

# Studies on Biosorption of Eosin Yellow Dye With Spicifera Powder and Optimization through Central Composite Design

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**Abstract-** In this study dried powdered of Spicifera, component were used for the removal of Eosin Yellow dye from aqueous solution by using a new biosorbent 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:** Eosin Yellow dye, spicifera, RSM,

## 1. INTRODUCTION

Textile industries consume large volumes of water and chemicals for the wet processing of textiles. The presence of very low concentrations of dyes in effluent discharged from these industries is highly visible and undesirable [1]. Due to their chemical structure, dyes are resistant to fading when exposed to light, water and chemicals [2, 3]. Dyes, usually, have a synthetic origin and complex aromatic molecular structures, which make them more stable and difficult to biodegrade. Dyes can be classified as follows [4]:

- Anionic: direct, acid, and reactive dyes.
- Cationic: basic dyes.
- Non-ionic: disperse dyes.

Brightly colored, water-soluble, reactive, acidic dyes are the most problematic, as they tend to pass through conventional treatment systems unaffected [5]. Various physical, chemical and biological methods have been used for the treatment of dye-containing wastewater. Some Chemical oxidations, such as Fenton reagent, ozone, UV plus H<sub>2</sub>O<sub>2</sub> or NaOCl, result in aromatic ring cleavage, which may generate chemical sludge or by-products that are likely to be even more toxic [6]. Aerobic biological treatment is known to be ineffective for dye removal [7], but anaerobic bioremediation enables water-

soluble dyes to be decolorized [8]. Although ion exchange resins can be regenerated easily, the high cost hinders their wide application for the treatment of dye-bearing wastewater. Consequently, various types of (bio) sorbents, which are able to bind dye molecules and be easily regenerated, have been extensively searched and tested [9,10]. A suitable sorbent has to meet the following criteria [11]: (1) high affinity and capacity for target compounds, (2) regeneration possible, (3) safe and economically viable treatment/disposal of regenerate, (4) tolerance for a wide range of wastewater parameters, and (5) usable for all or nearly all-reactive dyes. Due to their cost-effectiveness, biosorbents have gained much attention. However, most are non-regeneratable throwaway products, such as bagasse pith [12], eucalyptus bark [13], and so on. Good sorption capacities for reactive dyes (60–420 mg g<sup>-1</sup>) were found for quaternized organic materials, such as cellulose [14], sugarcane bagasse [15], rice husk [16] and coconut husk [17] however, no successful regeneration has been reported here either.

## 2.0 EXPERIMENTAL PROCEDURE

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

The experimental procedure consists of the following steps:

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

### 2.1. Preparation of the biosorbent

*Spicifera* algae was 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 Eosin yellow 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 Eosin Yellow dye (1000 mg/L) was prepared by dissolving 1.0 g of 99.9 % analytical grade Eosin Yellow 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 hypnea musciformis 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 carmine dye were evaluated using single step optimization process

Table 1

Experimental conditions for biosorption of Eosin Yellow 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, mg/L	20, 50, 100, 150 and 200
3	Initial 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

3.1 Effect of agitation time

The below discussions are about the effects of various parameters on the EY dye by spicifera powder biosorption. The experiment is carried out by varying time from 1 to 180 minutes. The fig. 3.1 shows the agitation time against the % biosorption and it is found to increase upto 40 min. At 60 min of agitation the max 67 % of biosorption is attained and becomes constant after 60min by indicating the attainment of equilibrium (67%).[18-19]

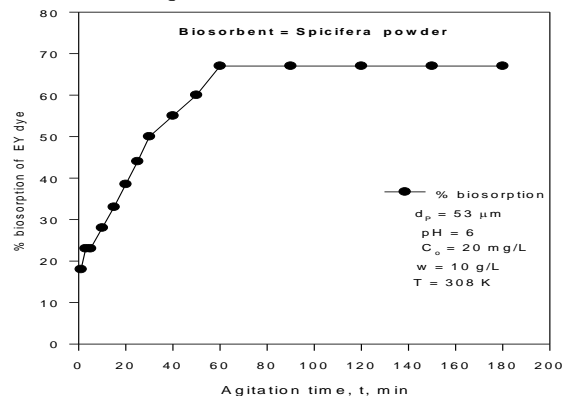


Fig 3.1. Effect of time on % biosorption of EY dye

5.13 Effect of biosorbent size

Fig 3.2 indicates the function of the particle size and % biosorption of EY dye by spicifera powder. The biosorbent size is increased from 53 to 152µm and its percentage is decreased from 67% to 52%. As the surface area of the biosorbent enhances and extra number of active sites on the biosorbent are available to the biosorbate and the size of the particle decreases [20-24].

