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Efficacy of a photo-catalyst towards the degradation of a pharmaceutical compound, 4-aminopyridine by application of response surface methodology

Sucharita Chakraborty, Suvanka Dutta, Rajnarayan Saha*, Sankar Chandra Moi , Dipankar Sukul, Sujit Sankar Panja

Department of Chemistry, National Institute of Technology, Durgapur-713209, West Bengal, India, email: schakrabaorty@gmail.com (S. Chakraborty), suvanka.dutta@gmail.com (S. Dutta), rajusaharupa@yahoo.com, rnsahanitd@gmail.com (R. Saha), sankarmoi67@yahoo.com (S.C. Moi), dipankar.sukul@gmail.com (D. Sukul), sujit.panja@gmail.com (S.S. Panja),

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ABSTRACT

The present study demonstrates an intensive experimental study on the photo-degradation of pharmaceutical compound (4-Aminopyridine) in batch photo reactor with low energy ultraviolet light (125 nm) and using zinc oxide as catalyst. 4-Aminopyridine (4-AP) has been used for many years, prescribed for people with multiple sclerosis. This study aims to analyze the influence of operating parameters and their interactive effect on the overall removal efficiency of the targeted component in water by response surface methodology (RSM). Time (A, min), catalyst (B, gm/l), H_2O_2 (C, mg), and pH (D) were chosen as independent variables to optimize the percent removal of 4-Aminopyridine as response. The highest COD removal 97% was obtained at pH (5.3), ZnO (0.3 gm/l), H_2O_2 (3757 mg) within 49 min treatment time. Model predicted values were found in good agreement with the experimental values, and the behavior of the model equation has supported the experimental observation with minor deviation. Furthermore, the degradation of 4-AP was confirmed by the UV-V is spectrophotometer which showed continuous degradation after every 10 min time interval within an hour study and the FTIR (Fourier transform Infrared) spectrophotometer analysis reveals the modification of the functional groups present in the target compound after photo-catalytic treatment.

Keywords: Chemical oxygen demand (COD) removal; Degradation; Experimental value; pharmaceutical; Photo reactor; Response surface methodology (RSM)

1. Introduction

Within the last few years, both the occurrence and fate of pharmaceutical residues and their metabolites in environmental matrices, have induced scientific interest [1]. The principle track of these pharmaceutical compounds for entering into the environment is the pharmaceutical industrial discharge or released by the people through disposal of unwanted and expired drugs directly into the domestic sewerage system or via leachate from landfills [2,3]. Also due to general aging of population, it can be assumed that greater quantities and a miscellaneous group of pharmaceutically energetic compounds will be consumed, with development of new compounds that have unknown effects on the environment, thus leading to the fast development of pharmaceutical industry [4].

4-aminopyridine (4AP), commercial available as Ampyra, has been used for many years, prescribed for people with multiple sclerosis. It is a potassium channel blocker that, when used correctly, improves walking and other activities. A case reports have shown that overdoses with (4-AP) can lead to parenthesis, seizure, atrial fibril-

*Corresponding author.

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lation [5] and some common side effects like kidney or bladder infections, headache, nausea, weakness, back pain etc [6].

Hence, eradication of these pharmaceutical compounds is a burning topic now a days and constant effort has been made by the researchers on the same. A range of treatment methods are reported in the literature but heterogeneous photo-catalytic advanced oxidation technology (AOT) has been placed in the forefront of vigorous research activity due to its efficiency of total destruction of pollutants, non-selectivity and formation of non-threatening products [7]. The effectiveness of this oxidation technology in the destruction of pharmaceuticals has been found in numerous studies [8–12]. Semiconductor photo-catalyst zinc oxide (ZnO) in bulk form is very influential in degradation of organic pollutants having band gap of about 3.3 eV. Pure ZnO is a white powder. This semiconductor has several favorable properties, including good transparency, high electron mobility, wide bandgap, and strong room-temperature luminescence. ZnO has higher excitonic binding energy about 60 meV and consequently longer lifetime at room temperature [13].

Response surface methodology (RSM) is a useful statistical method commonly used for experimental design and widely applied to model and optimize several wastewater treatments, like photo-catalytic wastewater treatment [14,15]. The development of mathematical model predicting the degradation of the target compound is one of the most important issues to be solved prior to the large scale for treatment of pharmaceutical compounds from wastewaters [16]. RSM is a collection of statistical and mathematical techniques used in developing, improving and optimizing a process in which response is of interest that is influenced by several variables and the objective is to optimize this response. When a combination of several independent variables and their interactions affect desired responses, response surface methodology (RSM) is an effective tool for optimizing the process [17]. Different parameters such as pH, catalyst dosage, reaction time and concentration of H_2O_2 could have effect on 4-aminopyridine compound degradation in photo-catalytic advanced oxidation process. RSM uses an experimental design such as the central composite design (CCD) frequently used for optimization of photo-catalytic treatment process [18] to fit a model by least squares technique [19,20].

