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"Studies on removal of Fast Green dye from wastewater using Thespesia-populnea powder and optimization using Central Composite Design"

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Abstract

The use of inexpensive and environmentally friendly biosorbents for the removal of dye from wastewater has been investigated. Biosorbents derived from Thespesia-populnea were successfully used in a batch process to remove Fast Green dye from an aqueous solution. Fast Green dye was adsorbing with Thespesia-populneapowder at various dye concentrations, adsorbent dosage, pH, and contact time. Initial dye concentrations ranging from 20 to 200 ppm reduced dye removal efficiency. While the contact time is 50 minutes and the pH is optimal at 6,

Key Words: **pH, time, FTIR, XRD and SEM**

1.0 Introduction

Convectional wastewater treatment, which relies on aerobic biodegradation, has a low removal efficiency for reactive and other anionic soluble dyes **[1-2]**. Dyes production industries and many other industries that used dyes and pigments generated wastewater. Because dyes degrade slowly, a convectional biological treatment process is ineffective for treating dye wastewater. Physical or chemical processes are typically used to treat it. However, these processes are prohibitively expensive and cannot be used to effectively treat a wide range of dye waste **[3-4]**. Adsorption is one of the most effective methods for removing dyes from waste effluent.Adsorption has an advantage over other methods due to its sludge-free clean operation and complete removal of dyes, even from diluted solutions **[5-6]**. Because of its high adsorption efficiency for organic compounds, activated carbon (powdered or granular) is one of the most widely used adsorbents. However, commercially available activated carbon is prohibitively expensive **[7-8]**. Furthermore, regeneration with a solution produced only a small amount of additional effluent, whereas regeneration with a refractory technique results in a 10-15% loss of adsorbents and their uptake capacity **[9-10]**.However, because the adsorption capacities of the adsorbents mentioned above are not very large, new adsorbents that are more economical, easily available, and highly effective are still required.

2.0 Experimental procedure

2.1 Reagents and materials

All of the chemicals used in this study were of analytical grade and were not purified further. By adding 0.1N HCL and 0.1NNaOH solutions, the pH of the dye solution was adjusted to the desired value.

2.2 Preparation of Biosorbent

Thespesia-populnea leaves used as biosorbent and the leaves were washed with water to remove dust, micro algae, and soluble impurities before being dried in the sun until crisp. The dried material was then finely powdered and sized by passing it through a series of sieves ranging in mesh size from 152 to 53.

2.3 Preparation of Fast Green stock solution

Analytical reagents and double-distilled water are used to make all of the required solutions. To obtain 1000 ppm (mg/L) of Fast Green stock solution, 1.0 g of 99 percent Fast Green is dissolved in distilled water in a 1 L volumetric flask up to the mark.

2.4 Studies on equilibrium biosorption:

The biosorption was carried out in a batch process by adding a pre-weighed amount of Thespesia-populnea leaves powder to a known volume of aqueous solution in an orbital shaker for a predetermined time interval. The procedures used to evaluate the various parameters, including agitation time, pH, initial concentration of FG dye in aqueous solution, biosorbent dosage, and temperature, are described below.

2.5 Experimental design for biosorption studies

In order to obtain the optimum condition for % removal of FG dye, four independent parameters were selected for the study. The range of study for pH (X_1), Concentration (X_2),w, dosage (X_3)& Temp (X_4) are chosen based on preliminary experiments. The relationship between the parameters and response were determined using Response Surface Methodology (RSM) of STATISTICA software. The RSM is chosen in this study as it is efficient, flexible and robust. Thirty experiments are conducted according to RSM design. The percentage of Fast Green dye removal was taken as a response (Y) of the experimental design. Samples taken after the desired period are analyzed with an UV-Spectrophotometer. The regression analyses and graphical analyses were done.