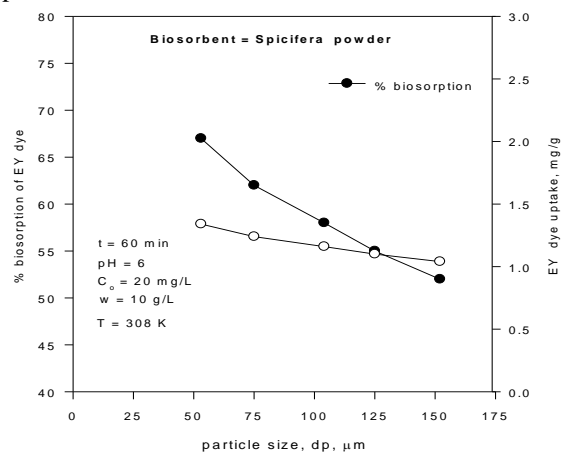


Fig 3.2. Effect of size on % biosorption of EY dye

The fig 3.3 is drawn to show the effect of pH of aqueous solution on percentage biosorption of EY dye by spicifera powder. As pH is increased from 2 to 8 and the % biosorption is increased from 46 to 52% as well as the pH is decreased from 5 to 8 and the % biosorption is decreased from 72 to 52%. The electro static interaction between biosorbent and biosorbate is the principle is the driving force for dye biosorption. As the interaction because the greater then biosorption of dye will be more. For forming part of the surface functional group, the EY dye by spicifera powder replace H<sup>+</sup> ions bound to the biosorbent with an interaction. Participation of =C-H of alkene or arena and symmetric -SO<sub>3</sub> stretching in which the predominant contributors in dye uptake are symmetric bending of CH<sub>3</sub> group. C≡N presenting in the poly acrylo nitrile and thio cynate (-SCN) which are directly involved in the biosorption and further followed by thio cynate, iso thio cynate, diazo in the aromatic combination groups. Hence the conclusions were reported when dye ions were adsorbed in the case of orange peel [25-29].

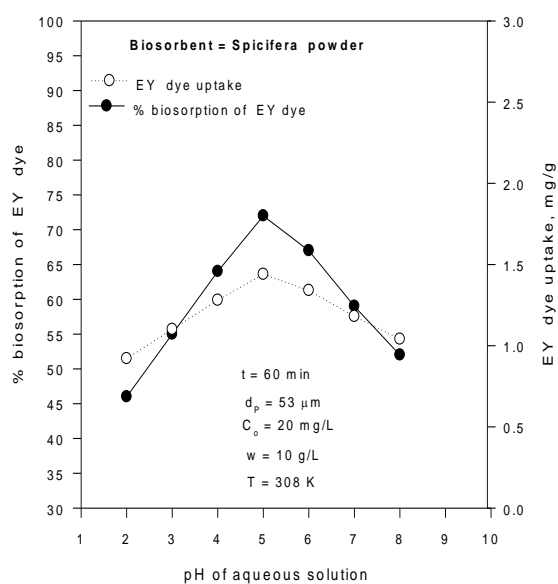


Fig 3.3. Effect of pH on % biosorption of EY dye

### 3.3 Effect of initial concentration of EY dye by spicifera powder

The below graph shown the function of initial concentration of EY dye by spicifera powder with the % biosorption of EY dye by spicifera powder and it is decreased from 72% to 54% as the initial concentration EY dye by spicifera powder while increasing aqueous solution from 20 to 200 mg/L. The uninterrupted number of freely active sites on the biosorbent can be attributed to the increase in the amount of biosorbate is the behavior observe fig 3.4 [76-80].

