STUDIES ON BIOSORPTION OF ALIZARIN RED DYE WITH SPICIFERA POWDER AND OPTIMIZATION THROUGH CENTRAL COMPOSITE DESIGN

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Abstract : Biosorption of Alizarin Red dye onto dried *Spicifera* biomass was studied with respect to pH, contact time, biosorbent and dye concentrations., The best practice for the removal of dyes is considered for the present investigation and is Biosorption. 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, Spicifera, RSM, CCD

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I. INTRODUCTION

Effluents discharged from textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries contain residues of dyes. Discharge of colored wastewater without proper treatment can results in numerous problems such as chemical oxygen demand (COD) by the water body, and an increase in toxicity. Many dyes may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system [1]. Organic dyes are harmful to human beings, the need to remove color from wastewater Effluents become environmentally important. It is rather difficult to treat dye effluents because of their synthetic origins and mainly aromatic structures, which are biologically non-degradable. During the previous several decades, a number of physical, chemical and biological methods for purification–decolorization were published and some of them were accepted by the textile industry. Among several chemical and physical methods, adsorption process is one of the effective techniques that have been successfully employed for color removal from waste water [2]. Activated carbons are widely used as adsorbents for the removal of dyes from wastewater. However, use of activated carbon for large scale removal of dyes is quite expensive. Consequently many researchers have studied the feasibility of using low-cost substances as alternative to costly activated carbons[3]. Materials like modified rice straw [4], fly ash [5,6], rice husk [7,8], neem leaf powder [9], chemically treated guava leaf powder [10],phoenix tree leaves [11], wheat shell [12], banana and orange peels [13], etc., can be used.

The contact between solid adsorbent and the liquid can be made by several systems. The present investigation is an attempt to explore the possibility of using a biosorbent to remove Bromo Cresol Purple dye in aqueous solution, since the raw material is harmless, cheaper, and plentiful.

The adsorption behavior of the dyes as a function of temperature, pH and agitation time was also studied. Adsorption data was fitted to Freundlich Eq., Langmuir Eq. and BET Eq. isotherms and their corresponding adsorption parameters such as K_F, n and K and V_m, respectively, have been calculated.

$$\ln x/m = \ln K_F + 1/n \ln C_s \quad \ldots.. \text{ Freundlich Eq.}$$

Where x/m is the amount adsorbed per unit mass of the adsorbate, C_s the equilibrium concentration, and $1/n$ and K_F are constants. The constant K_F is related to the degree of adsorption, n provides the rough estimation of the intensity of the adsorption:

$$C_s x/m = 1/K V_m + C_s V_m \quad \ldots\ldots \text{ Langmuir Eq}$$

$$C_s/C_0 x/m (1 - C_s/C_0) = 1/x_m C + (C - 1) C_s/x_m C C_0 \quad \ldots\ldots\ldots \text{ BET Eq}$$

where K is the adsorption coefficient, V_m the monolayer capacity, x_m the amount of dye required to form the monolayer over the surface of adsorbent and C is the constant.

In order to fully understand the nature of adsorption, the thermodynamic studies play an important role. This paper also presents the thermodynamics parameters related to the adsorption of dyes such as free energy change (ΔG), enthalpy change(ΔH) and entropy change (ΔS), which have been calculated using following equations [14-17].

$$\Delta G = -RT \ln K$$
$$\ln K = \Delta S/R - \Delta H/RT$$
$$\Delta G = \Delta H - T\Delta S$$

2.0 EXPERIMENTAL PROCEDURE

The present experimentation is carried out both batch-wise and column, on biosorption of Indigo caramine dye from aqueous solutions on the biosorbent – hypnea musciformis 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

Spicifera alage 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 spicifera 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 Alizarine red dye (1000 mg/L) was prepared by dissolving 1.0 g of 99.9 % analytical grade Alizarine 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 Spicifera 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 Alizarine red dye were evaluated using single step optimization process

TABLE 1

EXPERIMENTAL CONDITIONS FOR BIOSORPTION OF AR 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	Biosorbent dosage, w, g/L	10, 20, 25, 30, 35, 30, 50, 60 and 80
5	Temperature, K	283, 293, 303, 313 and 323

3.0 RESULTS AND DISCUSSIONS

Experimental data are generated in a batch mode of operation to study the effect of various parameters for the removal of AR dye from the aqueous solution using spicifera (red algae) powder as biosorbent. The effect of various parameters was studied on the biosorption of AR dye. Various experimental runs are conducted in the present study the following parameters.

The parameters are:

3.1. Effect of Agitation time
3.2. Effect of size of biosorbent.
3.3. Effect of dosage of biosorbent
3.4. Effect of initial concentration of the solution, C_0 (mg/L)
3.5. Effect of pH of the solution
.6. Effect of temperature, T, (K)

3.1 Effect of agitation time:

The above fig 3.1 is drawn against the % biosorption of AR dye by spicifera powder, and agitation time. In first 20 min of agitation the 41.5 % biosorption is gradually increased and their plots are found and the biosorption is more or less constant. Hence the equilibrium agitation time is 50 min 64 % biosorption. In the agitation time period of 1 to 180 min, experiment which is typically made with 50 mol of aqueous solution adding 10g/L of 53 μm size biosorption, the % biosorption is increased from 14% to 64%-time period of 1 to 180 min and dye uptake is 0.28 to 1.28 mg/gm. The % rate of biosorption is higher in the initial stages. It is maintained high because of the biosorbent ad-equal surface area is available for the biosorption of AR dye by spicifera powder.[1-5]
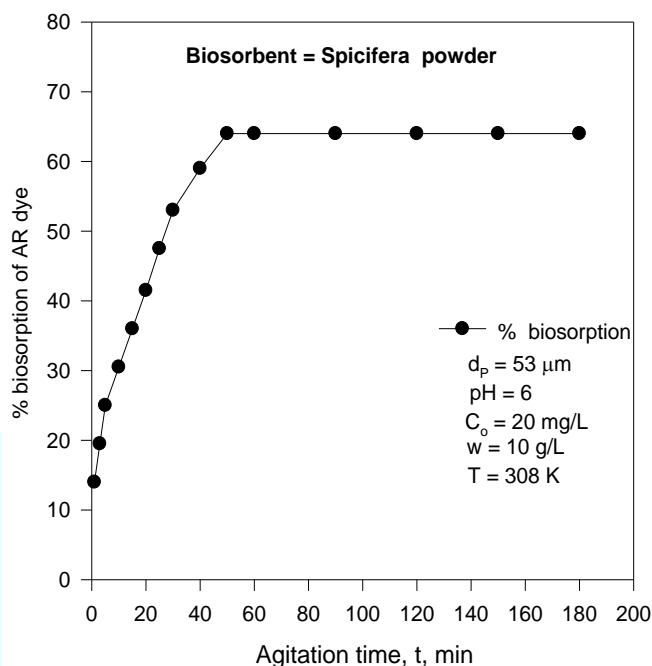

