo-first order reaction rate constant (cm^2 mJ^{-1}) and H' = fluence of the UV lamp (mJ cm^{-2}).

(E) Experimental design:

In this work, RSM-CCD statistical tool was employed to optimize the photochemical process. In order to assess the effect of different influencing parameters on photochemical degradation of wastewater containing CTAB, four factors – dose of H_2O_2 (X_1), initial CTAB concentration (X_2), pH (X_3) and NO_3^- concentration (X_4) were selected. Each parameter was performed at five levels: $-\alpha$, -1, 0, $+1$ and $+\alpha$ (Table 1). In CCD model, thirty experimental runs at 16 cube points, 8 axial points and 6 replications at the centre point were employed in this work. Design-Expert 7.0 software was used to analyse the experimental data. Correlation between dependent and independent variables is given below:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 \qquad (2)$$

where, Y = dependent variable, X_i's = independent process variables, b_0 = the coefficient of intercept. The coefficients, b_i, b_{ii} and b_{ij} are regression coefficients for linear, quadratic and interaction effects. Regression analysis of the experimental data was assessed by the analysis of variance (ANOVA). Fitness of the model was evaluated by the adjusted R^2 and adequate precision. The interaction and individual effects of the process variables on response within the design range was evaluated by the three-dimensional surface plots and two-dimensional contour plots. The process optimization and validation process were also done to evaluate optimum level of process variables for maximum response and to check validity of the polynomial model equation.

Table 1. Independent variables and its levels

Variables	Real values with coded levels				
	$-\alpha$	-1	0	$+1$	$+\alpha$
H_2O_2 dose (X_1) (mol/mol)	0	1.0	2.0	3.0	4.0
CTAB conc. (X_2) (mg L^{-1})	50	100	150	200	250
pH (X_3)	5	7	9	11	13
Nitrate conc. (X_4) (mM)	0	0.25	0.50	0.75	1.0

Results and discussion

(A) Degradation of CTAB by UV/H$_2$O$_2$ AOP:

In order to determine the effectiveness of the UV/H$_2$O$_2$ process, the CTAB degradation experiment was performed at pH 7 with hydrogen peroxide dose of 1 mol of H$_2$O$_2$ per mol of CTAB and CTAB concentration of 100 mg L^{-1}. The nitrate concentration of the solutions was 0.25 mM. Fig. 1 shows that more than 90% transformation of CTAB was obtained within 5 min. Kinetic analysis revealed that CTAB degradation followed pseudo-first order kinetic model. The fluence-based, constants was calculated to be 0.0049 cm^2 mJ^{-1} (Fig. 2).
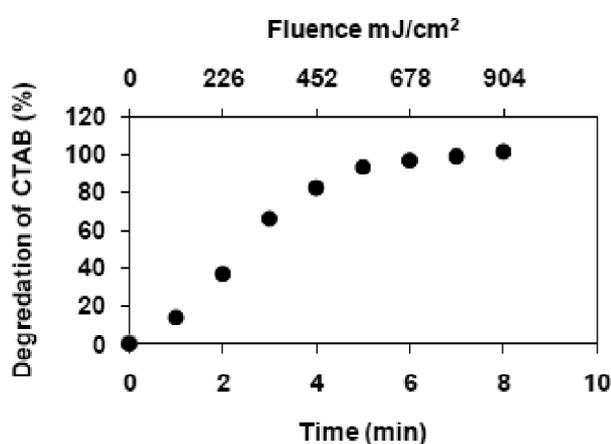
Fig. 1. Degradation of CTAB solution containing 100 mg L^{-1} by UV/H$_2$O$_2$ process with H$_2$O$_2$ dose = 1 mol/mol at pH 7 and nitrate concentration = 0.25 Mm.
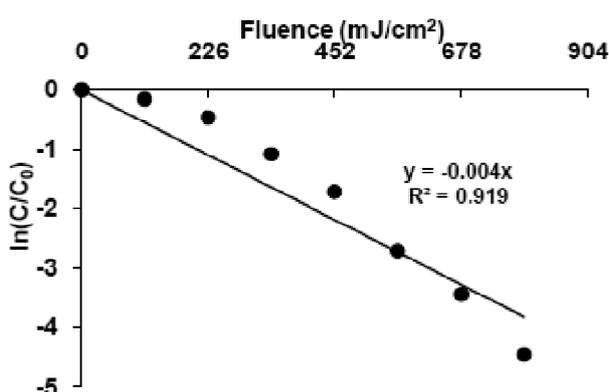
Fig. 2. Linearized plot of first order kinetic model for degradation of CTAB solution containing 100 mg L^{-1} by UV/H$_2$O$_2$ process with H$_2$O$_2$ dose = 1 mol/mol at pH 7 and nitrate concentration = 0.25 Mm.

