Anionic surfactant degradation by UV-H$_2$O$_2$ advanced oxidation process and optimization of process parameters

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This work deals with the degradation of widely used anionic surfactant, sodium dodecyl sulfate (SDS) by UV-H$_2$O$_2$ advanced oxidation process (UV-H$_2$O AOP) and the use of a statistical tool, central composite design (CCD) based response surface methodology (RSM), and to investigate the effects of essential process parameters such as peroxide dose, initial target pollutant concentration, pH and nitrate concentration on SDS degradation individually and interactively. Experimental results indicated that an increase in surfactant and nitrate concentrations adversely affects the degradation rate. Higher peroxide dose and pH showed an increasing trend in the fluence-based rate constant up to a maximum, followed by a decrease in degradation rate upon a further increase in either factor's concentration. The maximum fluence-based rate constant (0.0059 cm^2/mJ) was obtained under the numerical optimization of initial surfactant concentration 100 mg/L, pH 7, and nitrate concentration 0.25 mM and peroxide dose 1 mol H$_2$O$_2$/mol of SDS.

Keywords: Anionic surfactant, UV-H$_2$O$_2$ AOP, rate constant, Design Expert, response surface methodology.

Introduction

Surfactants or surface-active agents are commonly used in households as detergents for cleaning, oil, paper, mining, textile industries, dying industries, and so on. All unused surfactants from these processes and their intermediates are discarded into the wastewater treatment plants and surface water bodies and pollute the different environmental components. Surfactants can imbalance the ecological system and create many health hazards and irritation for human beings. For example, surfactants generate foams, which reduces the reoxygenation rate or oxygen levels of aquatic animals[1]. When surfactant concentration is high in wastewaters, algae, and other microorganisms' growths are affected and decrease their primary productivity. Long-term use of surfactant can cause skin irritation, dermatitis, damage to enzyme activities, and other physiological alterations of human beings[2].

Various physicochemical methods can treat surfactants bearing wastewater like coagulation[3], phase separation process[4,5], oxidation process[6]. Each of the above methods has individual merits and demerits though in general, the treatment of wastewaters with high surfactant concentrations is very difficult using any of the conventional methods. The concentration of surfactants in textile wastewater and laundry wastewater was reported to be more than 3000 mg/L in terms of CTAB (cationic surfactants)[7] and more than 5000 mg/L in terms of SDS (anionic surfactants)[2]. This apart, there are specific constraints with the use of any of the conventional methods. The application of the reverse osmosis process is costly to run. Massive sludge is generated in the coagulation process. Moreover, these processes produce a concentrated surfactant bearing solution, which again requires treatment. The adsorption processes are just a phase separation process and require post-treatment for complete elimination. On the other hand, the biological process is an eco-friendly and low-cost treatment option but suitable only for a low concentration of surfactants.

Due to this fact, many researchers have explored AOPs for the mineralization of different organic compounds like surfactants. In AOP, hydroxyl radicals, which have an oxidation potential of +2.8 eV, are generated. These have a highly excited unpaired electron and react immediately with organic compounds in various ways such as hydrogen abstraction, radical addition, and electron transfer[8]. Furthermore, AOP is used as pre-treatment for highly concentrated wastewater to increase the biodegradability of recalcitrant organics. The AOPs such as UV-H$_2$O$_2$, O$_3$-H$_2$O$_2$-UV[9,10], TiO$_2$/UV[11], and photo-Fenton processes[12] are generally used to degrade organic compounds in wastewater. The ozonation process is very costly as it consumes high electric power for generating ozone. Fenton or photo-Fenton process is applicable to the acidic solution. In photocatalytic process, uniform UV irradiation is required. In the present study, SDS degradation has been studied by UV-H$_2$O$_2$ AOP.