Fig 3.1. Effect of agitation time on % biosorption of AR dye

3.2 Effect of biosorbent size

The above fig. 3.2shows the variation in % biosorption of AR dyes by spicifera powder with biosorbent size. As the biosorbent size increased from 53to 152μm, the % biosorption is decreased from 64 to 40% and dye uptake is 1.28 to 0.8 mg/gm, the biosorbent surface area increases as the size of the particle decreases. The biosorbate is better exposed to the number active sites of the biosorbent[6-10].
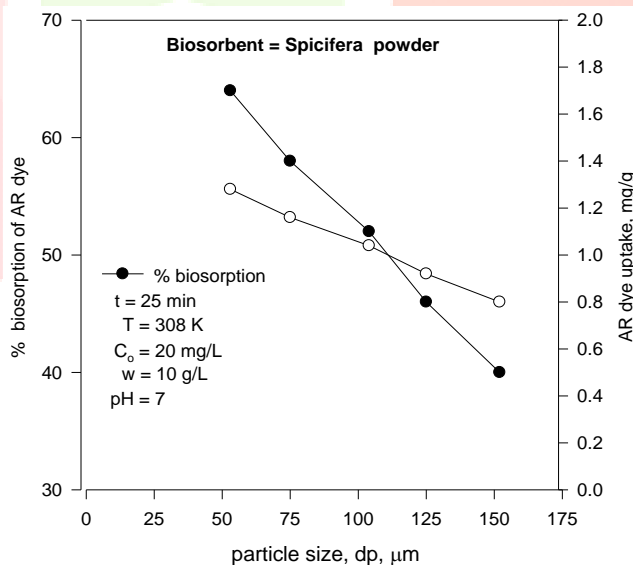

Fig 3.2. Effect of biosorbent size on % biosorption of AR dye

3.3 Effect of pH in aqueous solution

The below plot is drawn in between pH of aqueous solution and biosorption AR dye by spicifera powder. The observation from the fig.3.3 is significant increase in % biosorption and pH is increased from 2 to 8. Above 6 the pH is increased (44t o 64%) and downward trend of the % biosorption is noted. The extent of biosorption is increased from 44to 50% in the pH range from 2 to 8 by adding biosorbent dosage of 10g/L of 53 μm size along with 50 ml of aqueous solution is a typical experiment done. The obtained result indicates that the chemical interactions may have been exchanged between the ions. Due to ion exchange involvement in biosorption, the presence of SO_3 stretching, S=O and C-S-O bands, from ester sulfonate groups are very rich.[11-15]
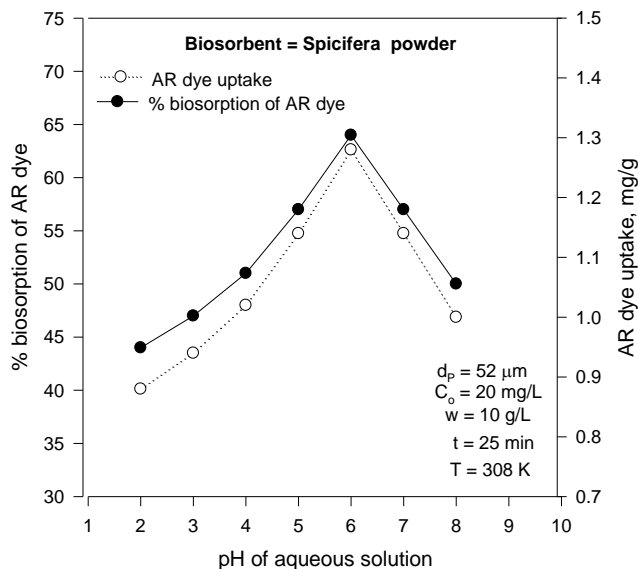
Fig 3.3. Effect of P^{H}on % biosorption of AR dye

3.4 Effect of initial concentration of AR dye by spicifera powder

The fig.3.4 shows the effect of initial concentration of AR dye by spicifera powder in the aqueous solution on the % biosorption at equilibrium agitation time. The % biosorption is gradually decreased from 64 to 46% (1.28 to 9.2 mg/gm) while increasing AR dye by spicifera powder concentration from 20 to 200 mg/L. In aqueous solution lesser % of AR dye by spicifera powder is removed from higher concentration of AR dye by spicifera powder. The available active sites on the biosorbent increases in the amount of biosorbate to the unchanging is the behavior observe. **[16-20]**
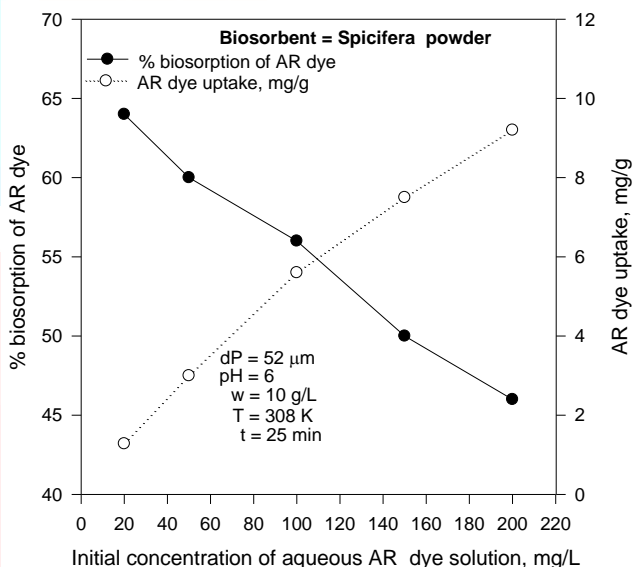

Fig 3.4. Effect of initial concentration for the biosorption of AR dye

3.5 Effect of biosorbent dosage

The fig. 3.5 represents biosorbent dosage from aqueous solution and its variation in % biosorption of AR dye by spicifera powder. The dosage is increased from 0.5 to 3gm/L and the % biosorption is increased from 64 to 92% as well as it increases in the biosorbent among with an increase in the aqueous face. This is so because the amount of biosorbent is increased and it would be more for the number of active sites available for dye uptake. The dosage is increased from 30 to 60 gm/L along with the increase in % biosorption is not appreciate (89 to 92%).**[21-25]**
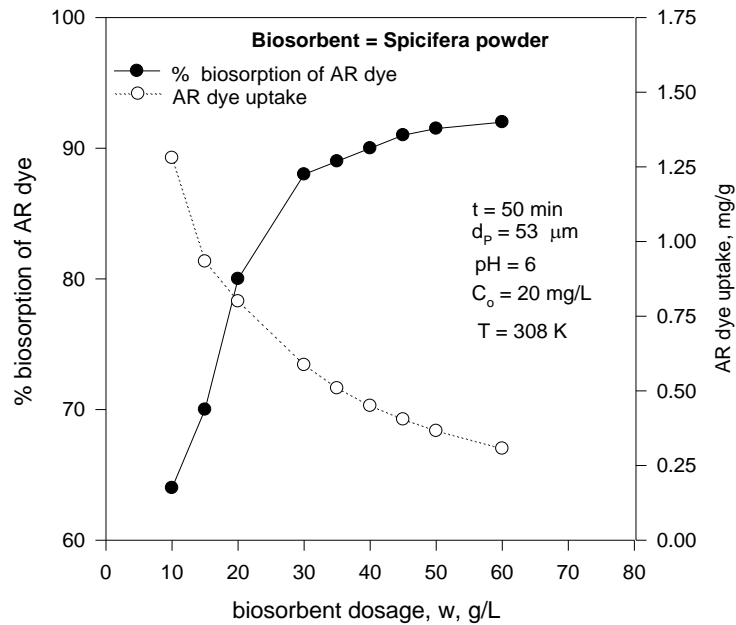
Fig 3.5. Effect of biosorbent dosage on % biosorption of AR dye

