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Optimization of COD Removal by Advanced Oxidation Process through Response Surface Methodology from Pulp & Paper Industry Wastewater

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Advanced oxidation process (AOP) is an efficient method to treat wastewater generated from pulp and paper industry. Hydroxyl radical ($^{\bullet}OH$) is responsible for the degradation of organic pollutant generated by the reaction of iron ion and hydrogen peroxide in the Fenton process. In this study, real wastewater was taken from pulp and paper industry, India. The lignin is mainly responsible for high Chemical Oxygen Demand (COD) in pulp and paper wastewater. For the present investigation, three independent variables were chosen COD: H_2O_2, H_2O_2: Fe^{2+} and time. The maximum 94% COD removal was found at the optimized value of 0.165, 0.0165 and 115 for the COD:H_2O_2, H_2O_2:Fe^{2+} and time respectively. The response surface methodology (RSM) was applied to optimize the operational parameters.

Keywords: Advanced oxidation process, Pulp and Paper wastewater, Lignin, Chemical Oxygen Demand, Response Surface Methodology

Introduction

Pulp and paper industry wastewater contains especially lignin and its derivatives along with some acidic components[1]. Direct discharge of industries based generated wastewater is harmful to the environment as well as to the ecosystem of aquatic life[2]. Zaied *et. al.,* (2009) used electrocoagulation method to treat black liquor from paper industry and around 98% COD was removed by the same method[3,4]. Himadri (2014) showed the synergistic catalytic action for the improvement in performance of lignin degradation by the advanced oxidation process[5-7]. Hermosilla et. al., (2016) reported that ozonation in AOP is very promising technique for the treatment of industrial wastewater[8]. Wang *et. al*., (2014) studied the syringyl lignin degradation using Fenton and UV/Fenton process[9]. Gu L *et al*., (2012) identified some intermediate product (isopropyl alcohol and benzaldehyde) using GC-MS during lignin degradation[10]. The aim of present work is to optimize the COD removal by Fenton process through RSM technique using central composite design (CCD) method. For the experimental work, three parameters were considered x_1, x_2 and x_3 as COD: H_2O_2 (wt:wt), H_2O_2:Fe^{2+} (molar ratio) and time (min) respectively.

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Materials and Methods

Wastewater was collected from pulp and paper mill in Chhattisgarh, India. The initial chemical oxygen demand (COD) of untreated pulp & paper industry wastewater was measured as 32000 mg/l, pH 3 and TDS 754 mg/l. Hydrogen peroxide supplied by Merck India was used as an oxidant. Reagent grade ferrous sulfate heptahydrate ($Fe_2SO_4 \cdot 7H_2O$) was supplied by Loba Chemie, India. For the estimation of COD, closed titrimetric method was used and COD reagent A and COD reagent B supplied by Merck, India. COD was computed as per equation no. 1:

$$\text{COD Removal Efficiency (RE) \%} = \{(C_0 - C_t)/C_0\} * 100 \quad \dots (1)$$

Where,
C_0 = Initial COD in mg/l.
C_t = COD at time t in mg/l.

Experimental Method

All experiments were performed in a batch reactor (1-liter glass beaker) with continuous and constant stirring (300 rpm) at room temperature. 300 ml of wastewater was used for the experiment with predetermined amount of hydrogen peroxide, ferrous sulfate and time. pH 3 was adjusted with 1 N sulfuric acid (H_2SO_4) and 1 N sodium hydroxide (NaOH). The samples were drawn at a regular time interval. MINITAB 16 (Trial version) software was used for the design of experiments.

Present work is designed with central composite design (CCD) to optimize the affecting parameters for highest removal efficiency. Central composite design (CCD) is the most common second-order model to design any experiment. The number of experiments conducted in the present work, was generated by giving the coded value using central composite design and optimum conditions were estimated by RSM (response surface methodology), adopting given formula (equations 2 and 3) :

$$N = 2^K + 2K + C_P \quad \dots (2)$$

Where K is a number of factors, Cp is the center point and N is a number of experiments.

