APPLICATION OF DOE (RSM-CCD) FOR DYE (CONGO RED) SEQUESTRATION FROM WATER EFFLUENTS

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ABSTRACT **-**In recent days, it has been found that Agricultural waste is alternate and cost effective adsorbent to replace Activated carbon. Ficus religosa are most famous abundantly available trees in India and Asian subcontinents. According to ayurveda the parts of this tree exhibit anti toxic properties. They shed their leaves at the onset of dry season. These dry leaves can be used to remove pollutants from industrial water streams. Textile and leather industries using volumes of synthetic dyes releasing its refuse in to water bodies making them unfit to reuse. Being stable & complex, these are non-biodegradable causing major environmental damage. In view of present huge water demand and scarcity it is obvious and essential to treat industrial water effluents with eco friendy and cost effective processes. Adsorption serves this purpose by using natural organic matter as an adsorbent. Hence Ficus religiosa leaf powder can be become a promising potential adsorbent for the removal of pollutants in particular Congo Red (CR) from aqueous solutions. In this study traditional adsorptive studies were replaced by statistical analysis to develop a suitable model that relates all the parameters affecting the process. Response surface methodology with central composite Design was used to generate the model and the model reliability was successfully verified.

KEYWORDS: **Congo Red, Ficus Religiosa, Biosorption, statistical studies, RSM, CCD.**

INTRODUCTION

Textile industry uses two thirds of dye stuff out of the total production of around $1x10^6$ TPA. In this 70 % of the dyes belong to azo dyes. Congo red is the widely used azo dye in textile industries. About 100 L of water is required to process 1 kg of dye and 10 to 15 % of the dye usually goes along with effluent. CR forms toxic amines in the water bodies. It causes skin and eye irritation and also a carcinogen. The treatment of CR is complicated due to its aromatic structure and thermal and optical stability. It is also resistant to bio and photo degradation (Mohan Rao and Basava Rao, 2016).

Mathematical modeling for water treatment process by classical methods is unreliable and complex due to its multi variative nature. Response surface method (RSM) is an alternative effective method that can be applied to these processes. Central composite design called as CCD considered to be superior with embided factorial design with center points augmented that allow estimation of curvature (Mohan Rao and Basava Rao, 2016).

Here, in the present study the biomass used was *Ficus Religiosa* leaf powder, contains different functional groups which can attract pollutants from water effluents. Batch adsorption studies were conducted to investigate the influence of parameters, initial concentration, adsorbent dosage, pH and Temperature on biosorption of Congo Red and to develop robust model to predict the Response of the process using RSM.

MATERIALS AND METHODS

Dry leaves of FR were washed and dried to a constant weight. And it was converted to powder and packed in desiccators. CR solution of concentration 1000 mg/L was prepared from dye powder supplied by Merk, Mumbai, and is diluted to the requirement. High end instruments like SHIMADZU – AX200 analytical balance, ELICO-L1 612 digital pH meter, REMI - CIS 24 BL orbital shaker, REMI C 24 Centrifuge, SYSTRONICS-117 UV-VIS Spectro photometer are used in the experimental studies.

RESULTS AND DISCUSSIONS

Effluent concentration (Co), dosage (Do), temperature (T) are considered to be influencing factors and hence selected for ststistical modelling. The details of experimental domain and the levels of each factor are given in the Table 1. Design – expert software (version: 8.0.7.1) is used to estimate number of runs. Based on the experimental levels and rages of process variable given in table 1. Total 20 runs were generated with 8 axial, 6 central and 6 factorial positions in the design matrix (Table 2).

Experiments were conducted according to the design matrix generated and the measured responses were presented in Table 2.

