Optimization of *In-situ* Electro-oxidation of Formaldehyde by the Response Surface Method

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This investigation attempted to study electrochemical oxidation of formaldehyde at lower concentrations. Experiments were carried out in a batch electrochemical reactor using commercially available RuO_2 coated titanium and SS as anode and cathode respectively and covering a wide range in operating conditions. Further, the statistical tool Response surface methodology by Box-Behnken design was used to examine the influence of individual parameters on electro-oxidation of formaldehyde, and the quadratic model for formaldehyde removal efficiency was derived. It was observed that the model predictions match well with experimental values with a R^2 value of 0.999.

Key words:
In-situ electro-oxidation, formaldehyde degradation, Response surface methodology, Box-Behnken design, optimization

Introduction

The quantum of wastewater generated is being increased with increase in process industries and development of human activities. Besides inorganic materials (heavy metals, acids and salts), industrial wastewater contains many toxic organic pollutants. Formaldehyde is one of the toxic pollutants that poses a serious threat as it is a carcinogen. The extensive industrial applications of formaldehyde have resulted in an increased concentration above the tolerance level in industrial wastewater. Conventionally, effluents containing formaldehyde are treated by chemical and biochemical methods. Murphy *et al.*[1] have studied formaldehyde oxidation using Fenton's reagent and reported more than 90 % oxidation. Garrido *et al.*[2] experimented oxidation of formaldehyde using the biochemical technique and observed that the formaldehyde degradation was effective only at lower concentration.

Treatment of organic pollutants using *in-situ* electro-generated hypochlorite ion has gained greater attention in recent years due to its capability of complete degradation without generating any solid waste. This technique has been successfully applied for the treatment of several industrial effluents.[3–5] Olivi *et al.*[6] experimented formaldehyde degradation through electrochemical technique and verified the effect of electrode structure on degradation. Do and Chin[7] studied formaldehyde degradation using *in-situ* electro-generated hydrogen peroxide and reported the influence of temperature and initial concentration on electro-oxidation. While Do *et al.*[8] have reported more than 90 % formaldehyde degradation using *in-situ* electro-generated hypochlorite ion. The objective of this investigation is to treat formaldehyde effluent by *in-situ* electro-oxidation using oxide coated anodes. Further, it was attempted to optimize the electro-oxidation process using the response surface method (RSM).

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Theory of electro-oxidation

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically, two different processes occur at the anode; on the anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on the metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where they are generated continuously (indirect electrolysis). In direct electrolysis, the rate of oxidation depends on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium or potassium are added for better conductivity and generation of hypochlorite ions.[9] The reactions of anodic oxidation of chloride ions to form chlorine is given as

Reaction at the anode

$$2Cl^- \xrightarrow{k_1} Cl_2 + 2e^- \quad (1)$$

While at the cathode, the water electrolyzed to hydrogen and OH^- radicals

$$2H_2O + 2e^- \xrightarrow{k_2} H_2 + 2OH^- \quad (2)$$

The liberated chlorine formed hypochlorous acid and further dissociated to give hypochlorite ion

$$Cl_2 + H_2O \xrightarrow{k_3} H^+ + Cl^- + HOCl \quad (3)$$

$$HOCl \xleftarrow{k_4} H^+ + OCl^- \quad (4)$$

The overall desired reaction for electrochemical treatment of formaldehyde can be given as

$$HCHO + OCl^- \xrightarrow{k_5} CO_2 + H_2O + Cl^- \quad (5)$$

The generated hypochlorite ions act as the main oxidizing agent in the pollutant degradation. The rate of electro-oxidation of organic pollutants depends on the electrode catalytic activity, organic compounds diffusion rate and applied current density. A generalized reaction scheme of electrochemical conversion/combustion of organics of pollutants on noble oxide coated anode is available in the literature.[10] The eq. (5) confirms that the formaldehyde present in the effluent is converted into CO_2 with the help of generated hypochlorite ions.

Materials and methods

Response surface method

Response surface method (RSM) is a statistical and mathematical technique used for modeling and optimization of process in which a response of interest is influenced by several variables. The RSM has important application in the design, development and formulation of new products, as well as in the improvement of existing product design. It defines the effect of the independent variables on the process either individually or collectively. Further, the experimental methodology generates a mathematical model, which describes the chemical or biochemical processes. Response surface method has been very popular for optimization studies in recent years. The design procedure of the RSM is as follows[11]

(i) Designing of a series of experiments for adequate and reliable measurement of the response of interest.