3.0 Results and discussion

3.1 Effect of agitation time:

The equilibrium agitation time is determined by plotting the % biosorption of Fast Green dye against agitation time as shown fig. 3.1 for the interaction time intervals between 1 to 180 min. For 53 µm size of 10 g/L biosorbent dosage, 38 % of Fast Green dye is biosorbed in the first 20 min. The % biosorption is increased briskly up to 50 min reaching 69 %. Beyond 50 min, the % biosorption is constant indicating the attainment of equilibrium conditions. The rate of biosorption is fast in the initial stages because adequate surface area of the biosorbent is available for the biosorption of Fast Green dye. As time increases, more amount of Fast Green dye gets biosorbed onto the surface of the biosorbent due to vanderwaal forces of attraction and resulted in decrease of available surface area**[11-12]**.

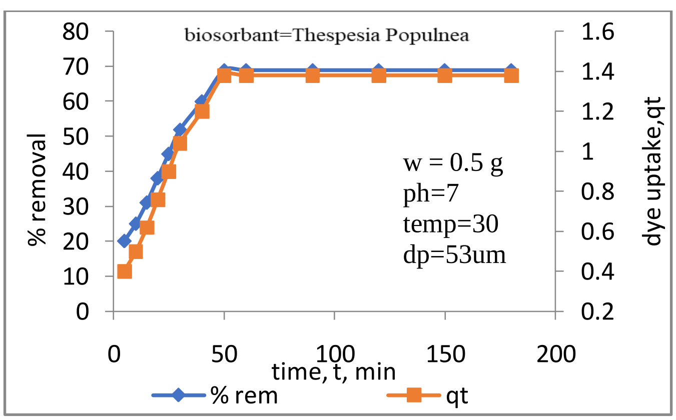

Fig. 3.1 Effect of time on % removal of Fast Green dye

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3.2 Effect of biosorbent size:

The variations in % biosorption of Fast Green dye from the aqueous solution with biosorbent size are obtained. The results are drawn in fig.3.2 with percentage biosorption of Fast Green dye as a function of biosorbent size. The percentage biosorption is decreased from 69 % to 50 % as the biosorbent size decreases from 152 to 53 µm. This phenomenon is expected, as the size of the particle decreases, surface area of the biosorbent increases; thereby the number of active sites on the biosorbent also increases**[13-14]**.

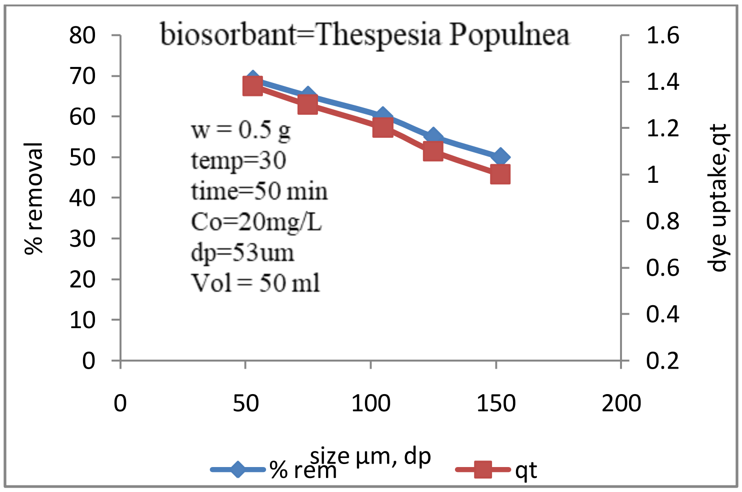

Fig. 3.2 Effect of size on % removal of Fast Green dye

3.3 Effect of pH:

The effect of pH of aqueous solution on % biosorption of Fast Green dye is shown in fig.3.3. The % biosorption of Fast Green dye is increased from 52 % to 75 % as pH is increased from 2 to 6 and decreased beyond the pH value of 6. % biosorption is decreased from pH 7 to 8 reaching 69 % from 62.5 %. Low pH depresses biosorption due to competition with H^+ ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and Fast Green dye ions replace H^+ ions bound to the biosorbent**[15-16]**.

