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Optimization of photocatalytic process parameters for the degradation of acrylonitrile using Box Behnken Design

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ABSTRACT

The present study involves the photocatalytic degradation of aqueous solution of acrylonitrile (ACN) which was carried out in a batch reactor under UV light. The degradation efficiency was evaluated with ZnO as a photocatalyst and hydrogen peroxide as an oxidant for a period of 5 h. The variables examined in this study included ZnO dose (0.5–3.0 g/L), pH (2–12), and H_2O_2 concentration (2.5–10 m mol/L). The rate of degradation was studied in terms of changes in concentration of the pollutant using spectrophotometry. The optimal values of operational parameters leading to degradation of ACN were obtained using Box Behnken design (BBD) under response surface methodology (RSM). The optimum conditions were found to be ZnO dose of 1.48 g/L; pH 7.0 and hydrogen peroxide (H_2O_2) concentration of 4.22 m mol/L. Under optimum condition, the degradation efficiency of ACN was found to be 89.6%. Optimization of photocatalytic process parameters for the degradation of ACN by BBD under RSM effectively copes with interaction between optimizing variables and its prediction agreed well with the experimental result.

Keywords: Acrylonitrile (ACN); Response surface methodology (RSM); Box Behnken Design (BBD); Degradation efficiency

1. Introduction

One of the important industrial chemicals, Acrylonitrile (ACN) is produced by catalytic reaction of propylene with ammonia [1,2]. It is used as a raw material in the manufacture of acrylic fibers, styrene plastics, and adhesives. Such fibers and plastics are components of clothing, furniture, appliances, construction materials, motor vehicles, food packaging, etc. ACN is mainly found in the acrylic industry wastewater and effluents discharged from chemical and latex manufacturing plants. It has been listed third in the EPA list of 129 priority pollutants [3]. It may reasonably be anticipated to be a carcinogen, according to the sixth annual report on Carcinogens, published by the National Toxicology Program of the US Department of Health and Human Services [4–9]. It is also classified by the US Environmental Protection Agency as a carcinogen in the national Toxic Release Inventory. ACN is toxic and irritant to humans who are exposed to it, which is mainly by inhalation or skin contact. Inhalation of ACN can lead to symptoms such as irritation of nose and throat, headache, nausea, dizziness, and vomiting. More severe exposures

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to ACN by inhalation can cause tremors, discoloration of the skin, convulsions, and collapse in some cases may result in death. Skin contact with ACN leads to severe irritation, with redness, blistering, and peeling. Cyanide bearing effluents cannot be discharged without detoxification into the environment.

Physical methods, such as adsorption [10,11] biological methods (biodegradation) [12] and chemical methods like chlorination and ozonation [13] are frequently used for the removal of organic contaminants from waste streams. Among these processes, biodegradation has received the greatest attention. However, many organic chemicals, especially which are toxic or refractory, are not amendable to microbial degradation. Ultimately, research activities centered on advanced oxidation processes (AOPs) for the destruction of synthetic organic species resistant to conventional treatment methods. AOPs rely on *in situ* generation of highly reactive radical species, mainly HO^* using solar, chemical, or other forms of energy [14,15]. The most attractive feature of AOPs is that this highly potent and strongly oxidizing radical allows the destruction of a wide range of organic chemical substrate with no selectivity. Among AOPs, heterogeneous photocatalysis has proved to be an efficient tool for degrading both aquatic and atmospheric organic contaminants [16]. Heterogeneous photocatalysis involves the acceleration of photoreaction in presence of semiconductor photocatalyst and UV irradiation.

Cheng-Nan et al. [17] utilized the ozone to decompose the organic nitrogen contained in ACN and styrene. Chang et al. [18] showed the removal of ACN increases by Fenton-microfiltration process. Yan-yang et al. [19] studied the treatment of ACN waste water by three AOP namely; Fenton oxidation, electro-Fenton oxidation, and electrochemical oxidation with iron promoting and found that all the three processes were able to treat ACN wastewater.

