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RESPONSE SURFACE OPTIMIZATION OF DYE REMOVAL BY USING WASTE PRAWN SHELLS

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ABSTRACT

A simple, highly efficient, locally and abundantly available, adsorbent was studied for removing dyes from synthetic industrial effluents. Experiments were conducted to study the efficiency of carbon prepared from waste prawn shells for removal of crystal violet (CV). The effect of various process parameters such as temperature, initial pH, contact time, adsorbent dosage and initial dye concentration of the solution were studied by running batch experiments in Erlenmeyer flasks. Response Surface Methodology was used to optimize the process parameters. ANOVA analysis was also studied to know the interaction effect of dye and adsorbent.

Key Words: Response Surface Methodology; Optimization; Prawn Shell Waste; Crystal Violet; Dye; ANOVA

1. INTRODUCTION

Dyes are extensively used in textile, plastic, leather, food, paper, cosmetics and pharmaceutical industries. Effluents from such industries are important sources of color pollution. Dyes present in water streams do not allow the passage of light through them and cause damage to the aquatic life. Disposal of dyes into water streams cause skin allergies, cancer and eye irritation in human beings. Among the various frequently used dyes crystal violet(CV) is important one which is used as biological stain, finger printing, veterinary medicine, poultry feed additive, dying and paper industries. Crystal Violet dye also causes mutagenic effects to human being hence it needs to be removed before discharging into water bodies [1-7].

Dyes in waste water are easily detectable and difficult to remove as they are not easily biodegradable, stable to oxidizing agents and light. Normal methods of dye removal such as flocculation, precipitation, coagulation and filtration, etc. are generally expensive and also produces large amount of sludge; disposal of which creates environmental problem. Hence, biosorption is used in this study which is simple, efficient, easy to run and cheap [8-10].

Researchers investigated the feasibility of using various materials as adsorbents such as orange peel, bentonite clay, bamboo dust, coconut shell, wheat bran etc. But still there is a need to develop cheap and effective biosorbent [11-17].

In this study, activated carbon prepared from prawn shell waste (PAC) was used as sorbent for the removal of crystal violet dye from synthetic industrial effluent. The various experimental parameters affecting the dye removal process such as temperature, initial pH, contact time, adsorbent dosage and initial dye concentration of the solution were also studied.

Designing of experiment and standardization of variables affecting the system is very critical in optimization process. Generally this optimization is carried out by using traditional one factor at a time method, which is simple, time and chemicals are consumed in large quantities. Moreover this method neglects the interaction effects of process variables. Hence, in the present study statistical approach such as Response Surface Methodology (RSM) was adopted to study the correlation among the process variables affecting the process and to optimize the process variables to give higher color removal [18-27].

2. MATERIALS AND METHODS:

2.1 Chemicals and Materials

The chemical HCl and NaOH used in this study were purchased from lotus enterprises, visakhapatnam, India. Analytical Grade Crystal violet (mol. formula $C_{25}H_{30}ClN_3$, mol. wt. 407.99, λ_{max} =590 nm) was procured from Fisher Scientific. All the solutions were prepared by using deionized water in this study.

The prawn waste was collected from the fish market at poorna market, Visakhapatnam, Andhra Pradesh, India. The waste prawn material was subjected to shell removal by hand and washed thoroughly with demonized water till no color is observed in effluent. This material was dried in sunlight for one day and grounded to powder using roll crusher. The crushed prawn shell powder was placed in muffle furnace at the temperature of 500^0C for 5 hours. Then it was screened to different particle sizes by using sieve shaker. The prawn shell powder retained on the mesh no-52 is collected as used as adsorbent through out in this study.