(ii) Developing a mathematical model of the second order response surface with the best fittings.

(iii) Finding the optimal set of experimental parameters that produce a maximum or minimum value of response, and

(iv) Representing the direct and interactive effects of process parameters through two and three-dimensional plots.

In the present study, the RSM has been used to determine the relation between percentage COD removal with operating parameters such as time, current density, effluent concentration and pH. Table 1 gives the parameters and the operating ranges covered in the present investigation. The electrolysis time, current density, initial concentration of formaldehyde and electrolyte pH are referred by uncoded variables as *A*, *B*, *C* and *D* respectively. The uncoded variables are converted as coded variables of *a*, *b*, *c* and *d* using the following equation[12]

$$a = \frac{A - \left(\frac{A_{max} + A_{min}}{2}\right)}{\frac{A_{max} - A_{min}}{2}} \quad (6)$$

Table 1 – *Range of independent variables used in formaldehyde degradation*

Factor	Variable	Unit	Range and level of actual and coded values		
			−1	0	+1
A	time	min	60	180	300
B	current density	A dm^{-2}	3	4	5
C	formaldehyde conc.	mg L^{-1}	156	298	440
D	pH	–	5	7	9

A general quadratic regression model equation relating the variables for a Box-Behnken design can be given as[13]

$$y = k_0 + k_a A + k_b B + k_c C + k_d D + k_{aa} A^2 + k_{bb} B^2 + k_{cc} C^2 + k_{dd} D^2 + k_{ab} AB + k_{ac} AC + k_{ad} AD + k_{bc} BC + k_{bd} BD + k_{cd} CD \quad (7)$$

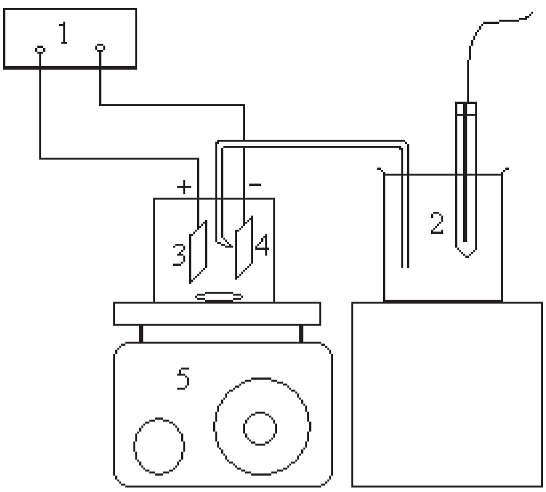
where *y* represents the predicted response; k_0 is a constant. The Box–Behnken experimental design has been chosen to find the relationship between the response functions and variables using a statistical tool MINITAB 14 (PA, USA). In the Box–Behnken method a total number of 29 experiments, with five centre points, were necessarily carried out to estimate the percentage COD removal of formaldehyde**.** The interaction between the variables and the analysis of variance (ANOVA) was studied by using RSM. The quality of the fit of this model is expressed by the coefficient of determination R^2 and adjusted R^2. The fit was confirmed by means of the absolute average deviation (AAD) defined as[12]

$$AAD = \left\{ \frac{\sum_{i=1}^{p} \left(\frac{\left| y_{i,\mathrm{exp}} - y_{i,\mathrm{pred}} \right|}{y_{i,\mathrm{exp}}} \right)}{p} \right\} \cdot 100 \qquad (8)$$

where $y_{i,\mathrm{exp}}$ and $y_{i,\mathrm{pred}}$ refer to the experimental and predicted responses and p refers to the number of experimental runs.