To design experimental runs, MINITAB 16 software is used considering three parameters given in Table 1. Twenty numbers of runs were given using equation 3 by the software. (N (20) = cube points 2^K (2^3) + axial points 2 K (2*3) + replications C_P (6)). Table 2 shows all the details of 20 experiments. Equation 3 is 2nd order polynomial response equation used to associate the parameters:

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{1 \le i \le j}^{K} \beta_{ij} X_i X_j + \sum_{j=1}^{K} \beta_{ii} X_i^2 + \epsilon \quad \dots (3)$$

Table 1 — Parameter considered in the experiments

Symbols	Variables	Coded Value -1	+1
x_1	$COD:H_2O_2$	0.3	0.8
x_2	$H_2O_2:Fe^{2+}$	0.03	0.08
x_3	Time (min)	28	93

Where,
Y= Predicted response,
K= Number of factors,
x_i and x_j= coded variables,
β_0= Offset term,
β_i, β_j and β_{ij}= first-order, quadratic, and interaction effects respectively,
i and j= Index numbers for factor,
ϵ = Residual error

Results and Discussions

Table 2 gives the details of all experimental parameters, actual COD RE %, predicted COD RE % and residual. All the experiments were done by Fenton method using RSM technique. Each experiment has its own significant value. Results also displayed the effects of x_1, x_2, and x_3 on % RE. Current experiments optimize the parametric condition. COD range varied between 4% to 94% and 6.17 % to 96.83 % for the actual and predicted COD RE % respectively. RSM identified optimized value for considered factors as x_1= 0.165, x_2= 0.0165 and x_3= 115 with maximum % COD removal efficiency. Results give the synergistic effects of $COD:H_2O_2$, $H_2O_2:Fe^{2+}$ and time. The effect of both x_1 (wt ratio) and x_2 (molar ratio) on % RE increases with the same time. The % RE increases with time and x_1 but increased molar ratio decreases the % RE. The ratio of $COD:H_2O_2$, H_2O_2: Fe^{2+} and time was very important and significant aspect for the removal of COD in Advanced oxidation processes[11].

Table 2 — Three-factor central composite design and experimental results

Run	Software design: $COD:H_2O_2$	$H_2O_2:Fe^{2+}$	Time (min)	Coded value: X_1	X_2	X_3	Actual COD RE%	Predicted COD RE%	Residual
1	0	0	0	0.165	0.0165	60.5	88	87.90906	0.090939
2	0	0	0	0.09	0.024	93	60	58.74384	1.256164
3	-1	1	-1	0.165	0.0165	60	88	87.84585	0.154146
4	-1.682	0	0	0.165	0.0165	115	94	96.83216	-2.83216
5	1	1	1	0.165	0.0165	5.84	82	83.00758	-1.00758
6	0	-1.682	0	0.165	0.0165	60.5	88	87.90906	0.090939
7	-1	1	1	0.165	0.0165	60.5	88	87.90906	0.090939
8	-1	-1	-1	0.24	0.024	93	42	40.01549	1.984514
9	0	0	0	0.03886	0.0165	60.5	23	25.82151	-2.82151
10	0	0	0	0.24	0.009	93	50	49.29154	0.708463
11	1.682	0	0	0.165	0.0165	60.5	88	87.90906	0.090939
12	0	0	1.682	0.291134	0.0165	60	32	33.00174	-1.00174
13	1	1	-1	0.165	0.0165	60	88	87.84585	0.154146
14	0	0	0	0.09	0.024	28	45	43.01133	1.988671
15	-1	-1	1	0.09	0.009	93	35	32.01989	2.980113
16	0	0	-1.682	0.09	0.009	28	22	21.28738	0.71262
17	1	-1	-1	0.24	0.024	28	34	34.27002	-0.27002
18	1	-1	1	0.24	0.009	28	50	48.54607	1.453929
19	0	1.682	0	0.165	0.0038866	60.5	4	6.17808	-2.17808
20	0	0	0	0.165	0.0291134	60.5	15	16.64543	-1.64543

Table 3 shows the analysis of variance (ANOVA) fit for the COD removal. At 95% confidence, the experimental results indicate that the influence of parameter was significant to COD removal efficiency. P values indicate that regression is significant ($P< 0.0001$)[15]. Table 3 showed the square terms of wt ratio ($COD:H_2O_2$) and the molar ratio (H_2O_2: Fe^{2+}) were significant (P-value< 0.05) but the square of the time were insignificant (P-value > 0.05). Identically, the individual effects of wt ratio and molar ratio were found significant but times were not significant. The interaction between wt ratio, molar ratio, and wt ratio, time was showed significant but the interaction between molar ratio and time displayed insignificant to the COD % RE. Statistical analysis showed that lack of fit is not significant at 95% confidence level. By the error analysis, predicted and observed values were compared in each experiment to get the residual error[12]. P-values for the response (> 0.05) were determined by ANOVA showed that response equation is suitable for central composite design experiments[13-15]. The coefficient of determination (R^2) controls the fitting model. COD removal using advanced oxidation process reports the very high R^2 value (99.72 %). In this work Adj-R^2 value is 99.47 %. For the better correlation of R^2 and Adj-R^2, the value for the same near to 1. ANOVA analysis gives the best explanation of parameters and response to the regression model.