2.3 Experimental procedure

The Crystal Violet stock solution was prepared by dissolving 1000mg of CV dye in 1000 ml of deionized water in volumetric flask. Different concentrations for CV dye (50 ppm -150 ppm) were prepared by diluting the stock solution with appropriate amounts of deionized water and stored in volumetric flasks. Different concentrations of dye solutions of 50 ml ranging from 50ppm-150ppm were transferred separately to different Erlenmeyer flasks. Appropriate amounts of adsorbent were added to the flasks and placed in orbital shaker for appropriate times at 120 rpm speed. Solutions pH's were maintained at different values by using 0.1N HCl and 0.1N NaOH. Concentrations of dye were measured by using UV-Vis Spectrophotometer at a wavelength of 590 nm.

The percentage removal of color from solution was calculated as

$$\% \text{ Removal of CV} = = \frac{(C_i - C_f)}{C_i} * 100$$

Where, C_i and C_f are the initial and final concentrations of the CV dye in liquid, mg/l.

2.4 Experimental Design and Data Analysis

The effect of various process parameters such as temperature (x_1), pH (x_2), time (x_3), adsorbent dosage (x_4) and initial dye concentration (x_5) on color removal was studied by using half fraction factorial Central Composite Design (CCD). A CCD with 32 experiments was used for the optimization of process parameters for removal of CV dye from synthetic industrial effluent solution. All independent variables were coded to five levels as X_i according to equation-1.

$$X_i = \frac{(X_i - X_{oi})}{\Delta X_i}, \quad i = 1,2,3,\ldots\ldots k \text{ ------------ } (1)$$

Where X_i is independent variable, x_i is the real value of an independent variable, x_{oi} is the real value of the independent variable at the centre point, and Δx_i is the step change. A polynomial (Equation-2) was developed to estimate the behavior of the percentage removal of color.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_{ii} X_i^2 \text{ ----------------------}(2)$$

Where Y is the response, β_0 was the intercept term, β_i were linear effects, β_{ij} were the squared effects and β_{ij} w-ere the interacting effects.

3. RESULTS AND DISCUSSION

The statistical analysis of the experimental results shows that percentage of dye removal was a function of temperature, pH, time, adsorbent dosage and initial dye concentration of the solution. The levels of independent process variables used in a Central Composite Design and the design matrix used with the observed responses obtained were shown in table -1 &2. Responses shown in table-2 were the average values of three replicates for all the experimental runs.

The main effects of all parameters on percentage dye removal were determined and shown in figure -1. A plot of temperature versus percentage removal of CV shows that the percentage removal of dye increased with increased temperature up to 30^0C and thereafter it showed a decrease in percentage dye removal. This might be due the exothermic nature of the process. At higher temperatures low percentage removal efficiency might be due to desorption of adsorbed dye particles from the adsorbent surface. Similar temperature effects were obtained with other adsorbents also [28]. The effect of pH on CV removal was studied in the range of pH 2-12. It is apparent from the figure -1 that percentage removal was decreased with increased pH and reached minimum at pH range of 4.5 to 9.5. At normal pH values electrostatic repulsion between protonated PAC and crystal violet dye might result lower removal efficiencies where as at higher pH conditions electrostatic attraction between CAC and basic dye may be resulted higher efficiencies. Similar observations were noticed for biosorption of CV from aqueous solution [8, 25]. Percentage removal of dye was increased with time up to 52.5 minutes beyond that the change in percentage dye removal was slower. This might be due to the fact that increased time allowed the particles to reach equilibrium hence, removal efficiency was increased. These results agree with the results obtained by other researches on dye removal [9,13].

It is noticed from the figure-1that percentage removal of CV has increased significantly with increased adsorbent dosage up to 0.6 g however, beyond the dosage of 0.6 g changes in percentage removal of CV was marginal. This is in accordance with the reports available on other dye removal processes [24, 29]. The percentage removal of CV dye increased slightly up to the concentration of 100 ppm after that removal again decreased as shown in figure. This might be due to the non availability of active sites on the adsorbent surface [30].

ANOVA gives the information about quadratic and interaction effects along with the normal linearised effects of the parameters.

