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Wet oxidation of coking wastewater: Optimization of degradation parameters through RSM

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Present study deals with the degradation of COD contained in coking wastewater using catalytic wet air oxidation process. The investigated experimental parameters were pH, temperature ($T^{\circ}\text{C}$), air partial pressure (p_{air}), catalyst loading (C_w) and time (t_R). Among various catalysts, copper chloride was found to best for degradation of COD. The optimum condition evaluated for the degradation of organic compounds using Response Surface Methodology (RSM) was $T = 159.93^{\circ}\text{C}$, $p_{\text{air}} = 5.80$ MPa, $C_w = 3.1 \text{ kg/m}^3$ and $t_R = 5.98 \text{ h}$. The central composite design (CCD) was used for the experimental design and optimization of the process. Analysis and interaction between the four most important operating variables T , p_{air} , C_w and t_R were studied. ANOVA analysis of variance showed the good regression coefficient with $R^2 = 0.977$ for the degradation of COD.

Keywords: Catalytic wet air oxidation, coking wastewater, response surface methodology, COD.

Introduction

Iron and steel industries are come under the profitable industries in India. It was the largest producer of raw steel and sponge iron in the world during 2014-2016¹. The wastewater produced by the iron and steel industries are called coking wastewater (CWW), and comes under hazardous effluent as it contains cyanide, thiocyanide, ammonium nitrogen, phenolic compounds, sulphate, polynuclear-aromatic etc. Most of them are highly toxic and causes harmful effects to environment and ecology too²⁻⁴. Thus, it must be treated before discharge into water bodies. CWW is produced during coke conversion process; in this process coal is heated at high temperature in absence of air to produce coke, which is the raw material of blast furnace to manufacture iron and steel⁵. Hot coke produced during carbonization is cooled by spraying of water, during this process huge amount of water was used and becomes polluted due to transfer of chemicals from coke to water. The polluted water is called coking wastewater (CWW) or coke oven wastewater.

Wet air oxidation (WAO) is the simplest oxidation technique⁶ for the treatment of industrial wastewater containing highly concentrated organic pollutants. In WAO process high temperature ($100\text{--}320^{\circ}\text{C}$) and high oxygen pressure ($1\text{--}20$

bar) is used as oxidize organic pollutants present in water and convert into CO_2 and H_2O ⁷. Although, WAO is the effective process, but it requires high temperature and high pressure which increases its cost⁸, thus, to reduce the cost and time WAO is performed in presence of catalyst called catalytic wet air oxidation. CWAO increases the rate of reaction and reduces temperature, pressure and treatment time⁸. Literature review of CWAO process shows it is an effective treatment technique for acetic acid present in solutions (aqueous) over noble metal catalysts⁹. Treatment of methylamine over manganese dioxide catalyst¹⁰. Removal of phenol studied using catalyst like Ru and Pt were supported on $\text{TiO}_2/\text{CeO}_2$ oxide for CWAO process and the catalyst were prepared by sol-gel process as TiO_2 , TiCe_5 , TiCe_{10} , TiCe_{25} , TiCe_{50} , TiCe_{75} , CeO_2 ¹¹ and the degradation of three phenolic compounds such as phenol, *o*-cresol and 2,5-dimethyl phenol has been studied by catalytic wet air oxidation¹².

In present study various type of catalysts were tested for the degradation of CWW. The parameters like T , p_{air} , C_w , t_R and pH were selected to find out its effects on oxidation of CWW. Optimization of COD removal was performed by using RSM. The experiments were designed using CCD which is good tool for the optimization of the process.

Experimental

Material:

Coking wastewater was arranged from BSP, Chhattisgarh, India. AR grade chemicals for analysis and LR grade chemicals for CWAQ were used. Chemicals were purchased from Merck and Rankem Ltd., India. Various catalysts like CuCl_2 , CuNO_3 , MnCl_2 , V_2O_5 , and CeO_2 were used for WAO. Among these performances CuCl_2 was best; therefore it was selected for RSM studies.