Parametric optimization of photocatalytic degradation of catechol and 2,4-dichlorophenol in aqueous solutions by response surface methodology (RSM) has been reported [20,21]. Kumar et al. [11] reported the optimization of process parameters for ACN removal by a low-cost adsorbent using Box Behnken Design (BBD). Optimization for UV-photocatalytic degradation of paraquat over titanium dioxide supported on rice husk silica using BBD has also been reported [22]. Ray et al. [23] applied a four-factor three-level BBD to describe the photocatalytic degradation of phenol in an aqueous media and studied the effect of four process variables i.e. Titanium dioxide (TiO_2) catalyst size, TiO_2 concentration, dissolved oxygen concentration, and phenol concentration. Pretreatment of ACN manufacturing wastewater by Fenton process has been studied and it was obsereved that Fenton treatment resulted in enhanced susceptibility to micro-organism degradation [24]. To the best of author's knowledge, there is no report available in the literature for the parametric optimization of photocatalytic degradation of ACN using ZnO with RSM.

In the present study, an attempt has been made to optimize the process parameters of photocatalytic degradation of ACN using ZnO as a photocatalyst by the application of BBD based on RSM. The variables studied included ZnO dose, pH, and H_2O_2 concentration.

2. Experimental procedure

2.1. Materials and chemicals

ZnO ($5\,m^2/g$) was purchased from Merck, Germany and used as received. ACN was purchased from Sigma Aldrich (USA), used in the present study. ACN (CH_2=CHCN) having CAS No. 107-13-1 is a colorless to pale yellow liquid with an unpleasant odor. It is soluble in water and most common organic solvents such as acetone, benzene, carbon tetrachloride, ethyl acetate, and toluene [25]. Stock solution of ACN (50 mg/L) was prepared by dissolving 62.5 μL ACN in 1 L of double distilled water. pH of the solutions was adjusted with 0.1 N HCI or 0.1 N NaOH. Hydrogen peroxide (30% w/v) obtained from S.D. fine-chemicals Ltd. was used as an oxidant.

2.2. Instrumentation

Photocatalytic treatment of ACN was performed in batch experiments. For photocatalytic treatment, UV reactor was made up of iron having rectangular shape with wooden roof. The reactor consists of seven UV tubes (36 W each) mounted on the roof having wavelength of 365 nm. The photocatalytic experiments were performed under slurry mode in specially designed double-walled glass reaction vessels having volume of 1,000 mL and surface area of $0.025\,m^2$. Temperature inside the reactor was maintained by an exhaust fan. The solution was kept under constant stirring using magnetic stirrers and aeration was carried out with the help of conventional aerators. The spectrum was taken with UV–vis Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer) and pH was measured using Thermo Orion 920A digital pH meter.

2.3. Photocatalytic degradation

For the degradation experiments, fixed quantity of photocatalyst was added to 200 mL of sample taken in

the reaction vessel (1,000 mL capacity) and the vessel was covered with the transparent thin foil to prevent evaportaion loss; air was also supplied by the aerator during the experiments. The aqueous suspension was magnetically stirred and subjected to irradiation under UV light for a period of 2 h. The sample was withdrawn at every 15 min interval, filtered through the syringe filter of 0.45 μm pore size, and absorbance was taken at 204 nm with the spectrophotometer. The degradation efficiency was calculated by change in the absorbance at given wavelength.

2.4. Design and analysis

The best performance of a BBD depends on some previous information of the system being optimized. The BBD can optimize the number of experimental runs needed to be carried out to ascertain the possible inter-parametric interactions and their effects on the photocatalytic degradation of ACN. The BBD requires an experimental run according to $N = k^2 + k + c_p$, where k is the factor number and c_p is the replicate number of the central point [26]. These designs are formed by combining 2^k factorials with incomplete block designs. BBD is a spherical, revolving design; and it consists of a central point and the middle points of the boundaries of the cube circumscribed on a sphere. The BBD consists of three interlocking 2^2 factorial designs having points lying on the surface of a sphere surrounding the center of the design. It has been applied for optimization of several chemical and physical processes; and the numbers of experimental run are resolute accordingly [27,28].

