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Sorption of Synthetic Bromo Phenol Blue Dye using Gelidium Cartilagineum Powder and Optimization using Central Composite Design

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ABSTRACT

The removal of synthetic bromo cresol purple dye was experimented using sargassum muticum algae powder. The parameters studied include agitation time, algae powder size, pH of the solution, Initial concentration of BCP dye solution, dosage of algae powder and temperature. Different isotherms like Langmuir, freundlich and temkin were also studied along with lagergren first order & pseudo second order kinetics and thermodynamics as well. Results indicated that the optimum pH and size of the biosorbent were obtained to be 5 and 53 μm. Entire total system followed Langmuir Isotherm and Lagergren First order Kinetics. Thermodynamics revealed that system is endothermic, spontaneous and irreversible.

Keywords: Bromo Phenol Blue, Equilibrium time, pH, dosage, Central Composite Design, Concentration, Temperature

INTRODUCTION

As we all know that demand and supply are proportional to each other on purely economic basis. The population increased the need for the products in turn increasing the utilization of natural resources for our present day industries to have products. So as we know that in our present day computerized world our natural resources are depleting day by day and aggravating the atmosphere through pollution. So being engineers for future generations, it is our responsibility to propose an alternative method in order to run the industries and decrease the pollution released by these industries. We had another alternative which is more advantageous than the other complex and complicated methods i.e. biosorption.

Methods for treating textile dye wastewaters consist of various chemical, physical and biological processes .Biosorption is a promising biotechnology for pollutant removal from their solutions. The materials of biological origin are used as sorbents in order to remove dyes from the solution. These ‘biosorbents’ contain a variety of functional groups which can catch complex dyes. Research in the field of biosorption suggests a number of advantages over other techniques such as: the material can be found easily as waste or by-products, materials can be recycled, no need of costly growth media, methods are simple, and requires less investment. Moreover, the process is ecofriendly, rapid, easy to operate and independent of the physiological constraints of living cells.

MATERIALS AND METHODS

The experimental procedure consists of the following steps:

2.1. Preparation of the Biosorbent.

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2.2. Preparations of the 1000 mg/L of BPB dye stock solution.

2.3. Studies on Equilibrium Biosorption Process.

Preparation of the Biosorbent

Gelidium cartilagineum algae were collected from Jodugullapalem beach in Visakhapatnam and were washed with water to remove dust and soluble impurities and dried in sun light till the algae became crispy and colorless. By passing it through a set of sieves ranging from 300 to 75 mesh sizes the dried algae were finely powdered and sized. The powder of 53, 75, 105, 125 and 152 micron meters were separated and stored in dry bottles with double cap and used as biosorbent.

Preparation of 1000 Mg/L of BPB Dye Stock Solution

To prepare 1000 ppm of BPB dye stock solution 1.0 g of 99 % BPB dye powder was dissolved in 1.0 L of distilled water. From this stock solution synthetic samples of different concentrations of BPB dye were prepared by appropriate dilutions. 100 ppm BPB dye stock solution was prepared by diluting 100 ml of 1000 ppm BPB stock solution with distilled water in 1000 ml volumetric flask up to the mark. Similarly solutions with different dye concentrations such as 20, 50, 100, 150 and 200 ppm were prepared.

Studies on Equilibrium Biosorption Process

The biosorption was carried out in a batch process by adding a pre-weighed amount of the Gelidium cartilagineum algae powder to a known volume of aqueous solution for a predetermined time interval in an orbital shaker. The procedures adopted to evaluate the effects of various parameters via. Agitation time, biosorbent size, pH, initial concentration, biosorbent dosage and temperature of the aqueous solution on the biosorption of BPB dye were evaluated using single step optimization process.

RESULTS AND DISCUSSION

The effects of various parameters on biosorption are studied. The measured data consist of initial and final concentrations of dye in the aqueous solution, agitation time, biosorbent dosage, biosorbent size, pH and temperature of the aqueous solution.

Effect of Agitation Time

Duration of biosorption equilibrium is defined, as the time required for dye concentration to reach a constant value during biosorption. The equilibrium agitation time is determined by plotting the % removal of BPB dye against agitation time in figure 1. in the interaction time intervals of 1 min to 180 min. For 53 μm size of 10 g/L biosorbent, 25% (0.5 mg/g) of BPB dye is biosorbed in the first 5 min. The % biosorption is increased briskly up to 25 min reaching 56 % (1.12 mg/g).

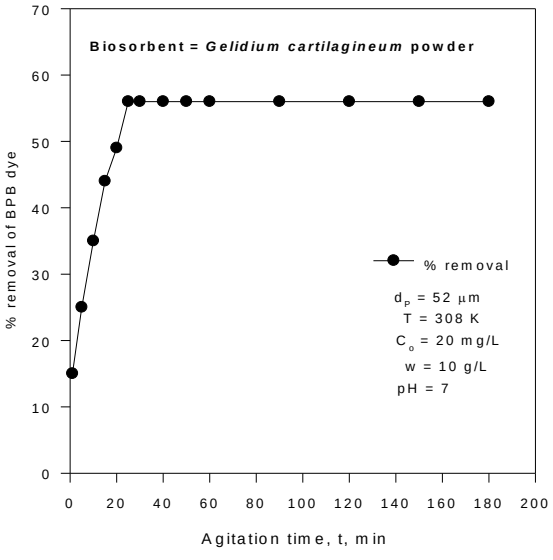


Fig1. *Effect of Agitation time*

From 25 to 180 min. the biosorption is constant indicating the attainment of equilibrium conditions. The maximum biosorption of 56 % (1.12 mg/g) is attained for 180 min of agitation time with 10 g/L of 53 µm size biosorbent mixed in 50 mL of aqueous solution (C0 = 20 mg/L). The rate of biosorption is fast in the initial stages because adequate surface area of the biosorbent is available for the biosorption of manganese. As time increases, more amount of manganese gets adsorbed onto the surface of the biosorbent due to Vanderwaal's forces of attraction and results in decreased of available surface area. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the biosorbent is exhausted **[01-17]**.