Model was developed from ANOVA to represent the effect of above parameters on percentage removal of crystal violet dye and was shown in equation-3.

$$Y_1 = -640.427 + 28.169X_1 - 18.601X_2 + 4.737X_3 + 146.959X_4 + 2.791X_5 - 0.434X_1^2 + 1.729X_2^2 - 0.009X_3^2 - 100.261X_4^2 - 0.009X_5^2 + 0.227X_1X_2 - 0.072X_1X_3 + 4.283X_1X_4 - 0.024X_1X_5 + 0.032X_2X_3 - 13.699X_2X_4 - 0.064X_2X_5 - 1.339X_3X_4 - 0.006X_3X_5 + 0.648X_4X_5 \text{ ------------ } (3)$$

Experimental data along with the predicted results obtained from the above model were shown in table-2. The proposed model was evaluated by regression coefficients, standard error, t-values, p-values and correlation coefficient (R). The model indicates that the adsorbent dose, temperature and pH had a strong effect; linear and quadratic terms had more influence in comparison to the interaction terms. From the tale-3 it is clear that all parameters effects were significant at 95% confidence levels. Here, the value of correlation coefficient (R= 0.999), R^2 (0.999) indicates a high agreement between the experimental and predicted values and its significance. The model adequacy was tested by using ANOVA (Table-

4). Lower P values for regression model equation imply that the second-order polynomial model fitted to the experimental results well. The graphical representations of the regression equation (3) were shown by the 3D response surfaces and 2D contour plots in figures 2-12. The optimum combination of all parameters effecting the percentage removal of dye was predicted by using prediction profiler of the software. The maximum removal efficiency was predicted to be 92% which was obtained at a temperature of 20^0C, pH of 12, contact time of 90 min, adsorbent dose of 0.41 g and initial dye concentration of 53 ppm (figure -13).

4. CONCLUSIONS

In this work, the optimum levels of process variables were determined by using statistical methods. A high percentage of color removal design was developed by using Central Composite Design. A highly accurate model was developed which showed that the percentage removal of CV dye was highly influenced by temperature, initial pH and adsorbent dosage. However the effects of contact time and dye concentration were marginal.

The optimum temperature of 20^0C, pH of 12, contact time of 90 min, adsorbent dose of 0.41 g and initial dye concentration of 53 ppm were obtained by using Response Surface Method, which resulted 92% of removal of CV dye from solution. This method produced 250% higher removal of CV dye efficiency as compared to that in original values. The above results suggest that activated carbon prepared from waste prawns could be used to remove the CV dye from aqueous solutions effectively. This method may results in reduction of environmental problems without compromising plant productivity. This method can also generate income to the fishermen and reduce the effluent treatment cost to the industries.

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Factor	Symbol	Level				
		-α	-1	0	1	+ α
Temperature, ^{0}C	x_1	20	25	30	35	40
pH	x_2	2	4.5	7	9.5	12
Time, min	x_3	15	33.75	52.5	71.25	90
Adsorbent dose, g	x_4	0.2	0.4	0.6	0.8	1.0
Initial dye concentration, ppm	x_5	50	75	100	125	150