Experimental

The schematic diagram of the experimental setup given in Fig. 1 consists of a glass beaker of 250 mL capacity. Proper provisions were made in the lid for electrode and periodic sampling. Commercially available oxide coated titanium and stainless steel with 7x5 cm^2 dimensions were used as anode and cathode respectively. Experiments were conducted using synthetic effluent prepared at various formaldehyde initial concentrations. The experimental conditions were designed by the Box-Behnken of Response surface methodology. All the experiments were carried out under galvanostatic conditions using a DC-regulated power source (HIL model 3161) of 0–5 A and 0–30 V. The electrode potentials were measured using reference electrode (saturated calomel electrode) connected to the working electrode and sufficient agitation was provided using a magnetic stirrer to the electrochemical cell to maintain uniform concentration. Samples were collected at regular intervals of time for COD estimation.[14]



F i g . 1 .– *Experimental setup: 1) DC power supply, 2) saturated calomel electrode, 3) anode, 4) cathode, 5) magnetic stirrer*

Results and discussion

Table 2 gives the experimental observations of formaldehyde oxidation under various operating conditions designed by Box-Behnken. The analysis

T a b l e 2 – *Actual design of experiments and response for formaldehyde degradation*

Run	*A*	*B*	*C*	*D*	COD removal %
1	60	3	298	7	28.2
2	60	4	440	7	37.3
3	60	4	298	9	42.7
4	60	5	298	7	62.2
5	60	4	298	5	40.2
6	60	4	156	7	48.7
7	300	5	298	7	91.1
8	300	4	298	9	87.4
9	300	4	298	5	76.1
10	300	3	298	7	79.1
11	300	4	440	7	77.3
12	300	4	156	7	92.4
13	180	3	298	9	64.8
14	180	5	440	7	77.6
15	180	3	156	7	69.6
16	180	4	156	9	84.9
17	180	5	298	5	81.8
18	180	5	156	7	93.2
19	180	3	440	7	58.1
20	180	4	440	9	65.8
21	180	4	440	5	62.4
22	180	5	298	9	86.2
23	180	3	298	5	54.8
24	180	4	156	5	71.8
25	180	4	298	7	70.1
26	180	4	298	7	71
27	180	4	298	7	70.7
28	180	4	298	7	70.8
29	180	4	298	7	71.2

was focused on COD removal and it could be observed from Table 2 that a maximum COD removal of 93 % was achieved under typical operating conditions. The mathematical relationship between the independent variables and their responses can be related in terms of coded variables as

$$\% COD = 70.76 + 20.34\,a + 11.46\,b - 6.84\,c + 3.73\,d - 8.11\,a^2 + 2.39\,b^2 + 1.44\,c^2 - 1.09\,d^2 - 5.5ab - 0.93\,ac + 2.2\,ad - 1.03\,bc - 1.4\,bd - 2.43\,cd \quad (9)$$

The eq. (9) can also be represented in terms of uncoded variables as

$$\% COD = -61.72 + 0.51A + 7.67B + 7.8\cdot 10^{-3}C + 9.37D - 6\cdot 10^{-4}A^2 + 2.39B^2 + 7\cdot 10^{-5}C^2 - 0.27D^2 - 4.6\cdot 10^{-2}AB - 5\cdot 10^{-5}AC + 9.2\cdot 10^{-3}AD - 7.2\cdot 10^{-3}BC - 0.7BD - 8.5\cdot 10^{-3}CD \quad (10)$$

The performance of model equations was verified under the following headings:

– Adequacy
– Significance of operating parameter
– Combined effect of the operating parameters on formaldehyde removal
– Optimization for maximum removal efficiency.

Adequacy

The model predictions using eq. (9) were compared with the experimental observations in Fig. 2 and it was ascertained that the model predictions matched satisfactorily with the experimental values. Further, the model equation was validated by a probability plot as given in Fig. 3 with normal residuals distribution. It can be noticed from Fig. 3 that the proposed model matches with experimental values satisfactorily. The adequacy of the model was also verified by absolute average deviation

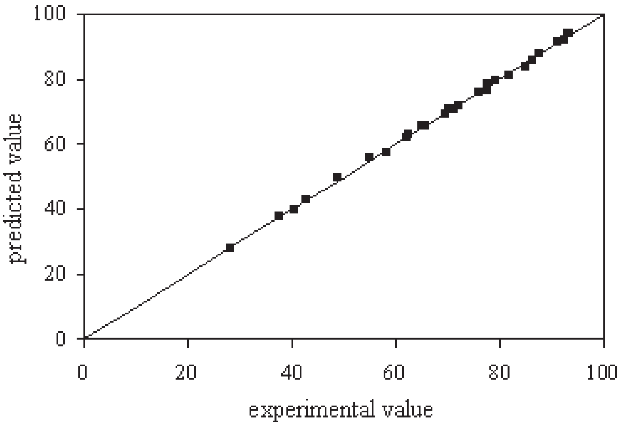


Fig. 2 – *Comparison of experimental observations of formaldehyde degradation with predicted value using eq. (9)*

