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Studies on Biosorption of Alizarin Red Dye onto Borassus Powder and Optimization Through Central Composite Design

Dr. Ch. A. I. Raju[1], P. Jagadeesh[2]

[1]Assistant Professor (Stage 3), Department of Chemical Engineering, Andhra University, Visakhapatnam, Andhra Pradesh, India

[2]Research Scholar Department of Chemical Engineering, Andhra University, Visakhapatnam, Andhra Pradesh, India

ABSTRACT

This work presents an alternative methodology for removal of a dyestuff Alizarin Red from aqueous solutions by using a new biosorbent, Borassus powder in a batch biosorption technique. The characterization of the biosorbent was performed by using FTIR and XRD techniques. The parameters investigated includes, agitation time, biosorbent size, pH, initial concentration of dye, dosage of biosorbent and temperature. The Kinetic study incorporated lagergren first order and pseudo second order models. The study also included thermodynamics and isotherms like Langmuir, Freundlich and Temkin. The experimental data was correlated for regression analysis and the data was very well fitted.

Keywords: Alizarine red dye, Borassus, RSM, CCD, kinetics.

I. INTRODUCTION

Effluents emanating from many industries contain dissolved heavy metals. If these effluents are discharged without treatment, they will have adverse effects on the environment. Numerous techniques have been proposed by various researchers for the treatment of heavy metal-bearing effluents. These include ion-exchange [1], chemical precipitation [2], electrochemical methods [3] and membrane technology [4]. Another method, which has gained momentum in recent years, is biosorption. The inherent advantages and applications of biosorption have been extensively reviewed by several investigators [5–7]. Several theoretical models were tested in order to fit the experimental data and to understand the possible physicochemical interactions involved in the sorption phenomenon between the biomass surface and the dye molecules. [8]

In the last decades, biomasses were widely used in waste liquid treatment. The usage of inactive microorganisms for the removal of heavy metals [9–10] and organics including dyes [11, 12], phenolics [13,14] and pesticides [15] from wastewaters have been widely studied. The special surface properties of bacteria, yeasts, fungi and algae enable them to adsorb different kinds of pollutants from solutions. The passive uptake of pollutants by inactive/dead biological materials is termed as biosorption [16]. In the concept of biosorption, several physical or chemical processes may be involved such as physical and/or chemical adsorption, ion exchange, coordination, complexation, chelation and microprecipitation. Biomass cell walls offer many functional groups which can bind metal ions and organics such as carboxyl, hydroxyl, sulphate, phosphonate and amino groups. In addition, biosorption processes offer the advantages of low operating costs, high selectivity and efficiency, good removal performance and regeneration ability. For FGD process, activated carbon and sewage sludge [17–19] were used to SO_2 adsorption at low temperature.

II. METHODS AND MATERIAL

The present experimentation is carried out both batch-wise and column, on biosorption of Alizarine red dye from aqueous solutions on the biosorbent – Borassus powder.

The experimental procedure consists of the following steps:

2.1 Preparation of the bisorbent
2.2 Characterization of biosorbent
2.3 Preparation of the stock solutions
2.3 Studies on Equilibrium Biosorption Process

2.1. Preparation of the bisorbent

Borassus leaves were collected from Jodugulla palem beach, near tenneti park, Visakhapatnam. The collected biosorbent was washed with water several times until the dirt particles are removed and finally washed with distilled water. The biosorbent was dried in sun light for fifteen days, cut into small pieces, powdered and sieved. In the present study, the obtained powder was used as biosorbent without any pretreatment.

2.2 Characterization of biosorbent

Biosorption of Alizarine red dye using Borassus powder has many affecting factors which include characterization (FTIR, XRD, SEM), Biosorbents were characterized by FTIR spectrometry using Spectrum GX of Perkin Elmer, XRD patterns were recorded from 10 to 700 For SEM studies, the dried powders and the corresponding loaded powders were first coated with ultra-thin film of gold by an ion sputter JFC-1100 and then were exposed under a Japanese make electron microscope (JEOL, JXA-8100) equilibrium studies (agitation time, biosorbent size, pH, initial concentration, biosorbent dosage, temperature), Isotherms (Langmuir, Freundlich, Temkin), Kinetics (Lagergren First Order, Pseudo Second Order), Thermodynamics (Entropy, Enthalpy and Gibb's Free Energy) and Optimization using Central Composite Design. XRD patterns were recorded from 10 to 700.

2.3 Preparation of stock solution:

The standard stock solution of Alizarin Red dye (1000 mg/L) was prepared by dissolving 1.0 g of 99.9 % analytical grade Alizarin Red dye in 1000 mL of distilled water. The concentration of dye in the aqueous solution was varied from 20 to 200 mg/L by diluting the stock solutions with required quantity of deionized water. The pH of the working solution was adjusted using either 0.1 N HCl or 0.1N NaOH.

2.3 Studies on Equilibrium Biosorption Process:

The biosorption was carried out in a batch process by adding a pre-weighed amount of the Borassus 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 Indigo caramine dye were evaluated using single step optimization process

Table 1 Experimental conditions for biosorption of Alizarin Red dye

S.No.	Parameter	Values Investigated
1	Agitation time, t, min	5, 10, 15, 20, 25, 30, 30, 50, 60, 90, 120, 150 and 180
2	pH of the aqueous solution	2, 3, 3, 5, 6, 7 and 8
3	Initial dye concentration, Co, mg/L	20, 50, 100, 150 and 200
3	Initia Biosorbent dosage, w, g/L	10, 20, 25, 30, 35, 30, 50, 60 and 80
5	Temperature, K	283, 293, 303, 313 and 323

III. RESULTS AND DISCUSSION

3.1 Effect of agitation time

Duration of equilibrium biosorption is defined as a time required for dye concentration to reach a constant value during biosorption. The fig 3.1 shows the equilibrium agitation time which is determined by plotting the % biosorption of AR dye against agitation for the interaction time intervals between 1 to 180 minutes. In the first five minutes, 25% of AR dye is biosorbed for the 53 μm size of 10 gm/L biosorbent dosage. By reaching 58%, the % biosorption is increased briskly upto 25 minutes. The equilibrium conditions of attainment indicate the constant % biosorption beyond 25 minutes. In 50 ml of aqueous solution (C_0= 20mg/L), the maximum biosorption of 58% is attained for 25 minutes of agitation with 10 gms/L of 53μm size biosorbent is mixed. In the initial stages the rate of biosorption is fast because adequate surface area of the biosorbent is available for the biosorption of AR dye. Due to vanderwall forces of attraction the time increases, more amount of AR dye gets biosorbed on to the surface of biosorbent and resulted in decrease of available surface area. Over the surface the biosorbate normally, forms a thin single molecule thick layer over the surface. The biosorption capacity is exhausted when this mono molecular layer covers the surfaces. At 40 minutes the maximum 69 % of biosorption. Therefore, all other experiments are conducted at this optimum agitation time. [**20-24**]