RSM has also been used in photo-catalytic removal of miscellany pharmaceutical agents [21–24]. To the best of our knowledge, few reports are there on the degradation of 4-aminopyridine [25,26], but till date, no attempt has been made to study the photo-degradation of 4-AP using ZnO. So the present investigation is an endeavor to explore the potential of ZnO for the photo degradation of 4-aminopyridine. The main aim of this study is to reduce the chemical oxygen demand (COD) level and also to find out the COD removal efficiency (RE) by varying the different parameters responsible for it. Thus, RSM has been used to optimize the chemical oxygen demand (COD) removal efficiency which is considered to be an essential parameter. Furthermore, degradation of the selected pharmaceutical compound was also aimed in this study which has been confirmed by UV-Vis spectrophotometer and FTIR (Fourier transform Infrared) spectrometer.

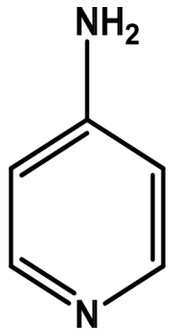
Regeneration of the catalyst is one of the most important attempts for the utilization of the catalyst and also for the environmental remediation. It would be vital owing to the rigid environmental safety for their disposal and economic benefit. Regeneration of the deactivated photocatalysts can be done by specific heat treatment or by UV irradiation. The efficiency of the regenerated catalyst towards degradation capability has been tested and reported good reusability in other research work [27–29].

2. Materials and methods

2.1. Chemicals and analytical methods

The pharmaceutical compound chosen for the study was 4-Aminopyridine (Fig. 1) purchased from Sigma Aldrich and its properties shown in (Table 1). Semiconductor employed as photo-catalyst is ZnO powder and commercial H_2O_2 solution (50% w/v) used in the oxidation process. KI, $K_2Cr_2O_7$, $Na_2S_2O_4$, starch were used for COD analysis. Samples were digested using COD thermo-reactor Orion COD 165, Thermo-scientific for COD analysis. The pH of the sample in the reaction vessel was adjusted according to the experimental design with calculated volume/weight of 1 N HCl or 1 N NaOH and measured in an Orion Star A2014, Thermo-scientific model. Na_2SO_3 was used for the quenching of H_2O_2 in the reaction mixture. All these laboratory chemicals were purchased from Merck (India) as per requirement without further purification. Milli-Q water was used for the entire study. The concentrations of 4-aminopyridine was measured in an UV-Vis spectrophotometer (Shimadzu UV-1601). Solutions of known concentration 0.2, 0.4, 0.6, 0.8, 1, 2, 3, 4 and 5 mg/L were prepared and UV-VIS spectra were recorded from 190 to 400 nm. The absorbance peak of 4-aminopyridine was observed at wavelength 265 nm. A standard absorbance vs. 4-aminopyridine concentration calibration curve was prepared by single wavelength mode (265 nm) using 4-aminopyridine standard. This curve was used to determine residual 4-aminopyridine concentrations in aqueous solution at different time intervals during the photo-catalytic treatment. Also, Thermo Nicolet iS 10 FTIR-spectrometer (4000–400 cm^{-1}) was used for the IR spectral measurements.

Table 1
Details of the pharmaceutical compound

Pharmaceutical compound	Chemical structure (Fig. 1)
Compound name - 4-aminopyridine Chemical formula - $C_5H_6N_2$ λ_{max} = 265 nm MW = 94.12 Boiling point - 273.5°C Water solubility - 50 mg/ml CAS No. - 504245	

2.2. Experimental Set-up

The photo-catalytic reactions were conducted in a batch process. All the experiments were performed in a cylindrical photo reactor with a total volume of 1.0 L (diameter 12 cm and height 13.3 cm). The catalyst (ZnO) was added to the reactor containing the sample. The unit configured with an annular cylindrical glass reactor (Fig. 2) with a quartz tube at the center of the reactor to house UV light (λ = 125 nm) source, jacket is provided for cooling purpose. Cooling media (water) was continuously circulated. The reactor was provided with inlets for feeding reactants, and ports for withdrawing samples. The reactor was open to air with a magnetic stirring bar placed in the bottom for homogenization. The reactor was covered with a wooden box to prevent the exposure of UV light. Samples were periodically withdrawn for analyzing the COD of the selected compound (4 AP).