RSM analysis methods:

Response surface methodology is generally used for the experimental designing, modeling and evaluation by using mathematical and statistical techniques for several independent variables to find out the optimum condition for desirable responses¹³. It is having two most common designs namely central composite design¹⁴ and box-behnken design¹⁵. In present study central composite design was used. The RSM was performed using MINITAB version 17.1.0.0. The percentage reduction of COD was calculated by using equation;

$$Z\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

where, C_0 = COD initial value, C_t = COD at different time, and Z = COD percentage reduction.

Experimental design and optimization:

CCD was generally used for designing the experimental data's and to determine the optimum condition for pollutants removal using RSM. It has been developed and well designed for fitting a quadratic equation, which generally works better for the optimization of different processes^{16,17}. The experimental data were designed and optimized through the software called MINITAB. Regression model was developed by choosing the levels and ranges of four independent variables including T , p_{air} , C_w and t_R ¹⁸, which is presented in Table 1. The experimental results obtained from the model and fitted in the equation given below:

$$Z = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j + e_i \quad (2)$$

where, Z = predicted response, b_0 = offset, b_i = first order,

Table 1. Selected parameter ranges and levels for Response surface methodology studies

Selected parameters	Factors	Range and levels		
		-1	0	1
Temperature (°C)	X1	100	130	160
p_{air} (MPa)	X2	2	4	6
Catalyst mass loading (kg/m ³)	X3	2	3.5	5
Reaction time (h)	X4	2.5	4.25	6

b_{ii} = quadratic and b_{ij} = interaction effects, n = number of factors, x_i and x_j = coded variables, i and j = index number for factor and e_i = residual error, presented by researcher¹⁵.

Results and discussion

Statically analysis and modeling:

Experiments were designed to get experimental and predicted COD percentage reduction of total 31 sets¹⁹. The reduction efficiency for each set of experiment was calculated by using eq. (3) and results are listed in Table 2. The experimental values are quite closure to predicted values obtained from eq. (3). Fig. 1 shows the predicted and actual values of COD reduction. The quadratic equation between the independent variables and response are given in terms of coded variables by eq. (3).

$$\begin{aligned} \% \text{ COD removal} = & 55.2 - 0.995 X_1 + 7.25 X_2 + 21.23 X_3 \\ & + 1.38 X_4 + 0.0035 X_1 X_1 - 0.569 X_2 X_2 - 2.249 X_3 X_3 + 0.251 \\ & X_4 X_4 - 0.01770 X_1 X_2 + 0.0330 X_1 X_3 + 0.0414 X_1 X_4 - 0.039 \\ & X_2 X_3 + 0.277 X_2 X_4 - 1.164 X_3 X_4 \end{aligned} \quad (3)$$

Analysis of variance:

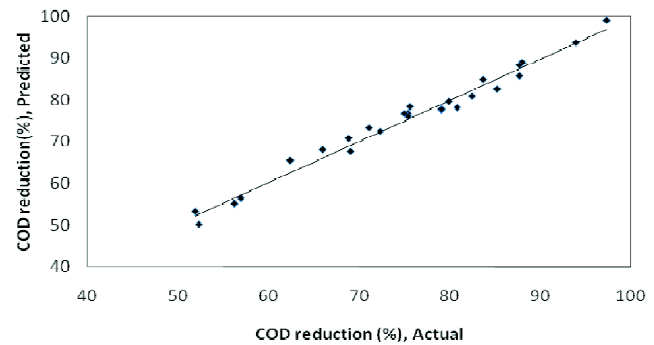
Analysis of variance was generally used to fit the model for statistical significance. It includes many mathematical terms such as mean square, sum of square (R^2), degree of freedom, R^2 predicted (pred.), R^2 adjusted (adj.), p (probability), F (Fischer's) value, and so on have been shown by some researchers^{20,21}. The experimental data signifies by two parameters and they are p value and F value. P is a probability value of independent variable on the dependent variables. F (>1) should be greater than one and p value should be less than 0.05 (<0.05) indicates better fit of the experimental data to the design model. R^2 is defining as the degree of fitness of model with the experimental data lies between 0 and 1. R^2 values must be higher and the value of R^2 adj and R^2 pred should be smaller than R^2 .