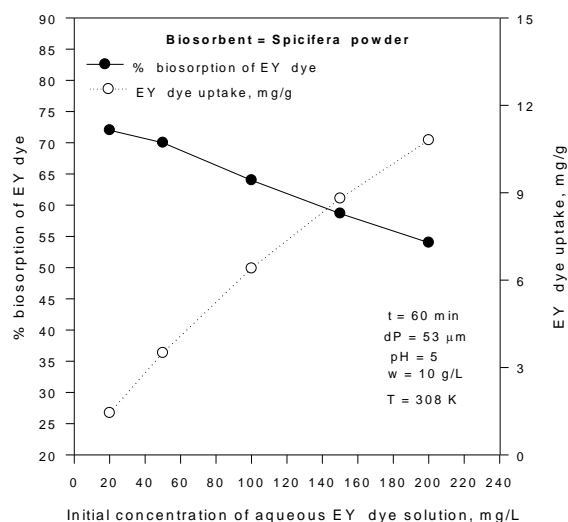


Fig 3.4 Effect of initial concentration on % biosorption of EY dye

### 3.4 Effect of biosorbent dosage

The fig 3.5 is drawn against biosorbent dosage and the % biosorption of EY dye by spicifera powder. The increase in biosorbent dosage with the increase in % biosorption. As dosage is increased from 0.5 to 3 gm/L, the % biosorption increases from 72 to 94% for a biosorbent size of 53 μm. For dye removal of the number of available sites where this behavior is obvious and it would be more as the amount of biosorbent increases [30-34].

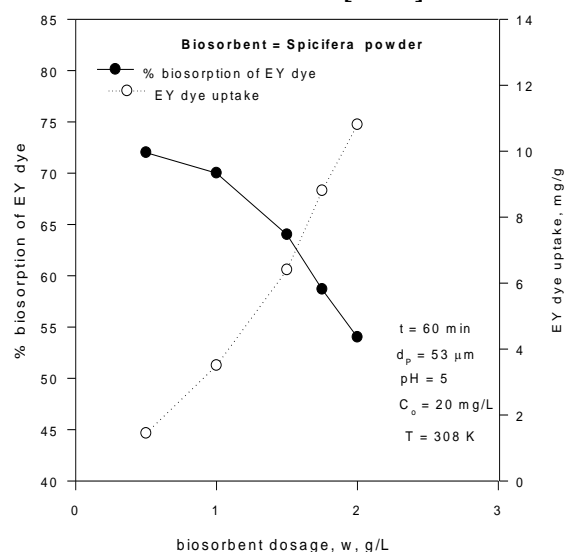


Fig 3.5. Effect of dosage on % biosorption of EY dye

### 3.5 Effect of temperature

On the equilibrium dye uptake was significant on the effect of temperature. The fig 3.6 shows the effect of changes in temperature on the EY dye by spicifera powder uptake. This system is an endothermic process which indicates that the biosorption of dyes and its capacity increased at higher temperatures. The experiment is carried out by varying temperature from 283 to 323K. The creation of new active sites or this may be attributed at higher temperatures to increase penetration of reactive dyes

inside micro pores. At higher temperature in the case of EY dye by spicifera powder to be achieved the formation of more than 1 molecular layer on the surface of spicifera powder.[35-39]

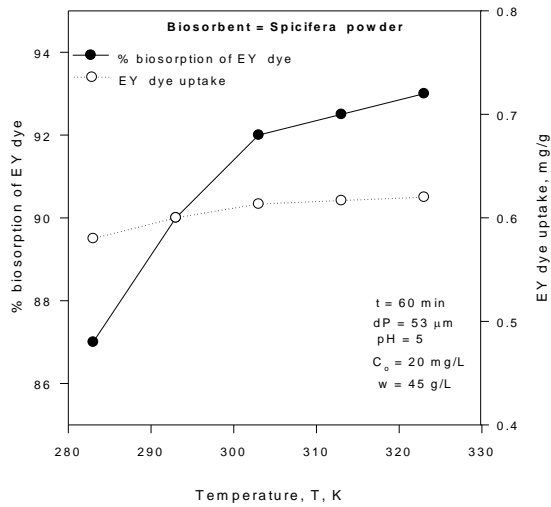


Fig 3.6. Effect of temperature on % biosorption of EY dye

3.6 Isotherms

3.6.1 Langmuir Isotherm:

Langmuir isotherm, drawn in fig. 3.7, for the present data has yielded the equation:

$$\left(\frac{C_e}{q_e}\right) = 0.0545 C_e + 3.5742$$

$$R^2 = 0.9978 \quad \text{----- (5.12)}$$

The correlation coefficient value of 0.9978 indicates strong binding of EY dye on to the biosorbent.