Influence of Independent Parameters

All Figures (Figure 1 to Figure 3) depicts the three-dimensional plot of parameters, which is basically for the estimation of COD removal. All Figures and their discussion are given below:

Table 3 — Analysis of variance (ANOVA) fit for the COD removal

Source	Degree of freedom	SS	MS	F -Value	Prob> F
Model	9	16752.1	1861.3	395.35	0
K-$COD:H_2O_2$	1	62.2	6155.3	824.26	0
L-$H_2O_2:Fe^{2+}$	1	132.3	9633.3	1307.37	0
M-Time	1	255.2	0.8	0.17	0.692
KL	1	648	648	137.63	0
KM	1	49.9	49.9	10.59	0
LM	1	12.5	12.5	2.65	0.134
K^2	1	4911	6165	1309.42	0
L^2	1	10703.8	10542.7	2239.24	0
M^2	1	7.3	7.4	1.56	0.239
Res.	10	47.1	4.7	*	*
LF	6	47.1	7.8	0.72	0.637

SS=Sum of Square, MS= Mean Square, Res. =Residual, LF = Lack of Fit

Influence of $COD:H_2O_2$ and $H_2O_2:Fe^{2+}$ on % COD removal

The influence of variation of wt ratio (COD: H_2O_2) and the molar ratio (H_2O_2: Fe^{2+}) on Fenton process of COD removal has been studied with the coded value of 0.3 to 0.8 and 0.03 to 0.08. Figure 1 depicts the 3D plot between $COD:H_2O_2$ and $H_2O_2:Fe^{2+}$ for COD removal using response surface method. As shown in Figure 1, % RE increases with increasing $COD:H_2O_2$ ratio.

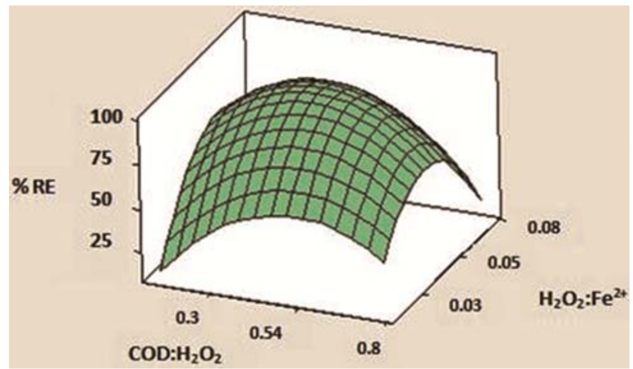

Fig. 1 — Plot of the influence of $COD:H_2O_2$ and $H_2O_2:Fe^{2+}$ on % COD RE.

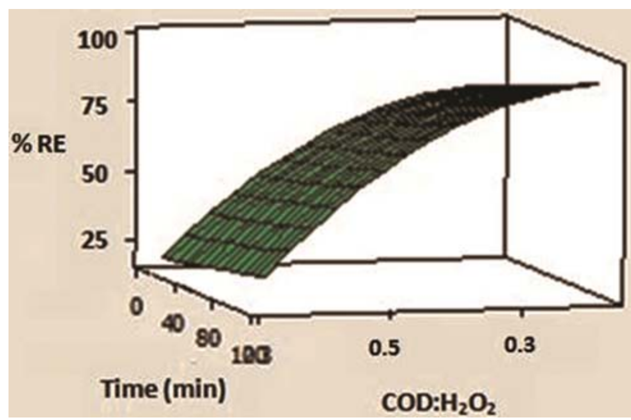

Fig.2 — Interactive effect between $COD:H_2O_2$ ratio and time (min) at $H_2O_2:Fe^{2+}$ ratio of 0.0165000