2.3. Design of the experiment

The standard RSM design called Central composite design (CCD) was used in this present work for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [30]. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c central runs [30]. The center points are utilized to evaluate the experimental error and the reproducibility of the data. Thus, for degradation process having four independent parameters (n = 4), the total number of experiments required was:

$$N = 2^n + 2n + n_c = 2^4 + (2 \times 4) + 6 = 30$$

The outcome of each experimental run was analyzed and the response was correlated with four input factors for degradation of 4-aminopyridine through an empirical second degree polynomial equation as given in the following.

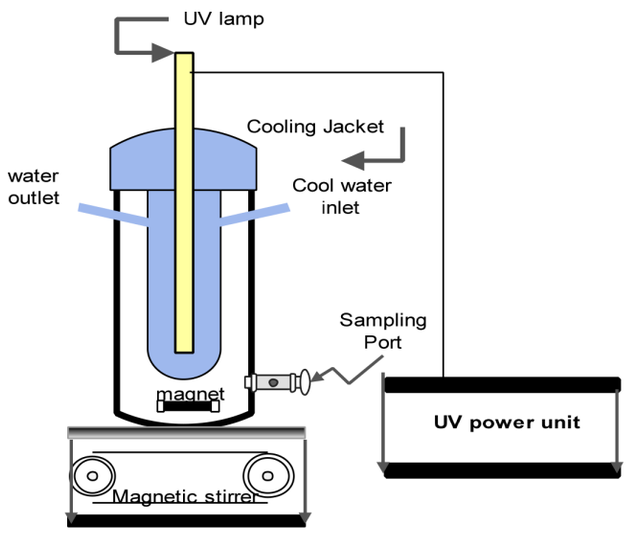


Fig. 2. A Photo-Catalytic reactor setup.

$$Y = \beta o + \Sigma \beta_i X_i + \Sigma B_{ii} X_i^2 + \beta_{ij} X_i X_j \quad (1)$$

where Y is the predicted response, $X_i X_j$ are the coded parameters, βo the constant coefficient, β_i the linear coefficients, β_{ij} the interaction coefficients and β_{ii} the quadratic coefficient [31]. To obtain the experimental results, the data was analyzed using the design expert software 7.0.

ANOVA was used to model the system represented by independent parameters and dependent output response and to optimize the system by estimating the statistical parameters. The minimum (–1) and maximum (+1) level of the independent variables i.e. time (A), photo-catalyst (ZnO) dosage (B), H_2O_2 (C) and pH (D) were 16 min and 60 min; 0.2 and 0.6; 1768 and 4420; and 3.55 and 10.55 respectively. The statistical experimental design as specified by the software is shown in Table 2.

2.4. Experimental procedure

The photo-catalysis under UV light was studied at ambient conditions. 250 ppm solution of 4-aminopyridine was prepared and was taken in a 1 liter reactor. At first, the pH was adjusted followed by addition of the photo-catalyst and then by the addition of H_2O_2 before UV light irradiation and stirring. The mixture was stirred in dark for 30 min in order to assure the adsorption/desorption equilibrium of ZnO catalyst on the solid surface, and then the solution was exposed to UV irradiation. At specified pre-selected time intervals, some aliquots of solution was taken from the solution and filtered by GF/C (25 mm) filter paper for COD analysis, residual H_2O_2 determination. The COD removal efficiency of 4-aminopyridine was calculated according to the following equation:

$$COD\,RE\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where C_0 is the initial 4-aminopyridine concentration and C_t is the 4-aminopyridine concentration after UV light irradiation of t, min.

Another photo-catalytic experiment with the same above conditions was run for an hour at the highest COD removal dosages to further confirm the photo-catalytic degradation. At every 10 min time interval some aliquot was collected and filtered to obtain the UV-Vis scan in the UV-Vis spectrophotometer. After completion of an hour run, the treated aqueous solution (100 ml) containing the selected compound was filtered and extracted in 250 ml ethyl acetate by solvent-extraction method in a separat-

Table 2
Experimental range and levels of independent variables for photo-catalytic degradation of 4-aminopyridine

Independent variables	Range and level			
	–1	+ 1	–α	α
Time (A, min)	27	49	16	60
Catalyst, ZnO (B, gm/l)	0.3	0.5	0.2	0.6
Oxidant, H_2O_2 (C, mg)	2431	3757	1768	4420
pH (D)	5.3	8.8	3.55	10.55

ing funnel for FTIR analysis. The sample was dried and mixed with KBr (1:20; 0.02 g of sample with KBr at a final weight of 0.4 g). The sample was ground and pressed to obtain IR- transparent pellets. The absorbance FT-IR spectra of the sample were recorded using an FTIR spectrometer. The spectra were collected within a scanning range of 400 to 4000 cm^{-1}.

