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Research Article

Process Parametric Study for Ethene Carboxylic Acid Removal onto Powder Activated Carbon using Box-Behnken Design

Ethene carboxylic acid removal from wastewater using powder activated carbon (PAC) requires a proper process parametric study to determine its optimal performance characteristics. Response Surface Methodology (RSM) is one of the advanced statistical analysis techniques for parametric studies involving a minimum number of trials. The Box-Behnken surface statistical design of experiments was carried out with three factors, i.e., dose, w, temperature, T, and time of contact, t, between the ethene carboxylic acid and the adsorbent, while maintaining the ethene carboxylic acid concentration, C_0 = 100 mg/L, as a fixed input parameter. The performance of the Box-Behnken design was analyzed and optimized using Design-Expert software for ethene carboxylic acid removal onto adsorbent using a batch system. The higher values of the correlation coefficients, lack-of-fit greater than 4 and p values < 0.05 are in good agreement with the optimum combination of process parameters, which proves the fitness of the selected model for analyzing the experimental data.

Keywords: Activated carbon, Adsorbents, Process optimization, Wastewater

Received: March 5, 2007; *revised:* March 30, 2007; *accepted:* March 31, 2007

DOI: 10.1002/ceat.200700084

1 Introduction

Ethene carboxylic acid, commonly known as acrylic acid, is widely used in several industries, e.g., paint, chemical fibers, adhesives, paper, oil additives and detergents. If it is released in effluent it can cause serious damage to the environment due to its high toxicity for aquatic organisms [1]. There are several routes for ethene carboxylic acid manufacture [2]. The molecule can be viewed as a combination of formic acid (HCOOH) and ethylene (CH_2=CH_2), and a conjugation effect occurs between the atomic orbitals of the two chemical groups. One can expect that the delocalization of the valence electrons of ethene carboxylic acid will give rise to changes in the adsorption modes compared to those of formic, acetic and propanoic acids [3]. Ethene carboxylic acid is a hazardous compound (U.S. EPA). Ethene carboxylic acid is released into wastewater during its production, and use in the manufacture of acrylic esters, water-soluble resins, dispersants, and flocculants. Light esters of ethene carboxylic acid are extremely odoriferous [4]. Detailed information concerning the hazardous nature of ethene carboxylic acid is presented elsewhere [5–12].

Activated carbon has been widely employed as the most popular adsorbent for the treatment of effluent [13]. The objective of the present study is to investigate the feasibility of using powder activated carbon (PAC) for the adsorption of ethene carboxylic acid. The study also reports important parameters, which affect the adsorption process, i.e., carbon concentration, w, time of contact, t, and temperature, T, using Box-Behnken designs [14].

2 Material and Methods

2.1 Adsorbent and Adsorbate

Commercial grade PAC was obtained from the HiMedia Research Laboratory, Mumbai, India and used in the present work as an adsorbent. The characterization of the PAC was carried out following the methods presented by Mahadeva [15] and the results are summarized in Tab. 1. Laboratory grade ethene carboxylic acid supplied by S.D. Fine Chemicals Ltd., Mumbai, and inhibited with 200 mg/L of hydroquinone mono-methyl ether, was used for the preparation of synthetic aqueous solutions of ethene carboxylic acid of initial concen-

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tration, C_0, of ca. 100 mg/L. The required quantity of adsorbate was accurately weighed and dissolved in a small amount of distilled water and subsequently made up to 1 L in a measuring flask by adding distilled water. Fresh stock solution was prepared daily as required and maintained at ambient conditions. The C_0 value was ascertained before the start of each experimental run.

Table 1. Characteristics of powder activated carbon.

Characteristic	
Proximate Analysis (Sample as Received)	
Moisture (%)	5.65
Ash (%)	8.74
Volatile matter (%)	4.46
Fixed carbon (%)	81.15
Bulk density (kg/m^3)	562
Calorific Value (MJ/kg)	4.59
Ultimate Analysis (dry basis)	
C	80.25
H	1.658
N	0.158
S	0.052
Chemical Analysis of Ash (%)	
Insoluble Matter	3.5
Silica	1.5
Ferric & Alumina	3.8
CaO	84.0
Mg	2.0
Surface area (m^2/g)	
BET	798.49
Langmuir	1007.37
t-plot micropore	804.26
t-plot external	203.12
Single point	790.06
BJH adsorption cumulative	192.63[a]
Pore Volume (cm^3/g)	
Single point total pore volume	0.76
t-plot micropore volume	0.25
BJH adsorption cumulative	0.30[a]
Particle Size	250 mesh
Pore size (Å)	
BET Adsorption average pore width	38.25
BJH adsorption average pore diameter	63.39

a Pores between 17 Å and 2000 Å.

