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Application of response surface optimization on biosorption of Congo red dye onto *Spathodea campanulata* leaves

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ABSTRACT

The present work aims to remove Congo red (CR) dye from their aqueous solution using *Spathodea campanulata* leaves powder as low-cost biosorbent in a batch study. The effect of parameters in a batch study was contact time, solution pH, initial CR dye concentration, biosorbent dosage, the average particle size of the biosorbent and temperature. The main objective of the response surface methodology is to determine the optimum operational variables of the process. It is also used to evaluate the relative significance of process variables even in the presence of complex interactions. The maximum removal efficiency was predicted to be 88.2% for Congo red on to *Spathodea campanulata* leaves.

Keywords: Congo red; *Spathodea campanulata*; RSM; Central composite design; Biosorption

1. Introduction

Water pollutants are of different types such as oxygen demanding wastes, diseases causing agents, synthetic organic compounds, plant nutrients, inorganic chemicals and minerals, oils, thermal discharge, and radioactive wastes. Of all these water pollutants, heavy metals and synthetic organic compounds cause the majority of water pollution. Industries like paper and pulp, tanneries, textiles, and coke ovens, pharmaceutical, food processing, metal packing, dye-stuff, and fertilizer discharge these pollutants into natural water bodies. Heavy metals and synthetic organic compounds are non–biodegradable and they can be accumulated living tissues causing various diseases and cause great damage to human habitation. So these impurities and waste shall be removed and water shall be purified before we use. Oil spillage from ships in the sea causes major pollution to the ecosystem. Some wastes from pharmaceuticals and petrochemical industries contain phenols which are toxic to the natural life of flora and fauna [1]. Recent studies state that 12% of the synthetic textile dyes used early are lost to wastewater streams. Approximately 20% of these enter the environment through effluents from wastewater treatment plants [2]. Color removal from the effluent is one of the most difficult requirements faced by the dye producers and consumers because of the toxic nature. The dye-based effluent is a considerable source of non-aesthetic pollution since the presence of a small amount of dye (below 1 ppm) is visible. Many researchers found that colorant may cause problems in the aquatic ecosystem in several ways as follows (a) Dyes can have an acute chronic effect on exposed organisms, depending on the dye concentration and on the exposure time. (b) The coloration of surface waters captures the attention of both the public and the authorities. (c) Dye present in the water affects the sunlight entering the water and have a drastic effect on the growth of bacteria and disturb the biological activity. (d) Dyes have complex molecules structure which can't be removed by municipal wastewater treatment operations biosorption technique was the most favorable procedure among all the physicochemical and adsorption, flocculation combined with flotation, membrane filtration, electrokinetic coagulation, ozonation, oxidation,

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precipitation and Ion exchange methods [3]. The response surface methodology (RSM) is a collection of useful mathematical and statistical techniques for analyzing the effects of several independent variables on the response of interest. RSM offers certain advantages in adsorption processess like improved percentage yield, closer confirmation of the output response to nominal and target requirements, reduced process variability and reduced developmental time and overall costs. Therefore, the present study aims to conduct Congo red biosorption onto *Spathodea campanulata* leaves biosorbent and to investigate the combined effects of various process variables on the percentage of biosorption using central composite design (CCD) in RSM.

2. Materials and methods

2.1. Preparation of dye solution

Stock solutions of Congo red concentration 1,000 mg/L were prepared by dissolving 1 g of 100% Congo red in 1,000 ml of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared dye solutions varied between 20 and 200 mg/L was prepared using the stock solution of individual dye.

2.2. Preparation of biosorbent

The green-colored *Spathodea campanulata* leaves used in the present study were collected from the College of Engineering, Andhra University, Visakhapatnam, India. The collected leaves were washed with deionized water several times to remove dirt particles. The washing process was continued until the wash water contains no dirt. The washed leaves were then completely dried in sunlight for 20 d. The dried leaves were then cut into small pieces and powdered using domestic mixie. In the present study, the powdered materials in the range of 53–152 mm particle size were directly used as biosorbents without any pretreatment.

2.3. Response surface methodology

Optimization of different process parameters depending on the dye removal is highly required for the effective design and accurate control of the biosorption technique. So, RSM is a time-saving and precise alternative to conventional optimization methods. The main objective is to optimize the response surface that is shaped under the influence of process parameters. The effect of different process parameters such as temperature (X_1), solution pH (X_2), biosorbent dosage (X_3) and initial dye concentration (X_4) on Congo red dye removal from aqueous solutions was studied by using full factorial rotatable CCD. Total thirty experiments, which include 16 cube point runs, 8 axial point runs and 2 center point, 4 dummy runs were required and all of them were done in duplicate. All the experiments were conducted at contact time (t) and a constant speed of agitation 180 rpm. All independent variables were coded to five levels as X_i according to Eq. (1).