3. Results and discussion

3.1. Optimization of COD removal conditions by response surface methodology

In this study, four parameters viz., time (A), molar ratio of pollutant to catalyst (B), molar ratio of H_2O_2 to ZnO (C), and pH (D) for degradation of the target compound have been optimized by RSM using Design Expert Software. The list of experiments as designed by RSM and the values of response (COD removal efficiency) for each sample obtained at corresponding experimental conditions are shown in Table 3. The regression analysis was performed to fit the response. As suggested by the software, no transformation was chosen and quadratic process order was selected to analyze the data. The final regression function for response in terms of coded factors used in making of statistical model is given below:

$$\begin{aligned}\text{COD RE\%} = {} & 70.50 + 13.3A + 1.50B + 8.25C + 3.25D \\ & - 0.75AB + 6.75AC + 5.25AD - 7.75BC \\ & + 11.25BD - 8.00CD - 4.79A^2 + 2.21B^2 \\ & - 10.92C^2 - 6.67D^2\end{aligned} \quad (3)$$

3.2. Analysis of variance (ANOVA)

Analysis of variance (ANOVA) values for the quadratic regression model obtained from CCD employed in the optimization of pharmaceutical degradation are listed in Table 4. The statistical significance of the second-order equation revealed that the regression is statistically significant ($P < 0.0001$) [32]; P values less than 0.05 indicate that the model terms are significant, whereas values greater than 0.1 are not significant. However, the "Lack of Fit F-value" of 0.52 implies the Lack of Fit is not significant relative to the pure error. There is 82.03% chance that a "Lack of Fit F-value" large could occur due to noise. Non-significant lack of fit is good. The results indicate that the Response equation proved to be suitable for the CCD experiment [33,34]. The model's F value 2425.186 in Table 4 implies that the model is significant for the degradation process. The large value of F indicates that most of the variation in the response can be explained by the regression equation. The fit of the models were controlled by the coefficient of determination R^2. Based on the ANOVA results, the models report high R^2 value of 99.96% for pharmaceutical degradation using photo-catalytic oxidation process. Also, an acceptable agreement with the adjusted determination coefficient is necessary. In this study, the Adj-R^2 value of 99.91% was found. The values of R^2 and Adj-R^2 are close to 1.0, which was very high and advocates a high correlation between the observed values and the predicted values. This indicates that the regression model provides an excellent explanation of the relationship between the independent variables and the response.

Table 3
Experimental design for COD removal

Run	(A) Time (min)	(B) ZnO (gm/l)	(C) H_2O_2 (mg)	(D) pH	COD removal efficiency (%)
1	38	0.4	3094	7.05	70
2	27	0.5	2431	8.8	63
3	27	0.5	3757	8.8	34
4	49	0.5	3757	8.8	84
5	49	0.5	2431	8.8	85
6	38	0.4	3094	7.05	70
7	27	0.3	2431	8.8	20
8	38	0.4	3094	7.05	71
9	16	0.4	3094	7.05	25
10	38	0.4	3094	3.55	37
11	38	0.4	3094	7.05	72
12	38	0.4	3094	7.05	70
13	38	0.4	1768	7.05	10
14	27	0.5	3757	5.3	32
15	49	0.3	2431	8.8	46
16	27	0.3	2431	5.3	31
17	38	0.2	3094	7.05	76
18	49	0.5	3757	5.3	60
19	38	0.4	3094	10.55	50
20	60	0.4	3094	7.05	77
21	49	0.3	3757	8.8	75
22	38	0.6	3094	7.05	82
23	38	0.4	3094	7.05	70
24	27	0.3	3757	8.8	23
25	27	0.3	3757	5.3	65
26	49	0.5	2431	5.3	30
27	27	0.5	2431	5.3	28
28	49	0.3	2431	5.3	35
29	38	0.4	4420	7.05	43
30	49	0.3	3757	5.3	97

3.3. Residual plots

Normal probability plot is a graphical method for determining residuals normality [35]. A normal probability plot of the residuals versus the response (Y) is presented in Fig. 3. Graphical data on the plot located in a position close to a straight line shows that the model sufficiently removed COD by UV/H_2O_2/ZnO process. The experimental and predicted values for Y are shown in Fig. 4. Observa-

Table 4
Analysis of variance (ANOVA) for fitting the COD removal efficiency from central composite design (CCD)