3.6 Effect of temperature

The effect of temperature was significant on the equilibrium dye uptake. The fig. 3.6 shows the effect of changes in the temperature on the AR dye uptake. The adsorption capacity of spicifera powder for the AR dye increased with the temperature is the result seen in the graph. Along with the temperature,283 to 323K it may be result of increase in the mobility of the large dye ion. Active sites at the surface undergo an interaction by increasing number of molecules may also required energy. Further the internal structure spicifera powder enabling large dyes to penetrate with the temperature increasing which may produce a swelling effect.[26-30]
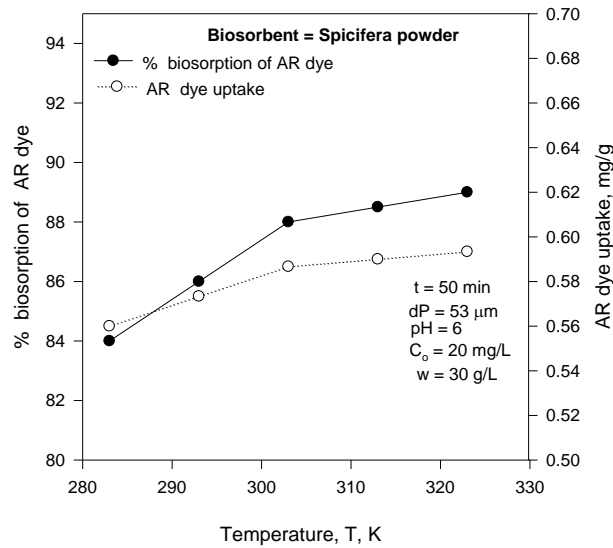

Fig 3.6. Effect of temperature on % biosorption of AR dye

3.7 Isotherms
3.7.1 Langmuir isotherm:

Langmuir isotherm is the most widely used simple two- parameter equation. This simple isotherm is based on following assumptions:

* Adsorbate is chemically adsorbed at a fixed number of well- defined sites
* Each site can hold only one adsorbate species
* All sites are energetically equivalent
* There are no interactions between the adsorbate species

The Langmuir relationship is hyperbolic and the equation is:

$$q_e / q_m = K_L C_e / (1 + K_L C_e) \qquad\qquad \text{-------- (3.1)}$$

The above equation can be rearranged as

$$(C_e / q_e) = 1/(K_L q_m) + C_e / q_m \qquad \text{------- (3.2)}$$

From the plots between (C_e/q_e) and C_e, the slope $\{1/ (K_L q_m)\}$ and the intercept $(1/q_m)$ can be calculated. Further analysis of Langmuir equation can be made on the basis of separation factor $[R_L = 1/ (1 + K_L C_e)]$.

$$0 < R_L < 1 \qquad\qquad \text{indicates} \qquad\qquad \text{favorable adsorption}$$
$$R_L > 1 \qquad\qquad \text{indicates} \qquad\qquad \text{unfavorable adsorption}$$
$$R_L = 1 \qquad\qquad \text{indicates} \qquad\qquad \text{linear adsorption}$$
$$R_L = 0 \qquad\qquad \text{indicates} \qquad\qquad \text{irrepressible adsorption}$$

Langmuir isotherm is drawn between C_e/q_e and C_e in fig. 3.7 for the present data. The resulting equation is

$(C_e/q_e) = 0.0603\ C_e + 5.3076$ ------ (3.3)

The (correlation coefficient of 0.9966) confirms strong binding of AR dye ions to the surface of spicifera powder.
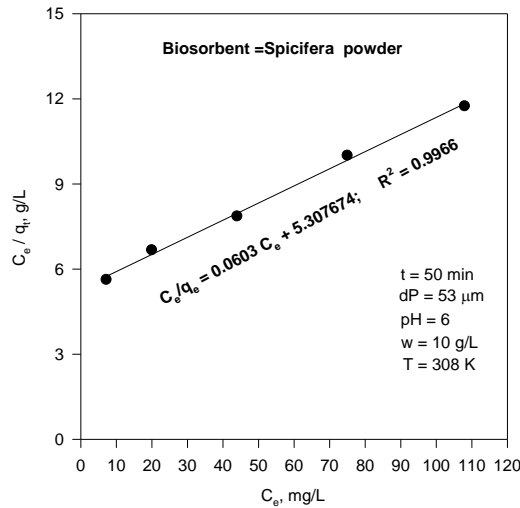

Fig. 3.7 Langmuir isotherm for biosorption

3.7.2 Freundlich isotherm:

Freundlich presented an empirical adsorption isotherm equation that can be applied in case of low and intermediate concentration ranges. The Freundlich isotherm is given by

$q_e = K_f\ C_e^{\ n}$ ----- (3.4)

Where K_f, mg/g represents the adsorption capacity at dye equilibrium concentration and n represents the degree of dependence of adsorption.

Taking LN on both sides, we get

$\ln q_e = \ln K_f + n \ln C_e$ ------ (3.5)

Freundlich isotherm is drawn between $\ln C_e$ and $\ln q_e$ in fig. 3.8, resulted in the following equation

$\ln q_e = 0.7334 \ln C_e - 1.1437$ ------ (3.6)

The equation has a correlation coefficient of 0.9926. The 'n' value of 0.7334 indicates favorable biosorption satisfying the condition of $0 < n < 1$.
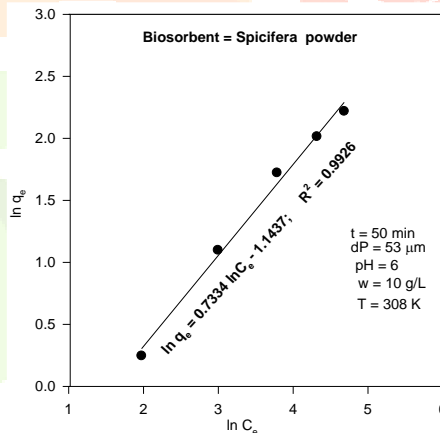

Fig.3.8 Freundlich isotherm for biosorption

3.7.3 Temkin isotherm:

Temkin and Pyzhev isotherm equation describes the behavior of many adsorption systems on heterogeneous surface and is based on the equation:

$q_e = RT \ln(A_T C_e)/b_T$ ------ (3.7)

The linear form of Temkin isotherm is

$q_e = (RT/ b_T)\ \ln(A_T) + (RT/b_T) \ln(C_e)$ ------ (3.8)

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

Slope, $b(1) = RT/ b_T$

Intercept, $b(0) = (RT/ b_T) \ln(A_T)$

Plot between q_e and $\ln C_e$ is shown in fig. 3.9. The equation for AR dye biosorption is

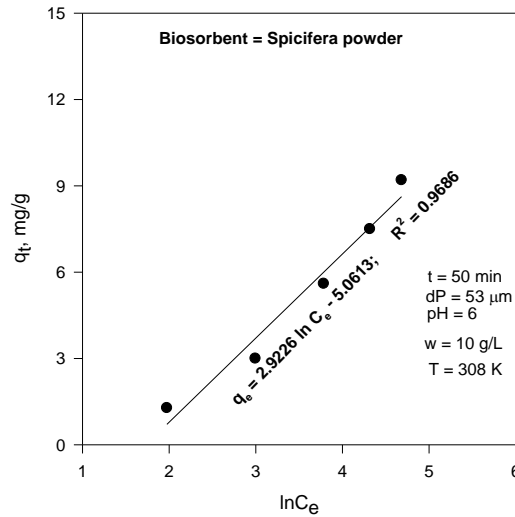$q_e = 2.9226 \ln C_e - 5.0613$ ------ (3.9)

Fig. 3.9 Temkin isotherm for biosorption

The isotherm constants are compiled in table-3.1. It is found that biosorption data are well represented by Langmuir isotherm ($R^2=0.9966$), Temkin ($R^2=0.9686$) and Freundlich isotherms ($R^2=0.9926$) **[31-35]**.