Table 1: Experimental range and levels of independent variables

Variables	Symbol	-1	0	1
Initial Concentration, mg/L	Co	10	55	100
Dosage, g	Do	0.01	0.06	0.1
Temperature, ^oC	T	20	35	50

Table 2: Experimental Design Matrix

Run	Concentration, mg/L	Dosage, g	Temperature, °C	Uptake, q, mg/g
1	100	0.01	20	74.84568
2	100	0.1	20	29.72222
3	55	0.06	20	30.04115
4	10	0.1	20	4.490741
5	10	0.01	20	20.37037
6	100	0.06	35	50.92593
7	55	0.01	35	221.4506
8	55	0.06	35	36.31687
9	55	0.1	35	23.07099
10	10	0.06	35	7.81893
11	55	0.06	35	36.31687
12	55	0.06	35	36.31687
13	55	0.06	35	36.31687
14	55	0.06	35	36.31687
15	55	0.06	35	36.31687
16	100	0.01	50	74.38272
17	100	0.1	50	36.40432
18	55	0.06	50	36.36831
19	10	0.1	50	4.351852
20	10	0.01	50	21.45062

Various models were tested with the experimental data to obtain the regression equations. And the model adequacy was tested with sequential F-test, lack-of-fit test and other adequacy measures were used for selecting the best model (Tarangini et al., 2009). Analyzing the measured responses, the fit summary output indicated that the quadratic polynomial model was significant for the present system. The General form of the quadratic model is

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

Where q is CR uptake, b_0 = constant coefficient, $b_{i,}$ b_{ii}, b_{ij}, are the interaction coefficients of linear, quadratic and second order terms respectively. n is the number of factor and e_i is the error (Ozer et al., 2008).

The uptake of CR varied from 4.35 (minimum) to 221.45 mg/g (maximum) in the present study. The ratio of minimum to maximum uptake of Congo red removal was 50.90, which was greater than 10 suggesting that transformation was required in the present system. Since CR removal in the present investigation represented skew ness with non-zero positive values, an inverse square root transformation was applied to the experimental data.

Analysis of variance (ANOVA)

The ANOVA of the predicted response for CR Removal efficiency was generated and the analysis has been displayed in Table 3. The model terms were significant if P>F values are less than 0.05, and are insignificant for values greater than 0.1 (Korbahti and Tanyolac, 2008) [46].

Table 3: Analysis of Variance Table

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	Prob>F
Model	0.22	9	0.025	466.94	< 0.0001
A-Co	*0.11*	*1*	*0.11*	*1990.46*	*< 0.0001*
B-Do	*0.060*	*1*	*0.060*	*1129.54*	*< 0.0001*
C-Tem	*1.036E-004*	*1*	*1.036E-004*	*1.96*	*0.1916*
AB	*0.020*	*1*	*0.020*	*371.47*	*< 0.0001*
AC	*4.669E-005*	*1*	*4.669E-005*	*0.88*	*0.3694*
BC	*3.014E-006*	*1*	*3.014E-006*	*0.057*	*0.8161*
A^2	*0.022*	*1*	*0.022*	*414.60*	*< 0.0001*
B^2	*1.321E-003*	*1*	*1.321E-003*	*25.00*	*0.0005*
C^2	*5.798E-004*	*1*	*5.798E-004*	*10.97*	*0.0078*
Residual	5.284E-004	10	5.284E-005		
Lack of Fit	*5.284E-004*	*5*	*1.057E-004*		
Pure Error	*0.000*	*5*	*0.000*		
Cor Total	0.22	19			

SD = 7.269E-003; PRESS = 5.539E-003, R^2 = 0.9976, R^2_{adj} = 0.9955, R^2_{pred} = 0.9751,
Adeq Precision = 80.115.

The model F-value (466.94) and low probability value (P>F<0.0001) indicate that the model was significant. The chance that the Model F- Value could occur due to noise is only 0.01%. In this case A, B, AC, A^2, B^2 are significant model terms. The values of Pred. R-Squared and Adj. R-Squared are 0.9751and 0.9955, representing good agreement. Signal to noise ratio is measured in terms of Adeq. Precision. A ratio of 80.115 indicates an adequate signal, whereas any value greater than 4 is desirable. All these results conclude that the proposed model can be used to navigate the design space.