2.2 Analytical Measurements

The concentration of ethene carboxylic acid in the aqueous solution was determined at 210 nm wavelength [16] using a high performance liquid chromatograph (HPLC) supplied by Waters (India) Pvt. Ltd., Bangalore. A Noval Pack, C_{18} column of size 3.9×150 mm was used in the analytical measurement of the ethene carboxylic acid. For ethene carboxylic acid analysis, a mixture of degassed organic free water, 4 % acetonitrile and 0.1 % H_3PO_4 was used as the solvent, while maintaining a flow rate of 1 mL/min, as per the specification given in the user manual of the instrument. The calibration curve of ethene carboxylic acid was plotted as the peak area versus concentration.

3 Experimental

3.1 Batch Experimental Programme

For each experiment, 50 mL of ethene carboxylic acid solution of known C_0 value and a known amount of the adsorbent were placed in a 100 mL airtight stoppered conical flask. This mixture was agitated in a temperature-controlled shaking water bath, at a constant speed for all experimental runs. The percentage removal of ethene carboxylic acid was calculated using the following relationship:

$$\text{Percentage removal} = 100\ (C_0 - C_t)/C_0 \quad (1)$$

where C_0 is the initial sorbate concentration (mg/L) and C_t is the equilibrium sorbate concentration (mg/L).

3.2 Box-Behnken Design

Box-Behnken designs require that a lower number of actual experiments be performed, which facilitates probing into possible interactions between the parameters studied and their effect on the percentage removal of ethene carboxylic acid. Box-Behnken is composed of a spherical, revolving design. It consists of a central point and the middle points of the edges of a cube circumscribed on a sphere [17]. It contains three interlocking 2^2 factorial designs and a central point. It has been applied for the optimization of several chemical and physical processes, and the number of experiments are decided accordingly [18]. In the present study, the three-level, three-factorial Box-Behnken experimental design is applied to investigate and validate adsorption process parameters, affecting the removal of ethene carboxylic acid onto PAC.

The adsorbent dose (2–36 g/L), temperature (30–70 °C) and agitation time (5–355 min) are variable input parameters, while the ethene carboxylic acid concentration of 100 mg/L was maintained as a constant input parameter, at its natural pH value of 4.12. The factor levels were coded as –1 (low), 0 (central point) and 1 (high) [17].

Tab. 2 shows the input parameters and experimental design levels used. RSM was applied to the experimental data using the statistical software, Design-Expert V6. Statistical terms and their definitions used in the Design-Expert software are given elsewhere [19]. Linear and second-order polynomials were fitted to the experimental data to obtain the regression equations. The sequential *F*-test, lack-of-fit test and other adequacy measures were used in selecting the best models [20]. To analyze a process or system including a response *Y*, where *Y* depends on the input factors x_1, x_2, ..., x_k, the relationship between the response and the input process parameters can be described as:

$$Y = f(x_1, x_2, ..., x_k) + \varepsilon \quad (2)$$

where *f* is the real response function with unknown format, and ε is the residual error, which describes the differentiation that can be included by the function *f*. Since the relationship between the response and the input parameters can be described as a surface of the x_1, x_2, ..., x_k ordinates in the graphical sense, the research into these relationships is known as a response surface study. The same statistical software was used to generate the statistical and response plots. A manual regression method was used to fit the second-order polynomial, Eq. (3), to the experimental data and to identify the relevant model terms. Considering all of the linear terms, square terms and linear by linear interaction items, the quadratic response model can be described as:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_{ii}^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where β_0 is a constant, β_i is the slope or linear effect of the input factor x_i, β_{ij} is the linear by linear interaction effect between the input factors x_i and x_j, and β_{ii} is the quadratic effect of the input factor x_i [21].