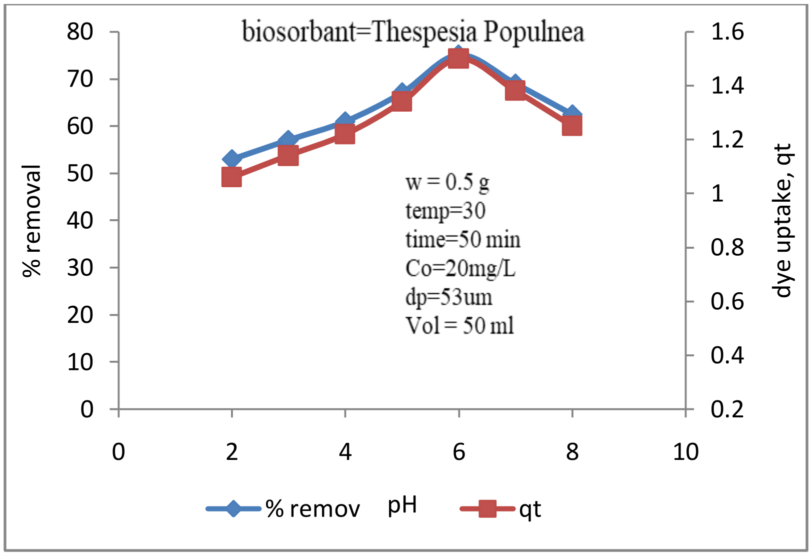

Fig. 3.3 Effect of pH % removal of Fast Green dye

3.4 Effect of initial concentration of Fast Green dye:

The effect of initial concentration of Fast Green dye in the aqueous solution on the percentage biosorption of Fast Green dye is shown in fig.3.4. The percentage biosorption of Fast Green dye is decreased from 75 % to 54.53 % with an increase in C_0 from 20 mg/L to 150 mg/L. Such behavior can be attributed to the increase in the amount of biosorbate to the unchanging number of available active sites on the biosorbent**[17-18]**.

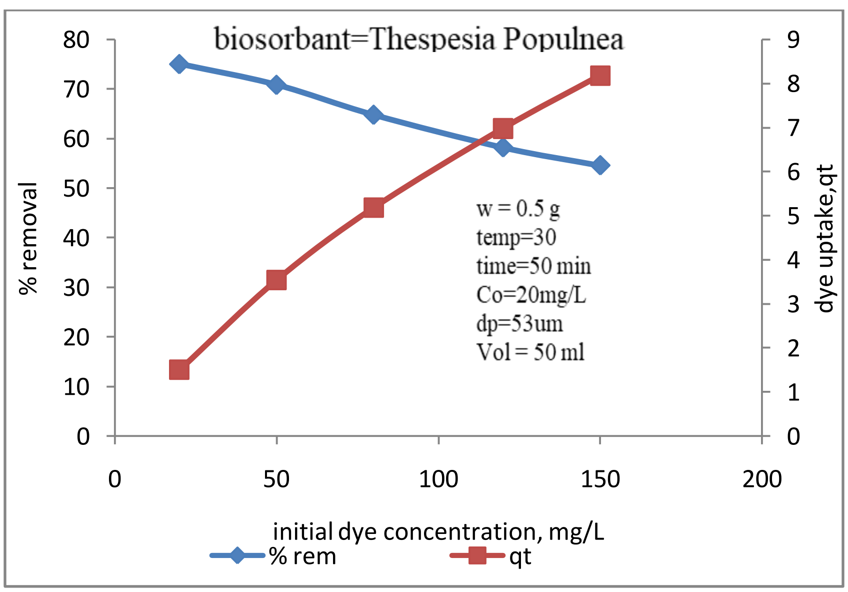

Fig. 3.4 Effect of initial concentration on % removal of Fast Green dye

3.5 Effect of biosorbent dosage:

The percentage biosorption of Fast Green dye is drawn against biosorbent dosage for 53µm size biosorbent in fig.3.5. The biosorption of Fast Green dye increased from 75 % to 85 % with an increase in biosorbent dosage from 10 to 25 g/L. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for Fast Green dye biosorption would be more. The change in percentage biosorption of Fast Green dye is marginal from 85 % to 86.5 % when 'w' is increased from 25 to 50 g/L. Hence all other experiments are conducted at 25 g/L dosage**[19-20]**.