Table - 3.1 sotherm constants

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
q_m = 16.5617 mg/g	K_f = 0.3186 mg/g	A_T = 0.17696 L/mg
K_L = 0.01137	n = 0.7334	b_T = 876.176
R^2 = 0.9966	R^2 = 0.9926	R^2 = 0.9686

3.8 Kinetics
3.8.1 Lagergren first order
Lagergren plot and pseudo second order kinetics plot for biosorption of AR dye are drawn in figs. 3.10 & 3.11. Table-3.2 summarizes the rate constant values for first and second order rate equations **[36-40]**. It is noted that both first and second order rate equations explain the biosorption interactions satisfactorily.
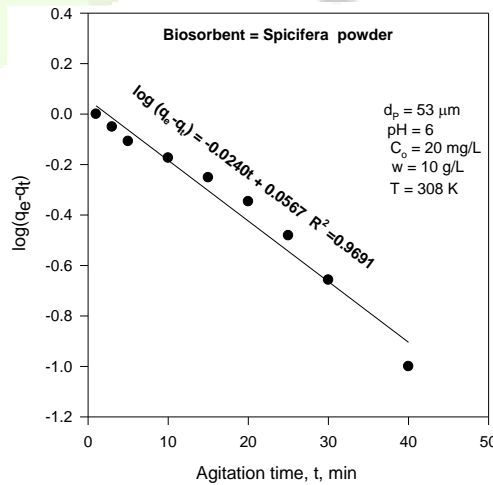
$\log (q_e-q_t) = -0.0240\, t - 0.0567$, $R^2=0.9691$

Fig.3.10 First order kinetics for biosorption

3.8.2 pseudo second order
Second order rate equations explain the biosorption interactions satisfactorily. the rate constant values for second order rate equations

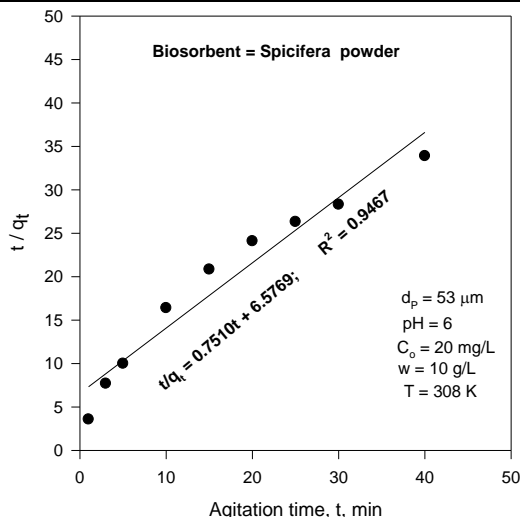$t/q_t = 0.7510\, t + 6.5769$, $R^2=0.9467$

Fig.3.11 Second order Kinetics for biosorption

Table – 3.2 Equations and rate constants

Order	Equation	Rate constant	R^2
Lagergren first order	$\log (q_e - q_t) = -0.0240\,t - 0.0567$	$0.0552\ \text{min}^{-1}$	0.9691
Pseudo second order	$t/q_t = 0.7510\,t + 6.5769$	0.0857 g/ (mg-min)	0.9467

3.9 Thermodynamics :

Van't Hoff's plot is drawn in fig. 3.12. From the data, Gibbs free energy change (ΔG) is calculated to be –4720.05 J/mol for biosorption of AR dye. The negative ΔG value indicates thermodynamically feasible and spontaneous nature of biosorption. The ΔH parameter is 8.36672 kJ/mol.K. The negative ΔH indicates the endothermic nature of biosorption. ΔS parameter is found to be 15.35199 J/mol K for AR dye biosorption **[41-45]**. The positive ΔS value suggests an increase in the randomness at the solid /solution interface during biosorption.
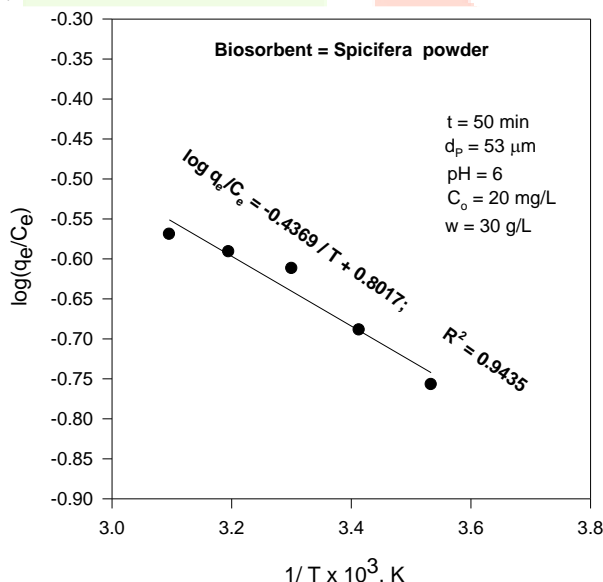

Fig.3.12 Vant Hoff's plot for biosorption

3.10 Optimization using Response Surface Methodology (RSM):

3.10.1 Optimization using CCD

The parameters that have greater influence over the response are to be identified so as to find the optimum condition for the biosorption of AR dye. The quadratic model is used in the present study, to relate four independent variables and percentage biosorption of AR dye. The regression equation for is % biosorption of AR dye is function of pH (X_1), C_o (X_2), w (X_3) and T (X_4) **[46-50]**.

The variations in the corresponding coded values of four parameters and response are presented in table-3.3

Table-3.3
Levels of different process variables in coded and un-coded form for
% biosorption of AR dye using spicifera powder

The

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	20	25	30	35	40
X_4	Temperature, T, K	283	293	303	313	323

following equation represents multiple regression analysis of the experimental data for the biosorption of AR dye:

$Y = -1600.82 + 47.94\,X_1 + 1.94\,X_2 + 0.84\,X_3 + 9.92\,X_4 - 4.06\,X_1{}^2 - 0.09\,X_2{}^2 - 0.01\,X_3{}^2$
$- 0.02\,X_4{}^2 + 0.11\,X_1X_2 - 0.00\,X_1X_3 - 0.00\,X_1X_4 + 0.00\,X_2X_3 + 0.00\,X_2X_4$
$- 0.00\,X_3X_4$ **------ (3.10)**