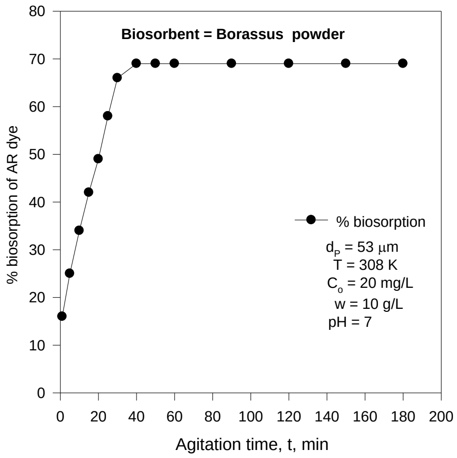

Figure 3.1. Effect of time on % biosorption of AR dye

3.2 Effect of biosorbent size

From the aqueous solution the variation in % biosorption of AR dye with biosorbent size are obtained. The figure 3.2 shows the results which are drawn with % biosorption of AR dye is a function of biosorbent size and it decreases from 53 to 152μm and increases from 69 to 45%. This is expected to phenomenon, as the size of the particle decreases there by the number of active and freely available sites on the biosorbent also enhances with the surface area of the biosorbent enhances. [**25-29**]

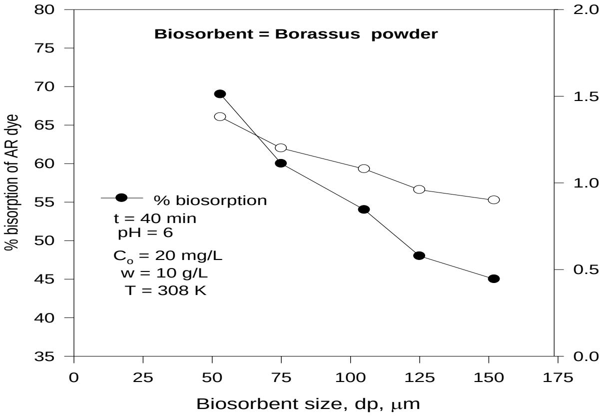

Figure 3.2. Effect of size on % biosorption of AR dye

3.3 Effect of pH

pH controls the degree of ionization and species of the biosorbate, biosorption by influencing the surface change of biosorbent. Using 10gm/L of 53 μm size biosorbent of the aqueous solution, AR dye biosorption data are obtained in the pH range of 2 to 8 in the present investigation made. The figure 3.3 shows the effect of pH of aqueous solution on % biosorption ofAR dye.Beyond the pH value of 6 it increased slowly and the margin is very less. For appropriate sites on the biosorbent surface the low pH depresses biosorption due to competition. The AR dye replace H+ ions bound to the biosorbent and with increasing pH, this competition weakens. [**30-34**]

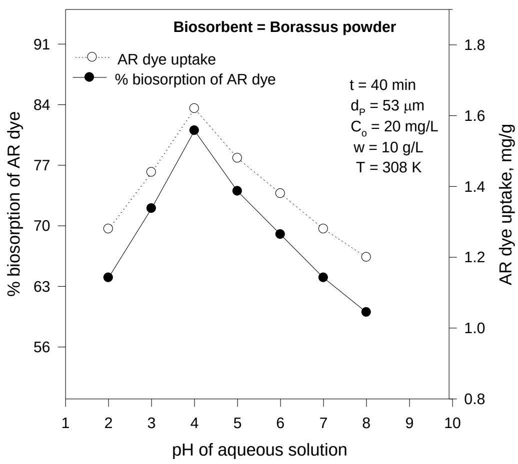

Figure 3.3. Effect of pH on % biosorption of AR dye

3.4 Effect of initial concentration of AR dye

The percentage of biosorption of AR dye shows in the figure 3.4 and its effect of initial concentration of AR dye in the aqueous solution. The precent biosorption of AR dye is increased in C_0 from 20 to 200mg/L (664-673) and decrease from 81 to 60%. The constant number of available active sites on the biosorbent and this behavior can be attributed to increase in the total amount of biosorbate. [35-39]

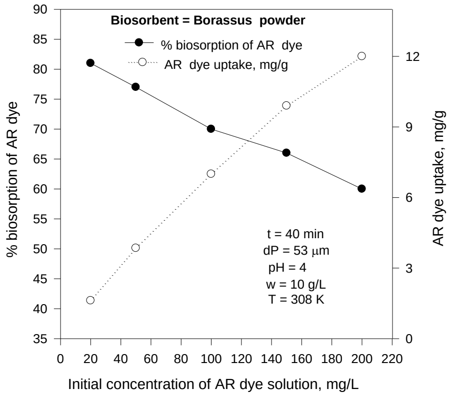

Figure 3.4. Effect of initial concentration on % biosorption of AR dye

3.5 Effect of biosorbent dosage

This figure 3.5 shows the percentage biosorption of AR dye which is drawn against the biosorbent dosage for 53 μm size biosorbent with an increase in the biosorbent dosage from 0.5to 4 gm/L and the biosorption of AR dye increased from 81 to 95%. The number of active sites available for AR dye biosorption would be more and this behavior is obvious because of the increase in biosorbent dosage. When dosage is increased from 40 to 70 gm/L the change in the biosorbent of AR dye is marginal from 92 to 95%. Hence all other experiments are conducted at 40 gm/L dosage. [40-44]

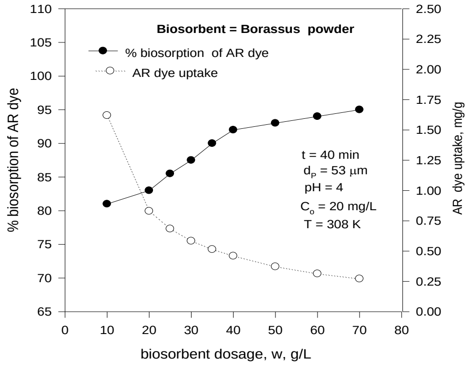

Figure 3.5. Effect of dosage on % biosorption of AR dye

3.6 Effect of temperature

Experiment is done varying temperature from 283 to 323K.On the equilibrium dye uptake the effect of temperature was significant. The figure 3.6 shows the effect of changes in the temperature on AR dye uptake. In the internal porus structure of surface high temperature favors the diffusion of dye molecules. [45-49]

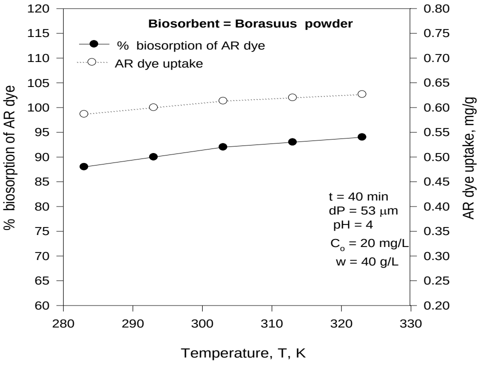

Figure 3.6. Effect of temperature on % biosorption of AR dye

3.7 Isotherms:

3.7.1 Langmuir isotherm:

Irving Langmuir developed an isotherm named Langmuir isotherm. It is the most widely used simple two- parameter equation. This simple isotherm is based on following assumptions:

Biosorbates are chemically biosorbed at a fixed number of well- defined sites

Each site can hold only one biosorbate specie

All sites are energetically equivalent

There are no interaction between the biosorbate species

The Langmuir relationship is hyperbolic and the equation is:

$q_e/q_m = bC_e / (1+bC_e)$ …….. (3.20)

Equation (6.1) can be rearranged as

$(C_e/q_e) = 1/(bq_m) + C_e/q_m$ …….. (5.20)

From the plots between (C_e/q_e) and C_e, the slope $\{1/(bq_m)\}$ and the intercept (1/b) are calculated. Further analysis of Langmuir equation is made on the basis of separation factor, (R_L) defined as $R_L = 1/(1+bC_e)$

$0< R_L<1$ indicates favorable adsorption

$R_L>1$ indicates unfavorable adsorption

$R_L = 1$ indicates linear adsorption

$R_L = 0$ indicates irrepressible adsorption

Langmuir isotherm is drawn for the present data and shown in Figure 3.7. The equation obtained is: $C_e/q_e = 0.0553C_e + 2.3358$ with a good linearity (correlation coefficient, R^2˜0.9887) indicating strong binding of AR dye to the surface of Borassuspowder.

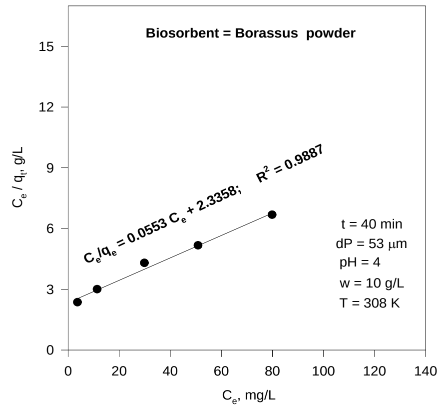

Figure 3.7 Langmuir isotherm for % biosorption of AR dye

3.7.2 Freundlich isotherm:

Freundlich 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

$q_e = K_fC_e^n$ …….. (3.21)

Where K_f (mg) represents the biosorption capacity when dye equilibrium concentration and n represents the degree of dependence of biosorption with equilibrium concentration Taking LN on both sides, we get

$\ln q_e = \ln K_f + n \ln C_e$ …….. (3.22)

Freundlich isotherm is drawn between $\ln C_e$ and $\ln q_e$ and is shown in Figure 3.8 for the present data. The resulting equation has a correlation coefficient of 0.9936.

$\ln q_e = 0.0553 \ln C_e - 0.3399$ …. (3.23)

The 'n' value in the above equation (n=0.6618) satisfies the condition of 0<n<1 indicating favorable biosorption.

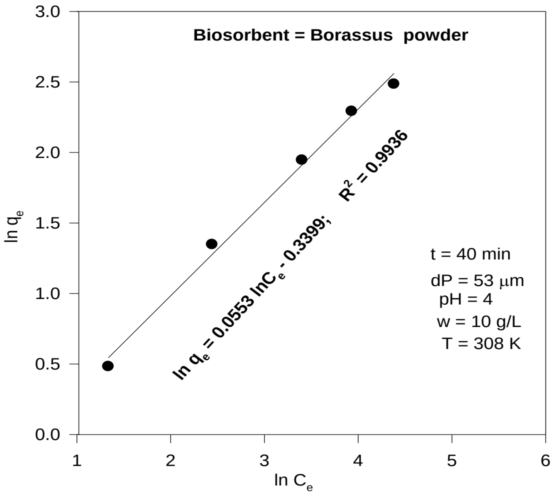

Figure 3.8. Freundlich isotherm for % biosorption AR dye

3.7.3 Temkin isotherm:

Temkin and Pyzhev isotherm equation describes the behavior of many biosorption systems on the heterogeneous surface and it is based on the following equation

$q_e = RT \ln(A_TC_e)/b_T$ …….. (5.24)

The linear form of Temkin isotherm can be expressed as

$q_e = (RT/b_T) \ln(A_T) + (RT/b_T) \ln(C_e)$ …….. (3.25)

Where

$A_T = \exp [b(0) \times b(1) / RT]$

$b(1) = RT/b_T$ is the slope

$b(0) = (RT/b_T) \ln(A_T)$ is the intercept and b= RT/b (1)

The present data are analysed according to the linear form of Temkin isotherm and the linear plot is shown in Figure 3.9. The equation obtained for AR dye biosorption is: $q_e = 3.4129 \ln C_e - 3.7009$ with a correlation coefficient 0.9834. The best fit model is determined based on the linear regression correlation coefficient (R). From the Figs 3.7, 3.8&3.9, it is found that biosorption data are well represented by Freundlich isotherm with higher correlation coefficient of 0.9936, followed by Temkin and Langmuir isotherms with correlation coefficients of 0.9638 and 0.9887[**50-59**] respectively.

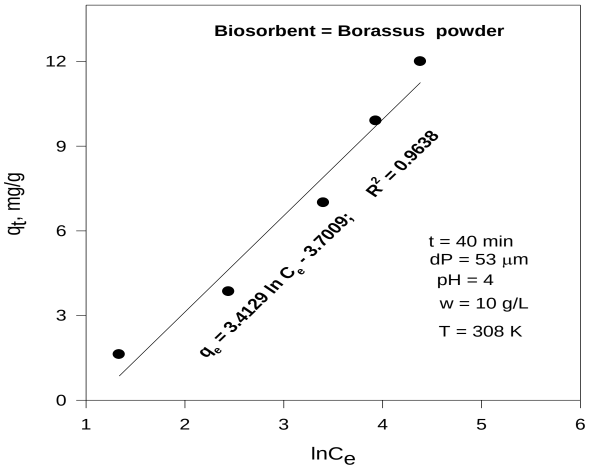

Figure 3.9. Temkin isotherm for % biosorption of AR dye

Table 1. Isotherm constants (linear method)

Langmuir isotherm	**Freundlich isotherm**	**Temkin isotherm**
q_m = 18.07011 mg/g	K_f = 0.71184 mg/g	A_T = 0.33811 L/mg
K_L = 0.02369	n = 0.6618	b_T = 738.117
R^2 = 0.9887	R^2 = 0.9936	R^2 = 0.9638

3.8 Kinetics of biosorption

3.8.1 Lagergren First order Kinetics

The order of biosorbate – biosorbent interactions have been described using kinetic model. Traditionally, the first order model of Lagergren finds wide application. In the case of biosorption preceded by diffusion through a boundary, the kinetics in most cases follows the first order rate equation of Lagrangen:

$(dq_t/dt)= K_{ad} (q_e - q_t)$ …….. (3.26)

where q_e and q_t are the amounts adsorbed at t, min and equilibrium time and K_{ad} is the rate constant of the pseudo first order biosorption.