Effect f Biosorbent Size

The variations in % biosorption of BPB dye from the aqueous solution with biosorbent size are depicted in fig. 2. The percentage biosorption is increased from 38 % to 56 % as the biosorbent size decreases from 152 to 53 µm. This phenomenon is explained, as the size of the particle decreases, surface area of the biosorbent increases; thereby the number of active sites on the biosorbent also increases **[17–34]**.

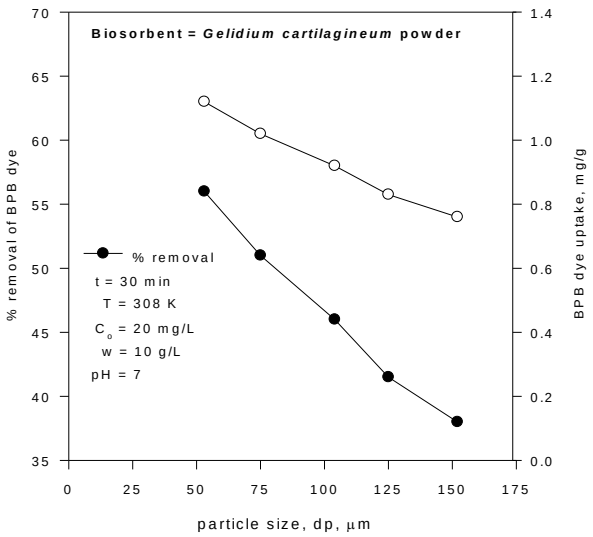


Fig.2. *% Biosorption of BPB dye as a function of biosorbent size*

Effect of Ph

The observations of pH along with % Biosorption of BPB dye are depicted in fig. 3. The % biosorption of BPB dye is increased drastically from 53 % to 74 % as pH is increased from 2 to 6 and beyond the pH value of 6 it decreased. 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 BPB dye ions replace H+ ions bound to the biosorbent **[35–51]**.

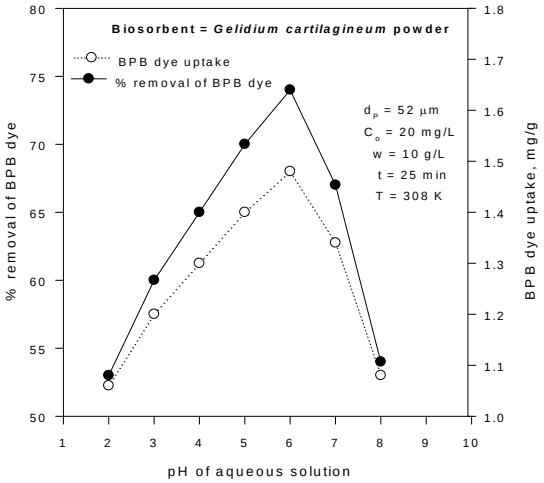


Fig3. *Observation of pH along with % biosorption of BPB dye*

Effect of Initial Concentration of BPB Dye

The percentage biosorption of BPB dye is decreased from 74 % to 44 % with an increase in C_0 from 20 mg/L to 200 mg/L and is presented in Fig. 4. Such behavior can be attributed to the increase in the amount of biosorbate to the unchanging number of available active sites on the biosorbent **[52-68]**.

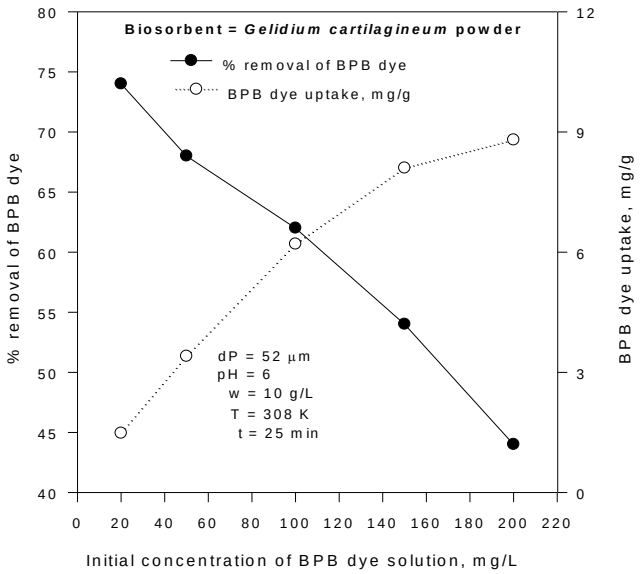


Fig4. *Variation of initial concentration with % biosorption of BPB dye*

Effect of Biosorbent Dosage

The biosorption of BPB dye as shown in Fig. 5 increased from 74 % to 90 % 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 BPB dye biosorption would be more. The change in percentage biosorption of BPB dye is marginal from 90 % to 94 % when 'w' is increased from 25 to 70 g/L. Hence all other experiments are conducted at 25 g/L dosage **[69-85]**.