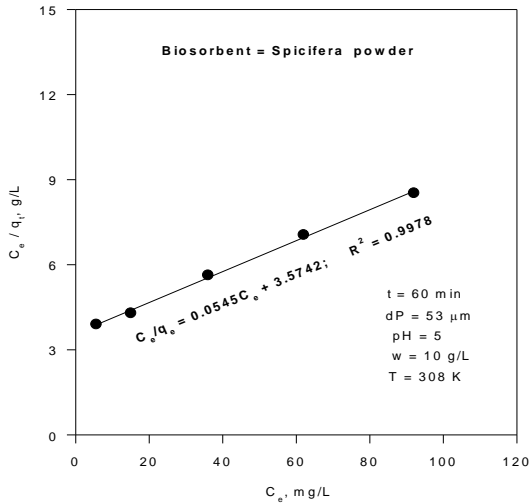


Fig. 3.7 Langmuir isotherm for biosorption of EY dye

3.6.2 Freundlich Isotherm:

Fig. 3.8, drawn between  $\ln C_e$  and  $\ln q_e$ , has resulted the equation:

$$\ln q_e = 0.7177 \ln C_e - 0.7865$$

$$\text{----- (5.13)}$$

The equation has a correlation coefficient of 0.9895. The 'n' value of 0.7177 satisfies the condition of  $0 < n < 1$ , indicating favorable biosorption.

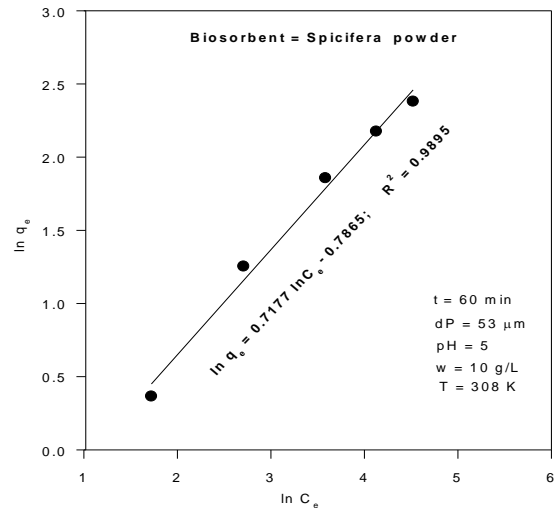


Fig. 3.8 Freundlich isotherm for biosorption of EY dye

3.6.3 Temkin Isotherm:

The present data are analysed according to the linear form. The linear plot of Temkin isotherm is shown in fig. 3.9. The equation obtained for EY dye biosorption is:

$$q_e = 3.3271 \ln C_e - 4.9002$$

$$\text{----- (3.1)}$$

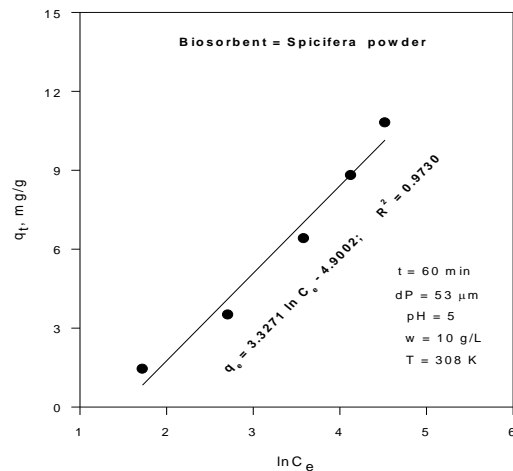


Fig. 3.9 Temkin isotherm for biosorption of EY dye

With a correlation coefficient 0.9730. The isotherm constants of the three isotherms are compiled in table-3.10. The equilibrium data are well explained by Langmuir isotherm (0.9978), Temkin (0.9730) and Freundlich isotherm (0.9895) [40-44].

Table – 3.10

Isotherm constants (linear method)

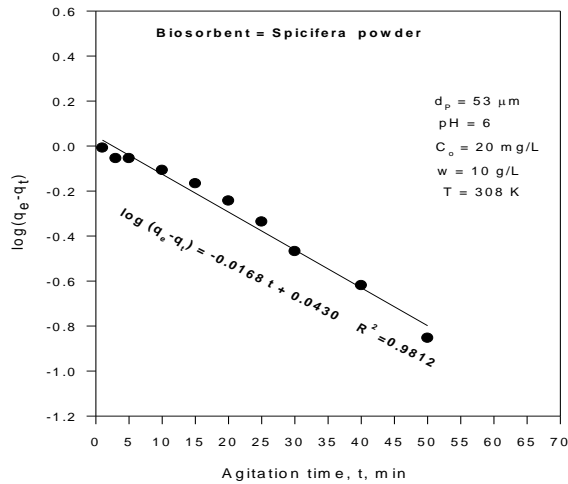
Langmuir isotherm	Freundlich isotherm	Temkin isotherm
$q_m = 18.3284 \text{ mg/g}$	$K_f = 0.4554 \text{ mg/g}$	$A_T = 0.22927 \text{ L/mg}$
$K_L = 0.01526$	$n = 0.7177$	$b_T = 757.1585$
$R^2 = 0.9978$	$R^2 = 0.9895$	$R^2 = 0.9909$