Source	Sum of squares (SS)	Degrees of freedom (DF)	Mean square (MS)	F value	p-value Prob > F
Model	16221.8	14	1158.7	2425.186	< 0.0001
A-time	4266.667	1	4266.667	8930.233	< 0.0001
B-ZnO dose	54	1	54	113.0233	< 0.0001
C-H_2O_2	1633.5	1	1633.5	3418.953	< 0.0001
D-pH	253.5	1	253.5	530.5814	< 0.0001
AB	9	1	9	18.83721	0.0006
AC	729	1	729	1525.814	< 0.0001
AD	441	1	441	923.0233	< 0.0001
BC	961	1	961	2011.395	< 0.0001
BD	2025	1	2025	4238.372	< 0.0001
CD	1024	1	1024	2143.256	< 0.0001
A^2	629.7619	1	629.7619	1318.106	< 0.0001
B^2	133.7619	1	133.7619	279.9668	< 0.0001
C^2	3268.762	1	3268.762	6841.595	< 0.0001
D^2	1219.048	1	1219.048	2551.495	< 0.0001
Residual	7.166667	15	0.477778		
Lack of fit	3.666667	10	0.366667	0.52381	0.8203

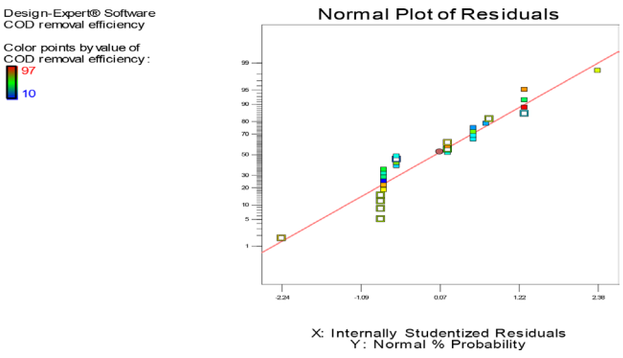


Fig. 3. Normal probability plot, COD removal efficiency.

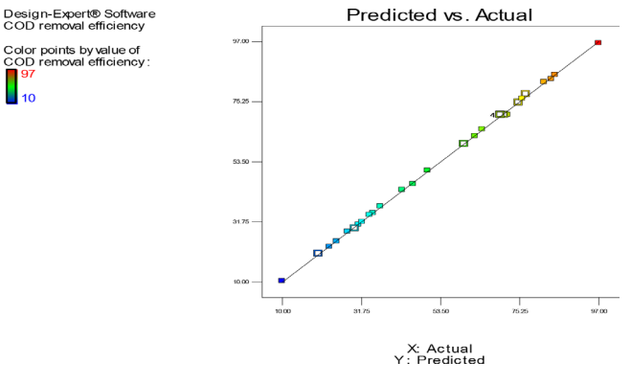


Fig. 4. Comparison between the experimental values and the predicted values of RSM model, COD removal efficiency.

tions indicate a very good correlation between the results obtained by experiments and the values predicted by the statistical model, which shows the success of this model.

3.4. Response surface analysis

A typical approach for graphical representation of regression equation for the optimization of reaction conditions is three-dimensional surfaces and contour plots which efficiently presents the status of reaction system. The effects of time, pollutant to catalyst ratio, H_2O_2 to ZnO ratio and pH of the reaction medium were illustrated by surface and contour plots for percent COD removal as shown in Figs. 5 and **6**. Response surface plots provided a method for predicting a response to different test variable values, and contour plots help to identify the types of interactions between the test variables. A 'slightly flat' response surface indicates that the responses can tolerate variation in independent variables value without the response being seriously affected, whereas a very pointed surface indicates that response would be sensitive to the independent variables [36]. Contour lines are parallel with either of the axes indicates, no interaction exists between the two variables under analysis. Elliptic contours indicate that there are striking interactions between the variables.

Fig. 5 illustrates the effect of independent variables on the removal efficiency by surface plot, which predicts the response at any combination of operational variables. The response surface was plotted against two variables keeping the third and fourth variable constant. The curvature in all the plots suggests 'quadratic relationship' of all process variables on the desired response. Fig. 5a implies that with