(B) Model fitting and analysis of variance:

The experimental fluence based, pseudo-first order rate constant for CTAB degradation by UV/H$_2$O$_2$ process and fluence based, pseudo-first order rate constant obtained by RSM-CCD model with four process variables such as H$_2$O$_2$ dose (X_1), initial concentration of CTAB (X_2), pH (X_3) and nitrate concentration (X_4) are presented in the Table 2. Results obtained from CCD model were analyzed by analysis of variance and tabulated in the Table 3. F-value of the model was found to be 41.03 which indicated model was significant. Further, *p*-values (<0.05) represented that model and process parameters are significant with 95% confidence interval. In this study, X_1, X_2, X_3, X_4, X_1X_2, X_2X_4, X_3X_4, X_2^2, X_3^2 and X_4^2 were found to be significant. X_1X_3, X_1X_4, X_2X_3 and X_1^2 were found to be insignificant (*p*-values > 0.10). The *p*-value of "Lack of Fit" was found to be 0.0001; which implied that lack fit of the model was significant.

The fitness of the model was expressed by regression coefficient (R^2). R^2 was found to be 0.9757, indicating 97.57% of the variability of predicated response might be evaluated by the model. Predicted R^2 of 0.8917 was in reasonable agreement with the Adj R^2 of 0.9324. Adequate precision i.e. signal to noise ratio was 20.25. As this value is greater than 4, the adequate precision is desirable. Therefore, quadratic model obtained for CTAB degradation by UV/H$_2$O$_2$ process may be used in the range of the independent variables. The second-order polynomial equation for CTAB degradation by UV/H$_2$O$_2$ process was obtainedas follows:

Fluence-based rate constant (cm^2 mJ^{-1}) = 0.0219 − 1.240×10^{-4}×H$_2$O$_2$ dose − 6.254×10^{-5}×initial conc. − 2.294×10^{-3}×pH − 0.0136×NO$_3^{3-}$ + 8.250×10^{-7}×H$_2$O$_2$ dose × initial conc. + 1.710×10^{-7}×initial conc.×NO$_3^{3-}$ − 1.090×10^{-4}× pH×NO$_3^-$ + 2.020×10^{-7}×initial conc.^{2} + 1.060×10^{-4}×pH^2 + 1.136×10^{-2}×NO$_3^{-2}$.

(C) Contour and response surface plots:

To optimize the level of four process variables and their interaction effects on CTAB degradation by UV-H$_2$O$_2$ process, three- and two-dimensional plots were made against any two process variables within the experimental ranges with other variables kept constant.

The effect of H$_2$O$_2$ dose and concentration of CTAB on its degradation when pH and nitrate concentration at constant level (i.e. pH = 7, concentration of NO$_3^-$ = 0.25 mM) are shown in Fig. 1(A) and (B). The response plot of fluence