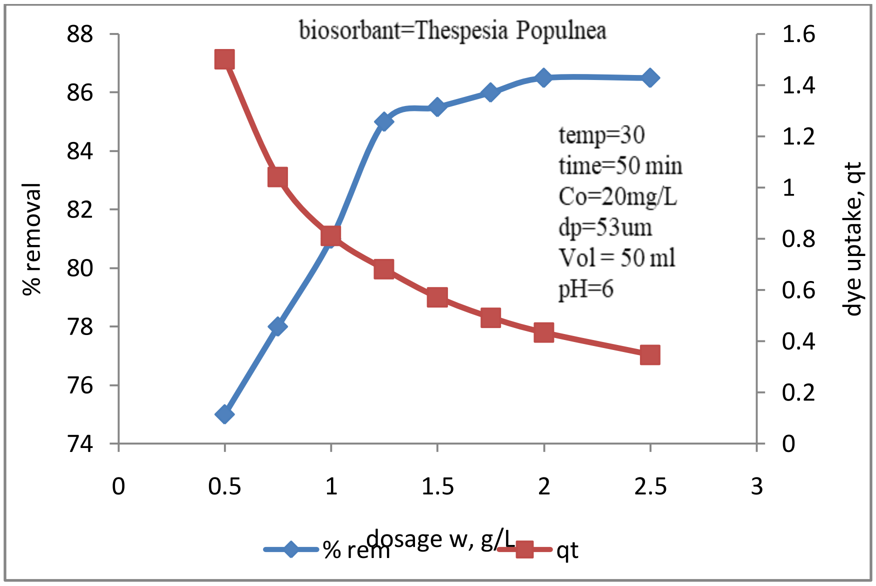

Fig. 3.5 Effect of dosage on % removal of Fast Green dye

3.6 Effect of Temperature:

The effect of temperature on the equilibrium dye uptake was significant. The effect of changes in the temperature on the Fast Green dye uptake is shown in Fig.3.6. When temperature was lower than 303 K, Fast Green dye uptake increased with increasing temperature, but when temperature was over 303 K, the results were on the contrary. This response suggested a different interaction between the ligands on the cell wall and the dye. Below 303 K, Physical biosorption reactions were normally exothermic, thus the extent of biosorption generally is constant with further increasing temperature**[21-22]**.

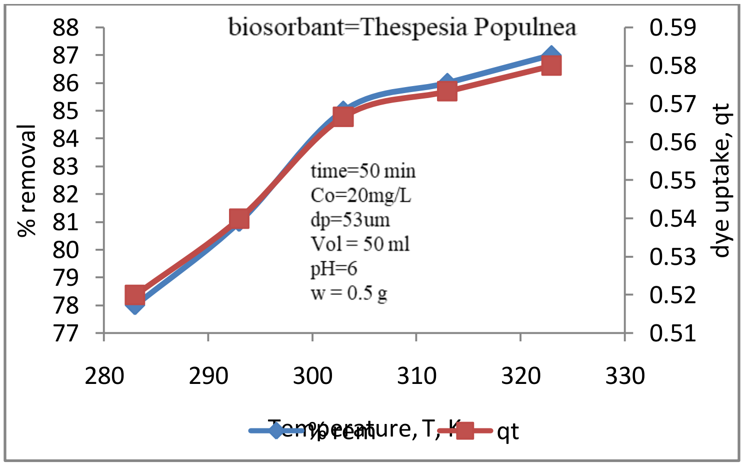

Fig. 3.6 Effect of temperature on % removal of Fast Green dye

3.7 Optimization using Response Surface Methodology (RSM):

3.7.1 Optimization using CCD

The parameters that have greater influence over the response are to be identified so as to find the optimum condition for the biosorption of Fast Green dye. The quadratic model is used in the present study, to relate four independent variables and percentage biosorption of Fast Green dye. The regression equation for is % biosorption of Fast Green dye (Y) is function of pH (X_1), C_o (X_2), w (X_3) and T (X_4) **[23-24]**.