According to Joglekar and May (1987), for a good fit of a model, the correlation coefficient should be at a minimum of 0.80. The value of correlation coefficient obtained in the present study is 0.9976. High R^2 value illustrates good agreement between the calculated and observed results within the range of experiment.

Based on the results, the response surface model constructed in this study was considered reasonable. In terms of actual factors, an empirical relationship between CR efficiency (uptake, q) and process variables can be expressed by the following second-order polynomial equation.

1/ Sqrt (q) = $0.29885 - 5.65673x10^{-3}C_o + 4.28448\,D_o + 4.48503x10^{-3}T - 0.024461\,C_oD_o - 3.57899x10^{-6}C_oT - 9.09308x10^{-4}D_0T + 4.40759x10^{-5}C_o^2 - 10.82298\,D_o^2 + 6.45322x10^{-5}T^2$

Usually, it is important to confirm if the selected model provides an adequate approximation of the real system. By applying the diagnostic plots provided by the software, such as normal probability plots of the studentized residuals, as well as the predicted versus actual value plots, the model adequacy can be judged. Fig. 1 shows the normal probability plot of the studentized residuals. A normal probability plot indicates if the residuals follow a normal distribution, in which case the points will follow a straight line. Since some scattering is expected, even with the normal data, we can assume that the data is normally distributed (Fig. 1). The values predicted by the model and the experimental values are in good agreement, as shown in Fig. 2.

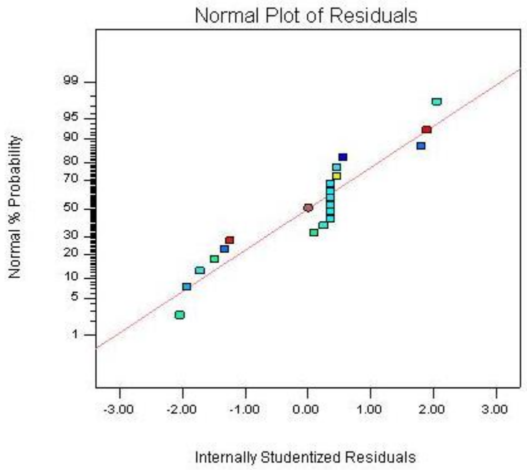

Figure 1

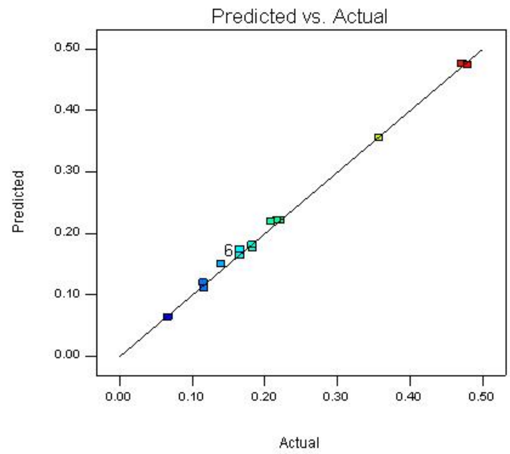

Figure 2

Figure 1: The studentized residuals and normal percentage probability plot
Figure 2: The actual and the predicted adsorption of Congo red uptake

Response surface graphs (Fig. 3 - 5) were generated to visualize the effect of initial concentration, dosage and temperature. Fig. 3 shows the interactive effect of dosage and initial concentrations. An increase in uptake observed at higher dosage and lower concentrations. Fig.4 and 5 shows the interactive effect of temperature - initial concentration and dosage – temparature. All the tree plots conclude that the removal of CR is influenced largely by dosage and initial concentration, but not with the temperature.

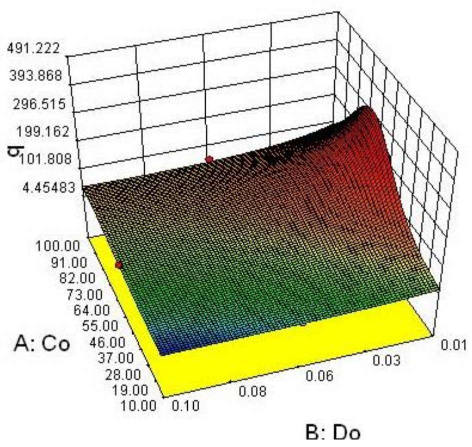

Figure 3: Effect of initial concentration and Dosage on CR Removal onto FRLP.

