STUDY OF BIOSORPTION AND OPTIMIZATION THROUGH BBD FOR THE REMOVAL OF METHYLENE BLUE ONTO FANWORT POWDER

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Abstract: The inequity in ecosystem is also a result of water pollution. Industrial wastes are also being the major cause, in a direct or indirect manner, of water pollution. This work comprises of discussions regarding the dye effluents removal methods as the dye effluents are one of the hazardous things that come through the industrial waste. The process of biosorption is the preferred method for removing the dye effluents. “Methylene Blue” is the dye that is to be removed from the effluent waters by using a bio material namely “Fanwort Powder”. The studies such as XRD, SEM, and FTIR will help in characterizing the bio material. Factors such as pH lying between 2 and 8, dosage of the biosorbent lying between 10mg/l and 60mg/l, time taken for the agitation lying between 1 and 180 minutes, Temperature lying between 283K and 323K and the Methylene Blue dye initial concentration lying between 20mg/l and 200mg/l are the process considerations. The study included the thermodynamics, kinetics and the isotherms involved in the process. The process optimization is carried out by the help of the BOX BEHNKEN design. Results have shown that the optimum time taken for the process of biosorption is 50 minutes at a pH value of 4 with a biosrbent dosage of 35g/l while the solution sample has an initial dye concentration of 20mg/l. The isotherm of freundlich is found to be the best suit likewise the kinetics of pseudo second order for the process.

***IndexTerms* – Methylene Blue, Fanwort powder, Box Benkhen design.**

I. INTRODUCTION

In many parts of the world fresh water is becoming a resource that is hard to find. As the pollution keeps on increasing by the next century, the chance of finding fresh water will become even harder. Other factors such as climatic changes and urbanization are also being the reasons for fresh water confinement. This confinement is not only a result of increased population but also the acts that pollute the fresh waters through human activities. As result, polluted water has to be treated which imposes extra costs and the supply of fresh water will be lowered. The uprising issues of industrialization, increasing population and urbanization all around the world are being the direct reasons for pollution of fresh water resources. The waste waters that come out of the industries are playing the major role in the total contamination of fresh waters. These contaminations do affect the ecosystems of fresh waters which ultimately lead to the environmental contamination. The contamination has grown to such great extents that there came the need of treating the water with various techniques such that it can come down to suitable life existing environmental conditions. Various techniques that are both physical and chemical in nature are used for the treatment of waters. Sedimentation and filtration are the physical treatments while flocculation, chlorination, oxidation, sand filtration, agglomeration and adsorption onto the surface of biomaterials (a biological method) are the chemical treatments. Out of all the treatment methods, the biological method of adsorption that includes the usage of a biomaterial seemed to be the best and effective technique cause of its ease of operation, cheaper costs and huge possibilities. The experimental procedure includes the treatment of Methylene Blue dye by using powdered Fanwort as the biomaterial. The optimization process of the obtained data is carried out by the help of Box Behnken design.

I. MATERIAL AND METHODS

The materials and the methods include the following steps.

Reagents and materials
Biosorbent preparation
Process of biosorption and equilibrium studies

Reagents and materials

All the materials and reagents used directly are of investigative grade in this study. Distilled water is used for the preparation of the Methylene Blue dye solution. The stock Solution of Methylene Blue dye is of 1000mg/l concentration. For altering the pH to the desired values, addition of the solutions such as 0.1M NaOH and 0.1M HCL are essential.

Biosorbent preparation:

The algae Fanwort is collected from the River Godavari at Rajahmundry. Washing the collected algae thoroughly will aid in removing the dust particles and the impurities that are present. The washed algae are crispy dried in the sunlight. The dried algae are then crushed and made into powders of various sizes by using different sieves. The range of the powder sizes is 53µm to 152µm. Thus each and every different sized powder is separated and stocked up in the bottles that have the facility of double capping. This feature of double capping allows the bottles to remain dry and any contact of moisture can be avoided. Hence the stored powder is called the biosorbent.

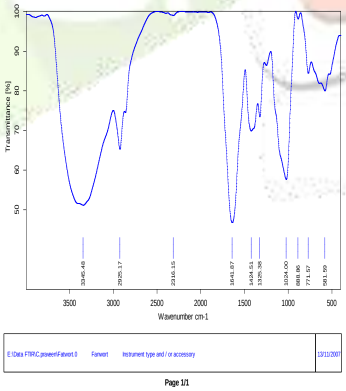
Process of biosorption and equilibrium studies

The biosorption process occurs in a batch. It starts by adding a measured quantity of biosorbent (Fanwort powder) to a specific volume of aqueous solution. It is then put in the orbital shaker for the pre-fixed interval of time. A variety of parameters like pH, dosage of the biosorbent, time taken for the agitation, initial concentrations, and temperature of the aqueous solution are evaluated for their effects on the Methylene Blue dye biosorption process. The evaluation is carried out by using single step optimization process. Additional optimizations are carried out by using the Box Behnken design.

II. CHARACTERIZATION OF FANWORT POWDER

FTIR spectrum of untreated fanwort powder

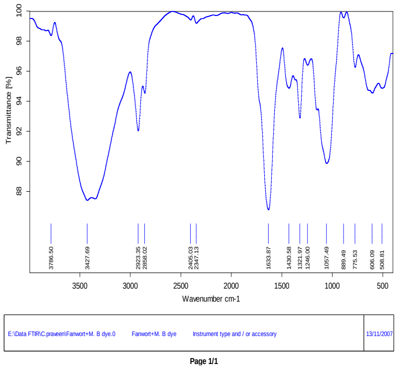
FTIR spectrum for untreated powder is shown in the below figure. A broad band at 573.85, 596.03, 617.25 and 663.54 cm^{-1} is due to the existence of C-Br stretch bands from alkyl halides. The broad absorption hits the highest point at around 758.06 cm^{-1} that shows the incidence of Aromatic C–H bending group. The bands at 855.47, 876.68 and 937.44 cm^{-1} are cause of the Al–O–H bending bonds. The bands at 1012.67 and 1024.25 cm^{-1} show the existence of C–F stretch bands from alkyl halides. The bands at 1037.75, 1053.18 and 1080.18 cm^{-1} are due to the incidence of C–F stretch bonds. The band at 1148.66 cm^{-1} implies the existence of Aromatic C–H bending bond. likewise the bands at 1211.35, 1233.53, 1242.21, 1319.37, 1339.62 and 1363.73 cm^{-1} are due to the incidence of =C–H bending alkenes.