The above equation can be presented as

$\int (dq_t/(q_e - q_t))= \int K_{ad} \, dt$ …….. (3.27)

Applying the initial condition $q_t = 0$ at $t = 0$, we get

$\log (q_e - q_t) = \log q_e - (K_{ad}/2.303)\, t$ …….. (3.28)

In the present study, the kinetics are investigated with 50 mL of aqueous solution (C_0= 20 mg/L) at 303 K with the interaction time intervals of 1 min to 180 min. Lagragen plots of log (q_e-q_t) versus agitation time (t) for biosorption of AR dye the biosorbent size (53 μm) of Borassuspowderinthe interaction time intervals of 1 to 180 min are drawn in Figure 3.10. log (q_e-q_t) = - 0.0380 t + 0.1862, R^2=0.8686 …….. (3.29)

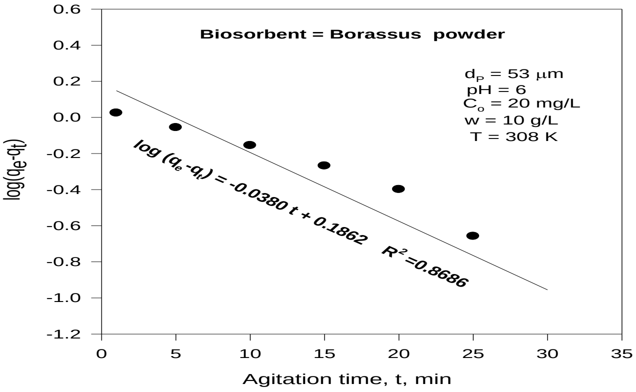

Figure 3.10. first order kinetics for % biosorption of AR dye

3.8.2 Pseudo Second order Kinetics

Plot of log (q_e–q_t) versus't' gives a straight line for first order kinetics, facilitating the computation of adsorption rate constant (K_{ad}). If the experimental results do not follow the above equation, they differ in two important aspects:

i) K_{ad} $(q_e - q_t)$ does not represent the number of available biosorption sites and

ii) log q_e is not equal to the intercept.

In such cases, pseudo second order kinetic equation: $(dq_t/dt) = K (q_e - q_t)^2$ …….. (3.30)

is applicable,

where 'K' is the second order rate constant.

The other form of the above equation is: $(dq_t /(q_e- q_t)^2)= Kdt$ …….. (3.31)

let $q_e - q_t = x$

$dq_t = dx$

$1/ x = K x + C$ …….. (3.31)

$C = 1/ q_e$ at t = 0 and $x = q_e$

Substituting these values in above equation, we obtain:

$1/(q_e - q_t) = Kt + (1/q_e)$ …….. (5.32)

Rearranging the terms, we get the linear form as:

$(t/q_t) = (1/ Kq_e^2) + (1/q_e) t.$ …….. (3.33)

The pseudo second order model 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. If the pseudo second order kinetics is applicable, the plot of (t/q_t) versus't' gives a linear relationship that allows computation of q_e and K.

$t/q_t = 0.6341 t + 6.165$, $R^2=0.8936$ ………………….. (3.34)

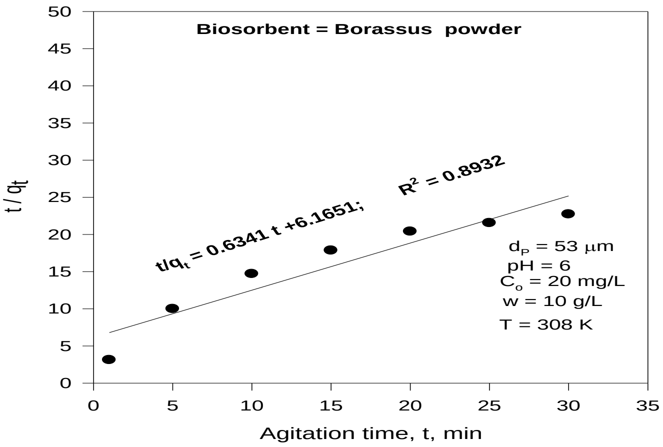

Figure 3.11. second order kinetics for % biosorption of AR dye

In the present study, the kinetics are investigated with 50 mL of aqueous solution (C_0= 20 mg/L) at 303 K with the interaction time intervals of 1 min to 180 min. Pseudo second order plot of t vs t/q_t for biosorption of AR dye with the biosorbent size (53 μm) of Borassus powderinthe interaction time intervals of 1 to 180 min is drawn in Figure 3.11[**60-64**].

Table 2. Equations and rate constants

Order	Equation	Rate constant	R^2
Lagergren first order	$\log (q_e-q_t) = -0.0380 t + 0.1862$	0.087514 min^{-1}	0.8686
Pseudo Second order	$t/q_t = 0.6341 t + 6.1651$	0.065219 g/(mg-min)	0.8932

3.8.3 Thermodynamics of biosorption:

Biosorption is temperature dependant. 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).

Enthalpy is the most commonly used thermodynamic function due to its practical significance. The negative value of ΔH will indicate the exothermic/endothermic nature of biosorption and the physical/chemical in nature of sorption. It can be easily reversed by supplying the heat equal to calculated ΔH.

The ΔH is related to ΔG and ΔS as

$$\Delta G = \Delta H - T\,\Delta S \quad \ldots\ldots\ (3.35)$$

ΔS < 1 indicates that biosorption is impossible whereas ΔS > 1 indicates that the biosorption is possible. ΔG < 1 indicates the feasibility of sorption.

The Vant Hoff's equation is

$$\log (q_e / C_e) = \Delta H/(2.303\ RT) + (\Delta S/2.303\ R) \ldots\ldots (3.36)$$

$$\log (q_e / C_e) = - 0.7590\ (1 / T) + 2.0730 \quad ..\ (3.37)$$

Where (q_e/C_e) is called the biosorption affinity.

If the value of ΔS is less than zero, it indicates that the process is highly reversible. If ΔS is more than or equal to zero, it indicates the reversibility of process. The negative value for ΔG indicates the spontaneity of biosorption. Whereas the positive value indicates is non spontaneity of sorption.

Experiments are conducted to understand the biosorption behavior varying the temperature from 283 to 323 K. The plot indicating the effect of temperature on biosorption of AR dye for different initial AR dye concentrations is shown in Figure 3.12. The values are ΔG = -12012.6, ΔH = 14.5326 and ΔS = 39.6935[**65-69**].