The sequential F-test and other adequacy measures are generally used for selecting the paramount model. To analyze a process or a system including a response Y, where Y depends on the input factors: x_1, x_2, …, x_k, the correlation between the response and the input process parameters are described as:

$$Y = u(x_1, x_2, \ldots, x_k) \pm \varepsilon \quad (1)$$

where u is the unknown but real response function with its format being unknown, and ε is the residual error which describes the differentiation that can be included by the function u. Since the relationship between the response and the input parameters can be described as a surface of the x_1, x_2, …, x_k coordinates in the graphical sense, the study of these relationships is named as the RSM. A statistical software, Design-Expert V_6 (trial version) was used to produce the statistical and response plots. A second-order polynomial Eq. (2) was used through nonlinear regression to fit the experimental data and to identify the relevant model terms. Considering all the linear terms, square terms, and the linear-by-linear interaction terms, the quadratic response model can be described as:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where β_0 is the constant, β_i the slope or linear effect of the input factor x_i, β_{ij} the linear-by-linear interaction effect between the input factors x_i and x_j, and β_{ii} is the quadratic effect of input factor x_i [29].

In the present study, a three-level, three-factorial BBD was applied to investigate the photocatalytic process parameters affecting the degradation efficiency of ACN in the presence of ZnO catalyst. The factor levels were coded as −1 (low), 0 (central point or middle), and 1 (high) [30]. The input parameters used in this study are given in Table 1. The range of process variables namely, ZnO dose, pH, and H_2O_2 concentration, were chosen based on preliminary experiments. Statistical terms and their definitions used in the Design-expert software are defined elsewhere [31]. Second-order polynomials were used to represent the experimental data to obtain the best-fit regression equations.

It is significant to take account of the second-order model to provide good prediction throughout the area of interest. The second-order response surface design can be rotated which means that the variance of the predicted response was the same at all points [32]. Rotatability is a reasonable basis for the selection of response surface design. The cubic model was found to be aliased and could not be used for modeling of the experimental data.

3. Results and discussion

3.1. UV–Vis spectra of ACN

The degradation efficiency of ACN (50 mg/L) was recorded in terms of change in the intensity of characteristic peak at 204 nm. Fig. 1 shows the UV–vis Spectra of 50 mg/L of ACN solution.

Table 1
Experimental design levels of chosen parameters

Variables	Levels		
Coded level	Low (–1)	Middle (0)	High (+1)
ZnO dose (g/L)	0.50	1.75	3.00
pH	2.00	7.00	12.00
H_2O_2 conc. (m mol/L)	2.50	6.75	10.00

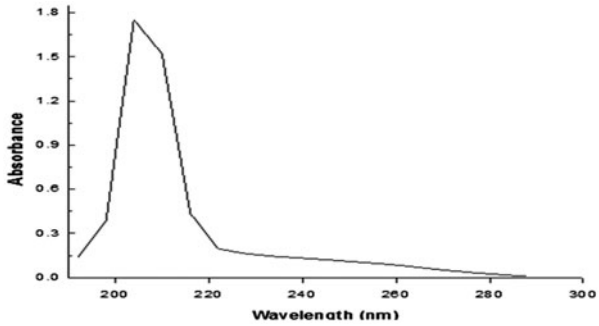

Fig. 1. Full scanning spectrum of ACN.