Degradation of SDS by UV-H$_2$O$_2$ AOP has been reported in a recent literature[13,14]. The effect of different process parameters like initial target pollutant concentration, UV irradiation time, applied peroxide dose, pH, presence of different interfering substances like nitrate, alkalinity, phosphate concentration, and dissolved organic matters have been reported. It has been observed that peroxide dose, surfactant concentration, pH, and nitrate significantly affect SDS degradation. In this present study, optimization of these process parameters using RSM based on CCD, and the influences of process variables on a specific response, have been focused. This work aims to determine the optimum operational conditions for the SDS degradation rate by the UV-H$_2$O$_2$ process.

Materials and methods

(A) Materials:

SDS (Technical grade, 98% pure; Merck, India) and 30% H$_2$O$_2$ (Merck, India) were used to prepare synthetic wastewater and advanced oxidation experiments. Reagent grade toluene, glacial acetic from Merck (India), and acridine orange II from MP Biomedical (France) were used as received without further purification.

(B) Instrumentation:

Experiments were performed in batch mode in a UV reactor (Make: M/s. Lab Tree, India). The reactor consists of eight monochromatic low-pressure mercury tubes (emission centered at 253.7 nm). The photon flux and fluence of the bulbs were determined using ferrioxalate actinometry method[14] and calculated to be 1.9 ($\pm$0.1)$\times$10^{-4} Einstein/L/min and 113 ($\pm$5.7) mJ/ cm^2/min respectively. After degradation, the remaining concentration of SDS was measured by a single-beam spectrophotometer (117, Systronics). The pH of the solution was measured by Digital pH meter (Orion 420A+, Thermo).

(C) Analytical method:

Measurement of SDS concentration was done by spectrophotometer[15]. An ion-pairing agent, acridine orange, was used to produce a color complex with SDS. The intensity of the color was measured at a wavelength of 467 nm. Solutions containing 10 mL volume of SDS (0.1 to 6.0 g/L) were taken in a 25-mL volume separating funnel. Then, 100 μL of acridine solution (5$\times$10^{-3} *M*) and 100 μL acetic acid were added in the funnel, followed by the addition of 5 mL toluene. The samples were shaken for at least 1 min, and then, the aqueous layer was separated. The absorbance of the separated toluene layer at a wavelength of 467 nm was measured. The calibration curve for SDS (at wavelength 467 nm) is shown in Fig. 1. The correlation coefficient was found to be 0.9976. The calibration equation was: Absorbance = 0.1121$\times$Concentration (mg/L) + 0.0213. From this equation, the unknown concentration of SDS can be found after measuring its absorbance.
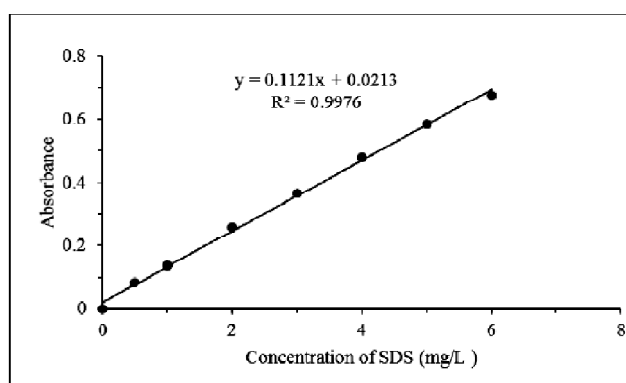

Fig. 1. Calibration curve for SDS.

(D) Degradation of anionic surfactant wastewater:

All batch-mode AOP kinetic experiments were performed for 6 min, and samples were collected at 1 min intervals of ultraviolet exposure. The data was analyzed using the pseudo-first order kinetic model[16].

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

In eq. (1), [SDS] = target pollutant concentration at any time t; $[SDS]_0$ = initial target pollutant concentration; k' = apparent fluence based rate constant (pseudo-first order) (cm^2/mJ) and H' = the fluence of the UV bulb corresponding to time t (mJ/cm^2).