Table 2. Level of variables chosen.

Variables	Levels		
Coded Level	1	0	–1
w: Dose (g/L)	4	20	36
T: Temp (°C)	30	45	60
t: Time (min)	5	180	355

4 Results and Discussion

The most important parameters, which affect the efficiency for ethene carboxylic acid removal onto PAC are adsorbent dose, *w*, temperature, *T*, and time of contact of adsorbate-adsorbent, *t*. In order to study the combined effect of these factors, investigations were performed for different combinations of the physical parameters using statistically designed experiments. The ranges selected for the input variables are given in Sec. 3.2.

The results of the *Y* response of ethene carboxylic acid onto PAC were measured according to the design matrix outlined in Tab. 3 and the measured responses are listed in Tab. 4. From

Table 3. Three-level Box-Behnken design of experiments with three independent variables.

Experiment No.	*w*	*T*	*t*
1	–1	–1	0
2	1	–1	0
3	–1	1	0
4	1	1	0
5	–1	0	–1
6	+1	0	–1
7	–1	0	+1
8	+1	0	+1
9	0	–1	–1
10	0	+1	–1
11	0	–1	+1
12	0	+1	+1
13	0	0	0
14	0	0	0
15	0	0	0
16	0	0	0
17	0	0	0

Table 4. Experimental and predicted values of *Y* for ethene carboxylic acid adsorption onto PAC.

Std. Run Order	*w*	*T*	*t*	Y[a]		ε
				Y_{exp}	Y_{pre}	
1	4	30	180	79.54	77.76	1.78
2	36	30	180	96.50	97.56	–1.06
3	4	70	180	73.61	72.55	1.06
4	36	70	180	89.92	91.70	–1.78
5	4	50	5	73.61	75.32	–1.71
6	36	50	5	96.34	95.21	1.13
7	4	50	355	71.40	72.53	–1.13
8	36	50	355	93.29	91.58	1.71
9	20	30	5	97.34	97.41	–0.074
10	20	70	5	89.13	88.48	0.65
11	20	30	355	90.16	90.81	–0.65
12	20	70	355	88.75	88.68	0.074
13	20	50	180	89.85	90.28	–0.43
14	20	50	180	90.05	90.28	–0.23
15	20	50	180	90.31	90.28	0.034
16	20	50	180	89.96	90.28	–0.32
17	20	50	180	91.21	90.28	0.93

[a] Y_{exp} and Y_{pre} are experimental and predicted responses.

analysis of the measured responses by the Design-Expert software, the fit summary output indicates that the quadratic model is statistically highly significant for the present adsorbate-adsorbent system. The cubic model was statistically recommended to be aliased for the ethene carboxylic acid-PAC system used in the present study, since the Box-Behnken matrix has sufficient data to interpret the outcome of the present system.

4.1 Analysis of Variance (ANOVA)

The statistical significance of the ratio of the mean square variation due to regression and mean square residual error was tested using analysis of variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [22]. According to the ANOVA in Tab. 5, the $F_{\text{Statistics}}$ values for all regressions were higher. The large value of F indicates that most of the variation in the response can be explained by the regression equation. The associated p value is used to estimate whether $F_{\text{Statistics}}$ is large enough to indicate statistical significance. A $p > F$-value lower than 0.01 indicates that the model is considered to be statistically significant [23].

The p values for all of the regressions were lower than 0.01. This means that at least one of the terms in the regression equation has a significant correlation with the response variable. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct [24].

The ANOVA result for the ethene carboxylic acid-PAC system, shows that the model F-value is 42.34, implying that the model is significant. There is < 0.01 % probability that a model F-value of this magnitude could be due to noise. The probability $p < 0.05$ indicates that the model terms are significant. In the present study w and w^2 are highly significant parameters, while T and t are significant parameters. Values of $p > 0.1000$ indicate that the model terms are insignificant. A lack-of-fit value of 19.69 also supports the fitness of the model. There is a 2.40 % possibility of this deviation being mostly due to noise. The predicted value of $R^2 = 0.7279$ for the same adsorption system is not close to the adjusted value of $R^2 = 0.9588$, as researchers might normally expect. This may indicate a large block effect or a possible problem with the model data. The high value of adequate precision at 19.799, which measures a signal-to-noise ratio greater than 4 is desirable in support of the fitness of the model [19].