3.2. Adsorption studies of ACN

The degradation adsorption of ACN on catalyst surface was studied by carrying out experiments under dark conditions through UV/ZnO and Dark/ZnO. The photocatalytic degradation of ACN under these experimental conditions is shown in Fig. 2. The degradation efficiency was recorded in terms of change in the intensity of characteristic peak at 204 nm. The experiments were carried out under dark conditions to assess the adsorption of ACN on the surface of photocatalyst which was observed to be 36.2%. This degradation efficiency refers to adsorption of ACN on catalyst surface. Then the UV-induced photocatalytic experiments were conducted using ZnO at substrate concentration of 50 mg/L and catalyst loading of 1.5 g/L at pH of 8.0 resulting in degradation efficiency of 86.7% within 60 min. This shows that degradation efficiency achieved was higher in photo-induced catalyzed reactions.

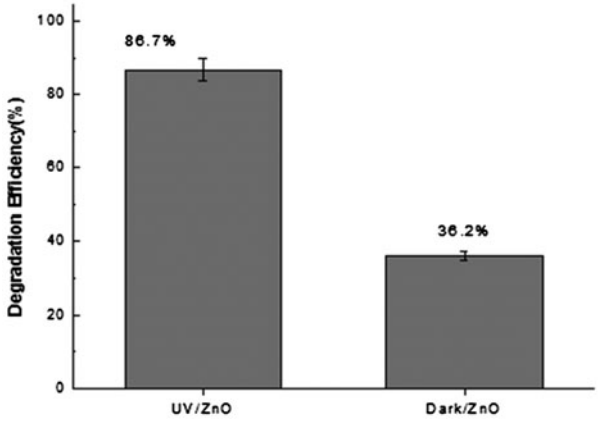

Fig. 2. Photocatalytic degradation of ACN under UV/Dark conditions. [ZnO] = 1.5 g/L, [Conc.] = 50 mg/L, [wavelength] = 204 nm, [Time] = 60 min.

3.3. Model fitting and statistical analysis

The experimental data were analyzed using the statistical software, Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, MN, USA), for regression examination to fit the equations developed and also for the estimation of the statistical significance of the equations. The results of the degradation efficiency of ACN (response) were measured according to the design matrix and are listed in Table 2.

The sequential *F*-test and other adequacy measures were used for selecting the best model [32]. A manual regression method was used to fit the second-order polynomial Eq. (2) to the experimental data and to identify the relevant model terms.

To make a decision about the adequacy of the model for the degradation efficiency of ACN, two different tests such as the Sequential model Sum of Squares and Model Summary Statistics were carried out as shown in Table 3 and p values for all the regressions were lower than 0.01 and the quadratic model. This means that at least one of the terms in the regression equation had a significant correlation with the response variable.

By selecting the manual regression method, which eliminated the insignificant model terms automatically, the resulting ANOVA for the reduced quadratic models summarizes the analysis of variance (ANOVA) of response and shows the significant model terms. Table 4 shows the ANOVA result for the degradation efficiency of ACN, with a model *F*-value of 62.75, implying that the model is significant.

Table 2
The experimental values and measured response

Std	Run	ZnO dose (g/L)	pH	H_2O_2 conc. (m mol/L)	Degradation efficiency (%)
3	1	0.50	12.00	6.25	No degradation
9	2	1.75	2.00	2.50	87.3
7	3	0.50	7.00	10.00	86.1
16	4	1.75	7.00	6.25	83.2
17	5	1.75	7.00	6.25	87.2
10	6	1.75	12.00	2.50	No degradation
15	7	1.75	7.00	6.25	88.9
11	8	1.75	2.00	10.00	85.0
1	9	0.50	2.00	6.25	83.9
14	10	1.75	7.00	6.25	88.2
2	11	3.00	2.00	6.25	84.5
6	12	3.00	7.00	2.50	81.09
5	13	0.50	7.00	2.50	74.2
12	14	1.75	12.00	10.00	No degradation
13	15	1.75	7.00	6.25	86.1
8	16	3.00	7.00	10.00	82.6
4	17	3.00	12.00	6.25	No degradation