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

where X_i is the dimensionless value of an independent variable, x_i is the real value of an independent variable, x_{0i} is the real value of the independent variable at the center point, and Δx_i is the step change. A second-degree polynomial equation (Eq. (2)) was developed to estimate the percentage of biosorption of dyes at different operating conditions of the biosorption process by using STATISTICA 6.0 (Stat Soft Inc.).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2$$
$$+ b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \tag{2}$$

where Y is the predicted response, X_1, X_2, X_3 and X_4 are independent variables: b_0 is an offset term; b_1, b_2, b_3, and b_4 are linear effects; b_{11}, b_{22}, b_{33} and b_{44} are squared effects and b_{12}, b_{13}, b_{14}, b_{23}, b_{24} and b_{34} are interaction terms.

3. Results and discussion

3.1. Effect of contact time

The percentage of biosorption was determined at different contact times and the results are shown in Fig. 1. The figure reveals that the percentage of biosorption Congo red was steeply increased with an increase in contact time from 5 to 40 min and thereafter reached plate after attaining equilibrium 40 min for Congo red. Therefore, the contact time of 40 min is sufficient for the removal of Congo red under the experimental conditions used in this study. The percentage of biosorption of *Spathodea campanulata* leaves as biosorbent for Congo red dye removal was increased from 11% to 64%, with an increase in contact time from 5 to 40 min for an initial dye concentration of 20 mg/L. For 200 mg/L, the percentage of biosorption increased from 7% to 56% mg/g, respectively with an increase in contact time from 5 to 40 min [4,5].

3.2. Effect of solution pH

The solution pH is one of the important controlling parameters of the biosorption process. The effect of solution pH on % biosorption for the removal of Congo red

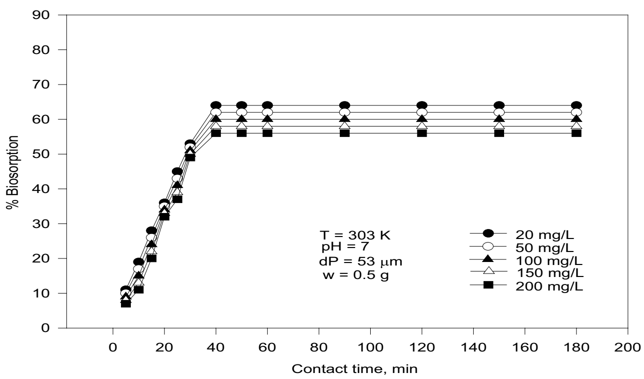

Fig. 1. Effect of contact time on % biosorption of Congo red using *Spathodea campanulata* leaves as biosorbent.

dye was studied from Fig. 2. It was observed that the increase in solution pH from 2 to 7 for Congo red resulted in an increase in the percentage of biosorption from 44% to 64% for Congo red for an initial concentration of 20 mg/L. As the pH of the solution increases, due to the absorption of OH^- ions by the biosorbent the number of positively charged sites decreases and negatively charged sites increase on the surface of the biosorbent. The higher biosorption rates at high pH were attributed to the fact that at high solution pH the surface of *Spathodea campanulata* leaves as biosorbent was in highly negative form thus strong electrostatic interactions developed between the positively charged dye and negatively charged biosorbent surface. This could be responsible for high values of % biosorption and dye uptake of biosorbent at high values of solution pH and the pH of the solution increases, biosorption percentage decreases due to strong electrostatic repulsions developed between positively charged dye ions and negatively charged biosorbent surface. For an initial concentration of 200 mg/L, the percentage of biosorption was increased from 36% to 58% for Congo red with an increase in solution pH from 2 to7 [6–12].

3.3. Effect of the initial concentration of dye

The effect of initial dye concentration on the percentage of biosorption is shown in Fig. 3. It is evident from the figure that the percentage of biosorption decreased with an increase in the initial concentration of dye from 20 to 200 mg/L at all temperatures. The percentage of biosorption of Congo red decreased from 60% to 36% and 66% to 42% for Congo red with an increase in the initial concentration of Congo red from 20 to 200 mg/L at the temperature of 283 and 323 K, respectively [13,14].