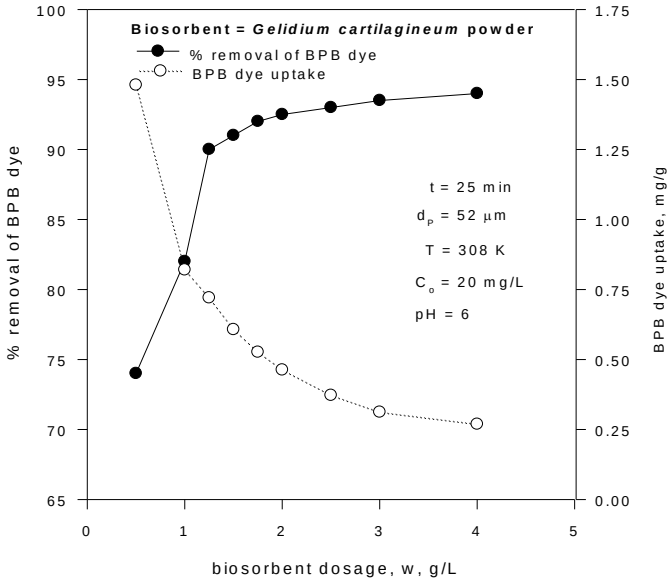


Fig5. *Dependency of % biosorption of BPB dye on biosorbent dosage*

Effect of Temperature

The effect of changes in the temperature on the BPB dye uptake is shown in Fig. 6. When temperature was lower than 303 K, BPB 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 metal. Below 303 K, chemical biosorption mechanisms

played a dominant role in the whole biosorption process, biosorption was expected to increase by increase in the temperature while at higher temperature, the plant powder were in a nonliving state, and physical biosorption became the main process. Physical biosorption reactions were normally exothermic, thus the extent of biosorption generally is constant with further increasing temperature **[86-103]**.

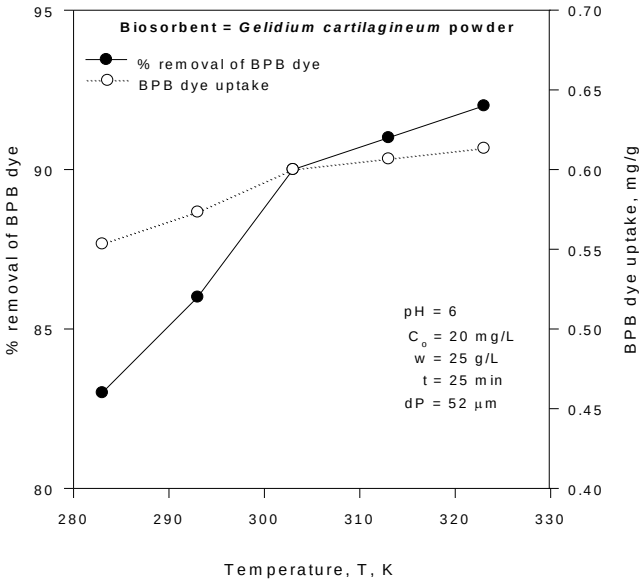


Fig.6. *Effect of temperature on % biosorption of BPB dye*

Langmuir Isotherm

Langmuir isotherm is drawn for the present data and shown in Fig. 7. The equation obtained 'n' C_e/q_e = 0.08404 C_e + 3.0812 with a good linearity (correlation coefficient, R^2~0.9946) indicating strong binding of BPB dye ions to the surface of Gelidium cartilagineum powder.

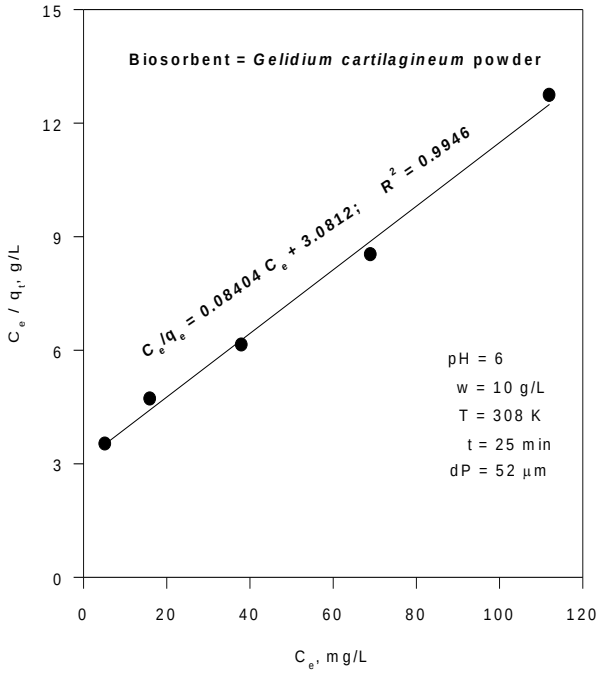


Fig.7. *Langmuir isotherm for % biosorption of BPB dye*

Freundlich Isotherm

Freundlich [**105**] presented an empirical biosorption isotherm equation, that can be applied in case of low and intermediate concentration ranges. It is easier to handle mathematically in more complex calculations. The Freundlich isotherm is given by $q_e = K_f C_e^n$.Freundlich isotherm is drawn between ln

C_e and ln q_e in Fig. 8 for the present data. Equation obtained is $\ln q_e = 0.600475 \ln C_e - 0.501594$; The resulting equation has a correlation coefficient of 0.97266. The 'n' value in the above equations satisfies the condition of 0<n<1 indicating favorable biosorption.