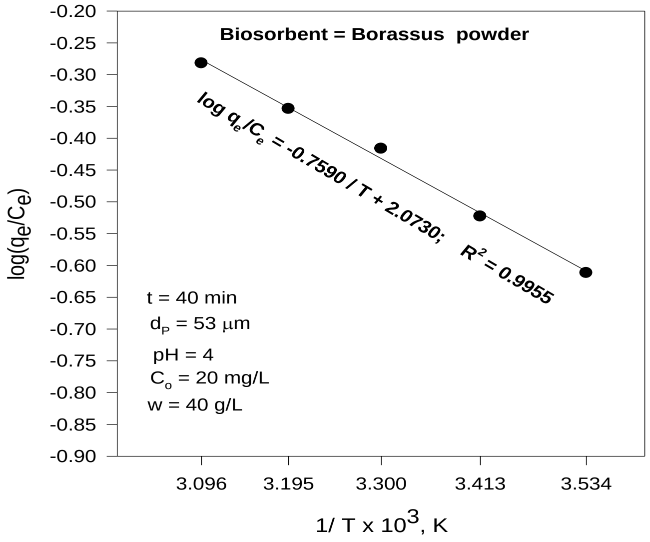

Figure 3.12. Vantoff's plot for % biosorption of AR dye

3.9. Optimization using Response Surface Methodology (RSM):

3.9.1 Optimization of biosorption conditions using CCD

The effects of four independent variables (pH, initial concentration of AR dye in aqueous solution, biosorbent dosage and temperature) on AR dye biosorption are analyzed using Central Composite Design (CCD) [**65-69**]. The optimum conditions for the four independent variables on the extent of AR dye biosorption are formed within the quadratic model.Levels of different process variables for percentage biosorption areshown in table–3.3.

Table 3. Levels of different process variables in coded and un-coded form for % biosorption of AR dye using Borassus powder

Variable	**Name**	**Range and levels**				
		-2	**-1**	**0**	**1**	**2**
X_1	pH of aqueous solution	2	3	4	5	6
X_2	Initial concentration, C_o, mg/L	10	15	20	25	30
X_3	Biosorbent dosage, w, g/L	30	35	40	45	50
X_4	Temperature, T, K	283	293	303	313	323

Regression equation for the optimization of biosorption is:

% biosorption of AR 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:

$Y = -1518.84 + 18.36\,X_1 + 6.52\,X_2 + 6.12\,X_3 + 9.13\,X_4 - 3.18\,X_1^2 - 0.11X_2^2 - 0.08X_3^2 - 0.01X_4^2 - 0.24\,X_1X_2 + 0.30\,X_1X_3 + 0.00\,X_1X_4 + 0.02\,X_2X_3 - 0.01\,X_2X_4 - 0.00X_3X_4$------- (5.38)

Table-5.22 represents the results obtained in CCD. The response obtained in the form of analysis of variance (ANOVA) from regression eq.3.38 is put together in table–3.4. 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.

Table 4. Results from CCD for AR dye biosorption by borassuspowder

Run No.	X_1, pH	X_2, C_o	X_3, w	X_4, T	% biosorption of AR	
					Experimental	Predicted
1	5	15	20	293	85.58000	85.58833
2	5	15	20	313	87.02000	86.97167
3	5	15	30	293	84.38000	84.39500
4	5	15	30	313	84.90000	84.90833
5	5	25	20	293	87.62000	87.61500
6	5	25	20	313	87.68000	87.70833
7	5	25	30	293	88.92000	88.87167
8	5	25	30	313	88.12000	88.09500
9	7	15	20	293	85.68000	85.68167
10	7	15	20	313	87.08000	87.12500
11	7	15	30	293	90.46000	90.42833
12	7	15	30	313	91.02000	91.00167
13	7	25	20	293	82.82000	82.80833
14	7	25	20	313	83.00000	82.96167
15	7	25	30	293	89.98000	90.00500
16	7	25	30	313	89.30000	89.28833
17	4	20	25	303	83.12000	83.14000
18	8	20	25	303	84.42000	84.42667
19	6	10	25	303	84.98000	84.97667
20	6	30	25	303	85.26000	85.29000
21	6	20	15	303	86.18000	86.17667
22	6	20	35	303	91.28000	91.31000
23	6	20	25	283	90.36000	90.37000
24	6	20	25	323	91.02000	91.03667
25	6	20	25	303	96.52000	96.52000
26	6	20	25	303	96.52000	96.52000
27	6	20	25	303	96.52000	96.52000
28	6	20	25	303	96.52000	96.52000
29	6	20	25	303	96.52000	96.52000
30	6	20	25	303	96.52000	96.52000

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 40 min and biosorbent size at 53 µm

Table 5. ANOVA of AR dye biosorption for entire quadratic model

Source of variation	SS	df	Mean square(MS)	F-value	*P*> F
Model	598.4132	14	42.7438	43175	0.00000
Error	0.0149	15	0.00099		
Total	598.4281				

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

R^2=0.99996; R^2 (adj):0.99992

Table 6. Estimated regression coefficients for the AR dye biosorption onto Borassus powder

Terms	Regression coefficient	Standard error of the coefficient	t-value	*P*-value
Mean/Int	-	6.09245	-249.299	0.0000

ercept	1518.84	3		0
Dosage, w, g/L (L)	18.36	0.253338	72.474	0.00000
Dosage, w, g/L (Q)	-3.18	0.006011	-529.708	0.00000
Conc, Co, mg/L (L)	6.52	0.050668	128.774	0.00000
Conc, Co, mg/L (Q)	-0.11	0.000240	-473.562	0.00000
pH (L)	6.12	0.052209	117.184	0.00000
pH (Q)	-0.08	0.000240	-323.425	0.00000
Temperature, T, K (L)	9.13	0.037241	245.053	0.00000
Temperature, T, K (Q)	-0.01	0.000060	-241.910	0.00000
1L by 2L	-0.24	0.001574	-155.645	0.00000
1L by 3L	0.30	0.001574	188.680	0.00000
1L by 4L	0.00	0.000787	1.906	0.07601
2L by 3L	0.02	0.000315	77.822	0.00000
2L by 4L	-0.01	0.000157	-40.976	0.00000
3L by 4L	-0.00	0.000157	-27.635	0.00000

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

The ANOVA of the regression model is sufficiently great, as proven from the Fisher's *F*-test and has a very low probability value ($P_{model}>F=0.000000$). Besides, the computed *F*-value 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. It is noted from table-5.24 that more significant corresponding coefficient term can be possessed by having high't' value and low 'P' value. By analyzing't' and 'p' values from table-5.24,all the variables have high importance to explain the individual and interaction effects of independent variables on biosorption of AR dye to anticipate the response. The model is reduced to the following form by excluding undistinguished terms in eq.3.39.

$$\mathbf{Y = -1518.84 + 18.36\,X_1 + 6.52\,X_2 + 6.12\,X_3 + 9.13\,X_4 - 3.18\,X_1^2 - 0.11X_2^2 - 0.08X_3^2 - 0.01X_4^2 - 0.24\,X_1X_2 + 0.30\,X_1X_3 + 0.00\,X_1X_4 + 0.02\,X_2X_3 - 0.01\,X_2X_4 - 0.00X_3X_4} \text{-------} \mathbf{(3.39)}$$

A positive sign of the coefficient represents an interactive effect i.e., response (% biosorption of AR 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 $R^2 \longrightarrow 1$, model is inviolable and the response is estimated better. In our study, $R^2 = 0.99996$suggests that 0.004 % 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.