Table-3.4
Results from CCD for AR dye biosorption by spicifera powder

Run no.	X_1, pH	X_2, C_o	X_3, W	X_4, T	% biosorption of AR dye	
					Experimental	Predicted
1	3	15	25	293	84.82000	84.82167
2	3	15	25	313	86.78000	86.82667
3	3	15	35	293	85.68000	85.68667
4	3	15	35	313	87.52000	87.47167
5	3	25	25	293	81.28000	81.30333
6	3	25	25	313	83.88000	83.86833
7	3	25	35	293	82.78000	82.78833
8	3	25	35	313	85.08000	85.13333
9	5	15	25	293	84.42000	84.41333
10	5	15	25	313	86.30000	86.26833
11	5	15	35	293	85.28000	85.26833
12	5	15	35	313	86.88000	86.90333
13	5	25	25	293	83.08000	83.10500
14	5	25	25	313	85.48000	85.52000
15	5	25	35	293	84.58000	84.58000
16	5	25	35	313	86.80000	86.77500
17	2	20	30	303	77.38000	77.35167
18	6	20	30	303	78.58000	78.58500
19	4	10	30	303	86.68000	86.70167
20	4	30	30	303	83.10000	83.05500
21	4	20	20	303	88.60000	88.56833
22	4	20	40	303	90.68000	90.68833
23	4	20	30	283	85.62000	85.60833
24	4	20	30	323	89.82000	89.80833
25	4	20	30	303	94.20000	94.20000
26	4	20	30	303	94.20000	94.20000
27	4	20	30	303	94.20000	94.20000
28	4	20	30	303	94.20000	94.20000
29	4	20	30	303	94.20000	94.20000
30	4	20	30	303	94.20000	94.20000

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

Table-3.5 represents the results obtained in CCD. Response obtained from regression in eq.5.10 in the form of ANOVA is presented. From the Fisher's F-test (F_{model} = 285.1025) and a very low probability value ($P_{model}>F$=0.000000), it is known from table–5.5 that the model is highly significant. At 5% level, the computed F-value ($F_{0.05\ (14.15)}$ = MS_{model}/MS_{error} = 285.1025) is greater than that of the tabular F-value ($F_{0.05\ (14.15)\ tabulars}$ = 2.42), indicating that the treatment differences are significant

Table-3.5

ANOVA of AR dye biosorption for entire quadratic model

Source of variation	SS	Df	Mean square(MS)	F-value	*P*> F
Model	619.7323	14	44.2665	38160	0.00000
Error	0.0174	15	0.00116		
Total	619.7497				

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

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

Table-3.6

Estimated regression coefficients for the AR dye biosorption onto spicifera powder

Terms	Regression coefficient	Standard error of the coefficient	t-value	*P*-value
Mean/Intercept	-1600.82	6.363520	-251.563	0.000000
Dosage, w, g/L (L)	47.94	0.272970	175.613	0.000000
Dosage, w, g/L (Q)	-4.06	0.006503	-623.987	0.000000
Conc, Co, mg/L (L)	1.94	0.053881	36.041	0.000000
Conc, Co, mg/L (Q)	-0.09	0.000260	-358.349	0.000000
pH (L)	0.84	0.026815	31.509	0.000000
pH (Q)	-0.01	0.000065	-175.747	0.000000
Temperature, T, K (L)	9.92	0.039973	248.242	0.000000
Temperature, T, K (Q)	-0.02	0.000065	-249.556	0.000000
1L by 2L	0.11	0.001703	64.888	0.000000
1L by 3L	-0.00	0.000851	-0.294	0.773079
1L by 4L	-0.00	0.000851	-4.404	0.000513
2L by 3L	0.00	0.000170	18.204	0.000000
2L by 4L	0.00	0.000170	16.442	0.000000
3L by 4L	-0.00	0.000085	-6.459	0.000011

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

$Y = -1600.82 + 47.94X_1 + 1.94X_2 + 0.84 X_3 + 9.92 X_4 - 4.06 X_1^2 - 0.09 X_2^2 - 0.01 X_3^2$
$- 0.02 X_4^2 + 0.11 X_1X_2 - 0.00 X_1X_3 - 0.00 X_1X_4 + 0.00 X_2X_3 + 0.00 X_2X_4$
$- 0.00 X_3X_4$ ------ (3.11)

The larger the value of t and smaller the value of P, the more significant is the corresponding coefficient term. The 't' and 'P' values are analyzed from table-3.6. It is found that the 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_2X_3 and X_2X_4 have high significance to explain the individual and interaction effect of independent variables on AR dye biosorption. The other terms (X_1X_2, X_1X_4, X_2X_3, X_2X_4 and X_3X_4) are insignificant and are not required to explain biosorption. A synergistic effect is indicated by positive sign of the coefficient which means response increases with an increase in effect, while an antagonistic effect is indicated by a negative sign which means response decreases with an increase in effect. In the observed response values, a measure of the models variability is provided by the correlation coefficient (R^2). In the present study, the value of the regression coefficient (R^2 = 0.9999) for eq.5.11indicates that 0.001 % of the total variations are not satisfactorily explained by the model. It is proved from that table that $F_{statistics}$ value for entire model is higher. This large value means that % biosorption can be adequately explained by the model equation. Generally P values lower than 0.05 indicates that the model is considered to be statistically significant at 95% confidence level. The % biosorption prediction from the model is shown in table-3.6.

It is implied from table-3.7 that all the squared terms of all the variables and the linear terms are significant ($P < 0.05$). Among the interaction terms, all the terms ($P < 0.05$) are insignificant on the biosorption capacity. Fig.3.13 and Fig.3.14shows pareto chart and normal probability plot (NPP) of residual values. It could be seen that the experimental points are reasonably aligned suggesting normal distribution.
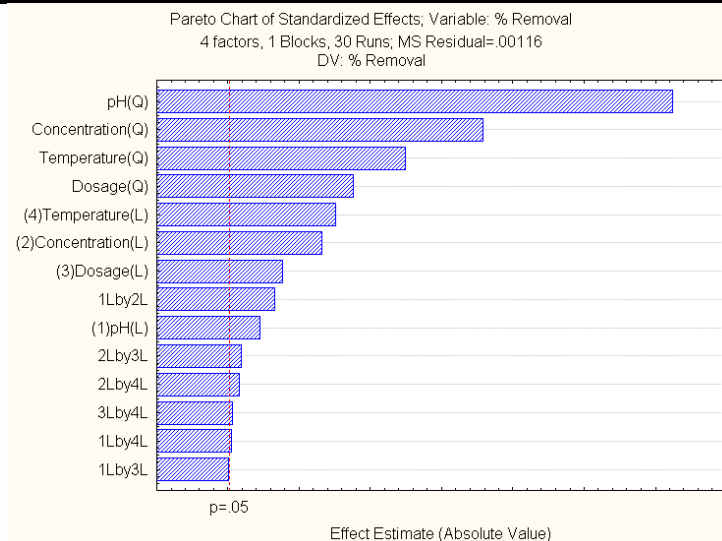
Fig. 3.13 Pareto Chart

The optimal set of conditions for maximum percentage biosorption of AR dye is pH = 6.0245, initial AR dye concentration = 19.1187 mg/L, biosorbent dosage = 32.1238 g/L, and temperature = 306.1201 K. The extent of biosorption of AR dye at these optimum conditions was 94.50421 %. 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.