Table-1: Levels of different process variables used in CCD for removal of CV dye

Run Order	X_1	X_2	X_3	X_4	X_5	% Removal of dye	
						Observed	Predicted
1	0	0	0	0	0	43.2849	43.3053
2	-1	-1	1	-1	-1	43.0642	43.9253
3	-1	1	-1	-1	-1	10.0890	10.0775
4	-1	-1	-1	-1	1	2.9755	3.3199
5	0	0	0	0	0	43.4041	43.3053
6	0	0	0	-2	0	5.6292	5.7661
7	1	1	-1	1	-1	47.2262	47.3290
8	1	-1	-1	1	1	57.0714	57.5301
9	-1	-1	1	1	1	58.7795	59.4130
10	1	1	1	-1	-1	50.6919	50.5016
11	2	0	0	0	0	0.6292	0.5376
12	0	0	0	2	0	49.7882	48.7609
13	0	0	2	0	0	49.5366	49.0954
14	0	0	0	0	0	42.7816	43.3053
15	0	0	0	0	-2	30.7436	29.2610
16	-1	1	1	-1	1	37.2184	36.6862
17	-1	1	1	1	-1	42.6715	42.9490
18	-1	1	-1	1	1	13.7097	13.4706
19	0	0	0	0	2	9.6119	10.2041
20	0	0	0	0	0	42.7816	43.3053
21	1	1	1	1	1	28.0929	27.6750
22	-2	0	0	0	0	0.0225	-0.7762
23	1	-1	-1	-1	-1	5.0222	5.7085
24	1	-1	1	1	-1	49.1167	50.0921
25	0	-2	0	0	0	91.4121	89.2178
26	-1	-1	-1	1	-1	28.7511	29.9052
27	1	1	-1	-1	1	3.6714	2.9644
28	0	0	0	0	0	45.0333	43.3053
29	1	-1	1	-1	1	3.0357	3.2013
30	0	0	0	0	0	41.6558	43.3053
31	0	2	0	0	0	82.5532	83.8573
32	0	0	-2	0	0	13.5100	13.0608

Table-2: CCD plan matrix in coded values and Responses

Term	Constant	SE	T	P
b0	-640.427	20.305	-31.54	0.000
b_1	28.169	0.7889	35.707	0.000
b_2	-18.601	1.341	-13.871	0.000
b_3	4.737	0.1788	26.492	0.000
b_4	146.959	16.8947	8.699	0.000
b_5	2.791	0.1414	19.745	0.000
$b_1 * b_1$	-0.434	0.0106	-40.805	0.000
$b_2 * b_2$	1.729	0.0426	40.624	0.000
$b_3 * b_3$	-0.009	0.0008	-11.49	0.000
$b_4 * b_4$	-100.261	6.6512	-15.074	0.000
$b_5 * b_5$	-0.009	0.0004	-22.151	0.000
$b_1 * b_2$	0.227	0.0288	7.863	0.000
$b_1 * b_3$	-0.072	0.0038	-18.783	0.000
$b_1 * b_4$	4.283	0.3602	11.888	0.000
$b_1 * b_5$	-0.024	0.0029	-8.379	0.000
$b_2 * b_3$	0.032	0.0077	4.13	0.002
$b_2 * b_4$	-13.699	0.7205	-19.014	0.000
$b_2 * b_5$	-0.064	0.0058	-11.086	0.000
$b_3 * b_4$	-1.339	0.0961	-13.941	0.000
$b_3 * b_5$	-0.006	0.0008	-7.765	0.000
$b_4 * b_5$	0.648	0.072	8.997	0.000

Table- 3: Response Surface Regression of percentage removal efficiency of CV dye

Source	DF	SS	MS(Adj)	F	p
Linear	5	5311	958.15	461.48	0.000
Square	5	9096	1819.2	876.19	0.000
Interaction	10	3038.1	303.81	146.32	0.000
Residual Error	11	22.8	2.08		
Lack of Fit	6	16.7	2.78	2.27	0.193
Pure Error	5	6.1	1.23		
Total	31	17468			
S = 1.441		R = 0.9995		R-Sq = 99.9%	R-Sq(adj) = 99.6%