The variations in the corresponding coded values of four parameters and response are presented in table-3.1

Table-3.1 Levels of different process variables in coded and un-coded form for % biosorption of Fast Green dye using *ThespesiaPopulnea*

Variable	Name	Range and levels				
		-2	-1	0	1	2
X_1	pH of aqueous solution	4	5	6	7	8
X_2	Initial concentration, C_o, mg/L	10	15	20	25	30
X_3	Biosorbent dosage, w, g/L	15	20	25	30	35
X_4	Temperature, T, K	283	293	303	313	323

The following equation represents multiple regression analysis of the experimental data for the biosorption of Fast Green dye:

$$\boldsymbol{Y = -1364.39 + 37.32 X_1 + 2.39 X_2 + 4.23 X_3 + 8.49 X_4 - 4.53 X_1^2 - 0.06 X_2^2 - 0.07 X_3^2 - 0.01 X_4^2 + 0.00 X_1X_2 - 0.01 X_1X_3 - 0.00 X_1X_4 + 0.00 X_2X_3 - 0.00 X_2X_4 + 0.00 X_3X_4} \text{------ } \mathbf{(3.1)}$$

Table-3.2 Results from CCD for Fast Green dye biosorption by *ThespesiaPopulnea*

Run no.	X_1, pH	X_2, C_o	X_3, W	X_4, T	% biosorption of Fast Green dye	
					Experimental	Predicted
1	3	15	25	293	85.98000	86.00583
2	3	15	25	313	87.50000	87.48833
3	3	15	35	293	88.08000	88.07167
4	3	15	35	313	89.58000	89.56917
5	3	25	25	293	84.08000	84.09833
6	3	25	25	313	85.52000	85.50583
7	3	25	35	293	86.52000	86.50917
8	3	25	35	313	87.90000	87.93167
9	5	15	25	293	86.40000	86.38500
10	5	15	25	313	87.78000	87.79250
11	5	15	35	293	88.18000	88.19583
12	5	15	35	313	89.62000	89.61833
13	5	25	25	293	84.48000	84.49250
14	5	25	25	313	85.80000	85.82500
15	5	25	35	293	86.62000	86.64833
16	5	25	35	313	88.02000	87.99583
17	2	20	30	303	77.86000	77.85917
18	6	20	30	303	78.32000	78.30250
19	4	10	30	303	91.58000	91.58583
20	4	30	30	303	88.08000	88.05583
21	4	20	20	303	87.36000	87.34250
22	4	20	40	303	91.58000	91.57917
23	4	20	30	283	89.28000	89.25583
24	4	20	30	323	92.08000	92.08583
25	4	20	30	303	96.22000	96.22000
26	4	20	30	303	96.22000	96.22000
27	4	20	30	303	96.22000	96.22000
28	4	20	30	303	96.22000	96.22000
29	4	20	30	303	96.22000	96.22000
30	4	20	30	303	96.22000	96.22000

Experimental conditions [Coded Values] and observed response values of central composite design with 2^4 factorial runs, 6- central points and 8- axial points. Agitation time fixed at 20 min and biosorbent size at 53 µm

Table- 3.3 represents the results obtained in CCD. Response obtained from regression in eq.3.1 in the form of ANOVA is presented.