Table 2. Optimization using RSM for COD degradation using CWAO

Run order	X ₁	X ₂	X ₃	X ₄	Experimental (% COD)	Predicted (% COD)
1	160	2	2.0	2.50	51.85	53.25
2	130	4	3.5	6.00	87.98	88.85
3	100	6	5.0	6.00	87.65	85.68
4	130	4	2.0	4.25	62.34	65.59
5	130	4	3.5	4.25	78.99	77.68
6	160	2	5.0	2.50	75.30	76.62
7	100	2	5.0	2.50	68.99	67.71
8	100	2	2.0	2.50	52.21	50.28
9	130	4	3.5	4.25	78.99	77.68
10	100	6	2.0	6.00	82.46	80.94
11	160	4	3.5	4.25	83.64	84.92
12	160	6	2.0	6.00	87.65	88.36
13	160	6	2.0	2.50	56.17	55.17
14	160	6	5.0	6.00	97.32	99.05
15	100	6	5.0	2.50	70.99	73.41
16	130	4	3.5	4.25	78.99	77.68
17	160	6	5.0	2.50	80.76	78.07
18	100	6	2.0	2.50	56.87	56.45
19	100	2	2.0	6.00	68.78	70.90
20	160	2	5.0	6.00	93.87	93.72
21	130	4	3.5	4.25	78.99	77.68
22	130	4	3.5	4.25	78.99	77.68
23	130	4	5.0	4.25	79.86	79.65
24	130	4	3.5	2.50	65.88	68.06
25	130	4	3.5	4.25	78.99	77.68
26	100	4	3.5	4.25	74.98	76.75
27	130	4	3.5	4.25	78.99	77.68
28	130	2	3.5	4.25	72.22	72.54
29	100	2	5.0	6.00	75.30	76.11
30	130	6	3.5	4.25	75.55	78.28
31	160	2	2.0	6.00	85.18	82.57

The F and p values obtained from analysis of variance for model are shown in Table 3. For COD reduction, F and p value obtained are 49.87 and 0.000. A large F and low p value signifies most of the variation in responses and explained by the regression and developed model²⁰. The COD removal through RSM has been studied and reported to F value = 9.92 and p value = <0.0001 for the treatment of distillery wastewater¹⁷. Our F and p values are comparatively good to these values. For COD $R^2 = 0.977$, R^2 (adj) = 0.958; and R^2 (pred) = 0.867 have been determined. The close val-

ues of R^2 (pred) and R^2 (adj) suggested the high significance and close relation experimental and predicted values obtained from eq. (3). The R^2 values are better in present case to $R^2 = 0.914$ reported for the treatment of distillery effluent²². The experimental and predicted values of pollutant (COD removal) are presented in Fig. 1 and the linear regression fit tendency was shown for COD removal.

**Fig. 1.** Experimental and predicted COD percentage reduction from RSM.

Effect of selected parameters:

Effect of four selected parameters on the COD removal by CWAO is presented in Fig. 2. The pollutants degradation was increased with increase in p_{air} , C_w , T , and t_R . The value of F and P are presented in Table 3 for COD degradation. The F values are high and p values are low for all T , C_w , p_{air} and t_R effect on treatment of CWW.