**3.7 Kinetics:**

**3.7.1 Lagergren first order rate equation**

The experimental data are tested for Lagergren first order rate equation and pseudo second order rate equation. Lagergren plot of  $\log (q_e - q_t)$  vs agitation time (t) is shown in fig. 3.10. Table-3.11 summarizes rate constant values for first and second order rate equations [45-49]. It is noted that both first and second order rate equations explain the biosorption interactions.

$$\log (q_e - q_t) = -0.0168 t + 0.0430, \quad R^2 = 0.9812 \quad \dots \dots \dots (3.2)$$

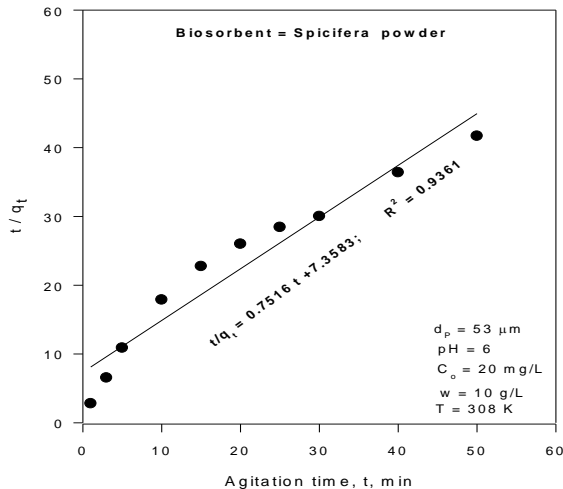


**Fig. 3.10 First order kinetics for biosorption of EY dye**

**3.7.2 Pseudo second order rate equation**

Pseudo second order kinetics plot between 't' vs 't/qt' for biosorption of EY dye is drawn in fig. 3.11. Table-5.11 summarizes 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.

$$t/q_t = 0.7516 t + 7.3583, \quad R^2 = 0.9361 \quad \dots \dots \dots (5.16)$$



**Fig. 3.11 Second order Kinetics for biosorption of EY dye**

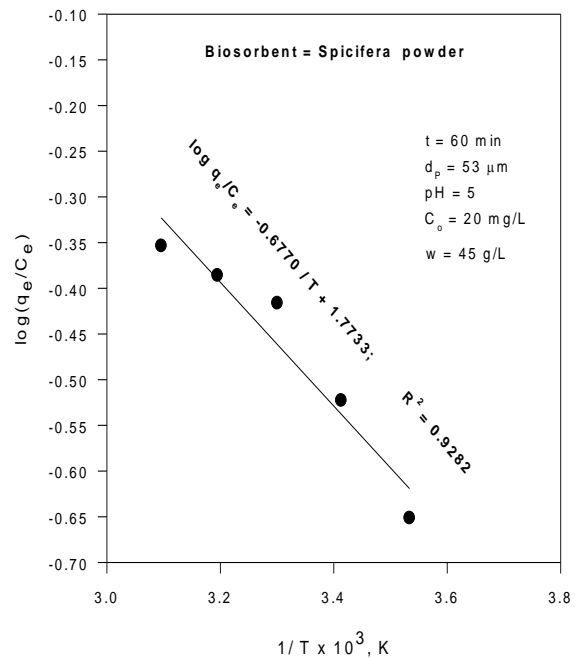
**Table–3.11**

**Equations and rate constants**

Order	Equation	Rate constant	R <sup>2</sup>
Lagergren first order	$\log (q_e - q_t) = -0.0168 t + 0.0430$	$0.03875 \text{ min}^{-1}$	0.9812
Pseudo Second order	$t/q_t = 0.7516 t + 7.3583$	$0.070677 \text{ g}/(\text{mg} \cdot \text{min})$	0.9361

**3.8 Thermodynamics:**

A series of thermodynamic parameters - change in Gibbs free energy ( $\Delta G$ ) change in enthalpy ( $\Delta H$ ) and change in entropy ( $\Delta S$ ) are determined.  $\Delta G$  value of  $-10275 \text{ J/mole}$  indicates that biosorption of EY dye by spicifera powder could take place spontaneously. Higher temperatures have benefitted biosorption and increased the equilibrium biosorption capacity. Positive  $\Delta H$  of  $12.9626 \text{ J/mole}$  indicates endothermic nature of biosorption while positive  $\Delta S = 33.9536 \text{ J/mole} \cdot \text{K}$  demonstrates the affinity of spicifera powder to EY dye[50-54].