FTIR spectrum of methylene blue untreated with *fanwort* powder

FTIR spectrum of treated fanwort powder

FTIR spectrum for treated powder is shown in the below figure. A broad band at 617.25 cm^{-1} hints the existence of C–Br stretch bands from alkyl halides. The band at 712.73 cm^{-1} is characteristic of Aromatic C–H bending bond. The band at 1495.86 cm^{-1} is due to the occurrence of Amine N–H stretch group. The bands at 3096.85, 3127.71, 3229.94, 3245.37, 3266.59 and 3287.81 cm^{-1} are the clues for the incidence of Amine N–H stretching bonds. The bands at 3299.38, 3355.32, 3362.07 and 3372.68 cm^{-1} contain –CH stretch bonds. The shifts in FTIR peaks are shown in table-6.10 and in turn validate that bisorption was attained.

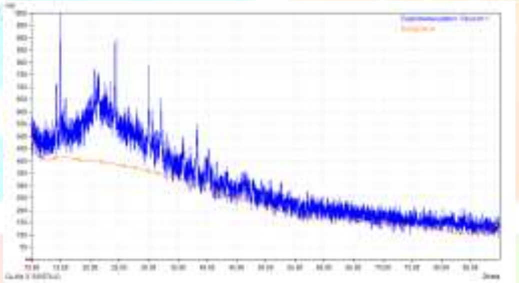


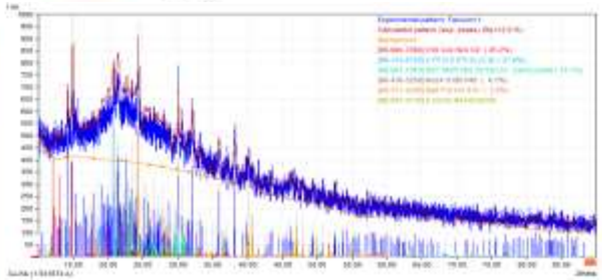
FTIR spectrum of methylene blue treated with *fanwort* powder

III. X RAY DIFFRACTION

XRD PATTERN SPECTRUM OF UNTREATED FANWORT POWDER

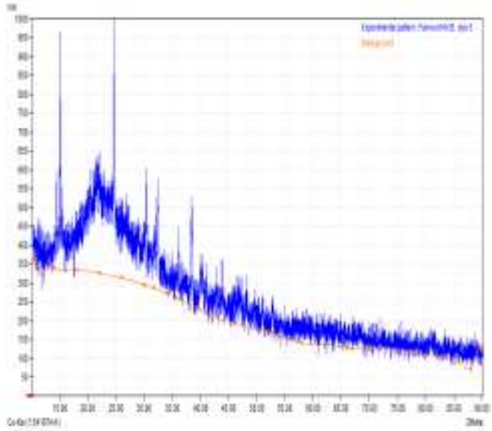
X-ray diffractogram of the untreated fanwort powder is shown in the below Figures. From the figure it can be seen that XRD pattern does not show apparently crystalline nature. The peaks at 2θ values of 0.3845, 0.6273, 0.5076, 0.6547 and 0.4937 confirm the presence of $NP_3O_{13}Se_3$, O_2Si, $Rb_{12}Si_{17}$, AuCs and $Al_{1.65}Na_{1.65}O_4Si_{0.35}$. Their equivalent d-values are 4.1049, 4.2516, 3.8633, 3.0189 and 2.5648

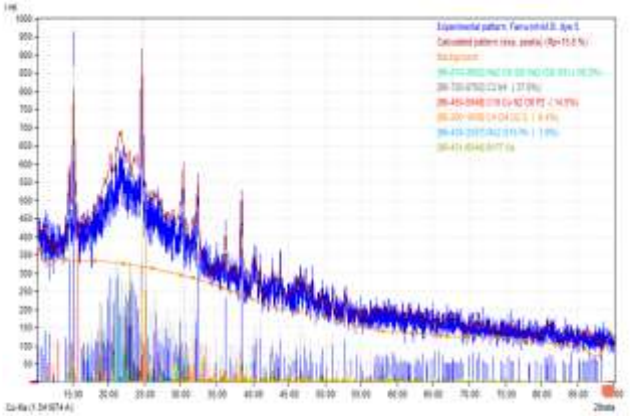




XRD pattern spectrum of treated fanwort powder

X-ray diffractogram of the treated fanwort powder is shown in the below diagrams. From the figure it can be seen that XRD pattern exhibits more amorphous nature and increase in its surface area and inflation in pores. The peaks at 2θ values of 0.4767, 0.6185, 0.5515, 0.5640 and 0.7138 supports the incidence of $C_{16}F_{10}N_4O_2$, BeF_2, O_2Si, N_2O and $Ca_{0.67}Cd_{0.33}(Co_3)$ (ICDD files). Their matching d-values are 3.6605, 1.9736, 1.8141, 1.6519 and 1.8601.

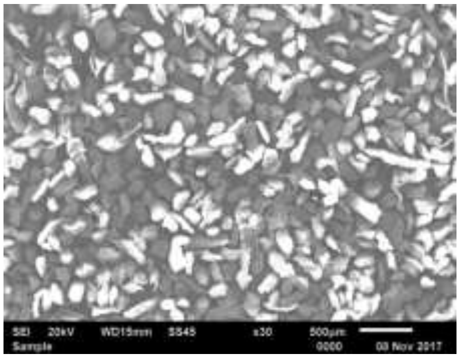


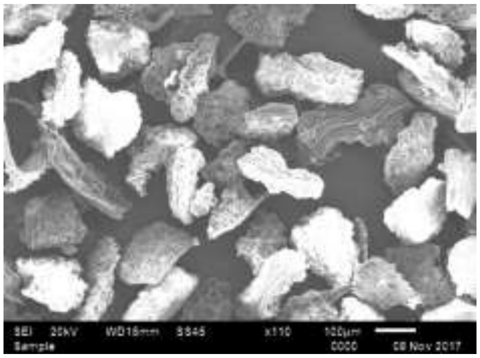


IV. SEM ANALYSIS

Scanning Electron Microscope (SEM) for untreated *fanwort* powder

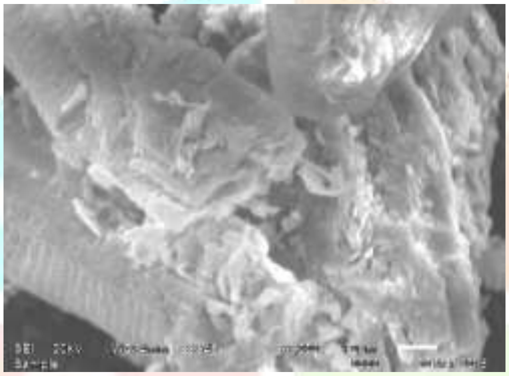
The SEM micrographs of *fanwort* powder before and after biosorption are analyzed. The sem images show that the algae powder is not at all even and lots of pores are accessible.