Interaction effects of selected parameters:

Effects of selected parameters such as T , C_w , p_{air} and treatment time for CWAO of CWW has been discussed²³ as below. The interaction effects between temperature and pressure on CWAO using RSM are shown in Fig. 2a. It indicates temperature and pressure both are influence to each other up to certain extent for the CWAO process. As the p_{air} increases, the degradation of organic pollutants of effluent also increases, until the completely consumption of p_{air} in the reaction medium. Similarly, as the temperature rises, degradation of organic pollutants increases due to collision increases between the species including air with pollutants. Fig. 2b shows the interaction effect between T and C_w for COD removal. When the temperature was increased with catalyst mass loading, the degradation of organic compounds was also increased²³. Fig. 2c shows, as the temperature in-

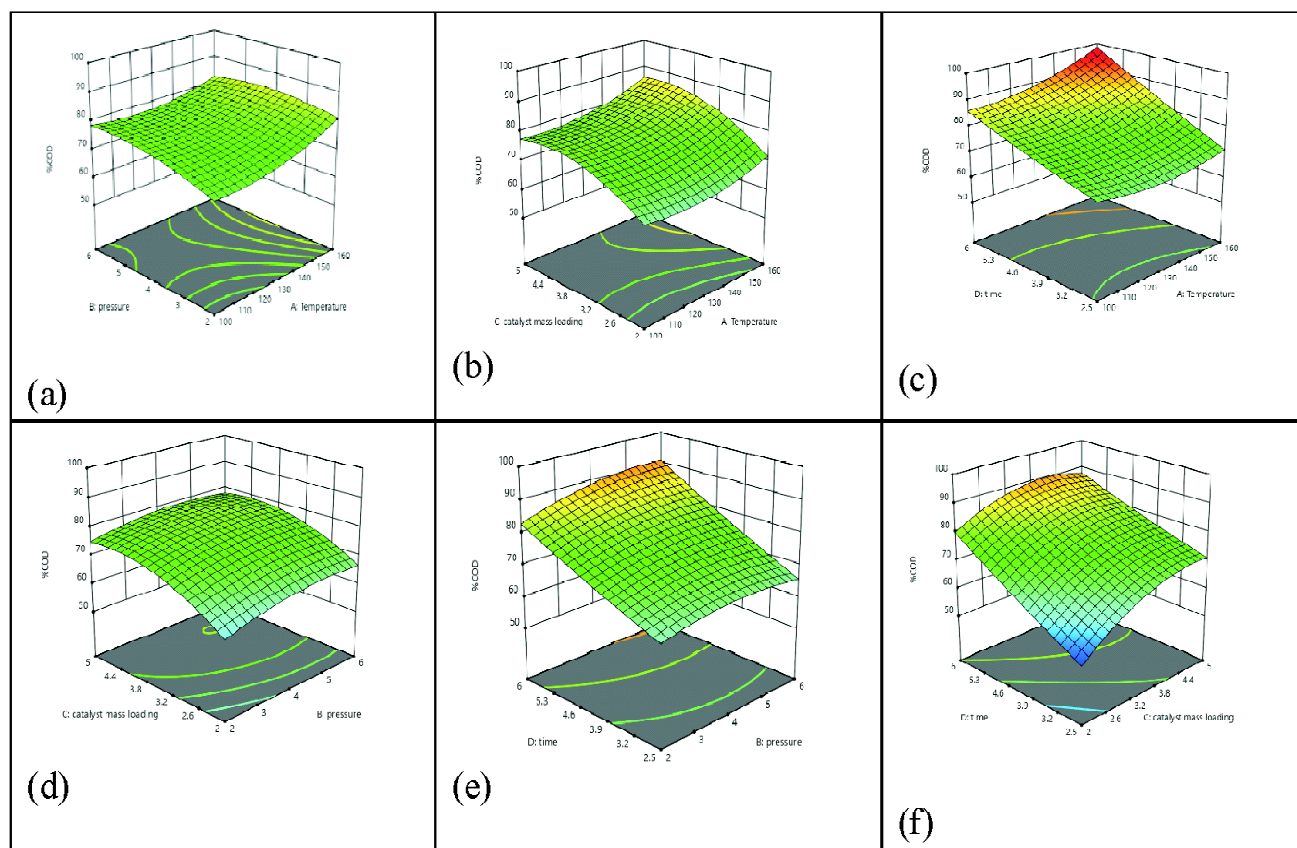


Fig. 2. Shows the COD reduction graph of three dimensional response.