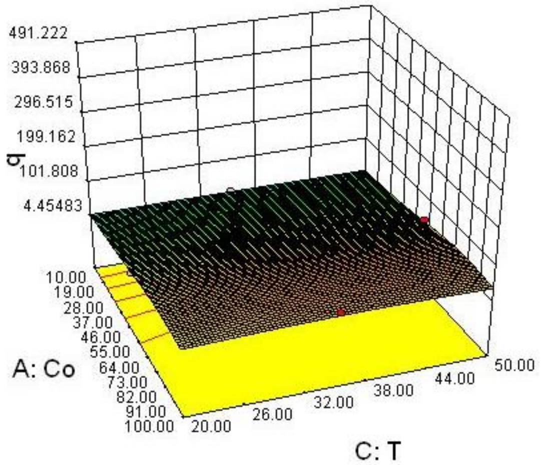

Fig. 4

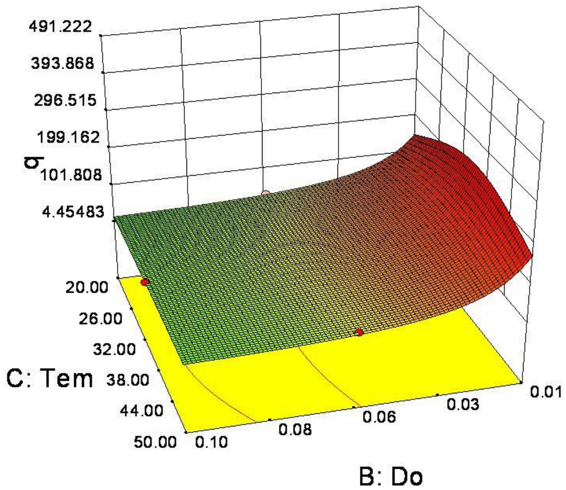

Fig.5

Figure 4:Effect of initial concentration and Temperature on CR Removal onto FRLP.
Figure 5: Effect of Temperature and Dosage on CR Removal onto FRLP.

Conclusions:

The effects of various parameters and their interactions were studied using the response surface methodology. Effluent concentration & Dosage were identified as most influential parameters and the second order effects of the same are also influencing the process. The statistical quadratic model was generated and its robustness were tested as per the standards given in the literature. 3D Response surface graphs and Contour plots were generated and analyzed.

REFERENCES

[1] Joglekar, A.M., May, A.T. Product excellence through design of experiments, *Cereal Foods World*,32: 857–868, 1987.
[2] Korbahti, B. K., Tanyolac, A. Electrochemical treatment of simulated textile wastewater with industrial components and Levafix Blue CA reactive dye: Optimization through response surface methodology, *J. Hazard. Mater.*,151: 422–431, 2008.
[3] Mohan Rao. T, Basava Rao. V.V., “Biosorption of Congo Red from aqueous solution by Crab Shell Residue- A Comprehensive Study.” Springerplus, 5:537, 2016
[4] Mohan Rao. T, Basava Rao. V.V. Process Modeling, Simulation, and Environmental Applications in Chemical Engineering. New Jercy, USA: Apple Academic Press, 2016.
[5] Ozer, A., Gurbuz, G., Calimli, A., Korbahti, B.K. Investigation of nickel (II) biosorption on Enteromorphaprolifera: optimization using response surface analysis. *J. Hazard. Mater.*, 152: 778-788,2008.
[6] Tarangini, K., Arvind Kumar, G., Satpathy, R., Vikas Kumar, S. Statistical Optimization of Process Parameters for Cr (VI) Biosorption onto Mixed Cultures of Pseudomonas aeruginosa and Bacillus subtilis, *Clean*, 37 (4 - 5): 319-327, 2009.