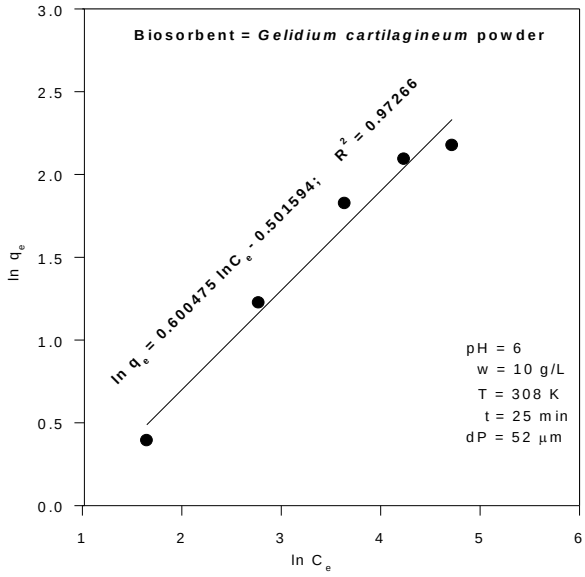


Fig8. *Freundlich isotherm for % biosorption BPB dye*

Temkin Isotherm

Temkin and Pyzhev isotherm **[106]** equation describes the behavior of many biosorption systems on the heterogeneous surface. The data are analysed according to the linear form of Temkin isotherm and the linear plot is shown in Fig. 9. The equation obtained for BPB dye biosorption is: $q_e = 2.527607 \ln C_e - 3.003648$ with a correlation coefficient 0.9834. The best fit model is determined based on the linear regression correlation coefficient (R). From the Figs 7, 8 & 9, it is found that biosorption data are well represented by Langmuir isotherm with higher correlation coefficient of 0.9946, followed by Temkin and Freundlich isotherms with correlation coefficients of 0.9834 and 0.97266 respectively.

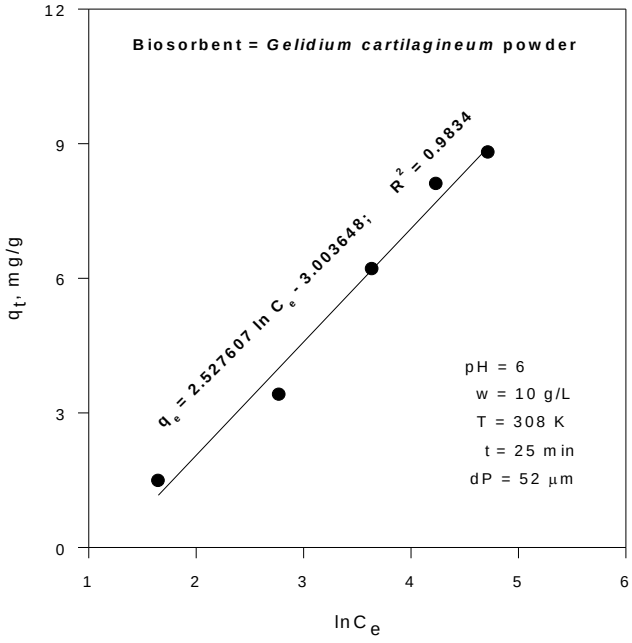


Fig9. Temkin isotherm for % biosorption of BPB dye

Lagergren First order Kinetics

The order of biosorbate – biosorbent interactions have been described using kinetic model. Traditionally, the first order model of Lagergren **[107]** finds wide application. Plot of log (q_e–q_t)

versus't' gives a straight line as presented in Fig. 10 for first order kinetics, facilitating the computation of adsorption rate constant (Kad =0.093746).

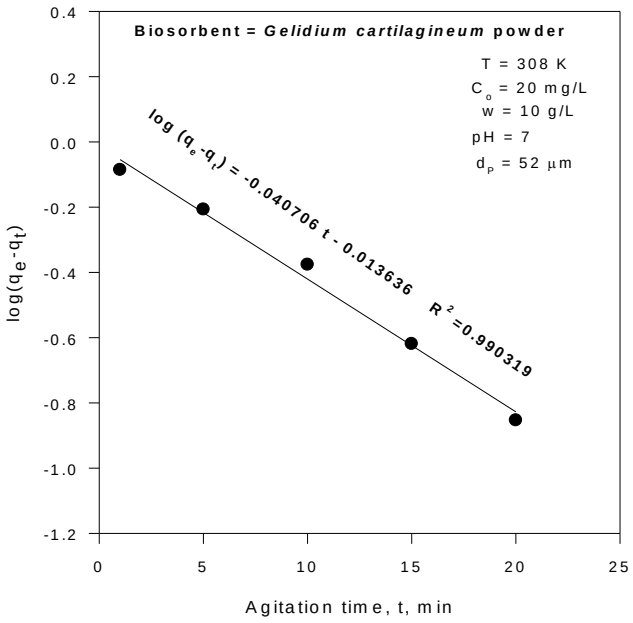


Fig10. First order kinetics for % biosorption of BPB dye

Pseudo Second Order Kinetics

The pseudo second order model **[108–109]** based on above equation, considers the rate -limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the biosorbate and biosorbent. The pseudo second order kinetics plot was presented in Fig. 11. If the pseudo second order kinetics is applicable, then the plot of (t/qt) versus 't' gives a linear relationship that allows computation of qe=1.1757 and K=0.1666.