(E) RSM modeling and process optimization:

Four important process parameters, such as peroxide dose (X_1), initial target pollutant concentration (X_2), pH (X_3), and nitrate concentration (X_4), were chosen as unconventional parameters for the RSM modeling. The coded value and its range are given in Table 1. Fluence-based pseudo-first order reaction rate constants were considered as the response of the RSM model. Considering the four-factorial,

Table 1. Range of the selected independent process variables and its levels in RSM

Process variables	Code	Real values of the coded levels				
		–2	–1	0	+1	+2
H_2O_2 dose (mol/mol)	X_1	0	1	2	3	4
Initial conc. (mg/L)	X_2	50	100	150	200	250
pH	X_3	5	7	9	11	13
Nitrate conc. (mM)	X_4	0	0.25	0.50	0.75	1.0

five-level CCD model, a total of 30 experimental runs (including six replications at the center point)[17,18] were performed. The Design-Expert 7.0 software was used to analyze experimental data and find a correlation between the conventional and unconventional parameters by the following polynomial equation:

$$Y = b_0 + \Sigma \, b_i X_i + \Sigma \, b_{ii} X_i^2 + \Sigma \, b_{ij} X_i X_j \qquad (2)$$

In eq. (2), Y = predicted reaction rate constant; X_i's = independent variables, b_0 = constant coefficient. The coefficients like b_i, b_{ii}, and b_{ij} are first-order, second-order, and interaction coefficients.

Results and discussion

(A) UV-H_2O_2 degradation of SDS:

To evaluate UV-H_2O_2 AOP effectiveness, SDS degradation was performed by ultraviolet light at 253.7 nm with hy-

drogen peroxide dose of 1 mol/mol (H_2O_2/SDS). The initial SDS concentration, pH, and nitrate concentration of the solutions were 100 mg/L, 7, and 0.25 mM, respectively. From Fig. 2, it was observed that more than 90% of SDS was degraded in 4 min (Fig. 2). The kinetic analysis represented that SDS degradation followed the pseudo-first order kinetic model. The fluence-based pseudo-first order rate constant was calculated to be 0.0062 cm^2/mJ (Fig. 3).
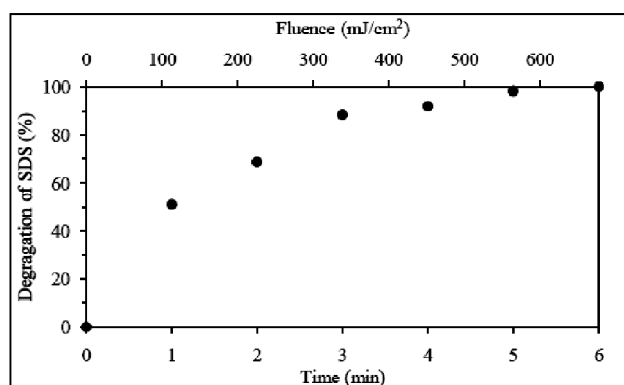

Fig. 2. Degradation of SDS (100 mg/L) by UV-H_2O_2 process when $[H_2O_2]/[SDS] = 1$, pH = 7.0 and nitrate concentration = 0.25 mM.
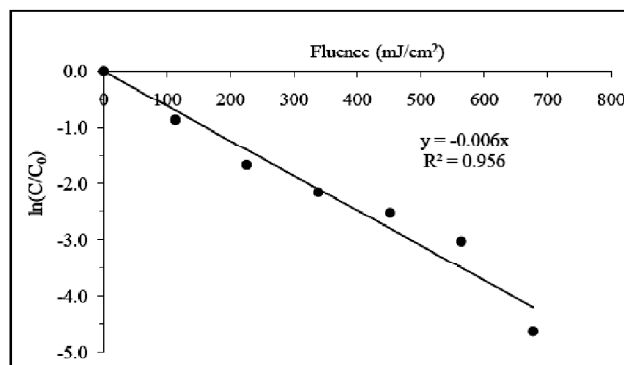

Fig. 3. Linearized plot for first order kinetic model for UV-H_2O_2 of SDS (100 mg/L) with $[H_2O_2]/[SDS] = 1$, pH = 7.0 and nitrate concentration = 0.25 mM.