Table 3
Selection of adequate model for degradation of ACN

Source	Sum of squares	d*f*	Mean square	*F*	*p*	Remark
Sequential model sum of squares						
Mean	3.19	1	3.19			
Linear	3.81	1	1.27	7.62	0.0034	
2FI	0.028	3	9497E-003	0.044	0.9868	
Quadratic	2.06	3	0.69	65.84	<0.0001	Suggested
Cubic	0.073	3	0.024	12408.95	<0.0001	Aliased
Residual	7.862E-006	4	1.956E-006	–	–	
Total	9.16	17	0.54	–	–	
Lack of fit tests						
Linear	2.17	9	0.24	1.225E+005	<0.0001	
2FI	2.14	6	0.36	1.813E+005	<0.0001	
Quadratic	0.073	3	0.024	12408.95	<0.0001	Suggested
Cubic	0.000	0	–	–	–	Aliased
Pure error	7.862E-006	4	1.965E-006	–	–	–
Model summary statistics						
Source	Std. dev.	R^2	Adj. R^2	Pre. R^2	Press	Remark
Linear	0.41	0.6375	0.5538	0.3267	4.02	
2FI	0.46	0.6423	0.4276	−0.4827	8.86	
Quadratic	0.10	0.9878	0.9720	0.8041	1.17	Suggested
Cubic	402E-003	1.000	1.0000		+	Aliased

Table 4
ANOVA results for response surface quadratic model

Source	Sum of squares	d*f*	Mean square	*F*	*p*	Remark
Model	5.90	9	0.66	62.75	<0.0001	Highly significant
Catalyst dose	0.014	1	0.014	1.37	0.2085	
pH	3.80	1	3.80	363.08	<0.0001	Highly significant
H_2O_2 conc.	1.749E-004	1	1.749E-004	0.017	0.9007	
(catalyst dose)^2	0.033	1	0.033	3.15	0.1194	
(pH)^2	1.99	1	1.99	190.56	<0.0001	Highly significant
(H_2O_2conc.)^2	0.030	1	0.030	2.88	0.1336	
Catalyst dose *pH	0.028	1	0.028	2.68	0.1457	
Catalyst dose *H_2O_2 conc.	1.333E-005	1	1.333E-005	1.275E-003	0.9725	
pH × H_2O_2 conc.	4.812E-004	1	4.812E-004	0.046	0.8362	
Residual	0.073	7	0.010			
Lack of fit	0.073	3	0.024	12,408.95	<0.0001	
Pure error	7.862E-006	4	1.965E-006			
Cor total	5.98	16				

The interaction of two factors (2FI) and the linear model was suggested to be insignificant using the RSM. The model summary statistic showed the regression coefficient ($R^2 = 0.9878$) was found to be highest for the quadratic model for the degradation efficiency of ACN. The regression coefficient was higher than the analyzed by Kansal et al. [33] for the photocatalytic degradation of catechol. The adequate precision was found to be 21.46 for the degradation efficiency of ACN. An adequate precision ratio above 4 indicates adequate model efficacy. It means that the model can be used to navigate the design space.

The ANOVA indicates a relationship between the degradation efficiency of ACN in terms of catalyst dose, pH, and H_2O_2 concentration. From ANOVA, it was clear that the pH is highly significant for the photocatalytic degradation of ACN employing ZnO catalyst. This is in agreement, that for photocatalytic degradation the pH and square of pH is significant [33,34].

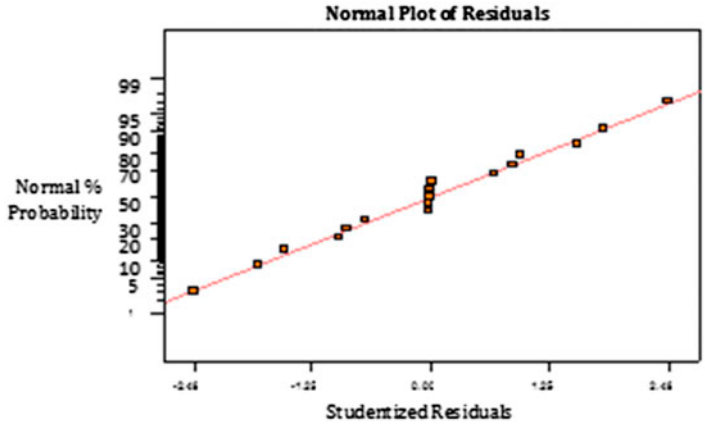

Fig. 3. Normal probablity plot of the residuals for percentage degradation.