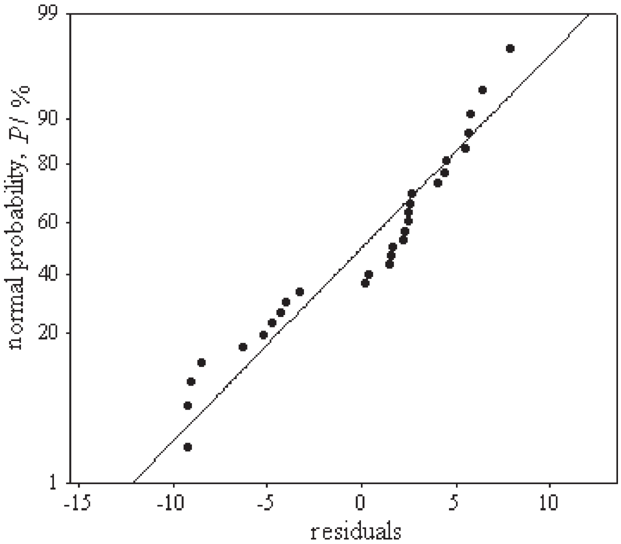


Fig. 3 – *Normal probability plot of the residuals obtained from the model for formaldehyde degradation*

(AAD) using the eq. (8). It has been observed an AAD value of 0.74176 % for the present experimental runs, which shows that model predictions match adequately with experimental values.

Significance of operating parameters

The significance of regression coefficents were analysed using *p*- and *t*-test. The '*p*', '*t*' and significant level (1-*p*) values of formaldehyde degradation are given in Table 3. Larger magnitude of '*t*' value

Table 3 – *Estimated regression coefficient and corresponding 't' and 'p' values for percentage COD removal*

Factor	Coefficient of the model in coded factors	'*t*' value	'*p*' value	Significance level
model	70.76	206.865	0.000	> 99 %
a	20.3417	92.128	0.000	> 99 %
b	11.4583	51.895	0.000	> 99 %
c	-6.8417	-30.986	0.000	> 99 %
d	3.725	16.871	0.000	> 99 %
axa	-8.1133	-27.016	0.000	> 99 %
bxb	2.3867	7.947	0.000	> 99 %
cxc	1.4367	4.784	0.000	> 99 %
dxd	-1.0883	-3.624	0.003	> 99 %
axb	-5.5	-14.382	0.000	> 99 %
axc	-0.925	-2.419	0.03	97 %
axd	2.2	5.753	0.000	> 99 %
bxc	-1.025	-2.68	0.018	> 98 %
bxd	-1.4	-3.661	0.003	> 99 %
cxd	-2.425	-6.341	0.000	> 99 %

and lesser values of '*p*' confirm the significance of variables in the model equations. In statistical modeling, more than 0.05 of *p*-value is not considered as a significant parameter.[15] It can be observed from Table 3 that for the present model the *p* values for linear, quadratic, and interaction terms are less than 0.05, which shows that the parameters are significant in the model equations.

The significant effect of process variables was verified using ANOVA and the results are presented in Table 4. The $F_{statistics}$ comparison was performed at 5 % level. It can be noticed from Table 4 that the $F_{statistics}$ values for percentage COD removal responses are higher, indicating that the variation in the responses can be explained by the present model. Further, the associated *P* value was used to estimate whether the $F_{statistics}$ values were large enough to indicate statistical significance.

Table 4 – *Analysis of variance (ANOVA) for percentage COD removal*

Source	Degree of freedom	Sum of squares	Mean squares	$F_{statistics}$	P
regression	14	8018.72	572.77	979.05	0.000
linear	4	7269.13	1817.28	3106.34	0.000
square	4	570.24	142.56	243.68	0.000
interaction	6	179.35	29.89	50.09	0.000
residual error	14	8.19	0.59		
lack-of-fit	10	7.5	0.75	4.33	0.085
pure error	4	0.69	0.17		
Total	28	8026.91			

R^2 = 0.999, R^2_{adj} = 0.998

The $F_{statistics}$ of the present model was significant at the 5 % level (i.e. $P < 0.05$), which shows the model matched with experimental values and can explain the significance of individual parameters. It can be noticed that the simulated $F_{statistics}$ value of 979.05 (Table 4) is much higher than the standard $F_{0.05\ (14,\ 14)}$ value of 2.49 showing that the COD removal is significant. Further, the simulated lack of fit value of 4.33 is less than the standard $F_{0.05\ (10,\ 4)}$ value of 5.96 at 5 % level shows that the present model can predict COD removal for the given range of variables.