Table-4: Analysis of Variance for Removal of CV dye using CCD

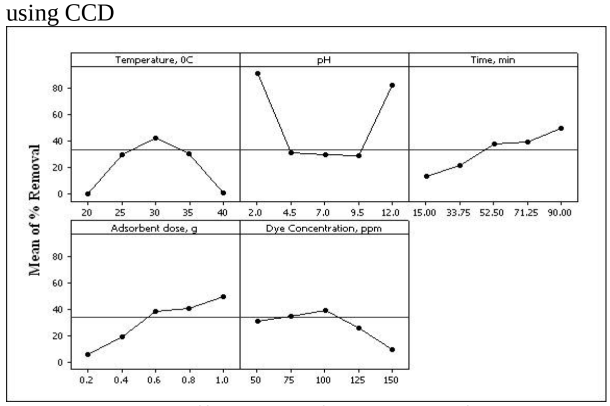

Fig-1: Main Effects plots of % Removal of CV Dye

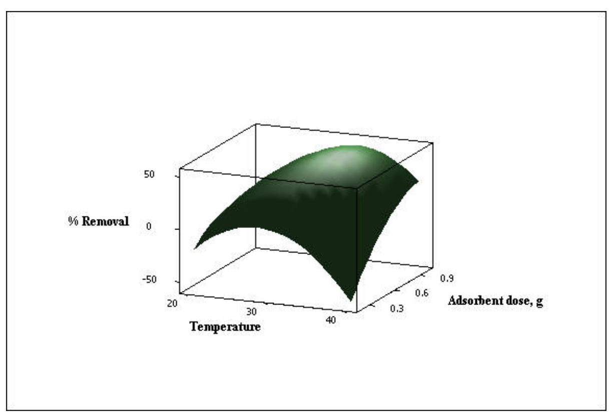

Fig-2: Surface plot of percentage removal of CV dye,Temperature and Adsorbent dose

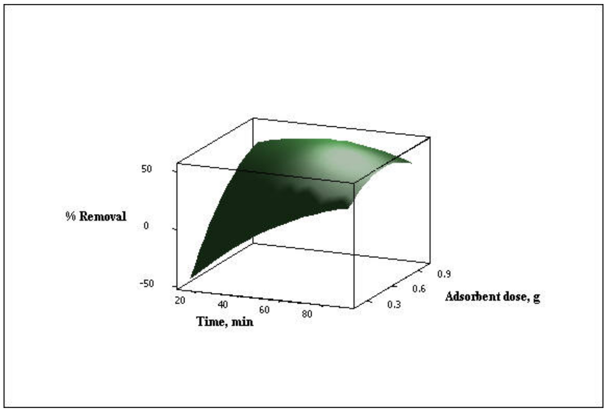

Fig-3: Surface plot of percentage removal of CV dye, Time and Adsorbent dose

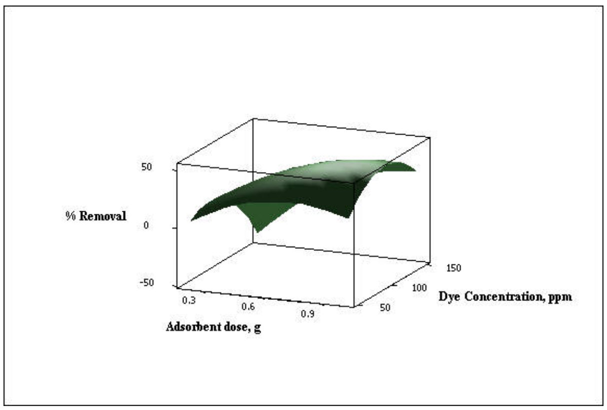

Fig-4: Surface plot of percentage removal of CV dye, Adsorbent dose and Dye concentration