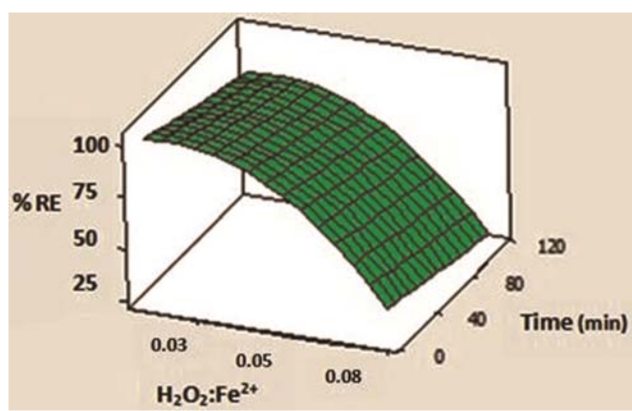

Fig. 3 — Influence of $H_2O_2:Fe^{2+}$ ratio and time (min) for Fixed $COD:H_2O_2$ ratio = 0.165

Similarly, % RE increases with increasing H_2O_2:Fe^{2+} up to 94 %. But for both the cases (COD:H_2O_2 and H_2O_2:Fe_2^+**)** after optimum value, % RE decreases. This occurrence might be due to the generation of hydroperoxy radical ($HO_2^•$) with the reaction of $^•OH$ radical and an excess amount of H_2O_2, which has very less oxidizing potential compared to $^•OH$ radical[6]. This is also defined as scavenging effect.

The interactive effect of COD/H_2O_2 ratio and time on % COD removal

The influence of variation of wt ratio (COD:H_2O_2) and time (min) on Fenton process of COD removal has been studied with a coded value of 0.3 to 0.8 and 28 to 93 min. Figure 2 depicts the interactive plot between COD:H_2O_2 ratio and time (min) at predetermined H_2O_2:Fe^{2+} ratio of 0.0165000. The figure shows that at a certain ratio of COD:H_2O_2, % RE attain a maximum value of 94% occurs at more than 90 min of the process, but again it decreases with the increase of COD:H_2O_2 due to excess amount of hydrogen peroxide with the ratio of 0.3 to 0.8. % RE increases with increase in time of 28 to 93 min but comparatively, it was very low.

Influence of H_2O_2:Fe^{2+} ratio and time on % COD removal

The influence of variation of molar ratio (COD:Fe^{2+}**)** and time (min) on Fenton process of COD removal has been investigated with a coded value of 0.03 to 0.08 with 28 to 93 min. Figure 3 depicts the 3D plot between H_2O_2:Fe^{2+} ratio and time with % COD removal. Figure shows that with a small ratio of H_2O_2:Fe^{2+} ratio and time, % COD removal of more than 90% occurs at 115 min. Figure 3 indicates that with the increase in time from 28 to 93 min, removal efficiency slightly decreases. With the certain molar ratio of COD:Fe^{2+} and time (min), % RE was maximum due to the generation of hydroxyl radical ($^•OH$) but after some time it decreases with less availability of hydrogen peroxide. The plot shows the performance effect of H_2O_2:Fe^{2+} ratio and time with % RE.

Experimental confirmation and optimization

The aim of present work is to achieve maximum COD removal. The Optimized condition for the factors of COD:H_2O_2 (wt:wt), H_2O_2:Fe^{2+} (molar ratio), time (min) and COD removal efficiency % were found 0.165000, 0.0165000, 115 and 94% respectively. This study shows the use of RSM for the optimization of COD removal with advanced oxidation process is significant because the values of P is less than 0.05 and regression value near to 1 which shows that model is significant[11]. Table 2 shows that with the optimized values of the experiment showed very less residual value i.e. observed results are nearer to the predicted value. It proves the significance of the model.

Conclusions

The present study was employed by the response surface methodology (RSM) for COD removal using Fenton process. Initial COD was 32000 mg/l and after treatment, it was decreased to 1920 mg/l. Influence of all the factors(x_1, x_2, and x_3) on COD removal was investigated and expressed in 3-D contour plots. Most of the terms were found significant from CCD design analysis (x_1, x_2, x_1x_2, x_1x_3 and square of x_1 and x_2). However, time, x_2x_3, square of x_3 and lack of fit were not found significant (P-value> 0.05). Predicted and observed values are very close (less residual value) which proves the significant experimental confirmation. In the present study, interactive influences of parameters were also studied, which gives the significant conclusion among them. Excess or less amount of hydrogen peroxide reduces oxidation reaction due to the formation of undesirable radicals. Optimized values for COD removal were: 0.165000, 0.0165000, 115, and 94% for COD:H_2O_2, H_2O_2:Fe^{2+}, time and % RE (COD) respectively. ANOVA (Analysis of Variance) gives the satisfactory regression value R^2 of 99.72 % and Adj-R^2 of 99.47 %, which proves the experimental data is fit for the model.

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