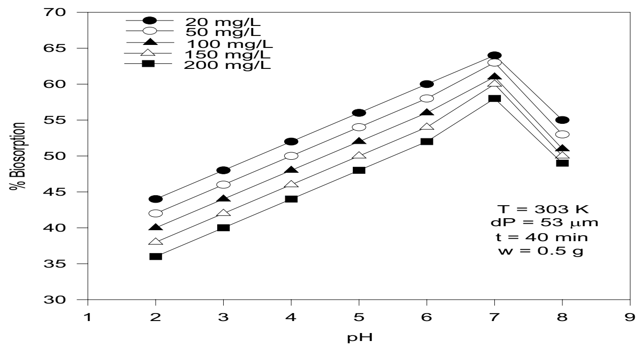

Fig. 2. Effect of solution pH on % biosorption of Congo red using *Spathodea campanulata* leaves as biosorbent.

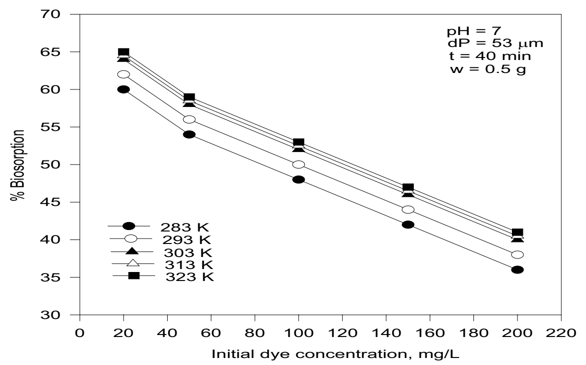

Fig. 3. Effect of the initial concentration of dye on % biosorption of Congo red using *Spathodea campanulata* leaves as biosorbent.

3.4. Effect of biosorbent dosage

The result obtained is shown in Fig. 4, illustrate that the percentage of biosorption was increased with an increase in biosorbent dosage. The percentage of biosorption increased from 64% to 86.5 % from biosorbent dosage 0.5 to 4 g for an initial concentration of Congo red 20 mg/L. For an initial concentration of Congo red 200 mg/L, the percentage of biosorption increased from 56% to 72.5% from biosorbent dosage 0.5–4 g [15–21].

3.5. Effect of particle size of biosorbent

The result obtained is shown in Fig. 5. The result indicated that the percentage of biosorption was decreased with an increase in the average particle size of biosorbent. The percentage of biosorption decreased from 79% to 59% and 70% to 51% with an increase in average particle size of biosorbent from 53 to 152 μm for an initial concentration of Congo red 20 and 200 mg/L, respectively [22–28].

3.6. Effect of temperature

The result obtained is shown in Fig. 6. The figure indicated that the percentage of biosorption was increased with

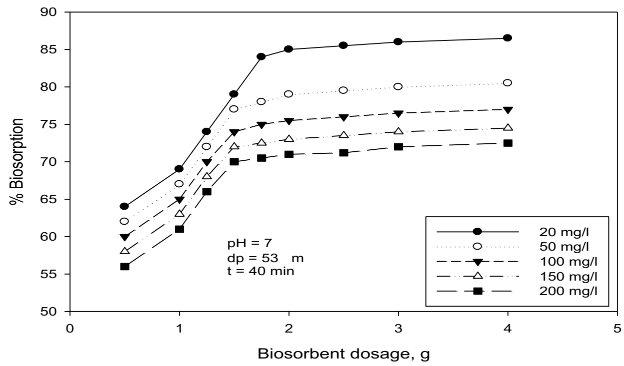

Fig. 4. Effect of biosorbent dosage on % biosorption of Congo red using *Spathodea campanulata* leaves as biosorbent.

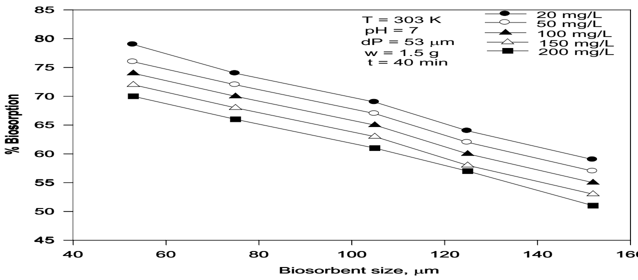

Fig. 5. Effect of average particle size on % biosorption of Congo red onto *Spathodea campanulata* leaves biosorbent.

an increase in the temperature of the solution. This suggests the endothermic nature of the biosorption process. The percentage of biosorption increased from 76% to 82% and from 70% to 75.5% with an increase in solution temperature from 283 to 323 K for an initial concentration of Congo red 20 and 200 mg/L, respectively [29–35].