The analysis of variance for the ethene carboxylic acid-PAC system indicates that for the ethene carboxylic acid concentration input model, the main effect of the dose, w, temperature, T, time, t, and the second-order effect of dose, w^2, are the most significant terms associated with the concentration input. The analysis also indicates that there is a linear relationship between the main effects of the dose, temperature and time, and a quadratic relationship with the second-order dose for the present adsorption system. The final mathematical equation in terms of significant effects (confidence level > 95 %) as determined by the Design-Expert software is given in Eq. (4):

$$Y = 87.16 + 1.67w - 0.51T - 0.31t - 0.03\,w^2 \quad (4)$$

A normal probability plot and a dot diagram of these residuals are shown in Fig. 1. The data points on this plot lie reasonably close to a straight line, lending support to the conclusion that w, T, t and w^2 are the only significant effects and that the underlying assumptions of the analysis are satisfied. Fig. 2 shows the relationship between the actual and predicted values of Y for adsorption of ethene carboxylic acid onto PAC. It is seen in Fig. 2 that the developed models are adequate because the residuals for the prediction of each response are minimum, since the residuals tend to be close to the diagonal line. Figs. 3 and 4 show 3D and contour plots of the relationship between dose and temperature and their effect on the percentage removal of ethene carboxylic acid. Both figures clearly indicate that the percentage removal of ethene carboxylic acid decreases with increasing temperature.

The point prediction option in the software is used for the optimization of the process parameters. The optimized param-

Table 5. ANOVA table for *Y*.

Source	Sum of Squares	d.f.	Mean Square	*F*-Value	*p*	Remark[a]
Model	1035.10	9	115.01	42.34	< 0.0001	Highly Significant
w	758.36	1	758.36	279.19	< 0.0001	Highly Significant
T	61.22	1	61.22	22.54	0.0021	Significant
t	20.54	1	20.54	7.56	0.0285	Significant
w^2	179.77	1	179.77	66.18	< 0.0001	Significant
Residual	19.01	7	2.72	–	–	–
Lack-of-Fit	17.81	3	5.94	19.69	0.0074	Significant
Pure Error	1.21	4	0.30	–	–	–
Corr. Total	1054.11	16	–	–	–	–

[a] $R^2 = 0.9820$, predicted $R^2 = 0.7279$, adjusted $R^2 = 0.9588$, adequate precision = 19.799.

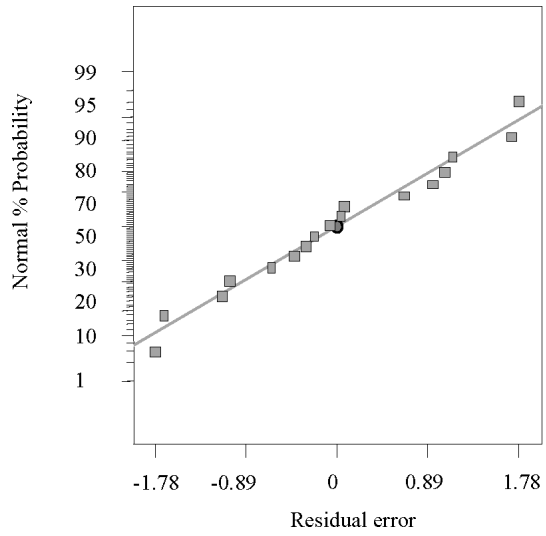

Figure 1. Normal % probability versus residual error.

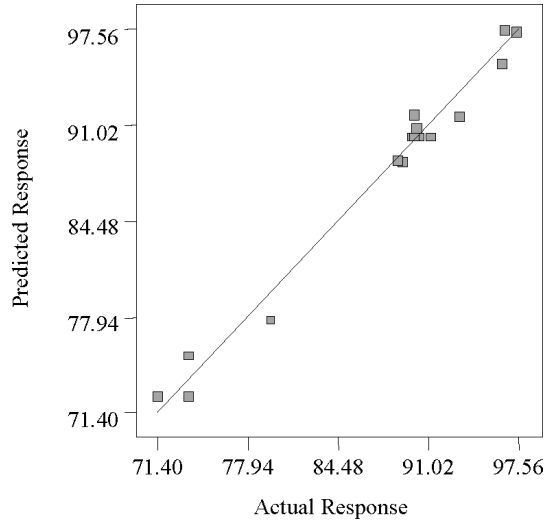

Figure 2. Scatter diagram of predicted response versus actual response for the ethene carboxylic acid-PAC adsorption system.