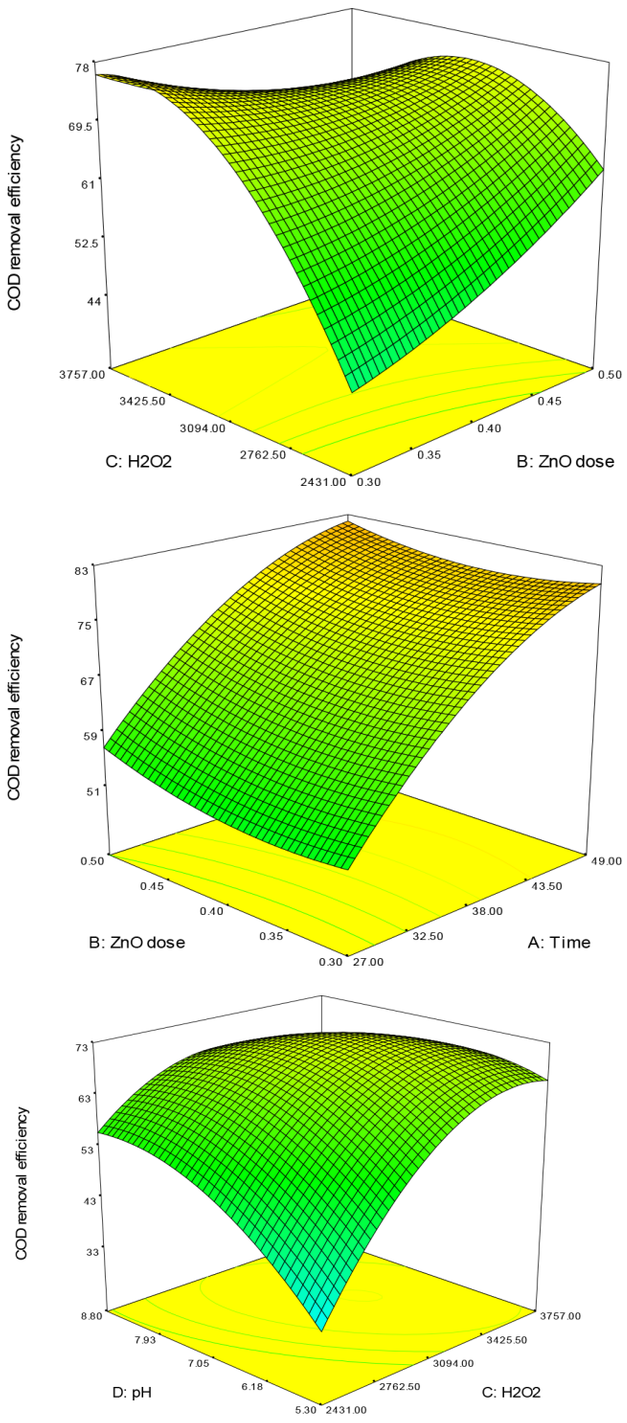


Fig. 5. (a) Response surface plot for the degradation of 4-aminopyridine illustrating interactive effect of catalyst dosage and time. (b) Response surface plot for the degradation of 4-aminopyridine illustrating interactive effect of catalyst dosage and oxidant (H_2O_2). (c) Response surface plot for the degradation of 4-aminopyridine illustrating interactive effect of the oxidant and reaction medium pH.