3.7. Equilibrium studies

3.7.1. Langmuir adsorption isotherm

The applicability of the Langmuir adsorption isotherm model was analyzed using the experimental data by plotting C_e/q_e vs. C_e. Fig. 7 shows the Langmuir plot for the biosorption of Congo red dye at a temperature 303 K and the separation factor (R_L) values at different initial dye concentrations for the dye was determined and shown in Fig. 8. Langmuir constants and maximum biosorption capacity are compiled in Table 1. The high correlation coefficient indicates that the biosorption of dyes onto *Spathodea campanulata* leaves biosorbent followed the Langmuir isotherm. The maximum biosorption capacity (q_m) values were found to be 11.73 mg/g for Congo red.

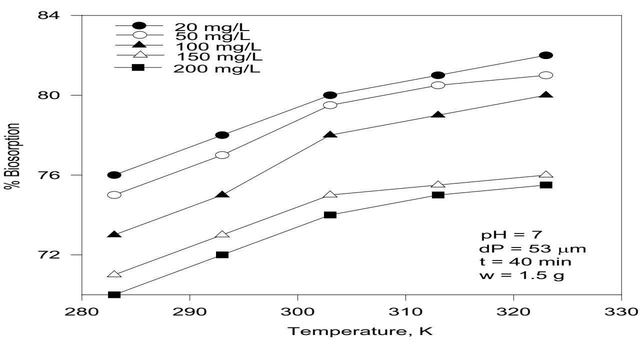

Fig. 6. Effect of temperature on % biosorption of Congo red onto *Spathodea campanulata* leaves biosorbent.

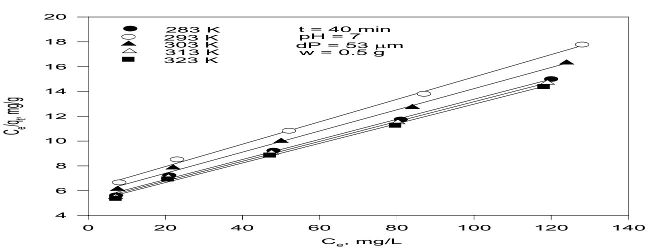

Fig. 7. Langmuir isotherm for biosorption of Congo red.

3.7.2. Freundlich isotherm

The experimental data were tested for the fitness of the Freundlich isotherm model by using a linear graphical method. The biosorption data was analyzed by plotting lnq_e vs. lnC_e shown in Fig. 9.

3.7.3. Temkin isotherm

Temkin isotherm studies were conducted to evaluate the biosorption potentials and to assess the variation of biosorption energies during the biosorption of Congo red dye using *Spathodea campanulata* leaves as biosorbent. The biosorption data were analyzed according to the linear form of the Temkin model and is shown in Fig. 10 for the removal of Congo red dye. The linear Temkin isotherm constants B_T and

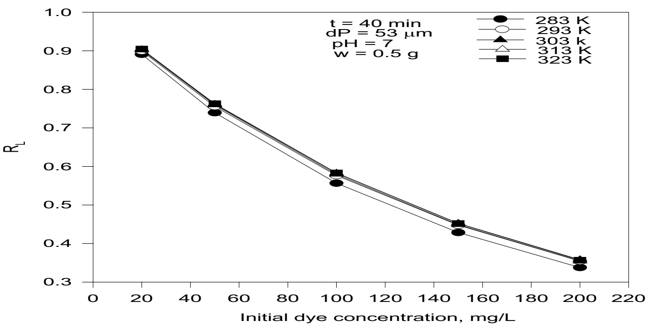

Fig. 8. Separation factor for biosorption of Congo red.

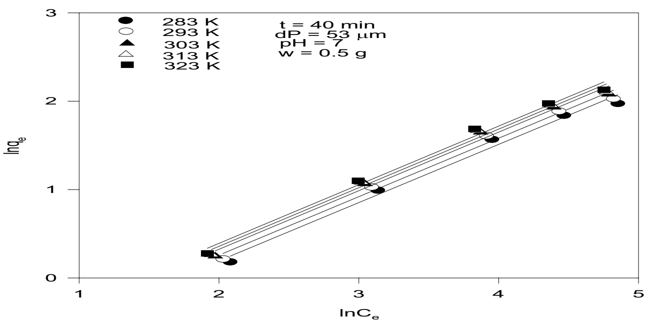

Fig. 9. Freundlich isotherm for biosorption of Congo red.