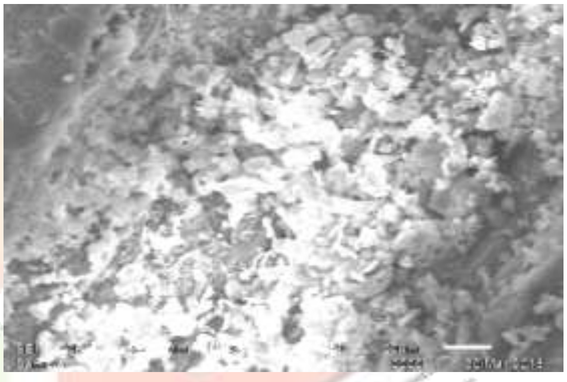




Scanning Electron Microscope (SEM) for treated fanwort powder

The micrographs presented exhibits clearly the dye loaded biosorbent coated by dye molecules over the whole surface. The dye molecules seem to have formed a void-free film covering the reliefs of particles and porosity of the aggregates.

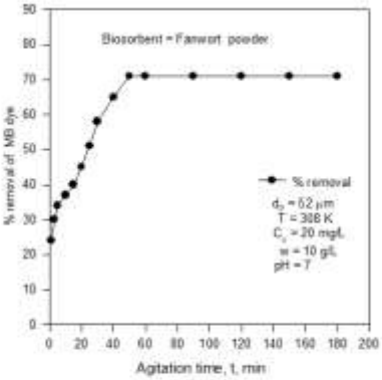




V. SINGLE STEP OPTIMIZATION PROCESS

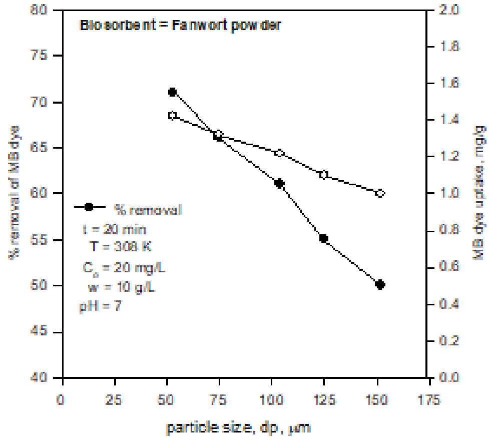
1. EFFECT OF AGITATION TIME

In the below mentioned graph, the percentage biosorption is plotted against agitation time. The % biosorption is found to increase up to 50 min. The maximum percentage of biosorption is attained at 50 min of agitation time and becomes constant after 50 min. indicating the attainment of the equilibrium.



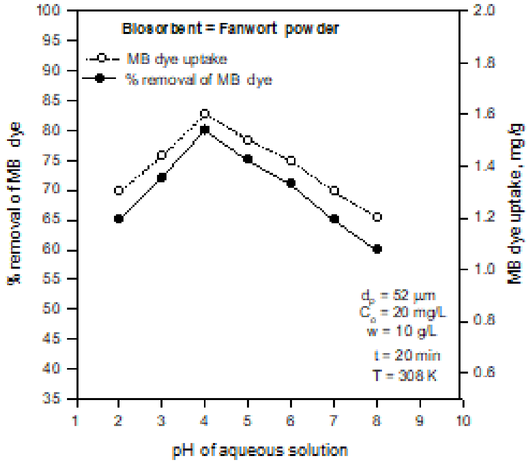
2. EFFECT OF BIOSORBENT SIZE

The below mentioned figure portrays the percentage biosorption of Methylene Blue as a function of particle size. The percentage biosorption is decreased from 71% to 50% as the biosorbent size is decreased from 53µm to 152 µm. As the size of the particle decreases, surface area of the biosorbent increases and additional number of active sites on the biosorbent are accessible to the biosorbate.



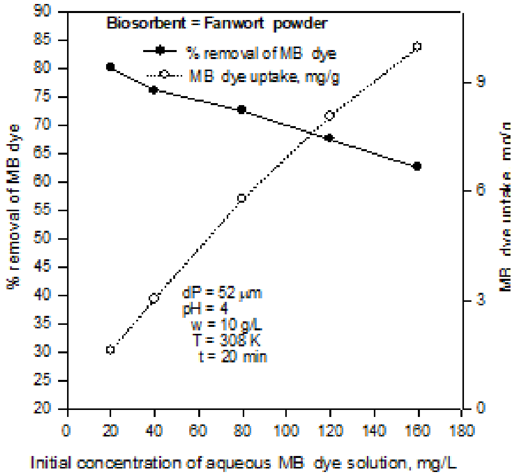
3. EFFECT OF PH

The effect of pH of aqueous solution on percentage biosorption of methylene blue is plotted in the below mentioned graph. The percentage biosorption is increased from 65 % to 80 % as pH is increases from 2 to 4. The percentage biosorption is decreased from 80 % to 60 % as pH increases from 4 to 8. The principal driving force for dye ion biosorption is the electrostatic interaction between biosorbent and biosorbate.



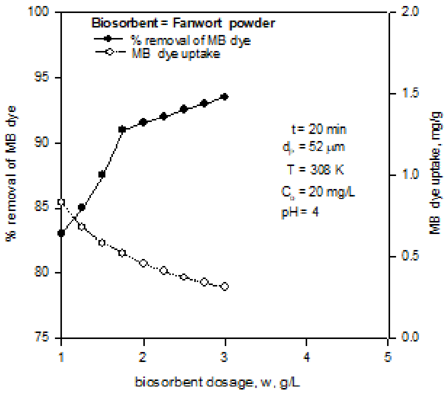
4. EFFECT OF INITIAL CONCENTRATION OF METHYLENE BLUE

The percentage biosorption is decreased from 80% to 62.5% as the initial concentration of methylene blue in the aqueous solution increases from 20mg/L to 160mg/L. Such behavior can be attributing to the increase in the amount of biosorbate to the continuous number of freely active sites on the biosorbent.