Table 2. Experimental design matrix and response proposed by CCD model

Run	Process parameters				Response (Y mJ cm^{-2})	
	Peroxide dose (mol/mol)	CTAB conc. (mg L^{-1})	pH	NO$_3^-$ (mM)	Experimental	Predicted
1	1	100	7	0.25	0.00490	0.00441
2	3	100	7	0.25	0.00433	0.00433
3	1	200	7	0.25	0.00450	0.00443
4	3	200	7	0.25	0.00432	0.00451
5	1	100	11	0.25	0.00311	0.00306
6	3	100	11	0.25	0.00304	0.00298
7	1	200	11	0.25	0.00322	0.00314
8	3	200	11	0.25	0.00303	0.00323
9	1	100	7	0.75	0.00375	0.00368
10	3	100	7	0.75	0.00338	0.00360
11	1	200	7	0.75	0.00395	0.00369
12	3	200	7	0.75	0.00376	0.00377
13	1	100	11	0.75	0.00257	0.00255
14	3	100	11	0.75	0.00229	0.00246
15	1	200	11	0.75	0.00265	0.00263
16	3	200	11	0.75	0.00256	0.00271
17	0	150	9	1.00	0.00087	0.00181
18	4	150	9	0.50	0.00182	0.00181
19	2	50	9	0.50	0.00351	0.00370
20	2	250	9	0.50	0.00390	0.00396
21	2	150	5	0.50	0.00447	0.00471
22	2	150	13	0.50	0.00229	0.00230
23	2	150	9	0.00	0.00507	0.00528
24	2	150	9	1.00	0.00399	0.00403
25	2	150	9	0.50	0.00189	0.00181
26	2	150	9	0.50	0.00189	0.00181
27	2	150	9	0.50	0.00189	0.00181
28	2	150	9	0.50	0.00189	0.00181
29	2	150	9	0.50	0.00189	0.00181
30	2	150	9	0.50	0.00189	0.00181

Table 3. ANOVA results of the model developed for degradation of CTAB solution by UV/H$_2$O$_2$ process on the basis of fluence based rate constant

Source	Sum of square	Degree of freedom	Mean square	F-Value	Prob >F
Model	3.313E–005	10	3.313E–006	41.03	0.0001
Residual	1.534E–006	19	8.076E–008		
Lack of Fit	1.534E–006	14	1.096E–007	0.0001	
Pure error	0.000	5	0.000		
R^2	0.9757				
Adjusted R^2	0.9324				
Predicted R^2	0.8917				
Adequate precision	20.25				

based rate constant gradually increased with increasing H$_2$O$_2$ dose after that decreased (Fig. 3). This was similar to the other investigation of researchers. Khataee and Habibi, 2010, reported that the removal efficiency of C.I. Basic Red 46 (BR46) increased with increasing H$_2$O$_2$ dose then decreased[12]. At the beginning of the degradation of CTAB, OH• attack the CTAB molecules that means in increase of rate constant generate intermediates which scavenge the hydroxyl radicals that results in decrease of rate constant.

Fluence-based rate constant of degradation of CTAB also depends on its own initial concentration and NO$_3^-$ concentration. At pH 7 and peroxide dose of 1 mol per mol of CTAB; its degradation rate constant decreased with increase in initial CTAB concentration. On the other hand, the degradation rate constant decreased with increase in concentration of nitrate when pH and H$_2$O$_2$ dose were 7 and 1 mol/mol respectively (Fig. 4). This might be due to the fact that nitrate consume significant amount of hydroxyl radical (Mondal *et al.*, 2017).

Fig. 5 shows the variation of fluence-based rate constant of CTAB degradation with change in pH and nitrate with con-

(A)

(B)
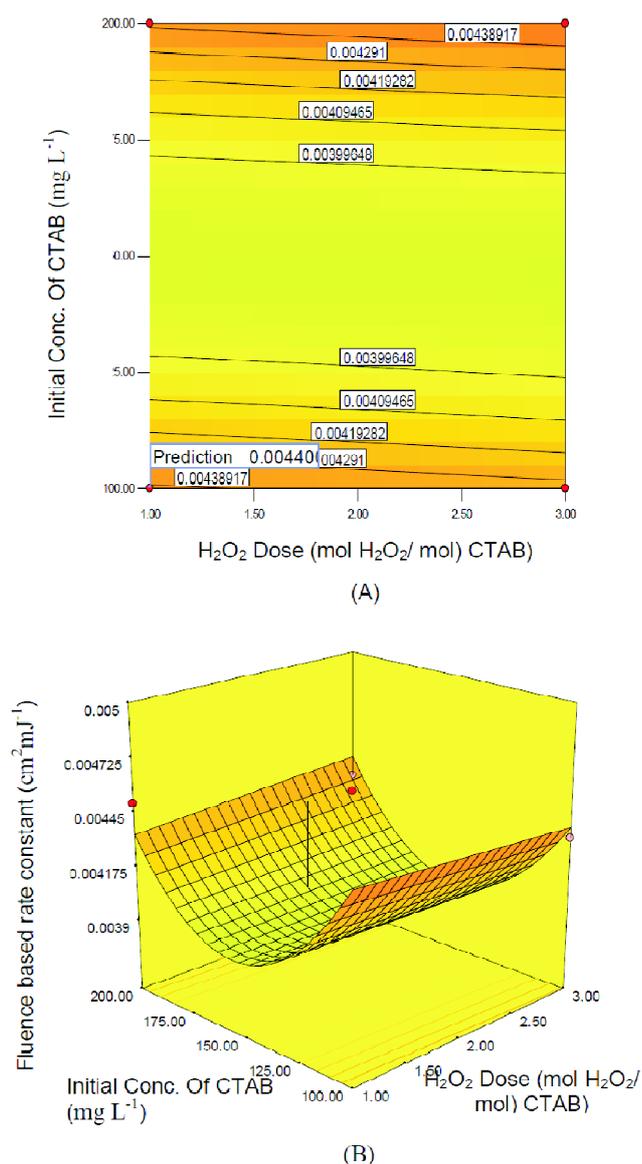
Fig. 3. 2-D (A) and 3-D (B) plots for the effect of CTAB concentration and peroxide dose on fluence based rate constant of CTAB at pH = 7 and NO$_3^-$ concentration = 0.25 mM.