Table- 3.3 ANOVA of Fast Green dye biosorption for entire quadratic model

Source of variation	SS	Df	Mean square(MS)	F-value	*P*> F
Model	120.7016	14	8.6215	285.1025	0.00000
Error	0.4536	15	0.03024		
Total	121.1552				

df- degree of freedom; SS- sum of squares; F- factor F; *P*- probability

R^2=0.99999; R^2 (adj):0.99998:

Table-3.4 Estimated regression coefficients for the Fast Green dye biosorption onto *ThespesiaPopulnea*

Terms	Regression coefficient	Standard error of the coefficient	t-value	*P*-value
Mean/Intercept	-1364.39	4.151260	-328.67	0.000000
Dosage, w, g/L (L)	37.32	0.175108	213.15	0.000000
Dosage, w, g/L (Q)	-4.53	0.004212	-1076.57	0.000000
Conc, Co, mg/L (L)	2.39	0.035022	68.25	0.000000
Conc, Co, mg/L (Q)	-0.06	0.000168	-379.79	0.000000
pH (L)	4.23	0.035482	119.12	0.000000
pH (Q)	-0.07	0.000168	-401.16	0.000000
Temperature, T, K (L)	8.49	0.025932	327.41	0.000000
Temperature, T, K (Q)	-0.01	0.000042	-329.35	0.000000
1L by 2L	0.00	0.001103	0.68	0.506897
1L by 3L	-0.01	0.001103	-11.56	0.000000
1L by 4L	-0.00	0.000552	-3.40	0.003960
2L by 3L	0.00	0.000221	15.64	0.000000
2L by 4L	-0.00	0.000110	-3.40	0.003960
3L by 4L	0.00	0.000110	0.68	0.506897

[a]insignificant ($P \geq 0.05$)

Among the interaction terms, all the terms ($P < 0.05$) are insignificant on the biosorption capacity. Fig. 3.7 and Fig. 3.8showspareto chart and normal probability plot (NPP) of residual values. It could be seen that the experimental points are reasonably aligned suggesting normal distribution.

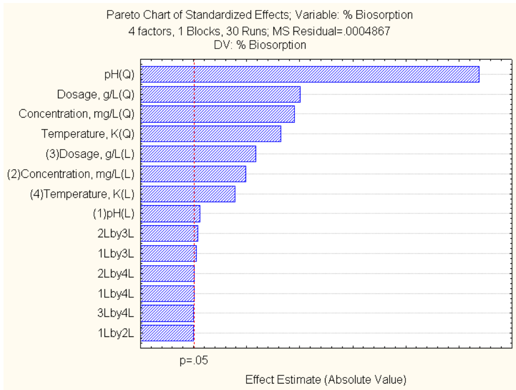

Fig. 3.7 Pareto Chart

3.7.2 Interaction effects of biosorption variables:

The three-dimensional view of response surface contour plots [Fig. 3.9 (a) to (f)] show % biosorption as a function of for various combinations of independent variables. The plots are represented as a function of two factors at a time keeping other factors fixed at zero level.

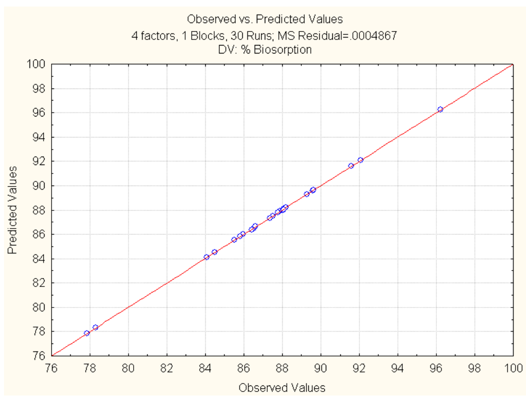

Fig. 3.8 Normal probability plot for % biosorption of Fast Green dye

The predicted optimal set of conditions for percentage biosorption of Fast Green dye is

pH of aqueous solution	= 4.0094
Initial Fast Green dye dye concentration	= 18.6548 mg/L
Biosorbent dosage	= 31.5332 g/L
Temperature	= 305.5716 K
% biosorption of Fast Green dye	= 96.5926

The optimal sets of conditions obtained with CCD are shown in table-3.5 along with experimental values.