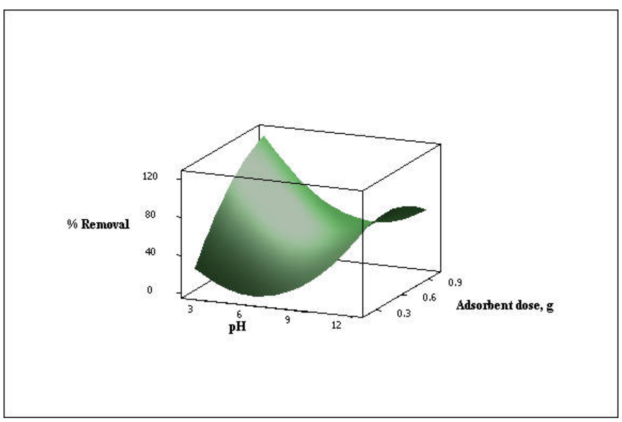

Fig-5: Surface plot of percentage removal of CV dye, Adsorbent dose and pH

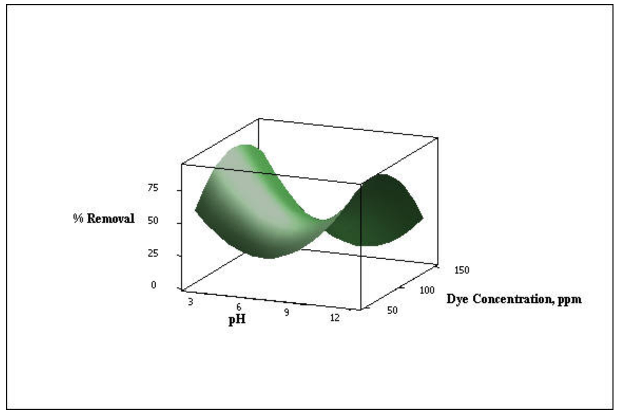

Fig-6: Surface plot of percentage removal of CV dye, Dye concentration and pH

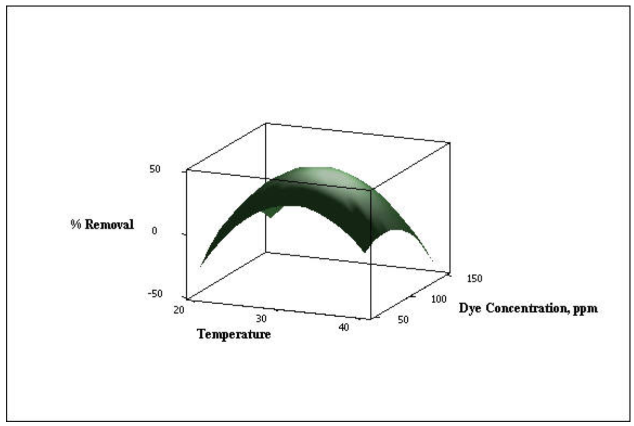

Fig-7: Surface plot of percentage removal of CV dye, Dye concentration and Temperature