3.10.2 Interaction effects of biosorption variables:

The three-dimensional view of response surface contour plots [Fig. 3.15 (a) to (f)] show % biosorption as a function of for various combinations of independent variables. The plots are represented as a function of two factors at a time keeping other factors fixed at zero level.
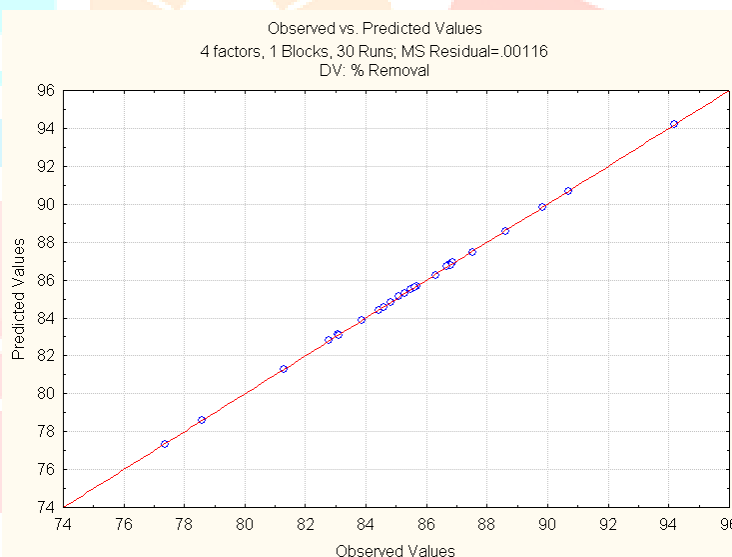

Fig. 3.14 Normal probability plot for % biosorption of AR dye

It is found from the response surface plots that the % biosorption is maximal at low and high levels of the input variables. However, there exists a region where neither an increasing nor a decreasing trend in % biosorption is observed. The biosorption variables should be optimum to maximize the % biosorption. The % biosorption of AR dye is strongly influenced by the pH as evident from figs. 3.15 (a)& (b).

The predicted optimal set of conditions for percentage biosorption of AR dye is

pH of aqueous solution	=	6.0245
Initial AR dye concentration	=	19.1187 mg/L
Biosorbent dosage	=	32.1238 g/L
Temperature	=	306.1201 K
% biosorption of AR dye	=	94.50421

The optimal set of conditions obtained with CCD is shown in table-5.7 along with experimental values.
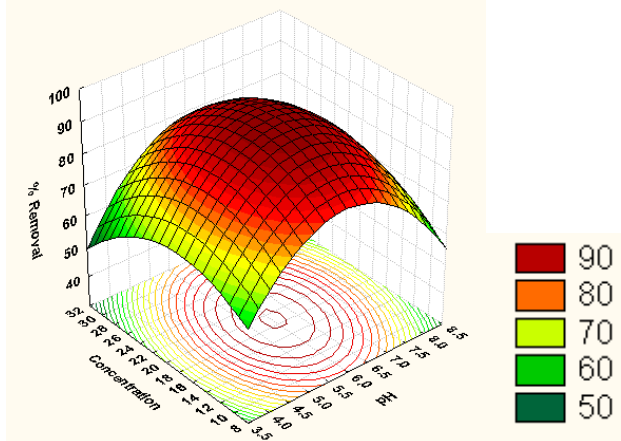
Fig. 3.15 (a) Surface contour plot for the effects of pH and initial AR dye concentration on % biosorption
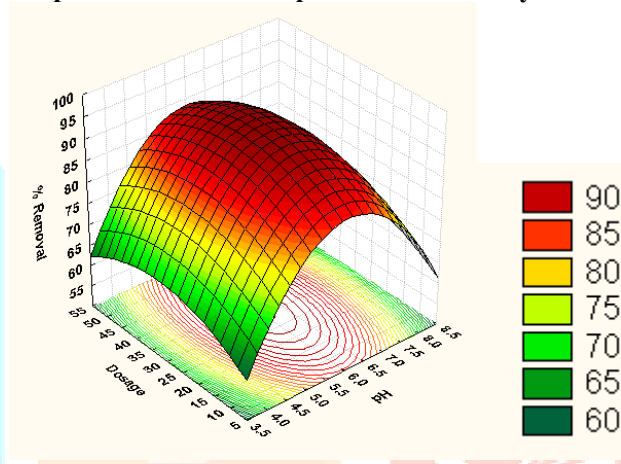

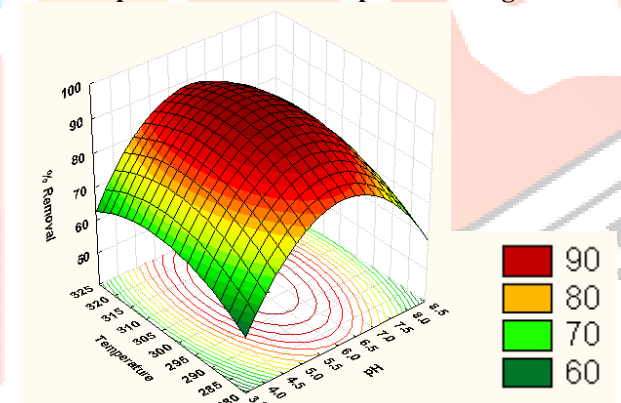**Fig. 3.15 (b) Surface contour plot for the effects of pH and dosage on % biosorption of AR dye**

Fig. 3.15 (c) Surface contour plot for the effects of pH and Temperature on % biosorption of AR dye
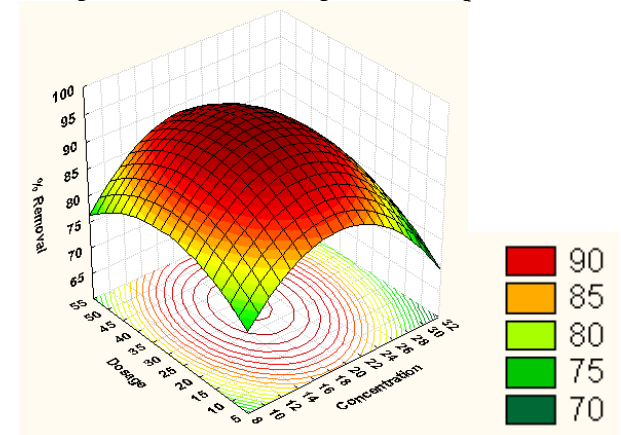

Fig.3.15 (d) Surface contour plot for the effects of initial concentration and dosage on % biosorption of AR dye
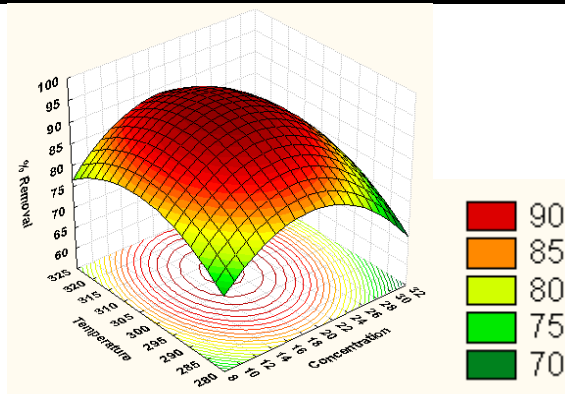
Fig. 3.15 (e) Surface contour plot for the effects of initial concentration and Temperature on % biosorption of AR dye
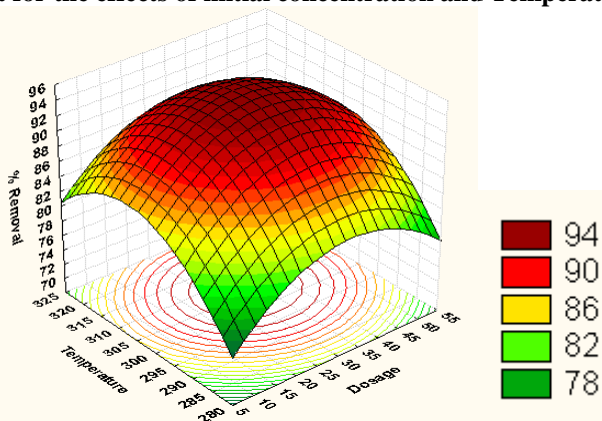

Fig. 3.15 (f) Surface contour plot for the effects of Dosage and Temperature on % biosorption of AR dye

Table – 3.7

Comparison between optimum values from CCD and experimentation

Variable	CCD	Experimental value
pH of aqueous solution	6.0245	6
Initial cobalt concentration, mg/L	19.1187	20
Biosorption dosage, w, g/L	32.1238	30
Temperature, K	306.1201	303
% biosorption	94.50421	95.0

3.11 Characterization ofspicifera powder
3.11.1 Fourier Transform Infra-Red Spectroscopy (FTIR)

Infrared spectroscopy belongs to the group of molecular vibrational spectroscopies which are molecule-specific and give direct information about the functional groups, their kind, interactions and orientations. Its sampling requirements allow the gain of information from liquids and gases and in particular from solid surfaces. Even if historically IR has been mostly used for qualitative analysis, to obtain structural information, nowadays instrumental evolution makes non-destructive and quantitative analysis possible [51-55] with significant accuracy and precision. The shift of the bands and the changes in signal intensity allow the identification of the functional groups involved in dye sorption.