The pH in the range of 5–10, no notable outcome from SDS degradation, has been reported in our previous work[13]. A significant decreasing rate was observed when the pH of the solution greater than 10. Nitrate concentration of 0 to 1 mM showed a significant adverse effect on SDS degradation. Significant impacts of initial SDS concentration and peroxide dose have also been reported. However, these effects

were studied individually. The combined results are of much importance and are described in the following sections.

(B) RSM model of SDS:

CCD modeled the relationship between kinetic rate constant (fluence-based) of SDS degradation by UV-H_2O_2 process and four parameters such as H_2O_2 dose (X_1), initial concentration of SDS (X_2), pH (X_3), and nitrate concentration (X_4). The details of the experimental design matrix and fluence-based rate constant are tabulated in Table 2. The observed values, the interaction between the response, and four unconventional parameters were determined using the RSM-CCD model from the table. The fluence-based rate constants of SDS degradation were fitted with a quadratic polynomial equation separately. The following fitted regression models were obtained to demonstrate the effects of independent process parameters for SDS degradation.

Table 2. Details of the experimental run and predicted fluence-based rate constant of RSM model

Run	Independent variables				Response (Y) (cm^2/mJ)	
	X_1 H_2O_2 dose (mol/mol)	X_2 Initial conc. (mg/L)	X_3 pH	X_4 NO_3^- (mM)	Experimental	Predicted
1	1	100	7	0.25	0.0062	0.0059
2	3	100	7	0.25	0.0057	0.0058
3	1	200	7	0.25	0.0052	0.0050
4	3	200	7	0.25	0.0047	0.0048
5	1	100	11	0.25	0.0050	0.0046
6	3	100	11	0.25	0.0045	0.0045
7	1	200	11	0.25	0.0039	0.0037
8	3	200	11	0.25	0.0035	0.0035
9	1	100	7	0.75	0.0040	0.0037
10	3	100	7	0.75	0.0035	0.0037
11	1	200	7	0.75	0.0020	0.0018
12	3	200	7	0.75	0.0013	0.0017
13	1	100	11	0.75	0.0027	0.0025
14	3	100	11	0.75	0.0024	0.0024
15	1	200	11	0.75	0.0009	0.0006
16	3	200	11	0.75	0.0003	0.0004
17	0	150	9	1.00	.00018	0.0016
18	4	150	9	0.50	0.0013	0.0014
19	2	50	9	0.50	0.0051	0.0054
20	2	250	9	0.50	0.0025	0.0025
21	2	150	5	0.50	0.0050	0.0050
22	2	150	13	0.50	0.0020	0.0024

Table-2 (contd.)

23	2	150	9	0.00	0.0070	0.007
24	2	150	9	1.00	0.0018	0.0019
25	2	150	9	0.50	0.0017	0.0015
26	2	150	9	0.50	0.0017	0.0015
27	2	150	9	0.50	0.0018	0.0015
28	2	150	9	0.50	0.0017	0.0015
29	2	150	9	0.50	0.0017	0.0015
30	2	150	9	0.50	0.0017	0.0015

Fluence-based rate constant (cm^2/mJ) = 0.027 + 1.898×10^{-5}×H_2O_2 Dose – 7.719×10^{-5}×Initial conc. – 2.782×10^{-3}×pH – 0.014×NO_3^- – 5.525×10^{-7}×H_2O_2 Dose×Initial conc. – 2.017×10^{-5}×Initial conc.×NO_3^- + 7.850×0^{-5}×NO_3^-×pH + 2.460×10^{-7}×Initial conc.^{2} + 1.367×10^{-4}×pH^2 + 0.012×NO_3^{-2}.