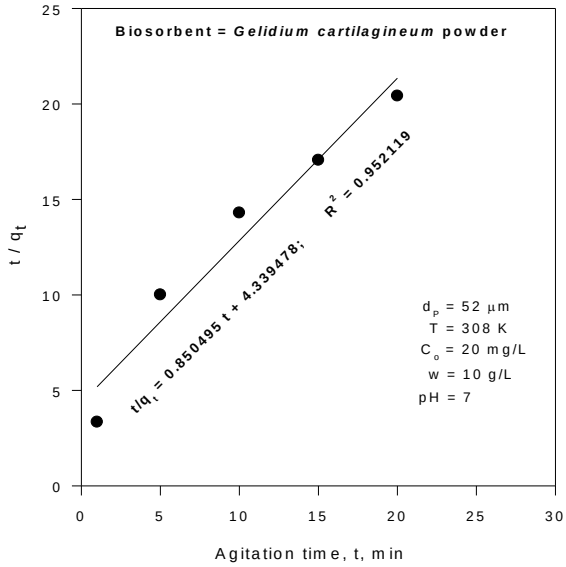


Fig11. *Second order kinetics for % biosorption of BPB dye*

Thermodynamics

Biosorption is temperature dependant **[110]**. In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of biosorption ((ΔH), change in entropy of biosorption (ΔS) and change in Gibbs free energy (ΔG). The investigation revealed that the endothermic nature of biosorption as ΔH (16.7816) is positive, irreversible nature of biosorption as ΔS (44.3838) is positive and spontaneity of biosorption as indicated by negative ΔG (ΔG = –13653.4 J/mole).

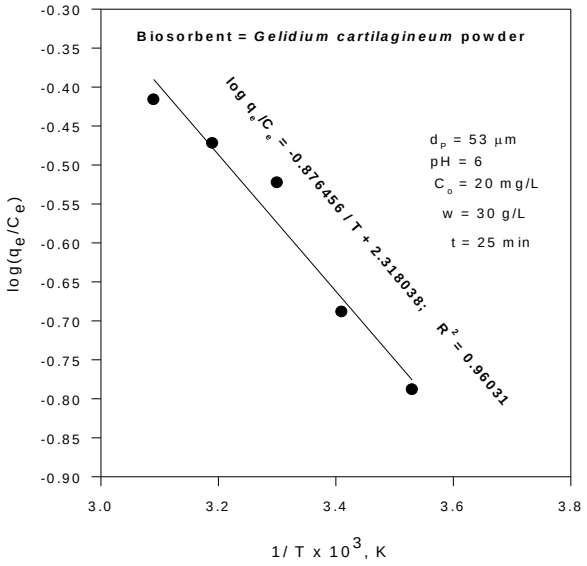


Fig12. *Vantoff's plot for % biosorption of BPB dye*

Response Surface Methodology

The effects of four independent variables (pH, initial concentration of BPB dye in aqueous solution, biosorbent dosage and temperature) on BPB dye biosorption are analyzed using Central Composite Design (CCD). The optimum conditions for the four independent variables on the extent of BPB dye biosorption are formed within the quadratic model. Levels of different process variables for percentage biosorption are shown in table–1.

Table1. *Levels of Different Process Variables in Coded and Un-Coded Form for % Biosorption of BPB Dye using Gelidium Cartilagineum Algae Powder*

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

Table2 Represents the results obtained in CCD. The response obtained in the form of analysis of variance (ANOVA) from regression equation (1) is put together in table–2. Fischer's 'F-statistics' value is defined as MS_{model}/MS_{error}, where MS is mean square. Fischer's 'F-statistics' value, having a low probability 'p' value, indicates high significance.

Table2. *Results from CCD for BPB Dye Biosorption by Gelidium Cartilagineum Algae Powder*

Run No.	X_1, pH	X_2, C_o	X_3, W	X_4, T	% biosorption of BPB dye	
					Experimental	Predicted
1	-1.00	-1.00	-1.00	-1.00	85.42	85.40
2	-1.00	-1.00	-1.00	1.00	88.38	88.39
3	-1.00	-1.00	1.00	-1.00	86.68	86.72
4	-1.00	-1.00	1.00	1.00	88.18	88.14
5	-1.00	1.00	-1.00	-1.00	86.78	86.83
6	-1.00	1.00	-1.00	1.00	88.22	88.19
7	-1.00	1.00	1.00	-1.00	87.92	87.90
8	-1.00	1.00	1.00	1.00	87.68	87.69
9	1.00	-1.00	-1.00	-1.00	86.38	86.43
10	1.00	-1.00	-1.00	1.00	87.82	87.79
11	1.00	-1.00	1.00	-1.00	87.12	87.10
12	1.00	-1.00	1.00	1.00	86.88	86.89
13	1.00	1.00	-1.00	-1.00	88.12	88.10
14	1.00	1.00	-1.00	1.00	87.82	87.84
15	1.00	1.00	1.00	-1.00	88.48	88.53