Table 1
Biosorption isotherm constants for Congo red removal using *Spathodea campanulata* biosorbent

Temperature, T(K)	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	q_{max}, (mg/g)	K_L, (L/mg)	R^2	N	K_f, (mg$^{1-1/n}$ L$^{1/n}$/g)	R^2	B_T, (J/mol)	A_T, (L/g)	R^2
283	12.36	0.01	0.99	0.65	0.32	0.98	1,059.75	0.18	0.98
293	11.08	0.01	0.99	0.66	0.34	0.98	1,045.22	0.18	0.97
303	11.73	0.01	0.99	0.66	0.36	0.99	1,033.24	0.19	0.97
313	12.51	0.01	0.99	0.66	0.37	0.99	1,044.84	0.20	0.97
323	12.67	0.01	0.99	0.66	0.39	0.99	1,056.33	0.20	0.97

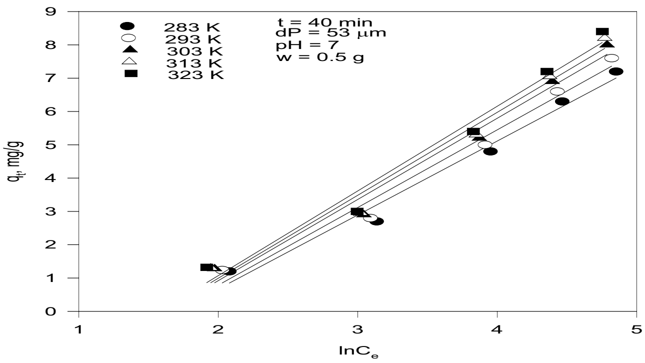

Fig. 10. Temkin isotherm for biosorption of Congo red.

A_T, were determined from the slope and intercept of the plots of q_e vs. $\ln C_e$ [36–40].

High correlation coefficient, R^2, values suggest that the biosorption process could be due to heterogeneous surface coverage. This is in good agreement with the result of Langmuir isotherm for Congo red dye.

4. Optimization of biosorption process parameters using RSM

The variables such as temperature, solution pH, the dosage of the biosorbent and initial dye concentration are all the four essential parameters of biosorption studies, significantly affected the percentage of biosorption of the dye of the biosorbent. Hence, these four variables were selected as independent variables to find the optimized conditions for the maximum percentage of biosorption of Congo red dye onto *Spathodea campanulata* leaves biosorbent using RSM. The influence of various process parameters such as temperature (x_1), solution pH (x_2), biosorbent dosage (x_3) and initial dye concentration (x_4) on the biosorption of Crystal violet onto the biosorbent was studied by using full factorial CCD. The response was expressed as the percentage of biosorption of Congo red dye. A CCD with 30 experiments, which includes 16 cube point runs, 8 center point runs, 2 axial point runs and 4 dummy runs, was used for the optimization of process variables for the removal of Congo red dye from aqueous solution. For statistical calculations, all independent variables were coded using Eq. (1). Based on the analysis of preliminary experimental results, the range of variables used in this design was selected and tabulated in Table 2 and the experimental design matrix along with the percentage of biosorption of Congo red tabulated in Table 3.

Fig. 11. represent the parity plots of Congo red dye which compare the experimental percentage of biosorption values with the predicted values obtained from the model. The parity plots shown in these figures demonstrate that the data points were distributed very close to the straight line for the dye which indicates the good agreement between the experimental and predicted values of percentage of biosorption of Congo red dye [41–45].

The results of the second-order polynomial regression model in the form of analysis of variance are compiled in Table 4. The statistical significance of the regression model

Table 2
Levels of different process variables used in CCD for the biosorption of Congo red dye onto *Spathodea campanulata* leaves as biosorbent

Variable	Name	Range and levels				
		–2	–1	0	1	2
X_1	Temperature, T (K)	283	293	303	313	323
X_2	pH of aqueous solution	5	6	7	8	9
X_3	Biosorbent dosage, w (g)	0.5	1	1.5	2	2.5
X_4	Initial concentration, C_0, mg/L	10	15	20	25	30

Table 3
Experimental design matrix along with the percentage of biosorption of Congo red dye onto *Spathodea campanulata* leaves biosorbent