All models or parameters were considered as significant with p-value < 0.05. As few models (X_1X_3, X_1X_4, X_2X_3, and X_1^2) or parameters were insignificant (p > 0.5), these were omitted from the model equation to improve the model and to optimize the data[19]. ANOVA was employed to examine the applicability of the model, and the results of ANOVA are represented in Table 3.

Table 3. ANOVA results of the quadratic polynomial model

Source	Sum of square	Degree of freedom	Mean square	F-Value	Prob >F
Model	9.445E-005	9	1.049E-005	52.80	0.0001
X_1	9.797E-008	1	9.797E-008	47.22	0.0001
X_2	1.273E-005	1	1.273E-005	61.33	0.0001
X_3	9.920E-006	1	9.920E-006	47.78	0.0001
X_4	4.223E-005	1	4.223E-005	203.65	0.0001
(X_1X_2)	1.221E-008	1	1.221E-008	59.02	0.0001
(X_2X_4)	1.017E-006	1	1.017E-006	49.20	0.0001
(X_3X_4)	2.465E-008	1	2.465E-008	62.0	0.0001
X_2^2	1.059E-005	1	1.059E-005	51.02	0.0001
X_3^2	8.378E-006	1	8.378E-006	40.35	0.0001
X_4^2	1.629E-005	1	1.629E-005	78.45	0.0001
Residual	3.957E-006	20	1.985E-007		
Lack of fit	3.957E-006	15	2.638E-007	99.73	0.0001
Pure error	3.957E-008	5	2.645E-009		
R^2	0.9599				
Adjusted R^2	0.9388				
Predicted R^2	0.9069				
Adequate precision	24.58				

The fitness of the model was determined by the regression coefficient (R^2). The predicted R^2 of 0.9069 was in reasonable agreement with the Adj R^2 of 0.9388. The diagnostic plot also suggested a good agreement between the experimental and predicted data (Fig. 4). The observed fluence-based rate constant of SDS varied in the range of 8.97×10^{-7} – 7.00×10^{-3} cm^2/mJ and the predicted rate constant values were also almost similar to these experimental results (Table 2). But in our present model, in experiment 16, an error was occurred within 20% between the experimental and predicted values due to intermediates' influence. However, in experiment 17, a very high error occurred between the observed and predicted values since no H_2O_2 was added, and the direct photolysis process is prolonged. In our previous study, the fluence-based reaction rate constant through direct photolysis was 460 times less than the calculated rate constant from SDS degradation through UV-H_2O_2[13].
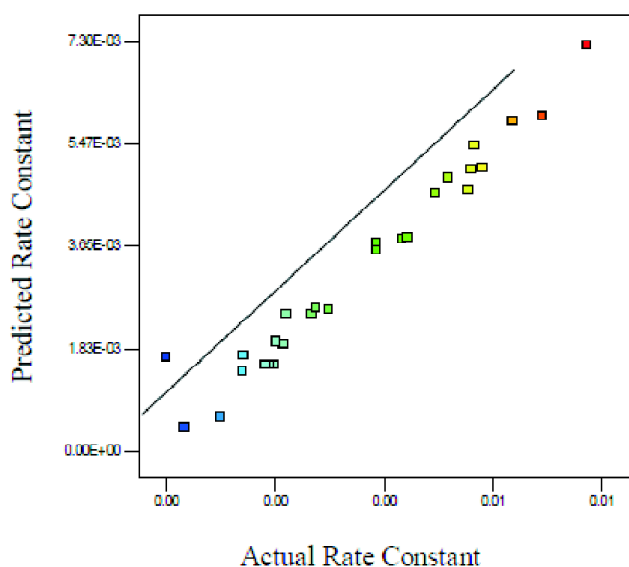

Fig. 4. Design-Expert plot for predicted and experimental rate constant.