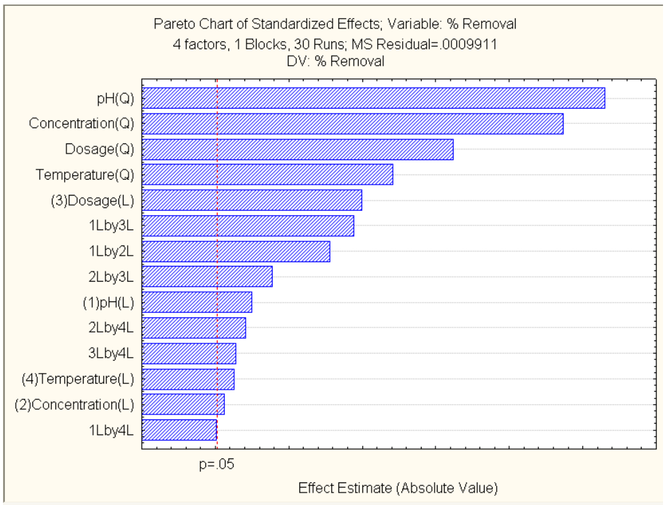

Figure 3.13. Pareto Chart

The optimal set of conditions for maximum percentage biosorption of AR dye is pH = 4.1354, initial AR dye concentration = 20.1222 mg/L, biosorbent dosage = 41.9207 g/L, and temperature = 303.2657 K. The extent of biosorption of AR dye at these optimum conditions was 96.79145%. It is evident that experimental values of % biosorption are in close agreement with that of predicted by Central Composite Design. Experiments are conducted in triplicate with the above predicted optimal set of conditions and the % biosorption of AR dye is 93 %, which is closer to the predicted % biosorption.**[70-74]**

3.9.2 Interpretation of residual graphs:

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. Figure 3.14 exhibits normal probability plot for the present data. It is evident that the experimental data are reasonably aligned implying normal distribution.

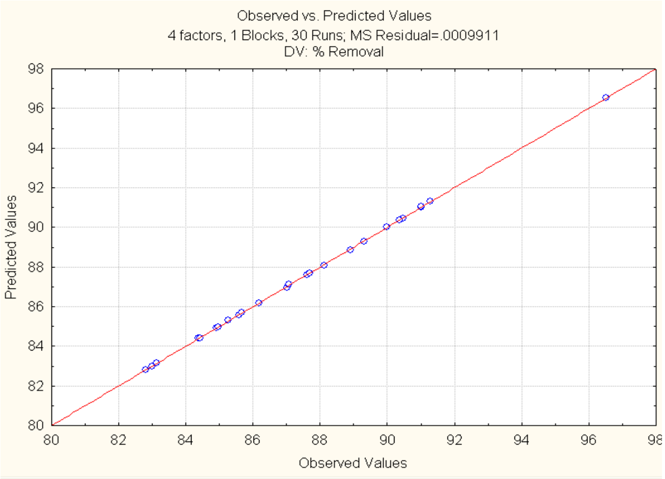

Figure 3.14. Normal probability plot for % biosorption of AR dye

3.9.3 Interaction effects of biosorption variables:

Three-dimensional view of response surface contour plots [Fig3.15 (a) to 3.15 (f)] exhibit % biosorption of the AR dye using borassus 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 confirms 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 AR dye and seen clearly from the plots. The predicted optimal set of conditions for maximum % biosorption of AR dye is:

pH of aqueous solution = 4.1354
Initial AR dye concentration = 20.1222 mg/L
Biosorbent dosage = 41.9207 g/L
Temperature = 303.2657 K
% biosorption of AR dye = 96.79145

The experimental optimum values are compared with those predicted by CCD in table-3.7. The experimental values are in close agreement with those from CCD.

Table 7. Comparison between optimum values from CCD and experimentation

Variable	CCD	Experimental
pH of aqueous solution	4.1354	4.0
Initial AR concentration, mg/L	20.1222	20
Biosorbent dosage, w, g/L	41.9207	40
Temperature, K	303.2657	303
% biosorption	96.79145	90

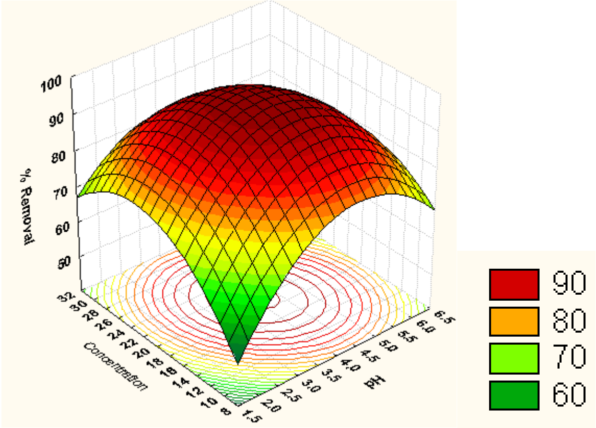

Figure 3.15. (a) Surface contour plot for the effects of pH and initial concentration of AR dye on % biosorption

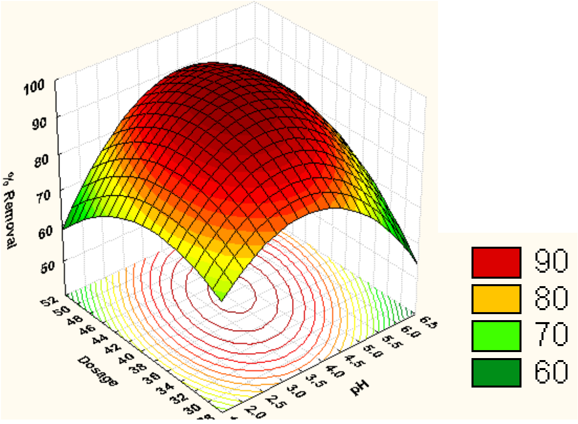

Figure 3.15. (b) Surface contour plot for the effects of pH and Dosage of AR dye in aqueous solution on % biosorption

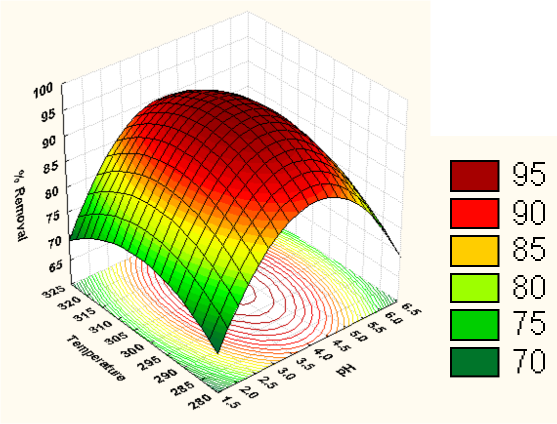

Figure 3.15 (c) Surface contour plot for the effects of pH and temperature of AR dye in aqueous solution on the % biosorption