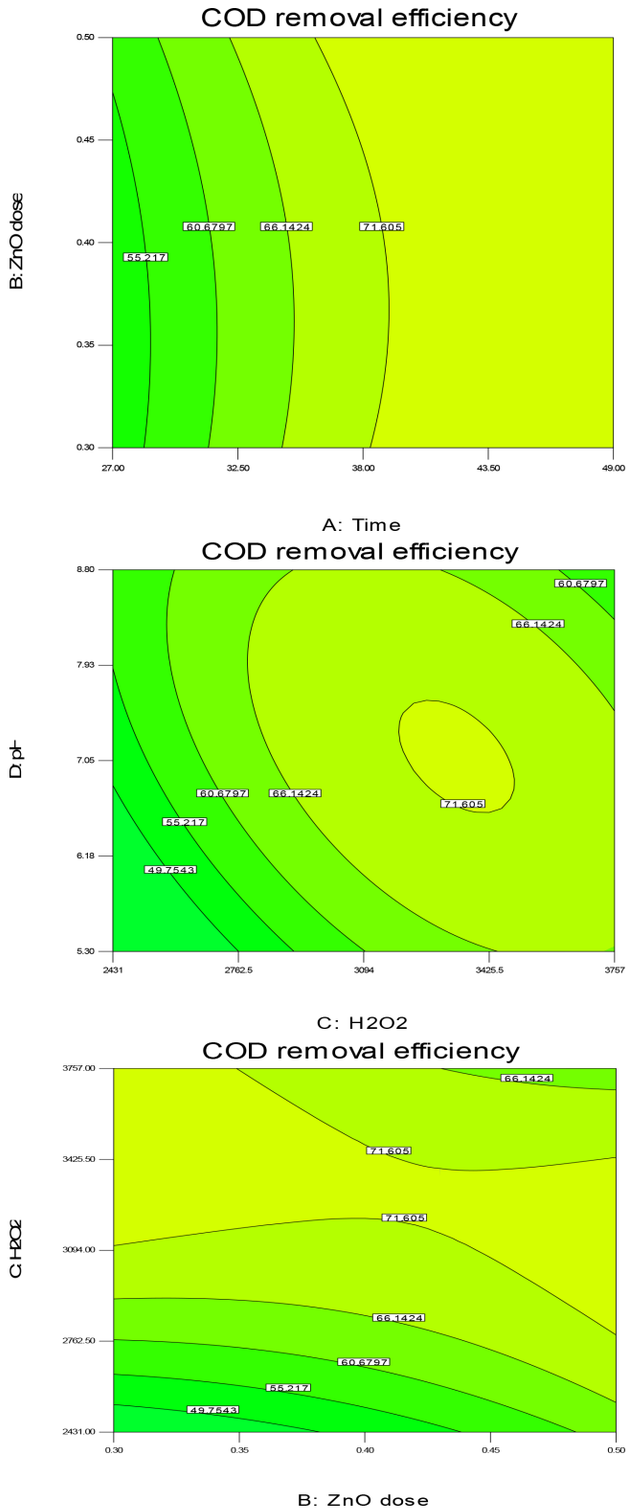


Fig. 6. (a) Contour plot for the degradation of 4-aminopyridine illustrating interactive effect of catalyst dosage and time. (b) Contour plot for the degradation of 4-aminopyridine illustrating interactive effect of oxidant (H_2O_2) and pH. (c) Contour plot for the degradation of 4-aminopyridine illustrating interactive effect of the oxidant and the catalyst dosage.

increasing catalyst dosage, percent removal remains almost same but increased with increase in time. The relatively flat surface of the plot indicates that the interactive effect of the medium time and pollutant to catalyst ratio was less significant. Fig 5b points up that with increasing the ratio of H_2O_2 to ZnO, percent removal value increases of the reaction medium. The curved surface illustrates the significant interactive effects between the catalyst dosage and time on the percent removal of COD. Fig. 5c also evidenced the substantial increase of the pH in the medium had escalated the removal percent.

Contour plots, Fig. 6a–c show the effects of the three factors on the 4-aminopyridine degradation. Fig. shows that with increasing time percent removal has increased. When pH and H_2O_2 values were low, the removal remained at 49.7% and when pH and H_2O_2 were at medium level, the removal remained at 71.6%. Thus the figures illustrates that at medium levels, COD removal achieved 71.6% which is maximum.

3.5. Degradation of 4-aminopyridine in UV-Vis Spectrophotometer

According to the experimental design, maximum COD removal was obtained at ph-5.3, ZnO dosage 0.3 gm/l and H_2O_2 3757 mg. Thus, the treated samples were scanned for UV-Vis range using spectrophotometer (Fig. 7) at the above-mentioned dosages at every 10 min time interval. The highest peak obtained was the initial concentration of the compound. The gradual decreasing of the peak confirmed the degradation of the compound after treatment.

3.6. Infra-red spectrum analysis

FTIR spectral comparison between 4-aminopyridine aqueous solution before and after photo-catalytic treatment of the same compound has been studied here. The FTIR spectra of initial 4-AP and the modification of the functional groups present in the compound after photo-catalytic treatment has been shown in Fig. 8. The initial selected compound possesses O–H stretch at 3436 cm^{-1} for alcohols and phenols, N–H stretch at 3300 cm^{-1} for amines and amides,

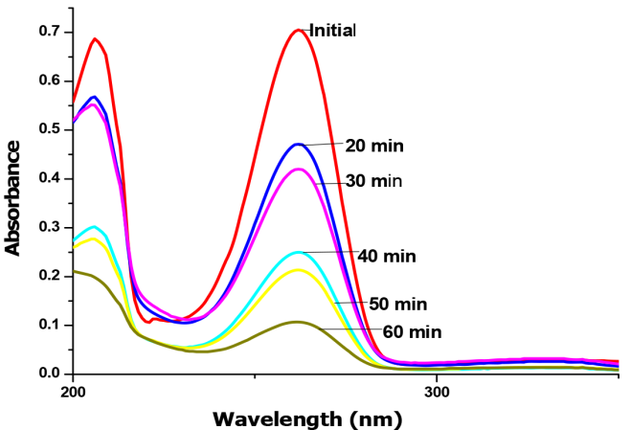


Fig. 7. Photo-catalytic degradation of 4-aminopyridine showing UV-Vis scan.