(*C*) *Process optimization and validation Experiments:*

Evaluation of optimum conditions for SDS degradation is necessary. For this purpose, the process parameters like as H_2O_2 concentration, target pollutant concentration, pH, and nitrate concentration of wastewater were designed as 'within range', while maximum rate constants were taken in the Design Experts software. Peroxide dose is considered a very useful parameter in applying the UV-H_2O_2 process because it has a destructive effect on further treatment. The optimal process parameters are presented in Table 4. A separate validation experiment was also conducted with an SDS concentration of 220 mg/L under the optimal conditions given in Table 4. The experimental and predicted value of fluence-based rate constants were 0.00412 cm^2/mJ and 0.00399 cm^2/mJ, respectively; which were relatively close to each other.

(*D*) *Contour and response surface plots for UV-H_2O_2 treatment of surfactant bearing wastewater:*

Two-dimensional (2D) contour and three-dimensional (3D) response surface plots were generated from the predicted model keeping two process parameters constant and varying the other parameters within the experimental ranges using Design-Expert software.

In Fig. 5, the reaction rate constant of SDS degradation depends on H_2O_2 concentration and SDS concentration of solution when pH of solution and concentration of NO_3^- were constant (i.e. pH = 7 concentration of NO_3^- = 0.25 mM). At constant pH and initial concentration of NO_3^-, the fluence-based rate constant was found to decrease with an increase in H_2O_2 concentration. Several researchers have investigated the effect of H_2O_2 in H_2O_2-based AOP for the removal of organic pollutants[13,20]. The decrease of the rate constant is due to the scavenging of hydroxyl radicals by H_2O_2 itself (eq. (3)).

$$H_2O_2 + HO^\bullet = H_2O + HO_2^\bullet \qquad (3)$$

For a constant H_2O_2 concentration (1 mol H_2O_2/mol SDS), the fluence-based rate constant significantly decreased with the increasing initial concentration of SDS. Thus, it is expected that hydroxyl radicals may not produce the same ratio at higher SDS concentration level.