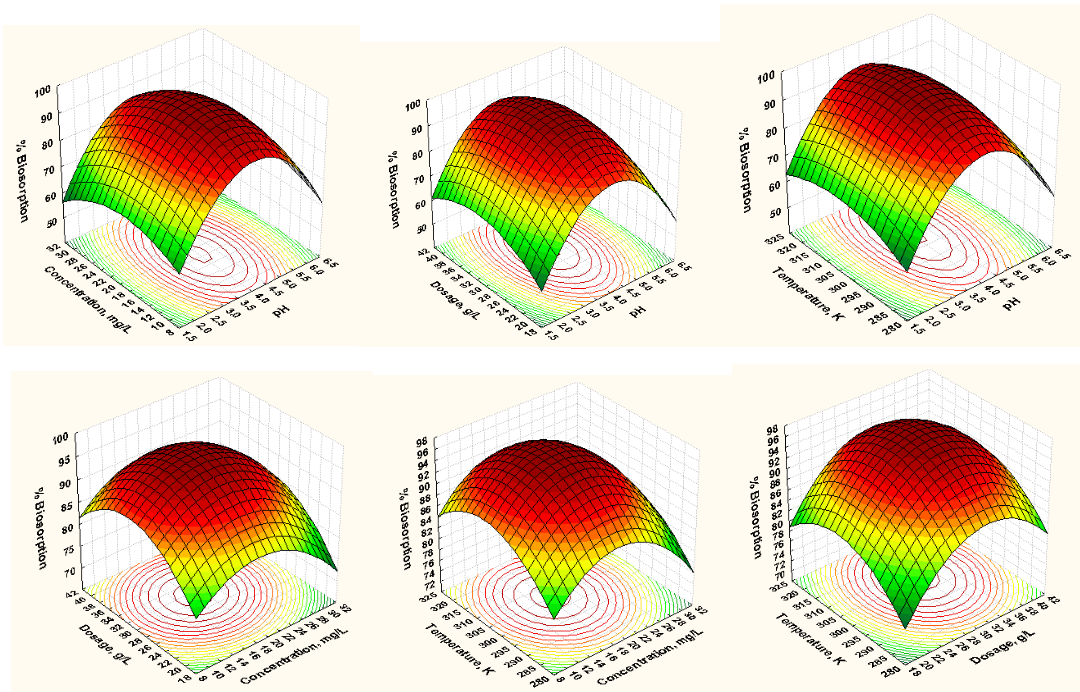

Fig. 3.9 (a-f) Surface contour plot for the effects of % biosorption of Fast Green dye

Table – 3.5 Comparison between optimum values from CCD and experimentation

Variable	CCD	Experimental value
pH of aqueous solution	4.0094	4
Initial Fast Green dye concentration, mg/L	18.6548	20
Biosorption dosage, w, g/L	31.5332	30
Temperature, K	305.5716	303
% biosorption	96.5926	95.0

4.0 CONCLUSIONS

The aim of this investigation is to determine the suitability of thespesia-populnea leaves powder as a biosorbent for the removal of Fast Green dye from aqueous solutions. The equilibrium, kinetic and thermodynamic studies are carried out for biosorption of FG dye experimentally and theoretically and results with the following conclusions. The equilibrium agitation time for dye biosorption is 50 minutes.The percentage biosorption of FG dye decreased with the increase in biosorbent size from 53 µm (69 %) to 152 µm (50 %). Percentage biosorption of FG dye from the aqueous solution increases significantly with increase in pH from 2 (53 %) to 6 (75 %).The optimum dosage for biosorption is 25 g/L.The maximum uptake capacity of 17.1526 mg/g is obtained at 303 K.The maximum biosorption of FG dye (83.57285 %) onto thespesia-populnea leaves powder is observed when the processing parameters are set as: pH = 6.0963, w = 42.12121 g/L and C o = 21.57143 mg/L using CCD.Hence the above said thespesia-populnea leaves powder is effective and efficient biosorbent and is capable of removing Fast Green dye.

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