3.11.1.1 FTIR spectrum of untreated AR dye:

FTIR spectrum of untreated spicifera powder is presented in fig. 3.16 (a). The sharp peak at 895.01 cm^{-1} denotes the involvement and participation of S=O and C–S–O from ester sulphonate in biosorption. The band at 609.57 cm^{-1} indicates the involvement of 2, 4 benzene deformation out of phase bond. The band at 1049.60 cm^{-1}assigns the C–H bending vibrations bond.
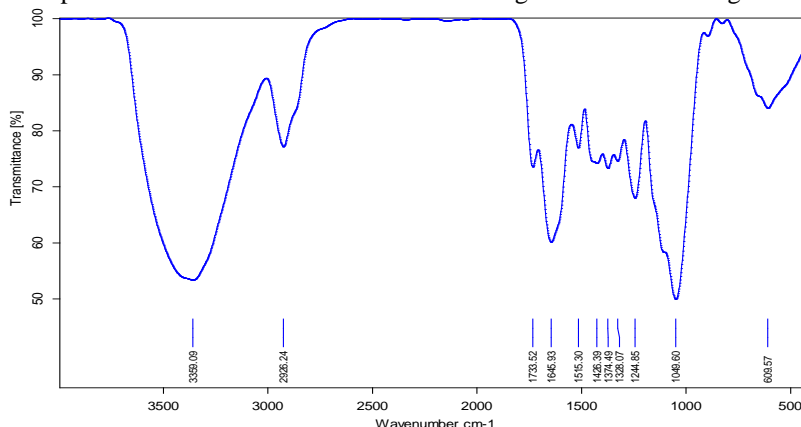

Fig. 3.16 (a) FTIR spectrum of AR dye untreated spicifera powder

The peaks at 1244.85^{-1} in native biomass designates the presence of -SO$_3$ stretching bonds and is not observed after loading AR dye. It indicates the direct involvement of C-O stretching in the ion-exchange process. The bands from 1328.07 and 1374.49 cm^{-1} denotes the presence of –CH$_2$ bending vibrations bonds. The peak at 1426.39 represents the C–N stretching bond. The peak at 1515.30 depict the Amide N–H bending vibrations. The peak at 1645.93 cm^{-1} assigned for Oleifinic C = C and Carbonyl C = O stretching bond in is shown in untreated powder. The sharp peak at 1733.52 cm^{-1} denots the presence of Assymetric stretching vibration of C = O. Further, the band peaks at 2926.24 cm^{-1} are assigned for the bounded CH$_2$ stretching vibrationsbonds.The peak at 3359.09 represents the –OH stretching or –NH$_2$ stretching bond.

3.11.1.2 FTIR spectrum of AR dye treated with spicifera powder:

FTIR measurements for AR dye loaded algal biomass are shown in fig. 3.16 (b). The sharp peak at 609.57 cm^{-1} is shifted to 609.99 cm^{-1} denoting the involvement and participation of 2,4 benzene deformation out of phase in biosorption. The shifting of band from 1048.53 cm^{-1} to 1049.60 cm^{-1} indicates the involvement of C–H bending vibrations. The bands from 1328.07 and 1374.49 cm^{-1} denotes the presence of –CH$_2$ bending vibrations bonds. The peak at 1426.39 represents the C–N stretching bond. The peak at 1515.30 depict the Amide N–H bending vibrations. The bands at 3359.09, 3361.05 cm^{-1} (assigned for the presence of C–OH stretching or –NH2 stretching respectively) are not shown in untreated biomass. The characteristic of stretching modes of O–H (indicated by the band at 3312.88 cm^{-1}) is also not seen in untreated biomass.
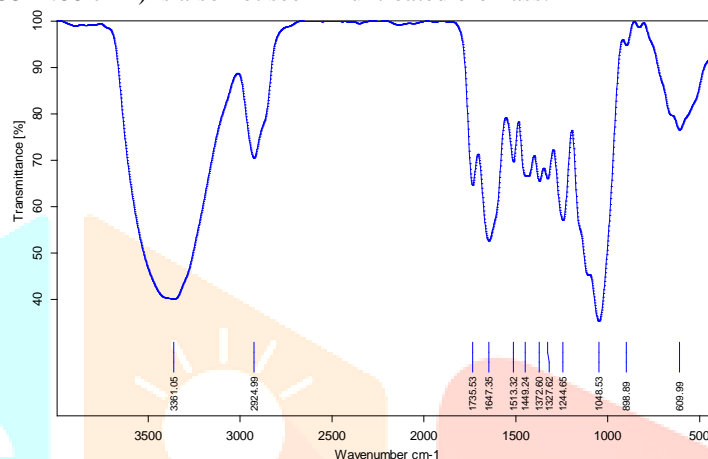

Fig. 3.16 (b) FTIR spectrum of AR dye treated spicifera powder
Table-3.9
Shift of FTIR peaks for untreated and spicifera powder treated AR dye

S. No.	Peaks in untreated powder, cm^{-1}	Peaks in treated powder, cm^{-1}	Description
1	609.57	---	2,4 benzene deformation out of phase
2	---	609.99	2,4 benzene deformation out of phase
3	---	898.89	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	---	1244.65	-SO$_3$ stretching
7	1244.85	---	-SO$_3$ stretching
8	---	1327.62	–CH$_2$ bending vibrations
9	1328.07	---	–CH$_2$ bending vibrations
10	---	1372.60	–CH$_2$ bending vibrations
11	1374.49	---	–CH$_2$ bending vibrations
12	1426.39	---	C–N stretching
13	---	1449.24	C–N stretching
14	---	1513.32	Amide N–H bending vibrations
15	1515.30	---	Amide N–H bending vibrations
16	1645.93	---	Oleifinic C = C and Carbonyl C = O stretching
17	---	1647.35	Oleifinic C = C and Carbonyl C = O stretching
18	1733.52	---	Assymetric stretching vibration of C = O
19	---	1735.53	Assymetric stretching vibration of C = O
20	---	2924.99	CH$_2$ stretching vibrations
21	2926.24	---	CH$_2$ stretching vibrations
22	3359.09	---	–OH stretching or –NH$_2$ stretching
23	---	3361.05	–OH stretching or –NH$_2$ stretching

The sharp peaks of 830.39 and 898.75 cm^{-1} arose suddenly after loading of AR dye due to the involvement of S = O and C–S–O bands from ester sulphonate respectively. Further, three additional peaks at 1328.50 and 1372.85 cm^{-1} denoting stretching of –CH$_2$ bending vibrations and 1450.19 cm^{-1} for C–N stretching have suddenly appeared in AR dye treated biomass. The peak appearing at 1648.60 cm^{-1} in AR dye treated powder is denoting Oleifinic C = C and Carbonyl C = O stretching and is not seen in

native biomass. The peaks at 1736.17 cm^{-1} are obtained in treated biomass due to the involvement of the Assymetric stretching vibration of C = O. This may be due to the adjustment of pH and physical disruption of cell walls upon the vigorous shaking.