In general, a *P* value of less than 0.01 is considered to be significant in statistical model. It can be noticed from Table 4 that *P* values obtained using eq. (9) or (10) is 0.000 show that the present model is significant. The present model equations were further checked by regression coefficients (R^2 and R^2_{adj}). It can be seen from Table 4 that the values of R^2 and R^2_{adj} closure to 1 indicates that the model is highly significant.

The combined effect of operating parameters on formaldehyde removal

The RSM was applied for degradation of formaldehyde effluent and the results are presented in both surface and contour plots. The analysis was carried out to check the influence of various operating parameters on pollutant degradation and the optimization was obtained based on the influence of individual parameters. The effects of variables on electro-oxidation of formaldehyde are depicted in Fig. 4–6.

The surface and contour plot of formaldehyde degradation is given in Fig. 4. It can be ascertained from Fig. 4a that the percentage removal of formaldehyde increases with increase in time and current

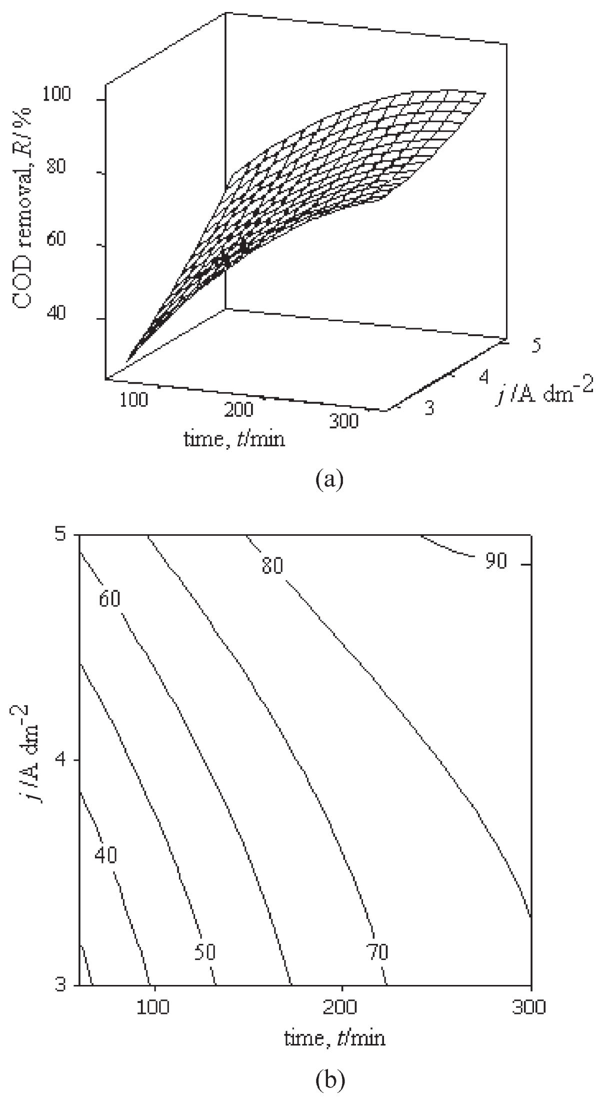
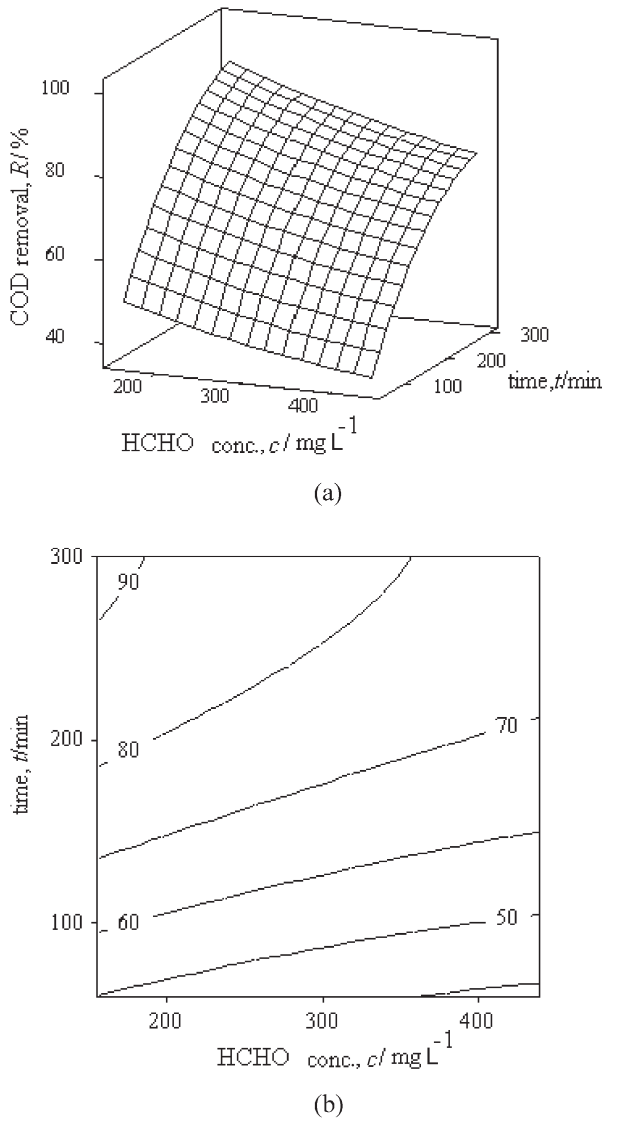
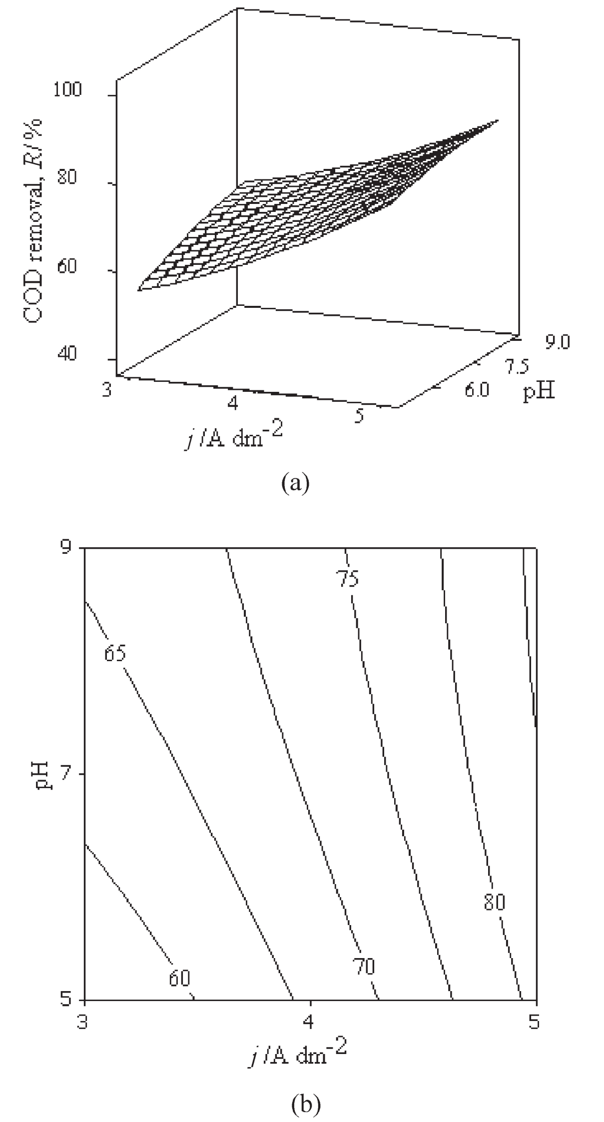


Fig. 4 – *Combined effects of current density and electrolysis time on percentage COD removal, (a) Response surface, (b) Contour plot; HCHO initial conc.: 298 mg L^{-1}; pH 7.0*



F i g . 5 – *Combined effects of formaldehyde concentration and electrolysis time on percentage COD removal, (a) Response surface, (b) Contour plot; j = 4 A dm*$^{-2}$*; pH 7.0*



F i g . 6 – *Combined effects of current density, pH on percentage COD removal, (a) Response surface, (b) Contour plot; electrolysis time: 180 min; HCHO initial conc.: 298 mg L*$^{-1}$

density. This can be explained that the generation of hypochlorite ion increases with current density, which eventually increases the formaldehyde degradation. It was also observed from contour plot (Fig. 4b) that the maximum COD removal can be achieved at maximum current density and time for the given operating range of variables.