Experimental run no.	x_1	x_2	x_3	x_4	% Biosorption of Congo red	
					Experimental	Predicted
1	–1	–1	–1	–1	73.2800	73.2775
2	–1	–1	–1	1	73.9800	73.9883
3	–1	–1	1	–1	76.3200	76.2683
4	–1	–1	1	1	77.0200	77.0542
5	–1	1	–1	–1	72.4200	72.3617
6	–1	1	–1	1	72.9000	72.9575
7	–1	1	1	–1	78.0200	78.0975
8	–1	1	1	1	79.0200	78.7683
9	1	–1	–1	–1	78.5800	78.7550
10	1	–1	–1	1	79.3200	79.2608
11	1	–1	1	–1	79.1200	79.0808
12	1	–1	1	1	79.6800	79.6617
13	1	1	–1	–1	74.9800	74.9642
14	1	1	–1	1	75.3800	75.3550
15	1	1	1	–1	78.1200	78.0350
16	1	1	1	1	78.4800	78.5008
17	–2	0	0	0	64.9000	64.9642
18	2	0	0	0	70.1800	70.1742
19	0	–2	0	0	81.6200	81.5675
20	0	2	0	0	79.3800	79.4908
21	0	0	–2	0	76.8200	76.7508
22	0	0	2	0	82.7600	82.8875
23	0	0	0	–2	78.1200	78.0908
24	0	0	0	2	79.1800	79.2675
25	0	0	0	0	88.2000	88.2000
26	0	0	0	0	88.2000	88.2000
27	0	0	0	0	88.2000	88.2000
28	0	0	0	0	88.2000	88.2000
29	0	0	0	0	88.2000	88.2000
30	0	0	0	0	88.2000	88.2000

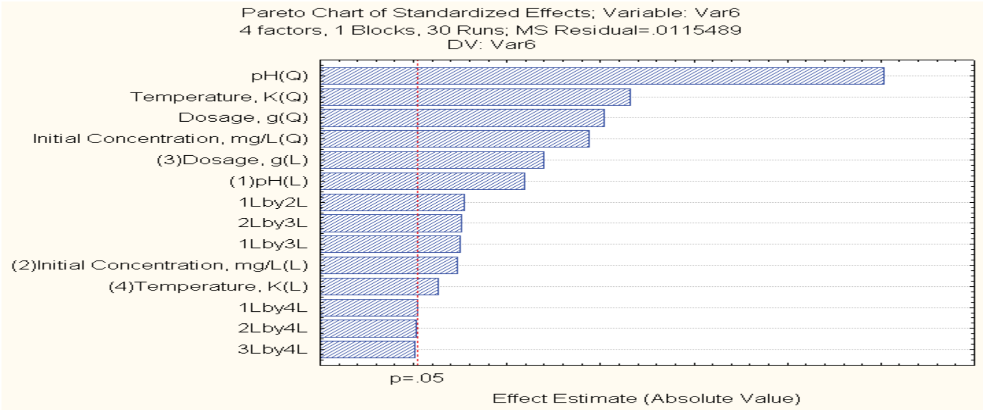

Fig. 11. Parity plot for Congo red biosorption.

Table 4
Response surface regression coefficients for the removal of Congo red

Term	Coeff.	SE coeff.	*t*-value	*P*-value
Const.	–2,458.40	20.34559	–120.832	0.000000
x_1	79.94	0.87392	91.470	0.000000
x_2	–5.16	0.02052	–251.355	0.000000
x_3	3.73	0.17111	21.818	0.000000
x_4	–0.08	0.00082	–93.457	0.000000
x_1^2	30.91	1.70322	18.149	0.000000
x_2^2	–8.38	0.08208	–102.108	0.000000
x_3^2	14.50	0.12650	114.589	0.000000
x_4^2	–0.02	0.00021	–115.997	0.000000
x_1x_2	–0.14	0.00537	–26.753	0.000000
x_1x_3	–1.33	0.05373	–24.799	0.000000
x_1x_4	–0.01	0.00269	–1.908	0.075777
x_3x_2	0.27	0.01075	25.543	0.000000
x_4x_2	–0.00	0.00054	–1.070	0.301488
x_3x_4	0.00	0.00537	0.698	0.495919