3.11.2 X-Ray Diffraction:

The X-Ray Diffractograms (XRD) of the powder samples are taken using a Rigaku Ultima model IV. The diffracted X-ray intensities are recorded as a function of 2θ by using copper target (Cu-Kα radiation with wave length, λ= 1.5492 A^0) at a scan speed of 2^0/min. XRD patterns are recorded from 3^0 to 90^0. Different phases of the samples are to be identified by comparing with a set of 'd' values and the corresponding intensities with the standards from the ICDD (International Center for Diffraction Data) files.

3.11.2.1 XRD for AR dye untreated with spicifera powder

XRD patterns of untreated powder are shown in figs.3.17 (a) & (b). XRD patterns shown in figs.3.17 (a) & (b) do not indicate sharp peaks, less crystallinity and exhibit little amorphous nature. The peaks at 2θ values of 0.7748, 0.7273, 0.7273, 0.7159 and 0.7035 corroborate the presence of $Fe_2H_{474}K_{44}$, $Eu_8K_{16.5}O_{206}$, $As_6ClCS_{3.9}$, $H_{168}K_3Li_{5.5}$ and $C_{40}K_{13}O_{368}$(ICDD files). Their corresponding d-values are 5.5771, 5.1148, 5.8082, 6.4302 and 6.6466 [56-60].
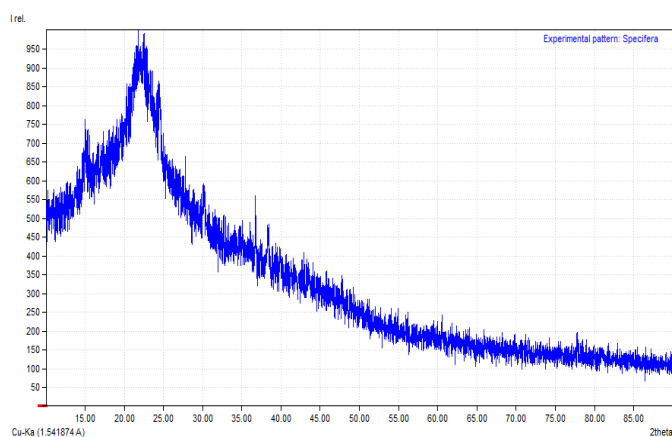

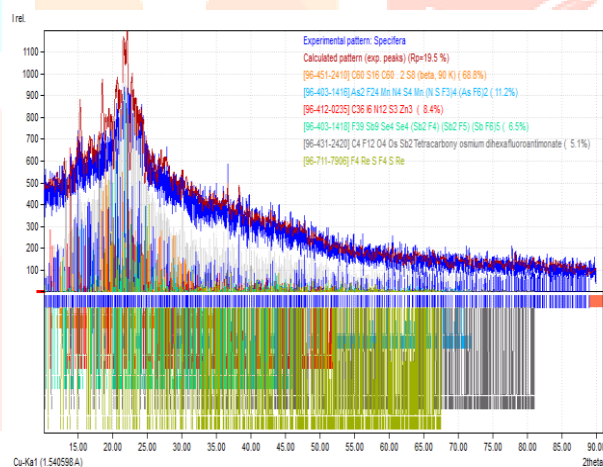**Fig. 3.17 (a) XRD pattern of AR dye untreated spicifera powder**

Fig. 3.17 (b)XRD pattern of AR dye untreated spicifera powder with matching compounds

3.11.2.2 XRD for AR dye treated with spicifera powder

XRD patterns for treated powder [Figs.3.17 (c) & 3.17 (d)] exhibit good crystallinity, more amorphous nature and increase in surface area and porosity. The peaks at 2θ values of 0.7765, 0.6899, 0.6084, 0.5983 and 0.5397 corroborate the presence of $Fe_{39}Sb_9Se_4$, $AS_{14}Cs_4Zn$, O_9P_3Y, F_7RuXe and $Cl_2H_{12}P_4Ru$. Their corresponding d-values are 3.9371, 3.7334, 3.4874, 3.4391 and 3.6449.
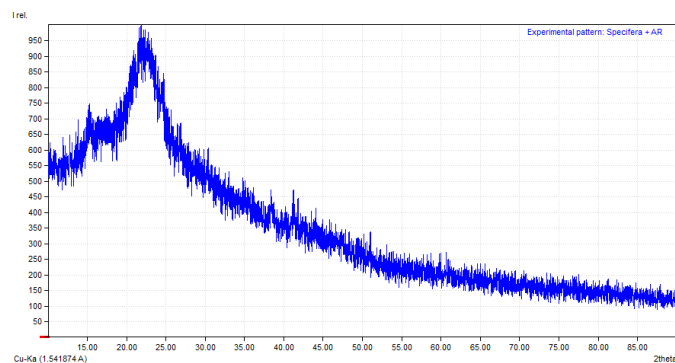

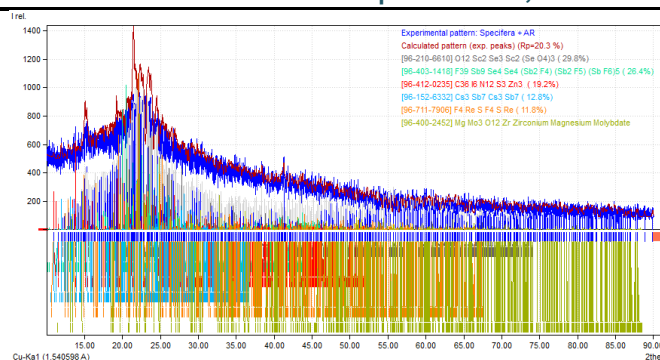**Fig. 3.17 (c) XRD pattern of AR dye treated spicifera powder**

Fig.3.17 (d) XRD pattern of AR dye treated spicifera powder with matching compounds

CONCLUSIONS

1. Theequilibrium agitation time for AR dye biosorption is 50 minutes.
2. Percentage biosorption of AR dye from the aqueous solution increases significantly with increase in pH from 2 (44 %) to 6 (64 %).
3. The optimum dosage for biosorption is 30 g/L (0.5866 mg/g).
4. The maximum uptake capacity of 16.56178 mg/g is obtained at 303 K.
5. The maximum biosorption of AR dye (94.50421%) onto spiciferapowder is observed when the processing parameters are set as: pH = 6.0245, w = 32.1238 g/L, C_0 = 19.1187 mg/L and T = 306.1201 K using CCD.
6. The thermodynamic data show that % biosorption of AR dye is increased with increase in temperature. The investigation also reveals the endothermic nature of biosorption as ΔH is positive (8.366727), irreversible nature of biosorption as ΔS is positive(15.35199) and spontaneity of biosorption as indicated by negative ΔG (ΔG = –4720.05 J/mole).

ACKNOWLEDGEMENTS

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