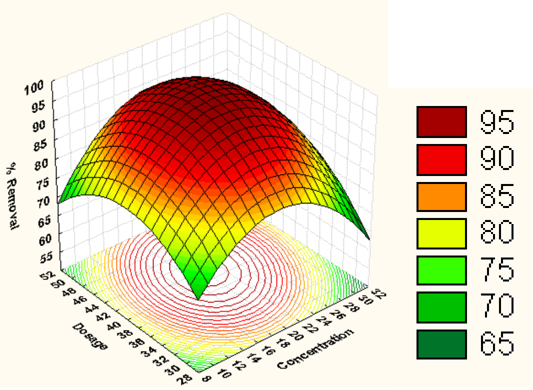

Figure 3.15. (d) Surface contour plot for the effects of concentration and dosage on % biosorption of AR dye

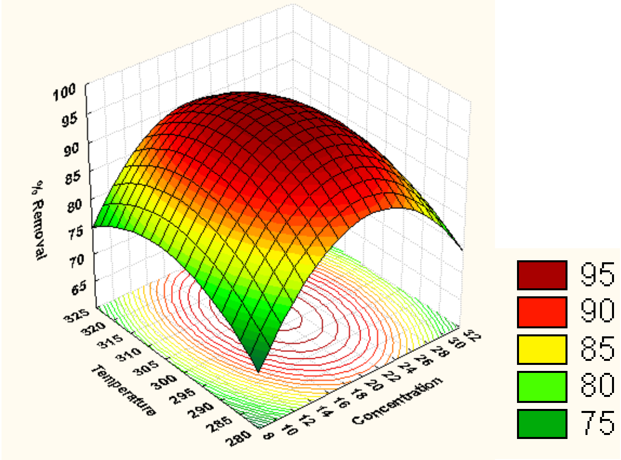

Figure 3.15. (e) Surface contour plot for the effects of concentration and temperature on % biosorption of AR dye

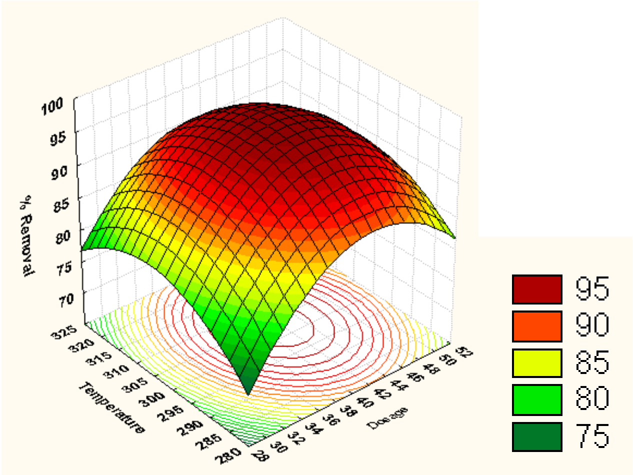

Figure 3.15. (f) Surface contour plot for the effects of Dosage and temperature on % biosorption of AR dye

3.10 Characterization of borassuspowder

3.10.1 FTIR spectrum

3.10.1 (a) FTIR spectrum of untreated Borassuspowder

FTIR measurements presented in Figure 3.16 (a) show the broad band at 3359.09 cm-1 is due to –OH stretching or –NH2 stretching. The band at 2926.24 cm^{-1} denote the presence of CH_2 stretching vibrations. The band at 1733.52 cm^{-1} suggests the presence of Assymetric stretching vibration of C = O. The band at 1645.93 cm^{-1} is may be due to the Oleifinic C = C and Carbonyl C = O stretching. Amide N–H bending vibrations of C=O is due at 1515.30 cm^{-1} band.

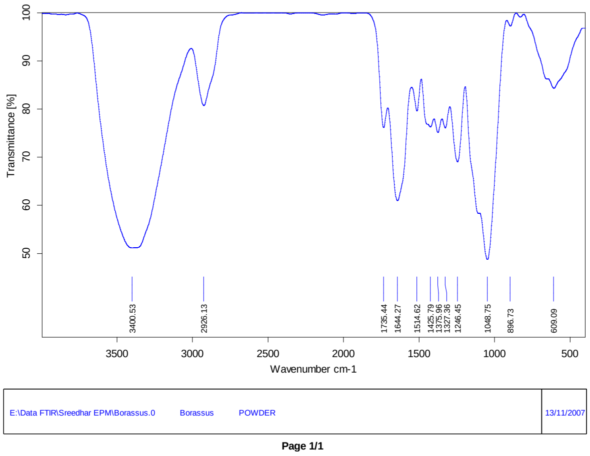

Figure 3.16. (a) FTIR spectru m of untreated Borassus powder

3.10.1(b) FTIR spectrum of treated Borassus powder

FTIR spectrum for treated powder is shown in fig 3.16(b). Broad band at 3359.17 cm-1 suggests –OH stretching or –NH2 stretching. The band at 2925.14 cm-1 due to the presence of CH_2 stretching vibrations. The band at 1737.91 cm^{-1} indicates the presence of Assymetric stretching vibration of C = O arising from group such as lactone, quinine and carboxylic acids. The Oleifinic C = C and Carbonyl C = O stretching, respectively appear at 1648.17 cm^{-1} band. The vibration at 1511.83 cm^{-1} be attributed to Amide N–H bending vibrations. Comparing IR spectra of Borassus before & after biosorption, the biosorption bands shifted to higher values. These shifts may be attributed to the changes in counter ions associated with carboxylate and hydroxyiate anions. This indicates that the main contributors in dye uptake are may be acidic groups, carboxyl and hydroxyl groups [75-79].