creased, the reduction of organic pollutant was also increased with time. Fig. 2d as pressure was increased with catalyst mass loading; rate of reaction or degradation of organic compounds was also increased. The p value is 0.842, respectively as presented in Table 3. Fig. 2e as p_{air} was increased with time keeping constant temperature, the degradation of CWW was also increased. Effect of interaction between catalyst and time at constant temperature and air pressure²³ is shown in Fig. 2f. As the catalyst mass loading was increased the degradation of pollutants with respect to time was also

Table-3 (contd.)

Table 3. Analysis of variance for COD percentage removal through CWAQ

Source	DF	Sum of square	Mean of square	F value	p value
Model	14	3725.47	266.10	49.87	0.000
Linear	4	3284.51	821.13	153.88	0.000
X1	1	300.21	300.21	56.26	0.000
X2	1	148.61	148.61	27.85	0.000

X3	1	889.44	889.440	166.68	0.000
X4	1	1946.26	1946.26	364.73	0.000
Square	4	147.29	36.82	6.90	0.002
X_1^2	1	25.75	25.75	4.83	0.043
X_2^2	1	13.43	13.43	2.52	0.132
X_3^2	1	66.44	66.440	12.45	0.003
X_4^2	1	1.54	1.54	0.29	0.599
2 way interaction	6	293.67	48.94	9.170	0.000
X_1X_2	1	18.04	18.04	3.38	0.085
X_1X_3	1	35.37	35.370	6.63	0.020
X_1X_4	1	75.73	75.73	14.19	0.002
X_2X_3	1	0.22	0.220	0.04	0.842
X_2X_4	1	15.04	15.04	2.82	0.113
X_3X_4	1	149.27	149.270	27.97	0.000
Error	16	85.38	5.34		
Lack of fit	10	85.38	8.54	*	*
Pure error	6	0.00	0.00		
Total	30	3810.85			

increased, because catalysis provides an alternate energy path which lowers the activation energy. The p value between the catalyst and time interaction is 0.000 which shows highly interaction effect.

From RSM studied, optimization of COD reduction was obtained. The optimum value of $T = 159.93^\circ\text{C}$, $p_{\text{air}} = 5.80$ MPa, $C_w = 3.19$ kg/m³ and $t_R = 5.98$ h was found with maximum 96.86% COD reduction. Thus the treated CWW has COD = 51 mg/dm³. The results are better to earlier studied reported by Demirel *et al.*²⁴, in which 89.5% COD reduction were obtained using expensive Ce-Cu (1:2) metal oxide catalyst and carrier $\gamma\text{-Al}_2\text{O}_3/\text{TiO}_2$ catalyst²¹. They have reported only COD reduction, RSM optimization has not been reported by investigators.

Conclusions

The degradation of COD was performed by using CWAO process. Results show that T , p_{air} , C_w and t_R played an important role in the process. As the temperature increases, collision between oxidant and catalyst also increases causes more degradation of pollutants. The process was optimized by RSM based on CCD model. The optimum operating conditions of the process was evaluated to $T = 159.93^\circ\text{C}$, $p_{\text{air}} = 5.80$ MPa, $C_w = 3.19$ kg/m³ and $t_R = 5.98$ h. At this operating condition, maximum percentage reduction of COD was 96.86%. The treated CWW has COD = 51 mg/dm³. The effect of four independent variables and there interaction on COD reduction were also studied. ANOVA showed the high regression coefficients for the COD reduction with $R^2 = 0.977$. Results show CWAO to be prominent method for the treatment of CWW for the reduction of highly concentrated pollutants.

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