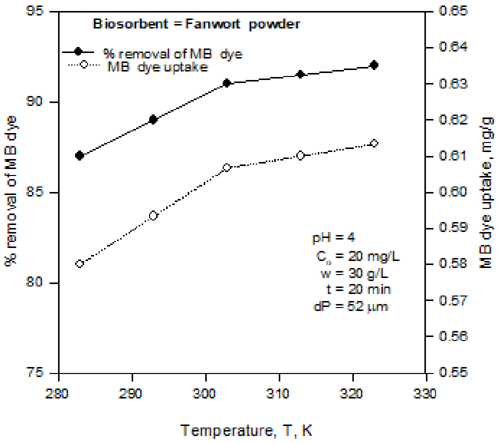
5. EFFECT OF BIOSORBENT DOSAGE

The percentage biosorption of methylene blue is plotted against biosorbent dosage and is shown in the following figure. The percentage biosorption increases with increase in biosorbent dosage. For a biosorbent size of 53μm, percentage biosorption increases from 80% to 91%, as dosage is increased from 10g/L to 35g/L. Such behavior is obvious because the number of available sites for dye removal would be more as the amount of the biosorbent increases.



6. EFFECT OF TEMPERATURE

The effect of changes in the temperature on the Methylene Blue uptake is represented pictorially in the below mentioned graph. The biosorption capacity of dye is increased at higher temperatures which shows that biosorption of dyes in this system is an endothermic process. This may be endorsed to increased penetration of reactive dyes inside micropores at higher temperatures or the creation of new active sites. The formation of more than one molecular layer on the surface of fanwort appears to be achieved in the case of Methylene Blue dye biosorption at higher temperatures.



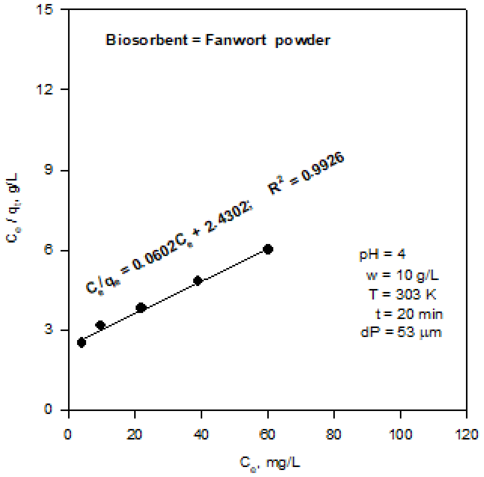
V. ISOTHERMS

7. LANGMUIR ISOTHERM

Langmuir isotherm, for the present data has yielded the equation

$(C_e/q_e) = 0.0602\ C_e + 2.4302$

The correlation coefficient value of 0.9926 shows the strong binding of methylene blue dye on to the biosorbent.



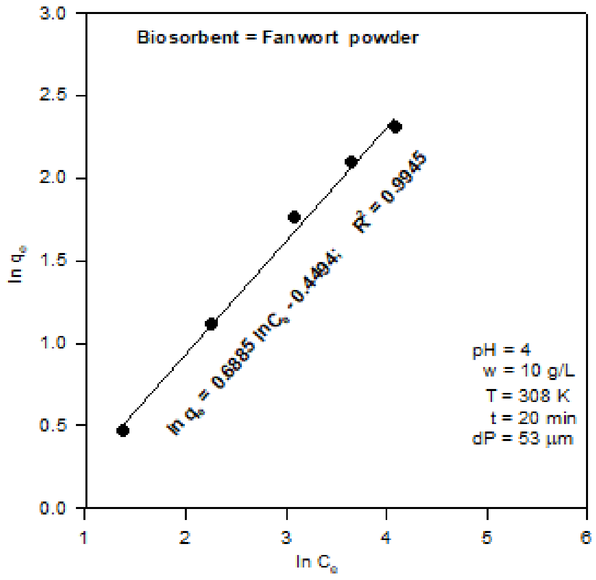
8. FREUNDLICH ISOTHERM

The graph is plotted between log C_e and log q_e, that has resulted the equation

$\ln q_e = 0.6885 \ln C_e - 0.4494$

The equation has a correlation coefficient of 0.9945.

The 'n' value of 0.6885 satisfies the condition of 0<n<1, indicates the favorable biosorption.

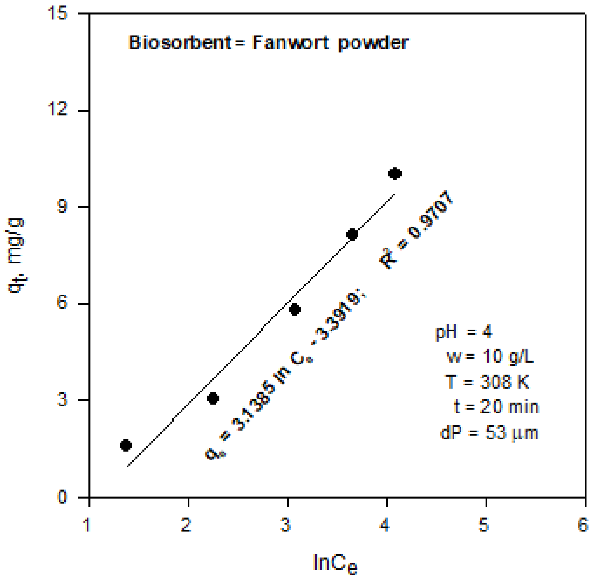


9. TEMKIN ISOTHERM

The present data are analyzed according to the linear form. The equation obtained for Methylene Blue biosorption is

$q_e = 3.1385\ln C_e - 3.3919$

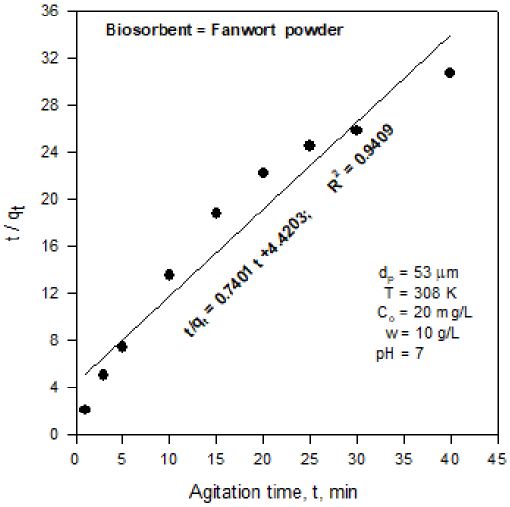
The correlation coefficient value of 0.9707

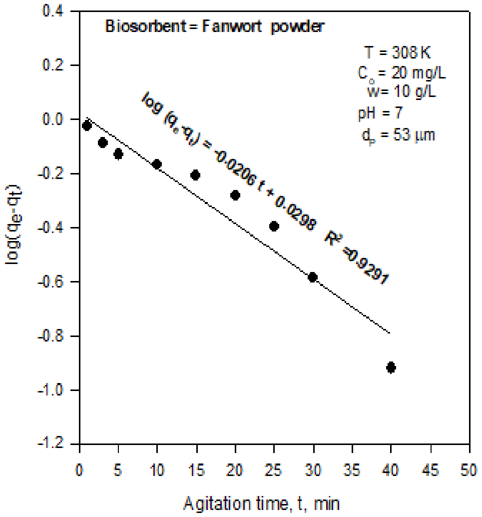


Langmuir isotherm	Freundlich isotherm	Temkin isotherm
q_m = 16.6113 mg/g	K_f = 0.6380 mg/g	A_T = 0.3393 L/mg
K_L = 0.02477	n = 0.6885	b_T = 802.658
R^2 = 0.9926	R^2 = 0.9945	R^2 = 0.9707

VI. KINETICS

The experimental data are tested for Lagergren first order rate equation and pseudo second order rate equation. Lagergren plot log (q_e-q_t) vs agitation time (t) and pseudo second order kinetics plot between 't'vs 't/q_t' for biosorption of methylene blue, summarizes the rate constant values for first and second order rate equations. It is noted that both first and second order rate equations explain the biosorption interactions.