Table 4. Optimized conditions from SDS degradation by UV-H_2O_2 process

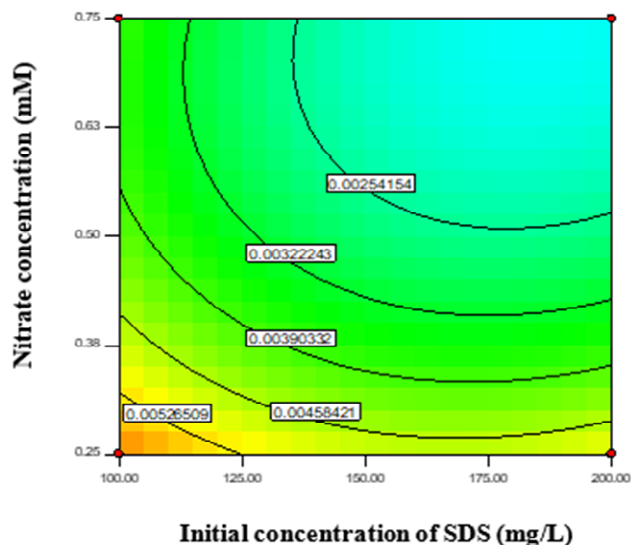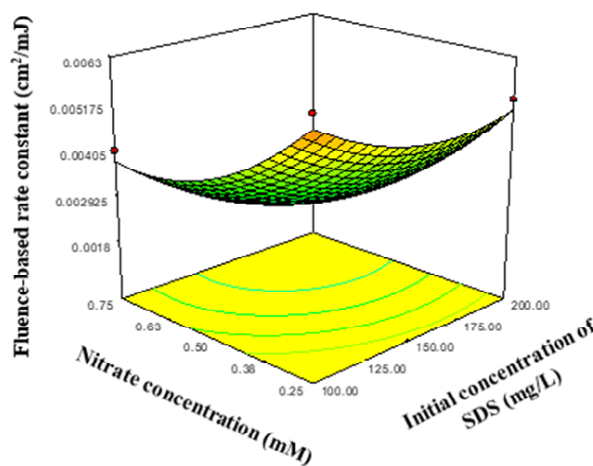| H_2O_2 Dose (mol/mol)	Initial conc. of SDS (mg/L)	pH	Nitrate concentration (mM)	Fluence-based rate constant (cm^2/mJ)	Desirability
1	100	7	0.25	0.0059	0.922
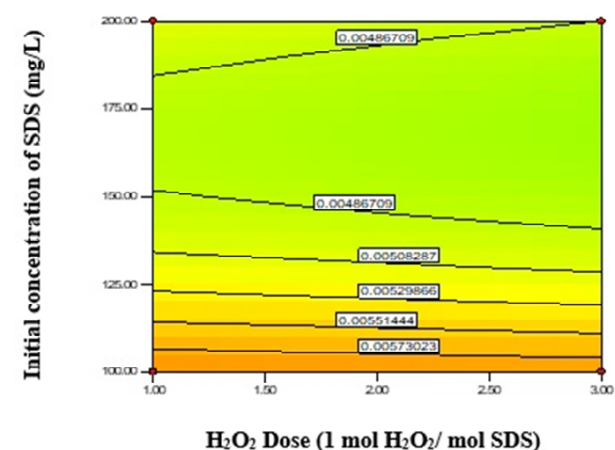
(a)
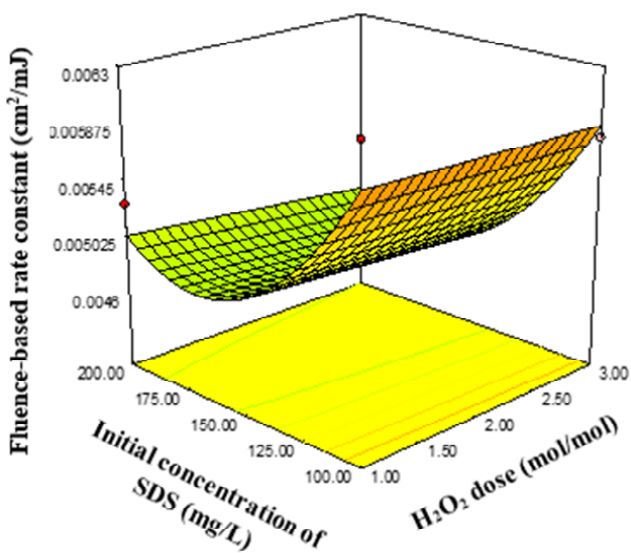
(b)

Fig. 5. 2D (a) and 3D (b) plots for SDS degradation when initial concentration of SDS and H$_2$O$_2$ concentration varied at constant of SDS at pH = 7 and concentration of NO$_3^-$ = 0.25 mM.
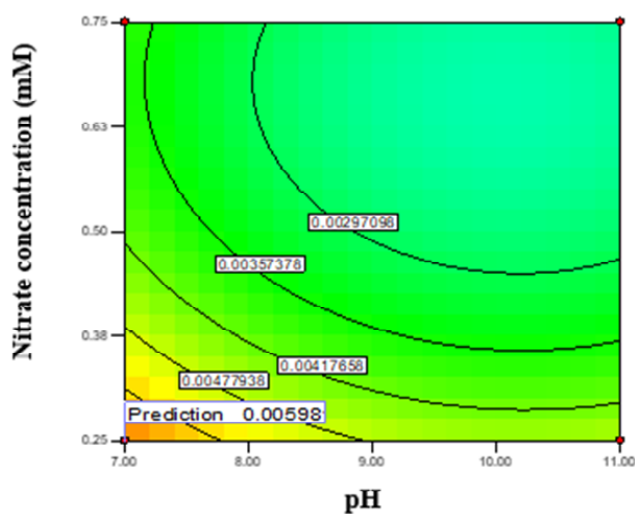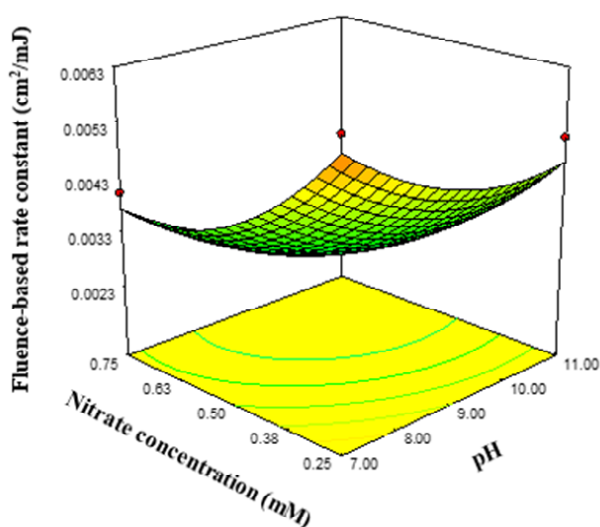