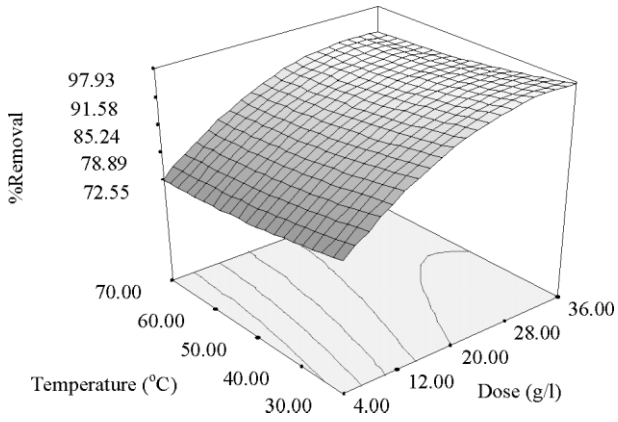

Figure 3. 3D response surface graph of adsorbent dose versus temperature at a holding time of 180 min for the ethene carboxylic acid-PAC adsorption system.

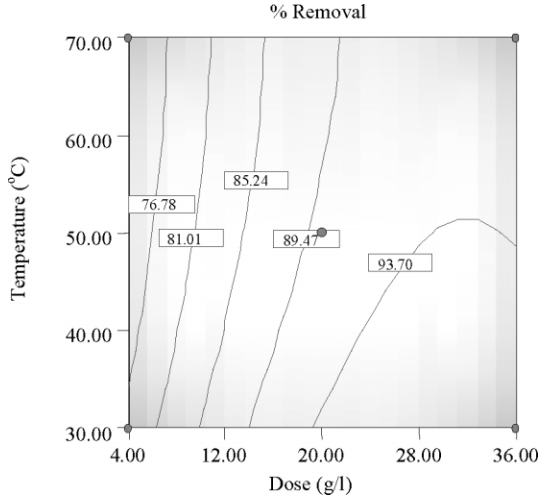

Figure 4. Contour graph of temperature versus adsorbent dose at a holding time of 180 min for the ethene carboxylic acid-PAC adsorption system.

Table 6. Optimum and confirmative values of the process parameters for maximum removal efficiency.

Processes Parameters	Optimized Values (Predicted Values)	Confirmation Values[a] (Actual Values)
% Removal (Y)	91.71	89.51
Dose (w)	20 g/L	20 g/L
Temperature (T)	30 °C	30 °C
Time (t)	5 min	5 min

[a] Percentage removal error = –2.40.

eters obtained from the statistical software are listed in Tab. 6. Tab. 6 summarizes the experimental conditions and the actual experimental values. For their validation, the experiment was conducted using the optimized parameters obtained and the percentage removal (response) of ethene carboxylic acid was observed to have an error of 2.40 %.

5 Conclusions

The following conclusions are drawn from this investigation:

– Box-Behnken design can be employed to develop mathematical models for predicting the geometry of ethene carboxylic acid removal.
– The desired quantity of removal of ethene carboxylic acid can be achieved by choosing the conditions predicted using the developed models.

– Parameters interacting together can be identified in a typical process such as adsorption. In the present study, the removal is more sensitive to carbon concentration.
– The high value of $R^2 > 98.2\,\%$ for the present mathematical model indicates the high correlation between the observed and predicted values.

Acknowledgements

The financial support for this investigation provided by the Ministry of Human Resources and Development (MHRD), New Delhi, India, is gratefully acknowledged. The authors wish to thank Dr. S. Paul, Sel. Gr. Lecturer in the Mechanical Engineering Department, Assam Engineering College, Guwahati, Assam-781 013, India, for his suggestions and advice on using the Design-Expert 6.0 (trial version) in the current study.

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