16	1.00	1.00	1.00	1.00	86.72	86.69
17	-2.00	0.00	0.00	0.00	80.08	80.09
18	2.00	0.00	0.00	0.00	80.12	80.11
19	0.00	-2.00	0.00	0.00	84.68	84.69
20	0.00	2.00	0.00	0.00	85.92	85.91
21	0.00	0.00	-2.00	0.00	91.32	91.31
22	0.00	0.00	2.00	0.00	91.48	91.49
23	0.00	0.00	0.00	-2.00	92.32	92.27
24	0.00	0.00	0.00	2.00	93.38	93.43
25	0.00	0.00	0.00	0.00	94.5	94.50
26	0.00	0.00	0.00	0.00	94.5	94.50
27	0.00	0.00	0.00	0.00	94.5	94.50
28	0.00	0.00	0.00	0.00	94.5	94.50
29	0.00	0.00	0.00	0.00	94.5	94.50
30	0.00	0.00	0.00	0.00	94.5	94.50

Experimental conditions [Coded Values] and observed response values of central composite design with 24 factorial runs, 6- central points and 8- axial points. Agitation time fixed at 25 min and biosorbent size at 53 µm

Table3. *ANOVA of BPB dye biosorption for entire quadratic model*

Source of variation	SS	df	Mean square(MS)	F-value	*P* > F
Model	460.5452	14	32.8960	25435.05	0.00000
Error	0.0194	15	0.001293		
Total	460.5646	29			

Regression equation for the optimization of biosorption is:

% biosorption of BPB dye (Y) is function of pH of aqueous solution (X_1), initial concentration (X_2), dosage (X_3), and Temperature of aqueous solution (X_4).

The multiple regression analysis of the experimental data has yield the following equation:

$$Y = -667.768+56.116X_1+6.198X_2+4.182X_3+3.132X_4-3.6X_1^2-0.092X_2^2-0.031X_3^2-0.004X_4^2-0.012X_1X_2-0.0033X_1X_3-0.041X_1X_4-0.003X_2X_3-0.008X_2X_4-0.008X_3X_4 \quad (1)$$

The ANOVA of the regression model is sufficiently great, as proven from the Fisher's F-test (Fmodel = 25435.05) and has a very low probability value (P_{model}>F=0.000000). Besides, the computed F-value [$F_{0.05}(14.15) = MS_{model}/MS_{error}$=25435.05] is much higher compared to F-value ($F_{0.05}$ (14.15) tabulars = 2.42) at 5% level, suggesting that the treatment differences are sufficiently great. Student's t-test can implicate regression coefficient of the parameter, while pattern of interactions amidst all the factors can be entailed by 'p' values. .

A positive sign of the coefficient represents an interactive effect i.e., response (% biosorption of BPB dye) steps up with increase in effect, whereas a negative sign implies an incompatible effect that means response lowers with an increase in effect.

Measure of the model's variability to the responses indicated is presented by correlation coefficient (R^2). As R^2 —> 1, model is inviolable and the response is estimated better. In our study, R^2 = 0.9996 suggests that 0.01 % of the total variations are not adequately explained by the model. Statistical relevance of the ratio of mean due to regression and mean square due to residual error is tested with the help of ANOVA. F-values implicate that % biosorption can be sufficiently explained by the model equation. If 'P' value is lower than 0.05, the model is considered to be statistically significant at the 95 % confidence level. All the linear, square and interaction terms of all variables (P < 0.05) are in good agreement.

Normal probability plot (NPP) is a graphical technique used for analyzing whether or not a data set is normally distributed to greater extent. The difference between the observed and predicted values from the regression is termed as residual. fig. 13 exhibits normal probability plot for the present data. It is evident that the experimental data are reasonably aligned implying normal distribution.

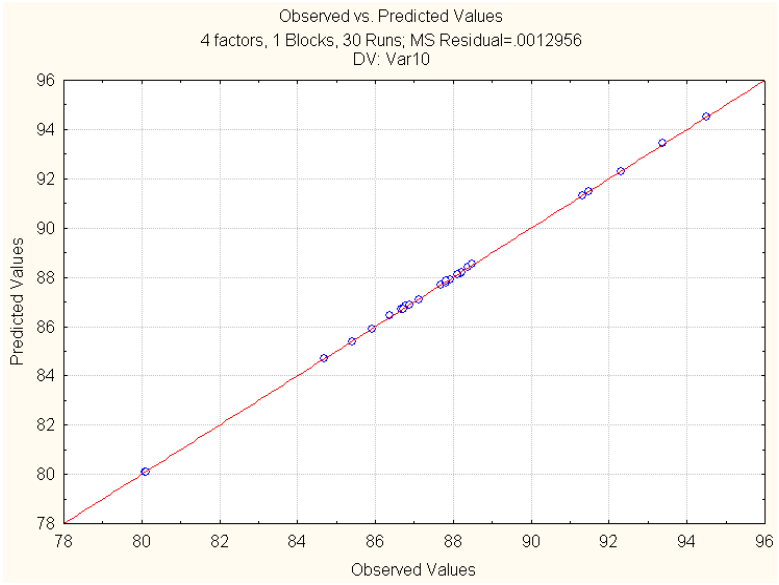


Fig13. *Normal probability plot for % biosorption of BPB dye*

The pareto chart can be explained in such a way that P > 0.05 are significant and is presented in Fig. 14. The red line in the x-axis is P = 0.05. All the linear, quadratic and interaction terms are significant as their p-values are less than 0.05.