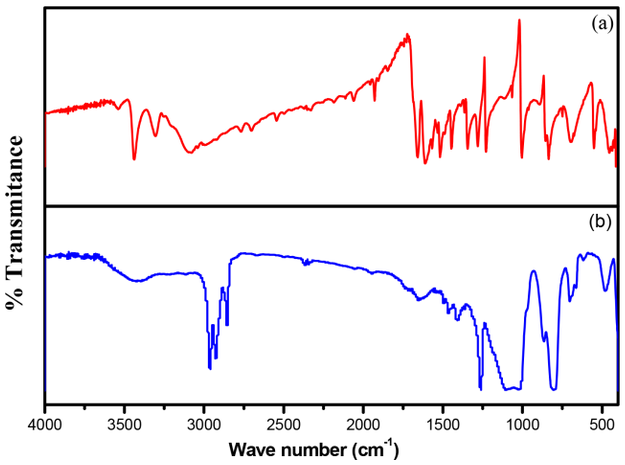


Fig. 8. (a) FT-IR Spectra of Initial 4-aminopyridine, (b) FT-IR Spectra of 4-aminopyridine after photo-catalytic treatment.

smaller peak at 3031 cm^{-1} for aromatics or alkenes, H–C=O stretch for aldehydes at higher frequency region. But at lower frequency region, alkenes at 1649 cm^{-1}, 1332 cm^{-1} for aromatic amines, 1216 cm^{-1} for aliphatic amines, 988 cm^{-1} and 821 cm^{-1} for alkenes. After the photo-catalytic treatment, IR spectrum showed significant changes in the position of the peaks when compared with the initial one. It showed peaks at 2925.98 cm^{-1} and 2854.90 cm^{-1} for alkyl C–H stretch, 1654.56 cm^{-1} for alkenyl C=C stretch and 703.46 cm^{-1} C–H bending for aromatics. The absence of N–H stretch and other functional groups signifies the degradation of 4-aminopyridine compound.

FTIR spectral comparison between ZnO which has been used as catalyst before and after photo-catalytic treatment of the target compound (4-aminopyridine) has been studied in Fig. 9. The FTIR spectra of initial ZnO indicated by a black line and the modification after photo-catalytic treatment have been indicated by red line. Initially ZnO possesses O–H stretch between 3400–3500 cm^{-1}, C–H

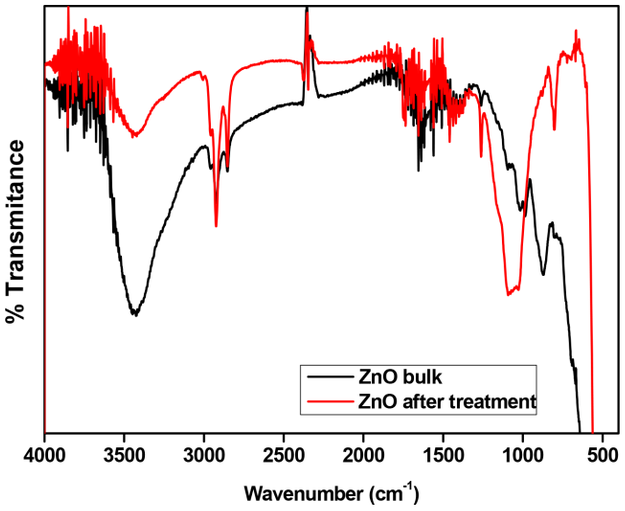


Fig. 9. FT-IR Spectra of ZnO before and after treatment.

stretch at 2850–3000 cm^{-1}, C–F and C–Cl stretch at 1300 cm^{-1} and 600–800 cm^{-1} respectively. All these functional groups present in the catalyst is due to the impurities present in it. After treatment, ZnO possesses all the functional groups as before but in reduced form as because of thorough washing with distilled water. This spectra proves that no adsorption of 4-aminopyridine took place on the surface of ZnO photocatalyst.

4. Conclusion

In this work, the degradation of a typical pharmaceutical, 4-Aminopyridine was studied by means of the most common type commercial photocatalyst, ZnO using ultra-violet irradiation. RSM was employed for optimization of COD removal and concentration degradation was studied in an UV-Vis spectrophotometer. By using the central composite design (CCD) method, four main parameters time, hydrogen peroxide concentration, pH and ZnO dosages were examined. A second-order polynomial model was developed using multiple linear regression analysis. Statistical test (ANOVA) indicated a good agreement between experimental data and the built model ($R^2 = 0.99$). The optimal operating conditions were determined using numerical optimization techniques. For this purpose, the maximum COD removal was optimized for pH (5.3), ZnO (0.3 gm/l), H_2O_2 (3757 mg) within 49 min treatment time. Accordingly, the removal efficiency of COD was 97% in terms of the independent variables. For further confirmation, experiment under optimum operating conditions showed concentration degradation in a UV-Vis scan and FTIR analysis. The efficiency of this photo-catalytic ($UV/H_2O_2/ZnO$) treatment process thus proved to be efficient enough to treat high concentrated pharmaceutical compounds.

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