A normal probability plot and a dot diagram of these residuals for the degradation efficiency of ACN are shown in Fig. 3. The data points on this plot lie reasonably close to a straight line, lending support to the conclusion that the underlying assumptions of the analysis were satisfied. Fig. 4 shows the relationship between the actual and predicted values of degradation efficiency of ACN. It can be seen that the residuals are in the proximity of the straight diagonal line. Therefore, developed models are considered to be adequate because the residuals for the prediction of each response are lowest. The 3D response surface plots of the effect of catalyst dose, pH, and H_2O_2 concentration for the degradation efficiency of ACN are visualized in Figs. 5–7.

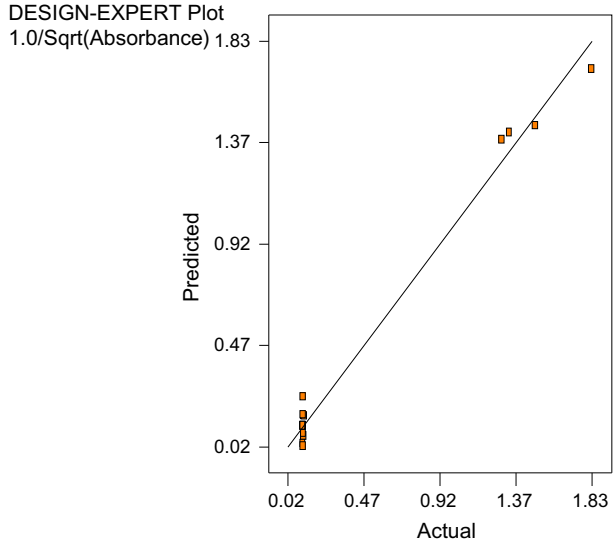

Fig. 4. Scatter diagram of predicted response versus actual response.

Using the point prediction option in the software, the response of the validation experiment was predicted using the previously developed models. To verify the adequacy of the developed models, the confirmation experimental runs were carried out using new experiment conditions, which were within the experimental ranges defined earlier. The optimum values for catalyst dose, pH, and H_2O_2 concentration, 1.48 g/L, 7.00, and 4.22 m mol/L respectively. At these values of catalyst dose, pH, and H_2O_2 concentration, the degradation efficiency of ACN was 89.9%. So the optimization of photo-catalytic degradation of process parameters can be carried out easily, as well as the number of experimental runs reduced significantly in doing so.

To confirm the adequacy of the model for predicting the maximum degradation efficiency of ACN, a verification experiment was carried out under the optimum conditions. A maximum degradation of 89.6% was obtained from the experiment, as shown in

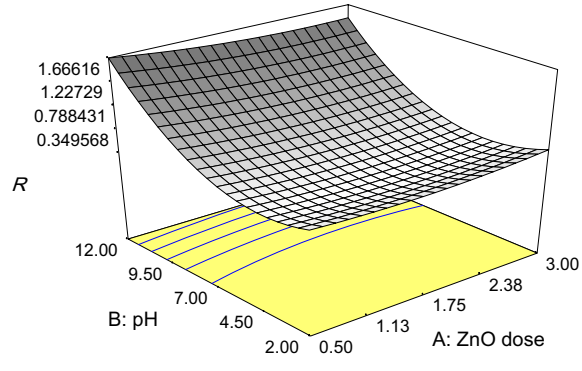

Fig. 5. Effect of pH and ZnO dose on degradation efficiency of ACN. R = 1.0/Sqrt (% degradation efficiency), X = A:ZnO dose, Y = B:pH, and Actual Factor C:H_2O_2 = 4.22 mM/L.