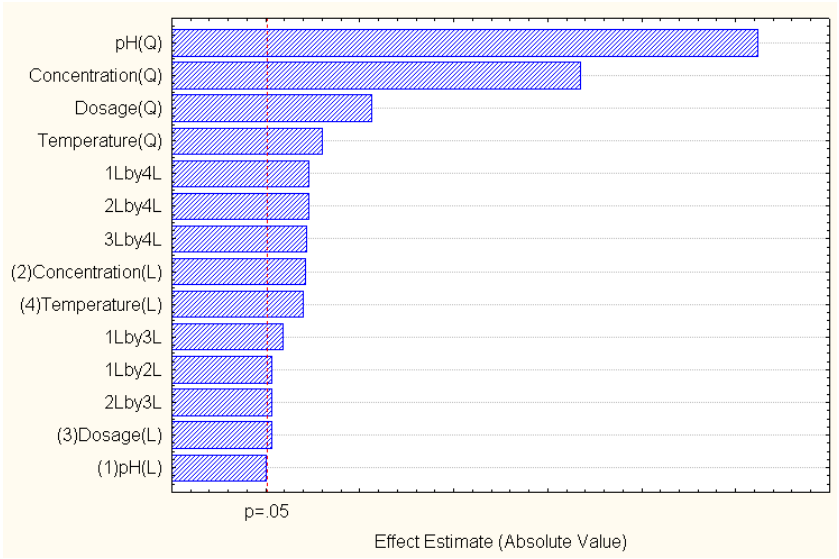


Fig14. *Pareto Chart*

Three-dimensional view of response surface contour plots [Fig. 15 (a) to (f)] exhibit % biosorption of the BPB dye using Gelidium cartilagineum algae powder for different combinations of dependent variables. All the plots are delineated as a function of two factors at a time, imposing other factors fixed at zero level. It is evident from response surface contour plots that the % biosorption is minimal at low and high levels of the variables. This behavior conforms that there is a presence of optimum for the input variables in order to maximize % biosorption. The role played by all the variables is so vital in % biosorption of BPB dye and seen clearly from the plots. The predicted optimal set of conditions for maximum % biosorption of BPB dye is:

pH of aqueous solution	=	5.9816
Initial BPB dye concentration	=	20.1713 mg/L
Biosorbent dosage	=	24.6702 g/L
Temperature	=	306.7304 K
% biosorption of BPB dye	=	94.5575

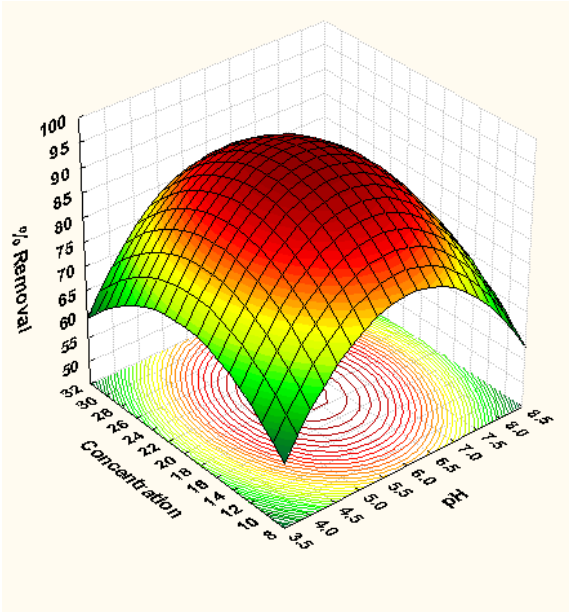
The experimental optimum values are compared with those predicted by CCD in table-4. The experimental values are in close agreement with those from and CCD. The comparison with other author works was also presented in table-5.

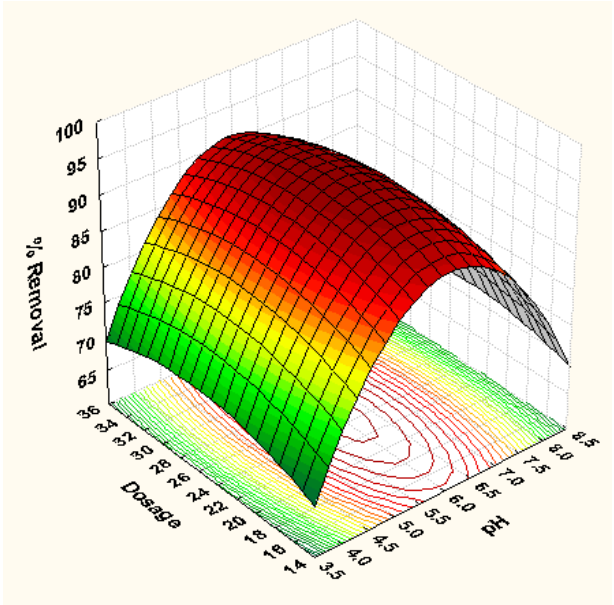
Table4. *Comparison between Optimum Values from CCD and Experimentation*

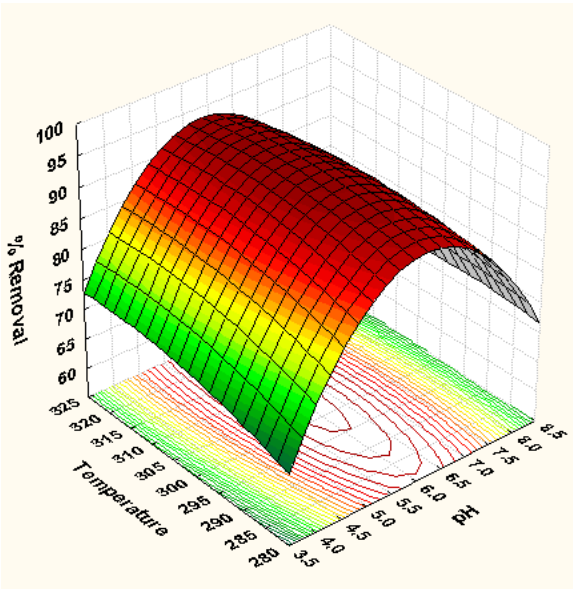
Variable	CCD	Experimental
pH of aqueous solution	5.9816	6
Initial BPB dye concentration, C_o, mg/L	20.1713	20
Biosorbent dosage, w, g/L	24.6702	25
Temperature, K	306.7304	303
% biosorption	94.5575	90