(A)

(B)
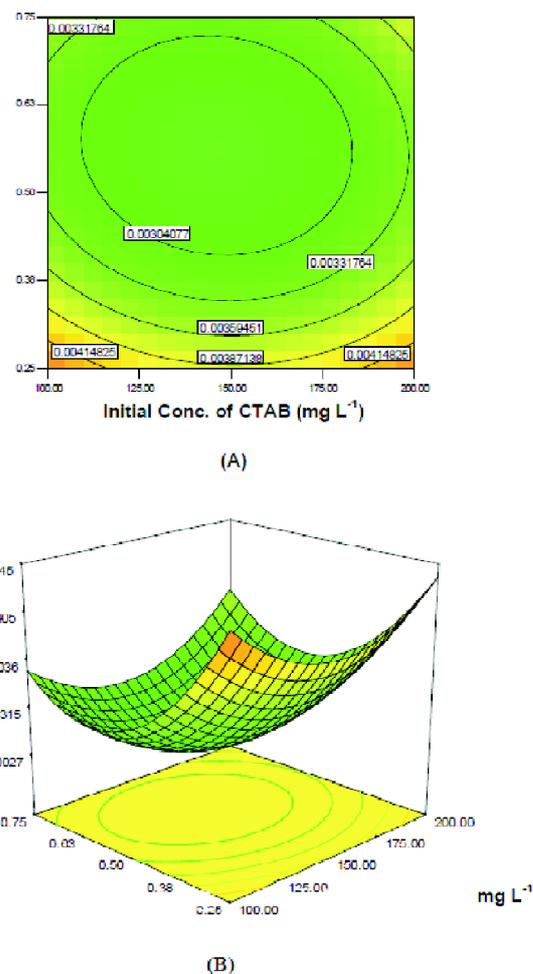
Fig. 4. 2-D (A) and 3-D (B) plots for the effect of CTAB concentration and NO$_3^-$ concentration on fluence based rate constant at pH = 7 and H$_2$O$_2$ dose = 1 mol/mol.
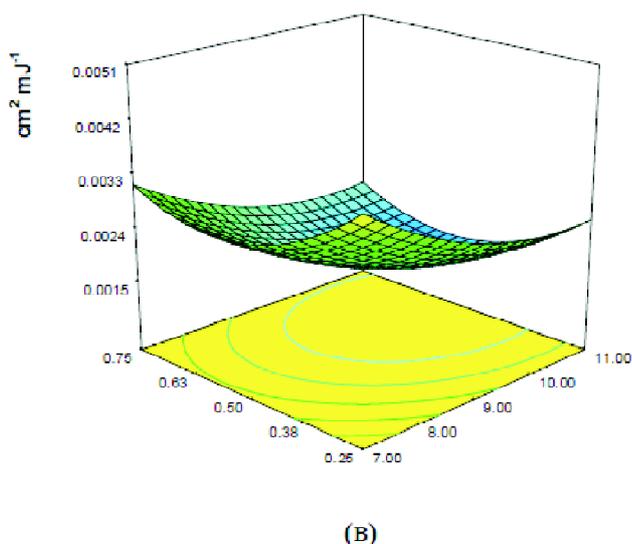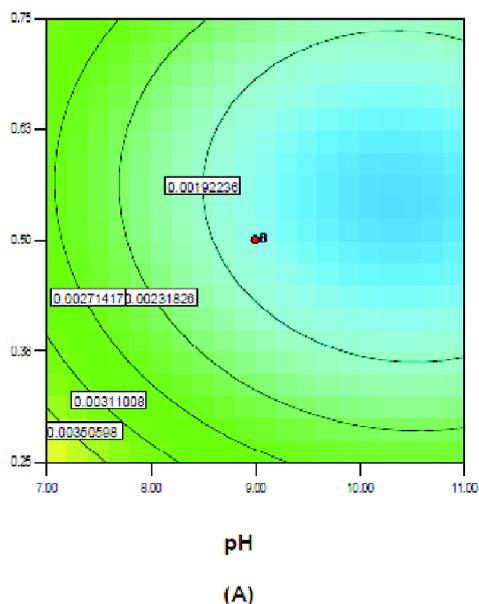
Fig. 5. 2-D (A) and 3-D (B) plots for the effect of nitrate concentration and pH on fluence-based rate constant at CTAB concentration = 100 mg L^{-1} andperoxide dose = 1 mol/mol.