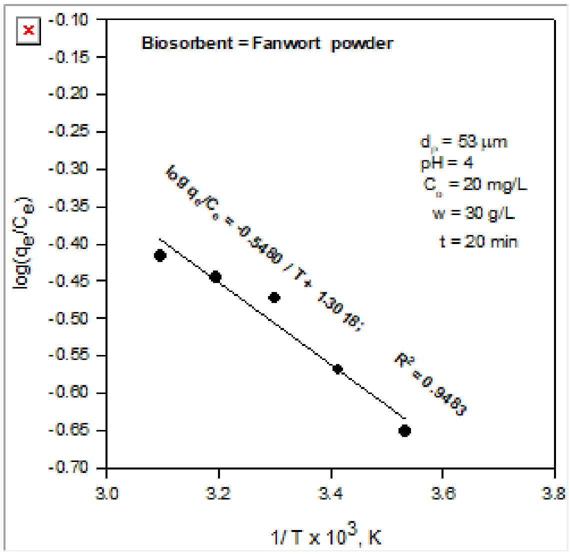


Equations and rate constants

Order	Equation	Rate constant	R^2
Lagergren first order	log (q_e-q_t) = -0.0206 t + 0.0298	0.0474 min^{-1}	0.9291
Pseudo Second order	t/q_t = 0.7401 t + 4.4203	0.1239 g/(mg-min)	0.9409

VII. THERMODYNAMICS

A series of thermodynamic parameters such as change in Gibbs free energy (ΔG) change in enthalpy (ΔH) and change in entropy (ΔS) are determined. ΔG value of –7542.01 J/mole indicates that biosorption of Methylene Blue by *fanwort* powder could take place spontaneously. Higher temperatures have benefitted biosorption and increased the equilibrium biosorption capacity. Positive ΔH of 10.4926 J/mole indicates endothermic nature of biosorption while positive ΔS = 24.9257 J/mole-K demonstrates the affinity of *fanwort* powder to Methylene Blue.



VIII. OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY (RSM)

Optimization using BBD

In the present study, the levels of four process input variables for % biosorption are studied.

Levels of different process variables in coded and un-coded form for % biosorption of Methylene Blue using fanwort powder

Variable	Name	Range and levels		
		-1	0	1
X_1	pH of aqueous solution	3	4	5
X_2	Initial concentration, C_o, mg/L	10	20	30
X_3	Biosorbent dosage, w, g/L	1.25	1.75	2.25
X_4	Temperature, T, K	293	303	313

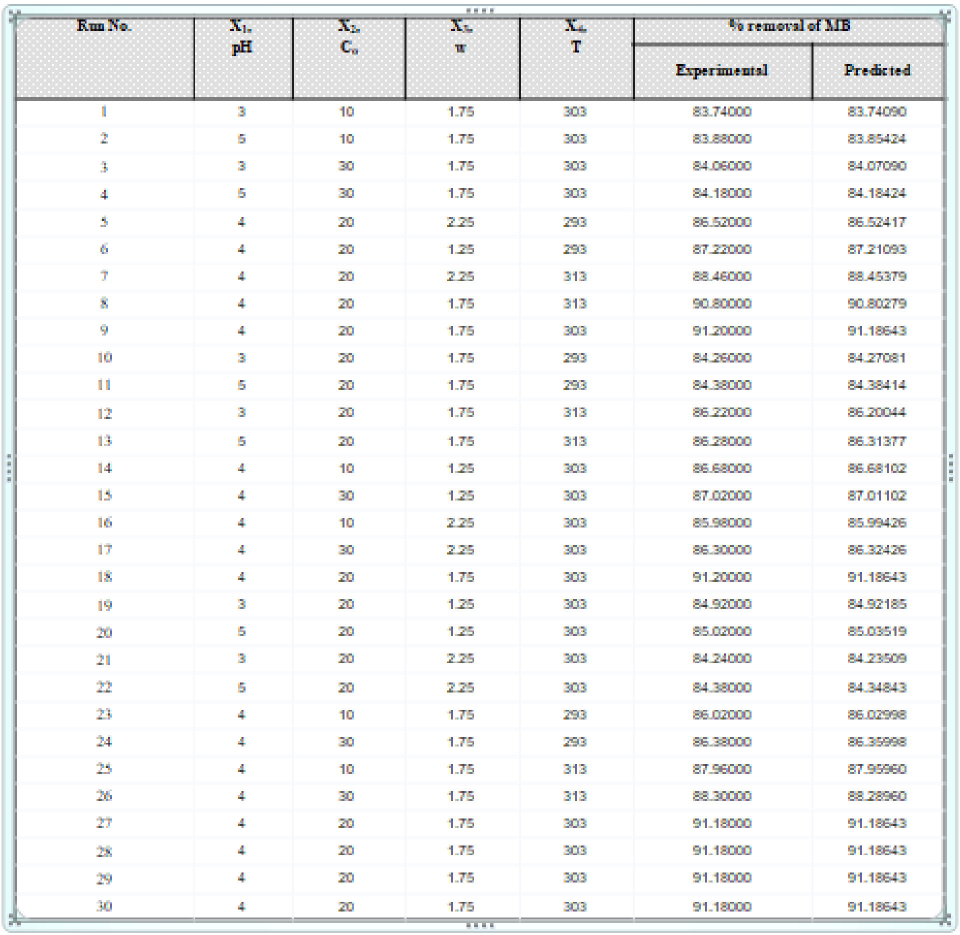
Regression equation for the optimization of removal is:

% removal of MB dye 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:

$$Y = -667.768 - 56.116X_1 + 6.198X_2 + 4.182X_3 + 3.132X_4 - 3.6X_1^2 - 0.092X_2^2 - 0.031X_3^2 - 0.004X_4^2 + 0.012X_1X_2 - 0.033X_1X_3 - 0.041X_1X_4 - 0.003X_2X_3 - 0.008X_2X_4 - 0.008X_3X_4$$

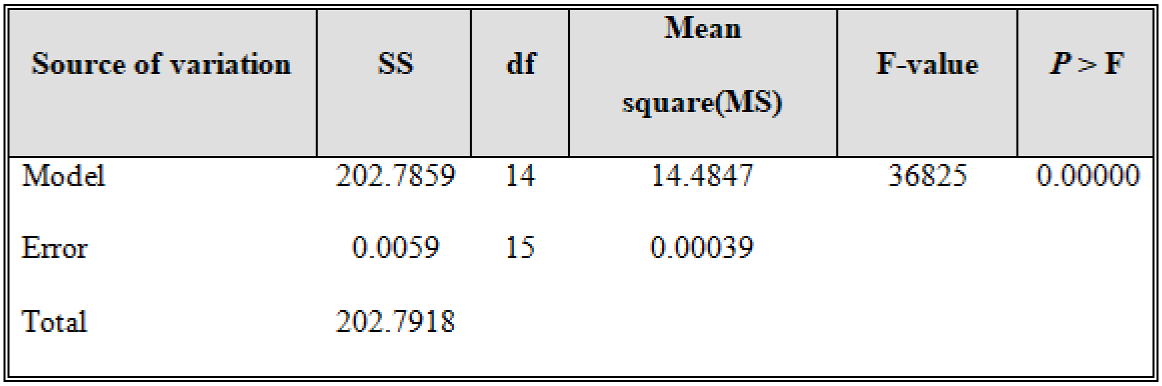
Results from BBD for MB dyeremoval by fanwortpowder



Run No.	X_1, pH	X_2, C_0	X_3, w	X_4, T	% removal of MB	
					Experimental	Predicted
1	3	10	1.75	303	83.74000	83.74090
2	5	10	1.75	303	83.88000	83.85424
3	3	30	1.75	303	84.06000	84.07090
4	5	30	1.75	303	84.18000	84.18424
5	4	20	2.25	293	86.52000	86.52417
6	4	20	1.25	293	87.22000	87.21093
7	4	20	2.25	313	88.46000	88.45379
8	4	20	1.75	313	90.80000	90.80279
9	4	20	1.75	303	91.20000	91.18643
10	3	20	1.75	293	84.26000	84.27081
11	5	20	1.75	293	84.38000	84.38414
12	3	20	1.75	313	86.22000	86.20044
13	5	20	1.75	313	86.28000	86.31377
14	4	10	1.25	303	86.68000	86.68102
15	4	30	1.25	303	87.02000	87.01102
16	4	10	2.25	303	85.98000	85.99426
17	4	30	2.25	303	86.30000	86.32426
18	4	20	1.75	303	91.20000	91.18643
19	3	20	1.25	303	84.92000	84.92185
20	5	20	1.25	303	85.02000	85.03519
21	3	20	2.25	303	84.24000	84.23509
22	5	20	2.25	303	84.38000	84.34843
23	4	10	1.75	293	86.02000	86.02998
24	4	30	1.75	293	86.38000	86.35998
25	4	10	1.75	313	87.96000	87.95960
26	4	30	1.75	313	88.30000	88.28960
27	4	20	1.75	303	91.18000	91.18643
28	4	20	1.75	303	91.18000	91.18643
29	4	20	1.75	303	91.18000	91.18643
30	4	20	1.75	303	91.18000	91.18643

The results obtained in BBD. The response obtained in the form of analysis of variance (ANOVA) from regression equation is put together in the table. 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. From the Fisher's *F*-test and a very low probability value ($P_{model} > F$=0.000000), the ANOVA of the model clearly explains that the model is highly significant. It shows that the treatment differences are significant.

ANOVA of MB dyeremoval for entire quadratic model



Source of variation	SS	df	Mean square(MS)	F-value	*P* > F
Model	202.7859	14	14.4847	36825	0.00000
Error	0.0059	15	0.00039		
Total	202.7918				

Df- degree of freedom;
SS- sum of squares;
F- factor F;

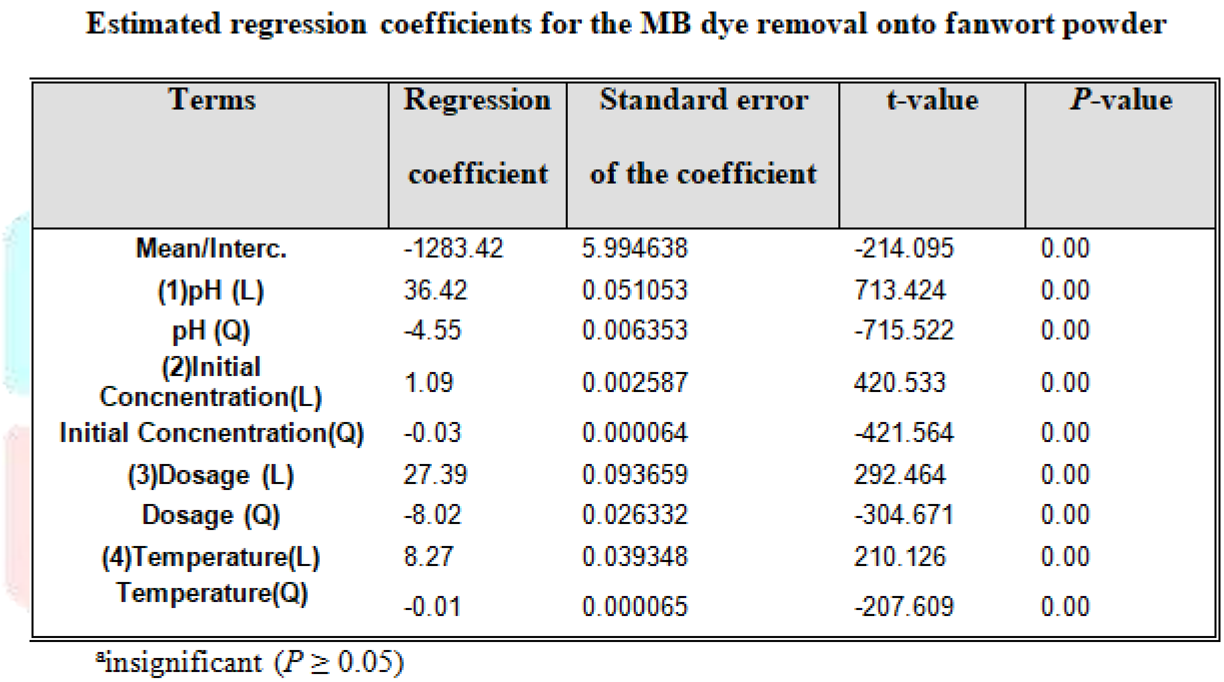
P- probability;
R^2=0.99996;
R^2 (adj):0.99992.