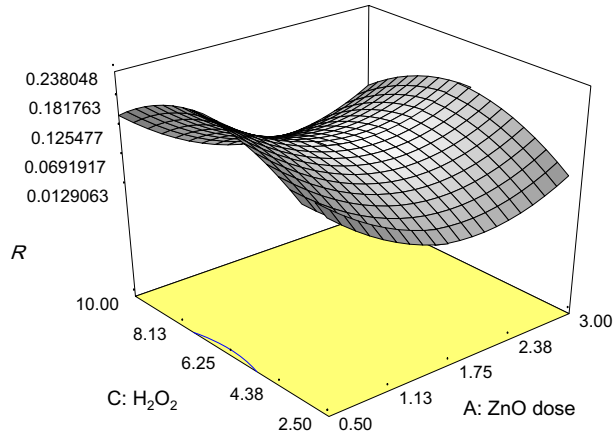

Fig. 6. Effect of H_2O_2 and ZnO dose on degradation efficiency of ACN. $R = 1.0/\text{Sqrt}$ (% degradation efficiency), X = A:ZnO dose, Y = C:H_2O_2, and Actual Factor B:pH = 7.00.

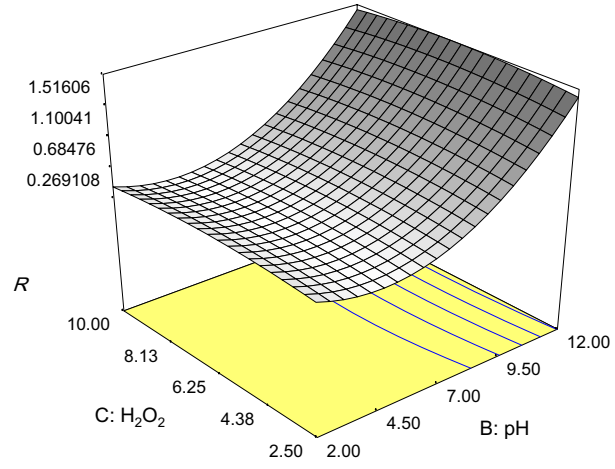

Fig. 7. Effect of H_2O_2 and pH on degradation efficiency of ACN. R = 1.0/Sqrt (% degradation efficiency), X = B:pH, Y = C:H_2O_2, and Actual Factor B:ZnO dose = 1.48 g/L.

Table 5
Optimum value of the process parameters for constraint conditions and their experimental values

Variables	Optimum value	ACN degradation (%)	
		Predictive	Experimental
ZnO dose (g/l)	1.48	89.9%	89.6%
pH	7.00		
H_2O_2 conc. (m mol/L)	4.22		

Table 5. The good agreement between the predicted value and the experimental value confirms the validity of the model for stimulating the photocatalytic degradation of ACN.

The results are in agreement with Tantriratna et al. [35], where BBD based on RSM was applied for the UV phototocatalytic degradation of paraquat and the results indicated that the quadratic model fitted well with the experimental data and the good agreement between the predicted and the experimental values confirmed the validity of the model.

4. Conclusion

The present study shows the efficacy of photocatalytic degradation of ACN employing ZnO catalyst. The study clearly showed that BBD was one of the appropriate methods to optimize operating conditions for the photocatalytic degradation of ACN. Graphical response surface and contour plots were used to locate the optimum point. The optimum condition yielded the highest degradation efficiency of 89.6% at 1.48 g/L ZnO dose, 7.0 pH, and 4.22 m mol/L H_2O_2 concentration which was in agreement with the predicted value. The degradation of ACN is sensitive to the pH in the present study. The value of $R^2 > 0.98$ for the present mathematical model indicates the high correlation between observed and predicted values.

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