stant H_2O_2 dose and CTAB concentration (i.e. H_2O_2 = 1 mol H_2O_2/mol CTAB and CTAB concentration = 100 mg L^{-1}). At the constant initial CTAB concentration and H_2O_2 dose, pH in the range of 5–10 showed no significant effect on degradation of CTAB. Further increase in pH beyond 10, showed negative impact of degradation i.e. rate constant decreased.

At very high alkaline pH, H_2O_2 (having pKa = 11.8) is dissociated to hydroperoxide ion (having molar absorptivity = 240 M^{-1} cm^{-1} at 254 nm). The molar absorptivity of hydroperoxide ion is higher than hydrogen peroxide (molar absorptivity = 18.6 M^{-1} cm^{-1} at 254 nm); effecting the dissociation of hydrogen peroxide to hydroxyl radical. Further, hydroperoxide ion can react both with hydrogen peroxide and hydroxyl radicals[13].

(D) Process optimization and validation experiments:

The maximum fluence-based rate constant for CTAB degradation by the UV/H_2O_2 process was determined. For this purpose, important influencing parameters 'peroxide dose' and 'nitrate concentration' kept either as 'minimize' or 'within the range', 'while rate constant' was considered as maximum in the CCD model. The desirability value was found to be 0.92. The optimum level of process parameters is listed in Table 4.

Table 4. Optimum process parameters for maximum fluence based rate constant for degradation of CTAB by UV/H_2O_2 process

Parameter	Optimum value
Peroxide dose (mol/mol)	1.0
Initial conc. of CTAB (mg L^{-1})	100
pH	7
Nitrate concentration (mM)	0.25

To know the model adequacy and validity of the optimization process, separate validation experiment was performed for CTAB concentration of 220 mg L^{-1} under other optimum conditions. Experimental and predicted fluence-based rate constants were 0.00412 cm^2 mJ^{-1} and 0.00399 cm^2 mJ^{-1} respectively, which were relatively close to each other. This result indicates that the RSM based on CCD is an efficient statistical tool for the optimizing the operational conditions for degradation of CTAB by UV/H_2O_2 process.

Conclusion

In the present work, the performance UV-H_2O_2 process for the degradation of cationic bearing wastewater was focused and the process parameters such as initial CTAB concentration, peroxide dose, pH and nitrate concentration of the solution were optimized by using widely used RSM-CCD model. The results reveled that RSM was an efficient statistical tool to optimize the operating condition of CTAB deg-

radation. The response models developed in this present work for predicting fluence-based rate constant of CTAB were considered adequately applicable. Under optimized conditions (peroxide dose = 1 mol of H$_2$O$_2$/mol of CTAB, initial CTAB concentration =100 mg L^{-1}; pH = 7 and nitrate concentration = 0.25 mM), the maximum rate constant was predicted to be 0.0044 cm^2 mJ^{-1}. Thus, it can be concluded that the optimized UV/H$_2$O$_2$ process parameter can be used as an effective treatment method under optimum conditions for CTAB degradation.

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