The‘t’ and ‘*P*’ values are analyzed to predict the response. It is found that X_1, X_2, X_3, X_4, X_1^2 , X_2^2 , X_3^2 , X_4^2 X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4 have high significance to explain the individual and interaction effects of input variables on biosorption of MB

The model is reduced to the following form by removing insignificant term (X_2).

$$\mathbf{Y = -467.638 + 30.507\, X_1 + 1.349\, X_2 + 1.7\, X_3 + 2.913\, X_4 - 2.761\, X_1^2 - 0.043\, X_2^2 - 0.033 X_3^2 - 0.005\, X_4^2 - 0.005\, X_1X_2 - 0.022\, X_1X_3 - 0.006\, X_1X_4 - 0.004\, X_2X_3 + 0.001\, X_2X_4 - 0.002 X_3X_4}$$

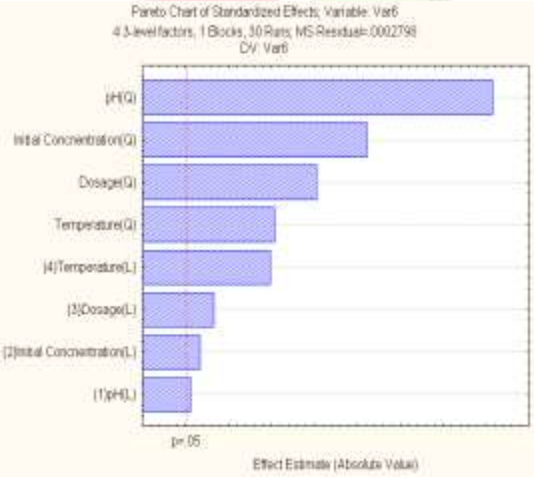
The regression coefficient value of 0.99996 indicates that 0.004 % of the total variations are not satisfactorily explained by the model

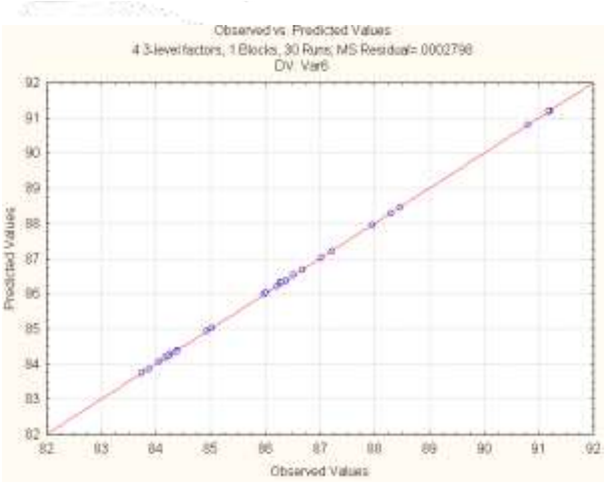


Estimated regression coefficients for the MB dye removal onto fanwort powder

Terms	Regression coefficient	Standard error of the coefficient	t-value	*P*-value
Mean/Interc.	-1283.42	5.994638	-214.095	0.00
(1)pH (L)	36.42	0.051053	713.424	0.00
pH (Q)	-4.55	0.006353	-715.522	0.00
(2)Initial Concnentration(L)	1.09	0.002587	420.533	0.00
Initial Concnentration(Q)	-0.03	0.000064	-421.564	0.00
(3)Dosage (L)	27.39	0.093659	292.464	0.00
Dosage (Q)	-8.02	0.026332	-304.671	0.00
(4)Temperature(L)	8.27	0.039348	210.126	0.00
Temperature(Q)	-0.01	0.000065	-207.609	0.00