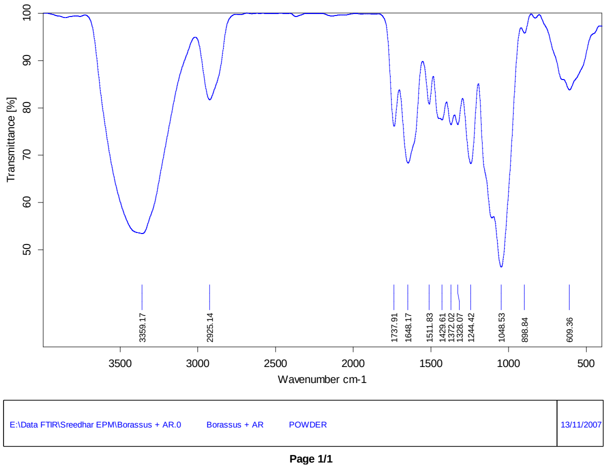

Figure 3.16 (b) FTIR spectrum of treated Borassus powder

Table 9. Shift of FTIR peaks for untreated and Borassus powder treated AR dye

S. No.	Peaks in untreated powder, cm^{-1}	Peaks in treated powder, cm^{-1}	Description
1	---	609.36	2,4 benzene deformation out of phase
2	609.57	---	2,4 benzene deformation out of phase
3	---	898.84	S = O and C–S–O

			bands from ester sulphonate
4	---	1048.53	C–H bending vibrations
5	1049.60	---	C–H bending vibrations
6	---	1244.42	-SO_3 stretching
7	1244.85	---	-SO_3 stretching
8	1328.07	1328.07	–CH_2 bending vibrations
9	---	1372.02	–CH_2 bending vibrations
10	1374.49	---	–CH_2 bending vibrations
11	1426.39	---	C–N stretching
12	---	1429.61	C–N stretching
13	---	1511.83	Amide N–H bending vibrations
14	1515.30	---	Amide N–H bending vibrations
15	1645.93	---	Oleifinic C = C and Carbonyl C = O stretching
16	---	1648.17	Oleifinic C = C and Carbonyl C = O stretching
17	1733.52	---	Assymetric stretching vibration of C = O
18	---	1737.91	Assymetric stretching vibration of C = O
19	---	2925.14	CH_2 stretching vibrations
20	2926.24	---	CH_2 stretching vibrations
21	3359.09	---	–OH stretching or –NH_2 stretching
22	---	3359.17	–OH stretching or –NH_2 stretching

3.10.2 XRD patterns

3.10.2 (a) X–Ray Diffractionfor untreatedBorassuspowder

XRD patterns shown in fig 3.17 (a) & (b) for untreated powder do not show very acute or keen and discrete peaks and exhibits minimum amorphous nature. The peaks at 2θ values of 0.3845, 0.6273, 0.5076, 0.6547 and 0.4937 corroborate 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 corresponding d-values are 4.1049, 4.2516, 3.8633, 3.0189 and 2.5648 [**80-84**].

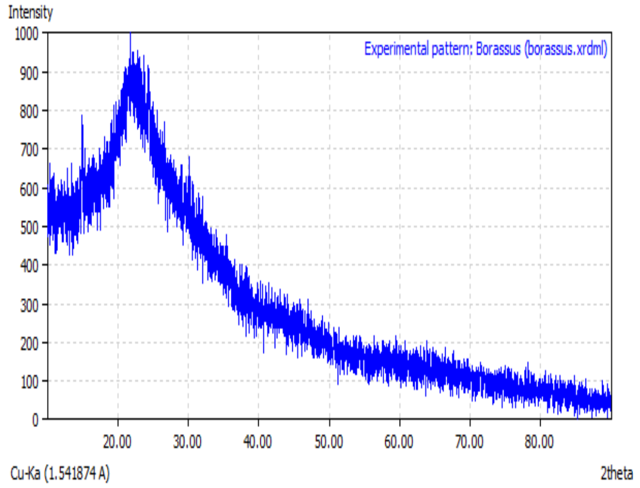

Figure 3.17. (a) XRD pattern of untreated Borassus powder

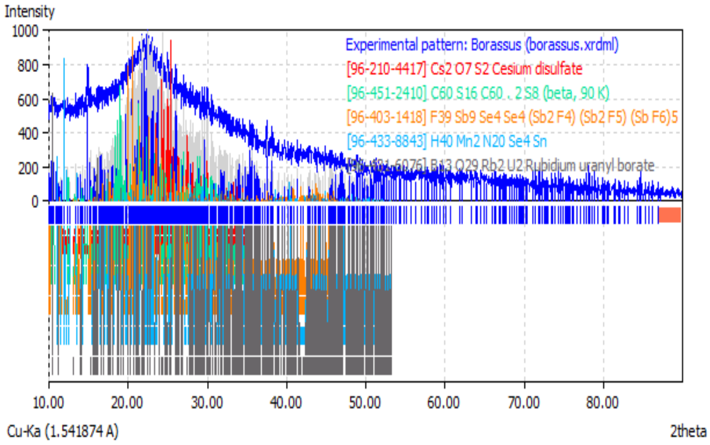

Figure 3.17. (b) XRD pattern of AR dye untreated Borassus powder with matching compounds

3.10.2 (b) X–Ray Diffractionfor treatedBorassuspowder

XRD patterns of treated AR dye, shown in figs 3.17(c), show very spiky and clear peaks and exhibit absolutely amorphous nature. The peaks at 2θ values of 0.4584, 0.6664, 0.5909, 0.6593 and 0.6948 corroborate the presence of $Ni(HN_2S_2)_2$, O_2Si, $CCaO_3$, $Cs_{23}O_{14.15}$ and C (graphite). Their corresponding d-values are 1.8171, 2.2843, 3.0168, 2.9714 and 2.1314 respectively.

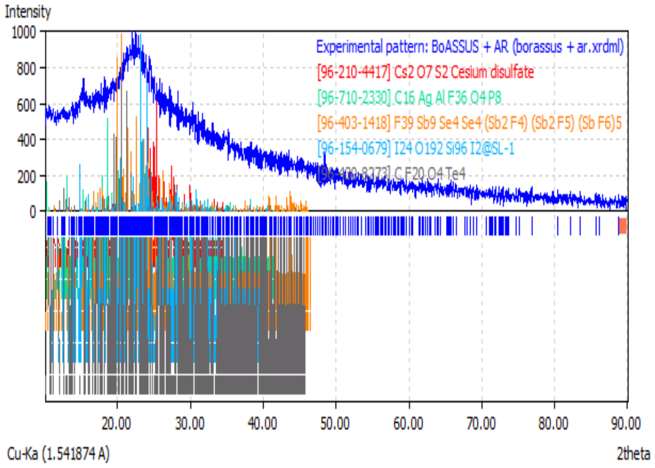

Figure 3.17. (c) XRD pattern of AR dye treated Borassus powder with matching compounds

IV. CONCLUSION

1. The equilibrium agitation time for biosorption of AR dye is 40 min.
2. The optimum dosage is 40 g/L
3. % biosorption is increased upto pH = 4.
4. The RSM optimized values are: w = 41.9207 g/L, pH = 4.1354, C_0 = 20.1222 mg/L, T = 303.2657 K and extent of biosorption = 96.79145%.
5. The experimental data are well represented by Langmuir (R^2 = 0.9887)and Temkin (R^2 = 0.9638) isotherms.
6. The kinetic studies show that the biosorption of AR dye is described by both first order(R^2= 0.8686) and pseudo second order kinetics(R^2 = 0.8932).

- The thermodynamic investigation reveal the spontaneity of the process –ΔG is negative (-1202.6J/mole), irreversibility–ΔS is positive (39.69356J/mole) and endothermic nature of biosorption–ΔH is positive (14.5326J/mole).

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