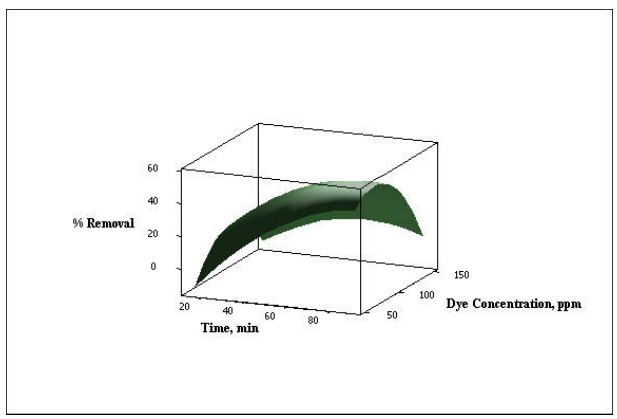

Fig-8: Surface plot of percentage removal of CV dye, Dye concentration and Time

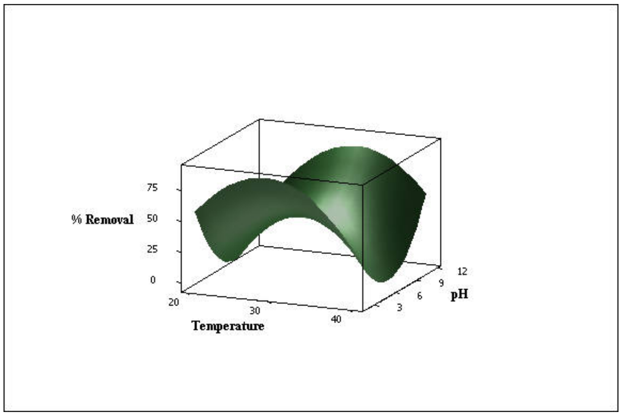

Fig-9: Surface plot of percentage removal of CV dye, Temperature and pH

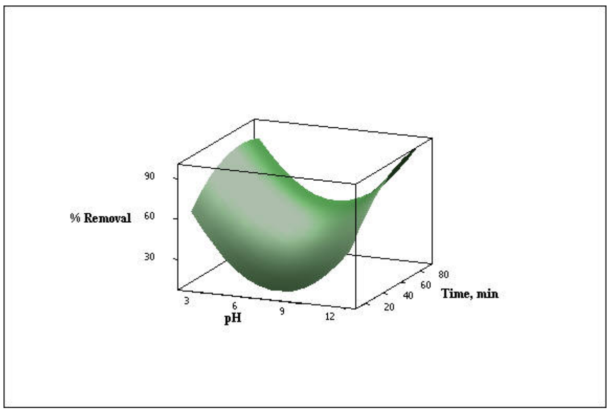

Fig-10: Surface plot of percentage removal of CV dye, pH and Time

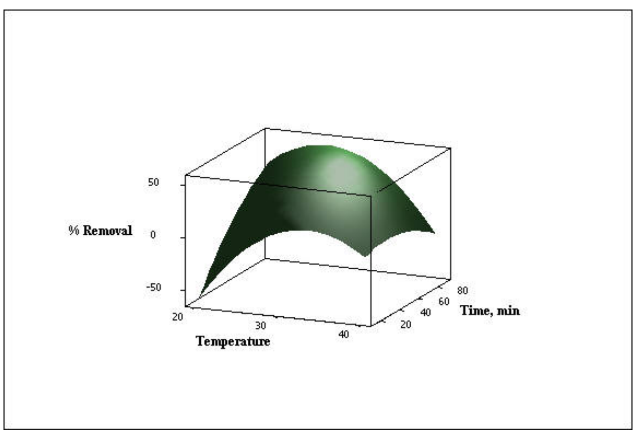

Fig-11: Surface plot of percentage removal of CV dye, Temperature and Time

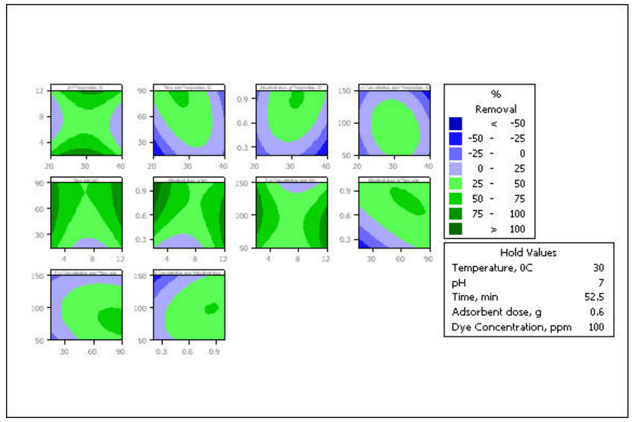

Fig-12: Contour plots of removal of CV dye

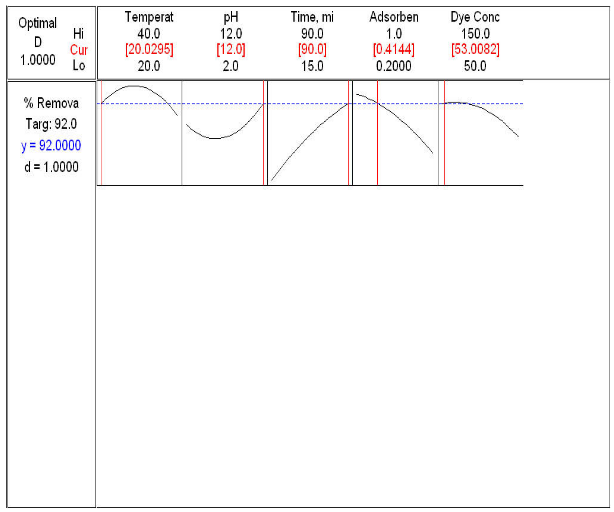

Fig-13: Response surface optimization plots for percentage removal of CV dye