Table 5
Analysis of variance for removal of Congo red dye

Factors	SS	Df	MS	*F*	*P*
x_1	40.7162	1	40.7162	3,525.55	0.000000
x_2	729.6536	1	729.6536	63,179.55	0.000000
x_3	6.4688	1	6.4688	560.12	0.000000
x_4	100.8715	1	100.8715	8,734.30	0.000000
x_1^2	56.4880	1	56.4880	4,891.21	0.000000
x_2^2	120.4086	1	120.4086	10,425.99	0.000000
x_3^2	2.0768	1	2.0768	179.83	0.000000
x_4^2	155.3936	1	155.3936	13,455.29	0.000000
x_1x_2	8.2656	1	8.2656	715.71	0.000000
x_1x_3	7.1022	1	7.1022	614.97	0.000000
x_1x_4	0.0420	1	0.0420	3.64	0.075777
x_3x_2	7.5350	1	7.5350	652.45	0.000000
x_4x_2	0.0132	1	0.0132	1.15	0.301488
x_3x_4	0.0056	1	0.0056	0.49	0.495919
Error	0.1732	15	0.0115		
Total SS	992.6524	29			

equations was evaluated by the *F*-test ANOVA. The significance of each variable was determined by *F*-values and *p*-values. It was observed in Table 5. That the *F* statistic values for all regression were higher, which indicates that the developed models were highly significant and adequate to represent the relationship between the percentage of biosorption of the dye and process parameters. The larger fisher *F*-value with a low probability values (<0.05) demonstrates that the developed mathematical models were fitted well to the experimental data. From the ANOVA results, it is evident that the linear and quadratic effects were highly significant in comparison with interaction effects for the dye. However, for Congo red, interaction effects of biosorbent dosage and initial dye concentrations were significant.

The response surface graphs were plotted to know the interaction of the process variables and to determine the optimum level of each variable for maximum response. The peak of the response surface graph shows the optimum value of the percentage of biosorption of dye. The response surface curves for a percentage of biosorption are shown in Figs. 12–17 for Congo red.

The optimization of process variables to get a maximum response of dye onto *Spathodea campanulata* leaves biosorbent was carried out. The optimal values of the variables from RSM for Congo red are as follows: temperature = 303.62 K, solution pH of 7.11, and initial dye concentration of 19.51 mg/L and biosorbent dosage of 1.66 g with the corresponding value of maximum percentage of biosorption 88.2% and biosorption capacity of biosorbent for the removal of Congo red dye is 11.73 mg/g.

5. Conclusion

The biosorption studies showed that a contact time of 40 min was sufficient for the maximum removal of Congo red dye from aqueous solution using *Spathodea campanulata*

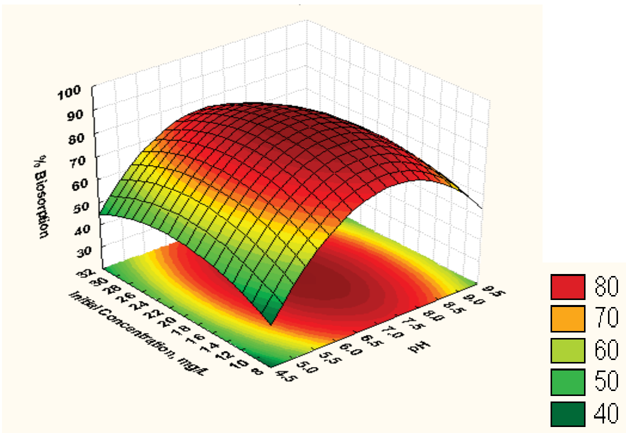

Fig. 12. Response surface plot of pH vs. initial dye concentration for the biosorption of Congo red.

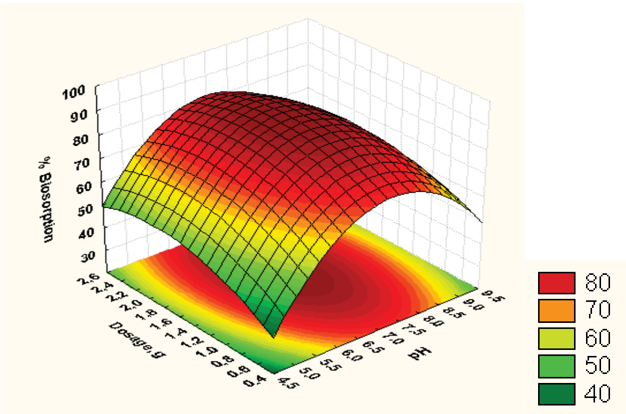

Fig. 13. Response surface plot of pH vs. Biosorbent dosage for the biosorption of Congo red.