The combined effect of formaldehyde initial concentration and the electrolysis time on formaldehyde degradation is given in surface and contour plots (Fig. 5). It can be ascertained from the Fig. 5a that the percentage removal of formaldehyde decreases with increase in formaldehyde initial concentration, which can be explained that the ratio of hypochlorite ion to formaldehyde decreases with increase in the formaldehyde initial concentration. Fig. 5b shows the combined effect of formaldehyde initial concentration and electrolysis time on formaldehyde degradation. It can be ascertained from the figure that the maximum COD removal is obtained at higher electrolysis time with minimum initial concentration. Finally, the combined effect of pH and current density on formaldehyde degradation is given in Fig. 6. It can be seen from Figs. 6a and 6b that the percentage of formaldehyde degradation increases with increase in pH and current density.

Optimization for maximum removal efficiency

The optimization of the parameters and their combination for effective degradation of formaldehyde has been analyzed and the optimized values are presented in Tables 5 and 6. The equations in Table 5 were derived for one particular parameter constant at their extreme optimal values for complete degradation. For example, row 1 of Table 5 gives an equa-

Table 5 – *Regression equations for predicting optimal conditions*

Sl. No.	Fixed parameters				Equation	R^2 value
	A	*B*	*C*	*D*		
1			156	9	$A = -113.25B + 763.87$	0.9999
2		5		9	$A = 0.0002C^3 - 0.1313C^2 + 24.451C - 1341.8$	0.997
3		5	156		$A = -11.839D^3 + 292.34D^2 - 2416.5D + 6896.5$	0.989
4	300			9	$B = -4E-05C^2 + 0.0263C + 0.9207$	0.9999
5	300		156		$B = -0.0367D^2 + 0.2028D + 5.2421$	0.9999
6	300	5			$C = -5.5865D^2 + 119.48D - 387.16$	0.9999
7			156	9	$B = -0.0088A + 6.7406$	0.9999
8		5		9	$C = -4E-06A^3 - 0.0033A^2 + 3.1439A - 305.76$	0.9999
9		5	156		$D = -3E-06A^3 + 0.0026A^2 - 0.7419A + 77.427$	0.9994
10	300			9	$C = 26.023B^2 - 149.03B + 330.31$	0.9999
11	300		156		$D = -0.7276B^2 + 3.9179B + 5.1489$	0.9999
12	300	5			$D = 0.0002C^2 - 0.0303C + 7.5526$	0.9996

Table 6 – *Optimum values of variables for complete COD removal*

COD removal %	Factors			
	A: time (min)	*B*: *j* (A dm^{-2})	*C*: HCHO conc. (mg L^{-1})	*D*: pH
100	300	5	156	6.5 – 9
100	300	5	156 – 235	9
100	300	4.1 – 5	156	9
100	197 – 300	5	156	9

tion for electrolysis time in terms of current density keeping other parameters (formaldehyde initial concentration and pH) constant. It can be noticed from Table 5 that the linear equation is significant with a R^2 value of 0.999. Similarly, rows 2 and 3 give equations for electrolysis time in terms of formaldehyde concentration and pH respectively, fitted with third degree polynomial for better R^2 value. Finally, Table 6 gives the optimized ranges of parameters for complete degradation of formaldehyde.

Conclusion

Experiments were carried out for formaldehyde degradation using electrochemical technique. The influence of individual parameters on formaldehyde degradation were critically examined using Response Surface Method (RSM) and a quadratic model for COD removal was developed using MNITAB14.

List of symbols

A – electrolysis time, min
B – current density, A dm^{-2}
C – formaldehyde concentration, mg L^{-1}
D – pH
k_a, k_b, k_c, k_d – linear coefficients
k_{aa}, k_{bb}, k_{cc}, k_{dd} – quadratic coefficients
k_{ab}, k_{ac}, k_{ad}, k_{bc}, k_{bd}, k_{cd} – interaction coefficients
j – current density, A dm^{-2}
t – time, min

List of abbreviations

SS – stainless steel
AAD – absolute average deviation
COD – chemical oxygen demand
RSM – response surface methodology
ANOVA – analysis of variance

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