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



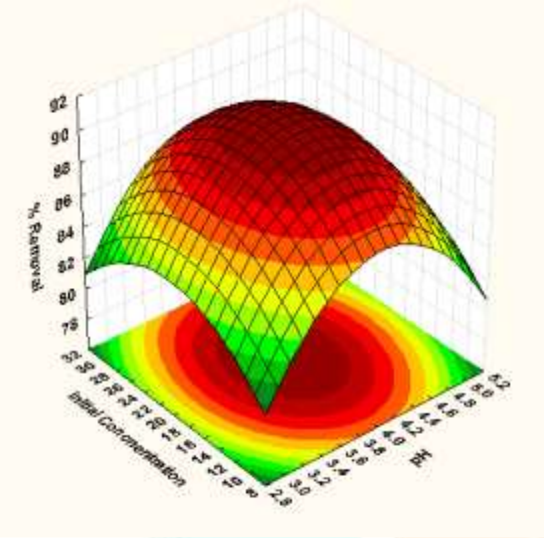


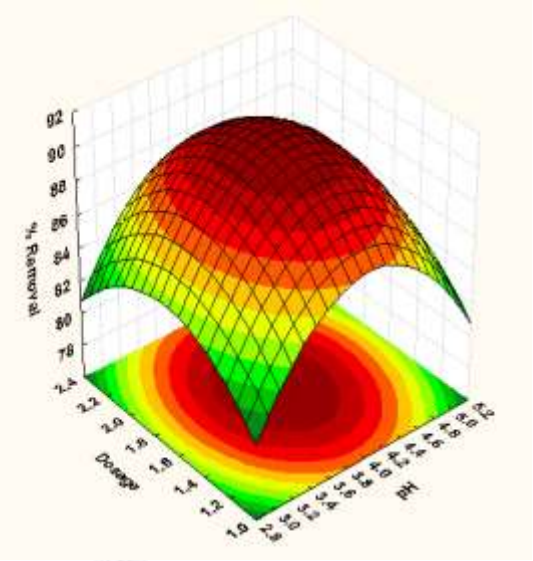
Pareto chart

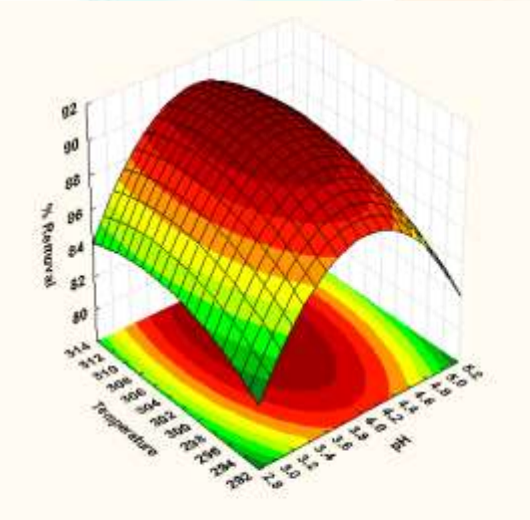
Normal probability % biosorption of MB

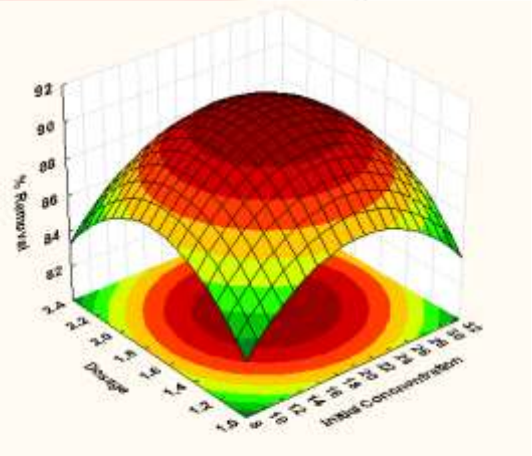
IX. INTERPRETATION OF RESIDUAL GRAPHS

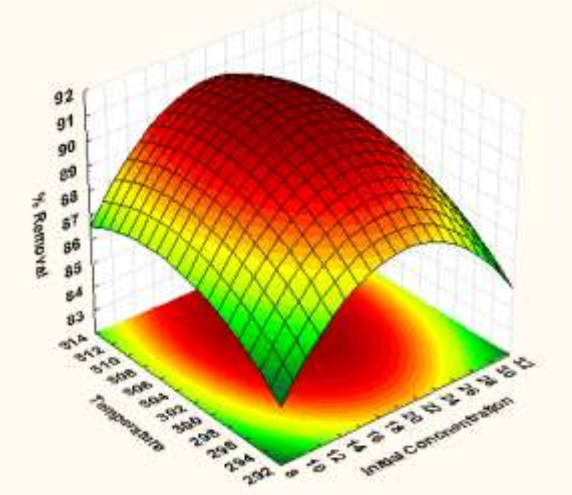
Normal probability plot of residual values are shown. The experimental values are in good agreement with predicted values with minimum error.

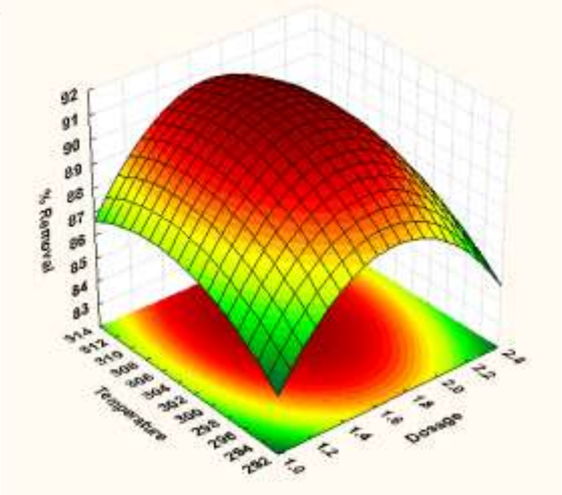






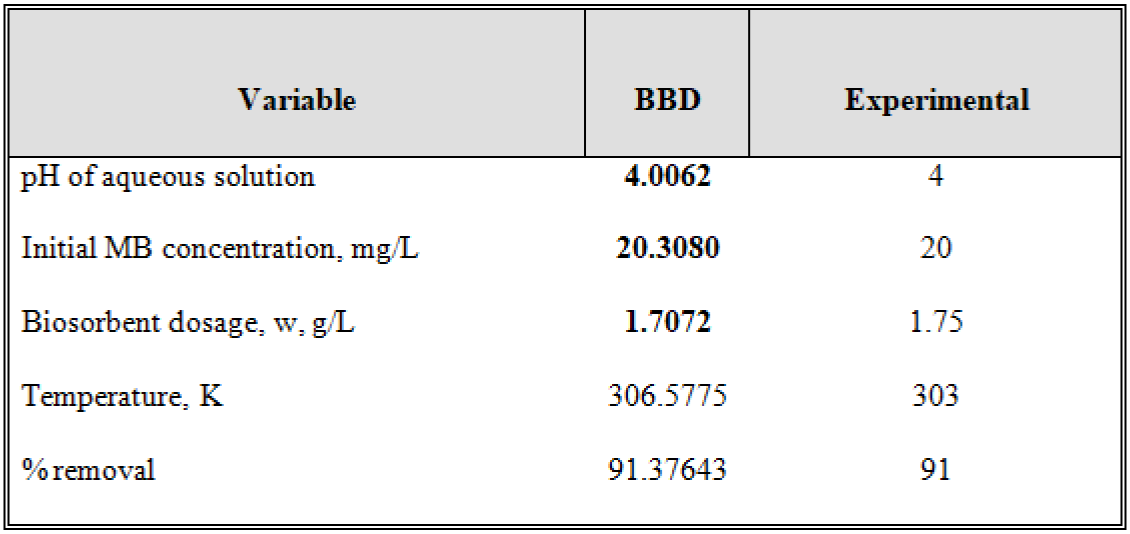






Surface contour plot for the effects of dosage and initial concentration on %, pH on %, Temperature on % biosorption of methylene blue.

Comparison between optimum values from BBD and experimentation



Variable	BBD	Experimental
pH of aqueous solution	**4.0062**	4
Initial MB concentration, mg/L	**20.3080**	20
Biosorbent dosage, w, g/L	**1.7072**	1.75
Temperature, K	306.5775	303
%removal	91.37643	91

X. CONCLUSIONS

The equilibrium agitation time for biosorption of MB dye is found to be 50 min. The optimum dosage is 1.75 g. % biosorption is increased upto pH = 4. The RSM optimized values are: w = 1.7072 g, pH = 4.0062, C_o = 20.3080 mg/L, T = 306.5775 K and extent of biosorption = 91.37643%. The experimental data are well represented by Freundlich (R^2 = 0.9945) and Langmuir (R^2 = 0.9926) isotherms. The kinetic studies show that the biosorption of MB dye is described by both first order (R^2 = 0.9291) and pseudo second order kinetics (R^2 = 0.9409). The thermodynamic investigation reveals the spontaneity of the process ΔG is negative (–7542.01 J/mole), irreversibility ΔS is positive (24.9257) and endothermic nature of biosorption ΔH is positive (10.4926 J/mole).

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