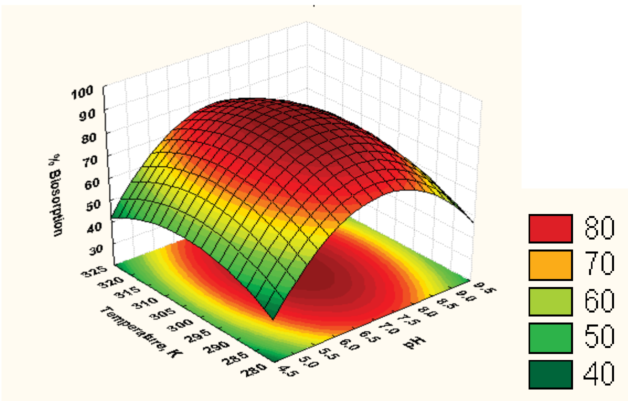

Fig. 14. Response surface plot of pH vs. temperature for the biosorption of Congo red.

biosorbent. The maximum removal efficiency was predicted to be 88.2% at a temperature of 303.62 K, solution pH of 7.11, and initial dye concentration of 19.51 mg/L and biosorbent dosage of 1.66 g and biosorption capacity of biosorbent for the removal of Congo red dye is 11.73 mg/g.

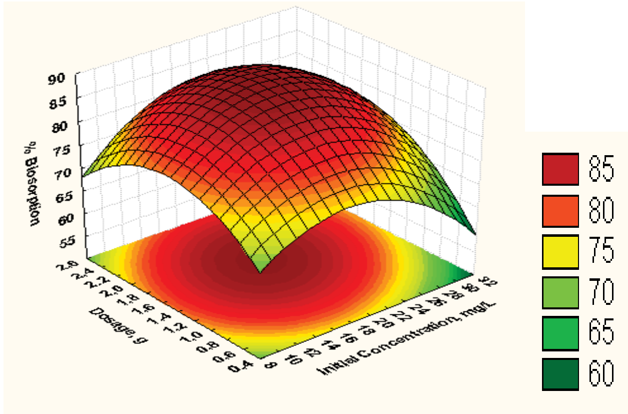

Fig. 15. Response surface plot of initial dye concentration vs. biosorbent dosage for the biosorption of Congo red.

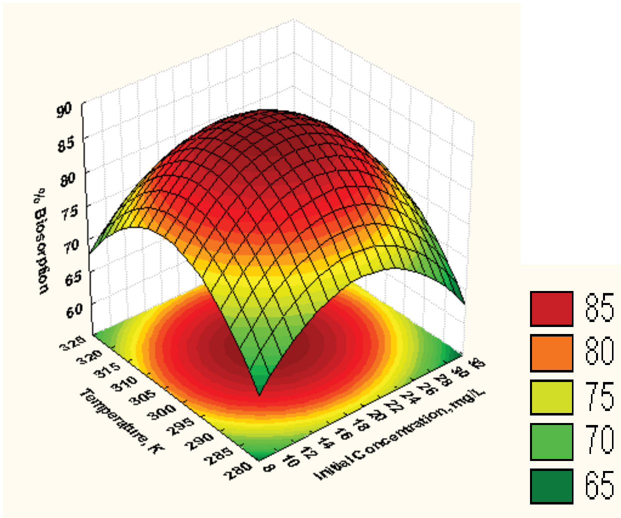

Fig. 16. Response surface plot of initial dye concentration vs. temperature for the biosorption of Congo red.

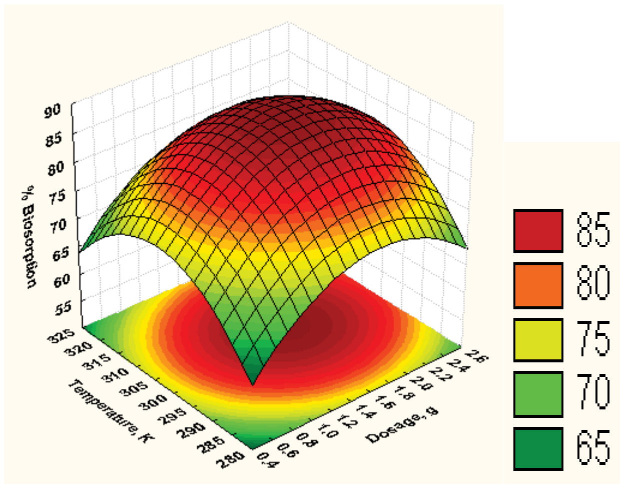

Fig. 17. Response surface plot of biosorbent dosage vs temperature for the biosorption of Congo red.

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