(a)

(b)

Fig. 6. 2D (a) and 3D (b) plots for SDS degradation when the initial concentration of SDS and concentration of NO$_3^-$ varied at constant at pH = 7 and H$_2$O$_2$ dose = 1 mol/mol.

The fluence-based rate constant of SDS also depends on the initial concentration of SDS and the concentration of NO$_3^-$. As shown in Fig. 6, at a pH of 7 and H$_2$O$_2$ dose of 1 mol H$_2$O$_2$/mol, the SDS degradation rate constant increases with decrease in initial concentration of SDS. On the other hand, the degradation rate constant increases with a decrease in nitrate concentration when pH and H$_2$O$_2$ dose were

7 and 1 mol/mol, respectively (Fig. 6). This is due to the scavenging of hydroxyl radicals by nitrate ions, resulting in fewer hydroxyl radicals reacting with SDS[13].

Fig. 7 shows the variation of the fluence-based rate constant of SDS with a change in pH and nitrate with constant H$_2$O$_2$ dose and SDS concentration (i.e. H$_2$O$_2$ = 1 mol H$_2$O$_2$/mol SDS and initial concentration of SDS = 100 mg/L). At the

(a)

(b)

Fig. 7. 2D (a) and 3D (b) plots for SDS degradation when pH and NO_3 varied at constant at initial concentration of SDS = 100 mg/L and H_2O_2 dose = 1 mol/mol.

given H_2O_2 dose and initial concentration of SDS, pH in the range of 5–10 had no adverse effect on the SDS degradation rate. Further increase in pH above 10, fluence-based rate constant decreases significantly. At higher pH, H_2O_2 (pKa = 11.8) starts to dissociate to hydroperoxide (HO_2^-). At pH 11, this is around 25% of the total H_2O_2. The molar absorp-

tivity of hydroperoxide at 254 nm is 240 M^{-1} cm^{-1}, which is much higher than that of hydrogen peroxide (molar absorptivity at 254 nm = 18.6 M^{-1} cm^{-1}). This hydroperoxide can react both with hydrogen peroxide and hydroxyl radicals resulting in less production of hydroxyl radicals[13].

Conclusion

This work demonstrated that the UV-H_2O_2 AOP process could effectively degrade the anionic surfactant SDS in wastewater. The UV-H_2O_2 process achieved more than 90% degradation of SDS. RSM-CCD model was used to optimize the rate constant of SDS by the UV-H_2O_2 process. A high connection was found between predicted and actual fluence based rate constant. Based on results, H_2O_2 dose had positive effects, and initial SDS concentration, pH and nitrate concentration had a negative effect on rate constant. Under optimized conditions (peroxide dose = 1 mol of H_2O_2/mol of SDS, initial SDS concentration = 100 mg/L; pH = 7 and nitrate concentration = 0.25 mM), the maximum rate constant was predicted to be 0.0059 cm^2/mJ. From ANOVA test results, the predicted model can be applied to navigate the design space to find the optimum conditions. Thus, it can be concluded that the optimized UV-H_2O_2 process parameter can be used as an effective treatment method under optimum conditions for SDS degradation.

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