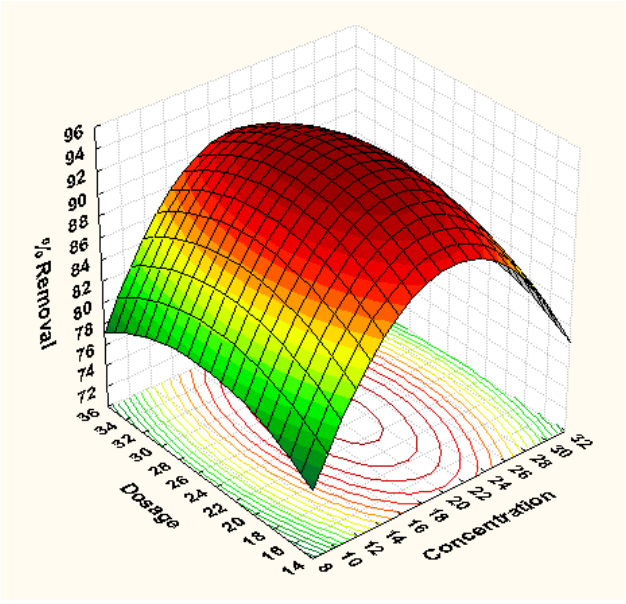
Table5. *Uptake Capacities for Different Biosorbents*

Authors	**Biosorbent**	**q_b, mg/g**
El-Naas et al. [58]	Chlorella vulgaris	169
Gupta et al. [59]	Spirogyra sp.	140.84
Flavio et al. [60]	Ponkan peel	112.1
Ruhan et al. [61]	Lactarius scrobiculatus	56.2
Matheickal et al. [62]	Powder activated carbon	20.7
Present investigation	**Borassus Fruit Waste powder**	**15.41782**









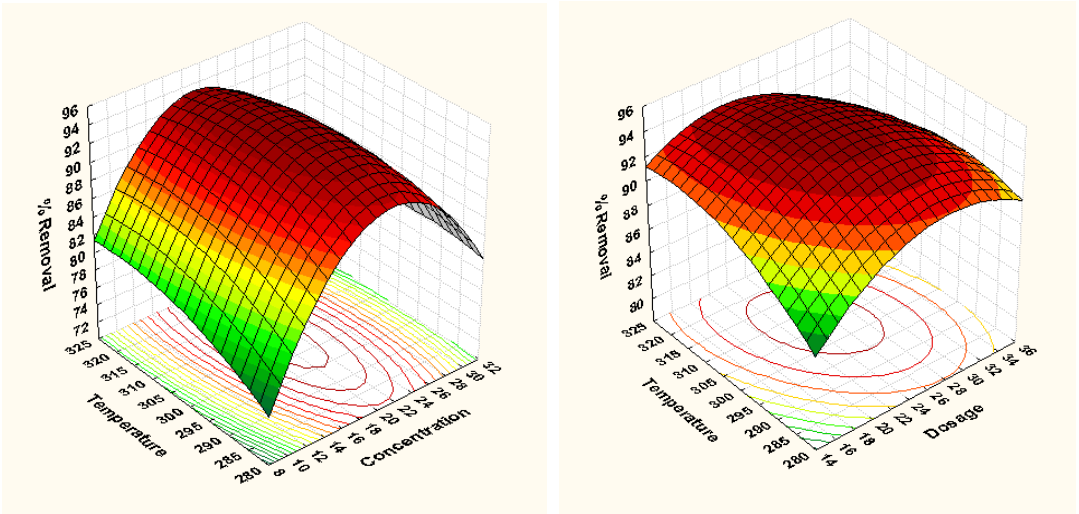


Fig15. (a to f). *Surface contour plot for the effects of dosage and initial concentration of BPB dye on % biosorption*

CONCLUSION

The equilibrium agitation time for BPB dye biosorption is 25 minutes. The percentage biosorption of BPB dye decreased with the increase in biosorbent size from 53 µm (56 %) to 152 µm (38 %). Percentage biosorption of BPB dye from the aqueous solution increases significantly with increase in pH from 2 (53 %) to 6 (74 %). The optimum dosage for biosorption is 25 g/L. The maximum uptake capacity of 11.8991 mg/g is obtained at 308 K. The maximum biosorption of BPB dye onto Gelidium cartilagineum powder is observed when the processing parameters are set as: pH = 5.9816, Concentration = 20.1713, w = 24.6702 g/L and Tempeature = 306.7304 K using CCD. The investigation also reveals the endothermic nature of biosorption as ΔH (16.78163) is positive, irreversible nature of biosorption as ΔS (44.3838) is positive and spontaneity of biosorption as indicated by negative ΔG (ΔG = –13653.4 J/mole). Hence the above said Gelidium cartilagineum powderis effective and efficient biosorbent and is capable of removing Bromo Phenol Blue dye.

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