**Fig.3.12 Vant Hoff's plot for biosorption of EY dye**

**3.9 Optimization using Response Surface Methodology (RSM):**

**3.9.1 Optimization using CCD**

In the present study, the levels of four process input variables for % biosorption are shown in table–3.12.

**Table – 3.12**  
Levels of different process variables in coded and un-coded form for % biosorption of EY dye using spicifera powder

Variable	Name	Range and levels				
		-2	-1	0	1	2
X <sub>1</sub>	pH of aqueous solution	3	4	5	6	7
X <sub>2</sub>	Initial concentration, C <sub>0</sub> , mg/L	10	15	20	25	30
X <sub>3</sub>	Biosorbent dosage, w, g/L	35	40	45	50	55
X <sub>4</sub>	Temperature, T, K	28	29	30	31	32
		3	3	3	3	3

The parameters that have greater influence over the response are to be identified so as to find the optimum condition for the biosorption of EY dye. For optimization of medium constituents, the regression equation is:

% biosorption of EY dye is a function of pH (X<sub>1</sub>), C<sub>0</sub> (X<sub>2</sub>), w (X<sub>3</sub>), and T (X<sub>4</sub>). The variations in the corresponding coded values of four parameters and response are presented in table-3.13 depending on experimental runs and predicted values proposed by CCD design. The following equation represents multiple regression analysis of the experimental data:  

$$Y = -2056.89 + 44.52 X_1 + 2.93 X_2 + 14.77 X_3 + 10.94 X_4 - 2.15 X_1^2 - 0.09 X_2^2 - 0.09 X_3^2 - 0.02 X_4^2 - 0.33 X_1 X_2 - 0.51 X_1 X_3 + 0.03 X_1 X_4 - 0.04 X_2 X_3 + 0.01 X_2 X_4 - 0.01 X_3 X_4 \dots\dots\dots (5.17)$$

**Table - 3.13**  
Results from CCD for EY dye biosorption by spicifera powder

Run No.	X <sub>1</sub> , pH	X <sub>2</sub> , C <sub>0</sub>	X <sub>3</sub> , w	X <sub>4</sub> , T	% biosorption of EY dye	
					Experimental	Predicted
1	-1	-1	-1	-1	84.22000	84.21583
2	-1	-1	-1	1	84.08000	84.10750
3	-1	-1	1	-1	90.72000	90.71750
4	-1	-1	1	1	88.42000	88.38917
5	-1	1	-1	-1	87.22000	87.19417
6	-1	1	-1	1	89.88000	89.91583
7	-1	1	1	-1	90.02000	90.02583
8	-1	1	1	1	90.52000	90.52750
9	1	-1	-1	-1	90.20000	90.19083
10	1	-1	-1	1	91.38000	91.40250
11	1	-1	1	-1	86.52000	86.51250
12	1	-1	1	1	85.48000	85.50417
13	1	1	-1	-1	86.58000	86.63917

14	1	1	-1	1	90.68000	90.68083
15	1	1	1	-1	79.32000	79.29083
16	1	1	1	1	81.08000	81.11250
17	-2	0	0	0	88.78000	88.78667
18	2	0	0	0	85.38000	85.34667
19	0	-2	0	0	87.20000	87.20333
20	0	2	0	0	85.82000	85.79000
21	0	0	-2	0	88.62000	88.58000
22	0	0	2	0	85.50000	85.51333
23	0	0	0	-2	87.62000	87.64000
24	0	0	0	2	89.40000	89.35333
25	0	0	0	0	95.68000	95.68000
26	0	0	0	0	95.68000	95.68000
27	0	0	0	0	95.68000	95.68000
28	0	0	0	0	95.68000	95.68000
29	0	0	0	0	95.68000	95.68000
30	0	0	0	0	95.68000	95.68000

Experimental conditions [Coded Values] and observed response values of central composite design with 2<sup>4</sup> factorial runs, 6- central points and 8- axial points. Agitation time fixed at 40 min and biosorbent size at 53 μm

The results of eq. 5.17 are presented in the form of ANOVA. From the Fisher’s F-test and a very low probability value (P<sub>model</sub>>F=0.000000), the ANOVA of the model clearly explains that the model is highly significant (Refer table 3.15). It shows that the treatment differences are significant.

**Table-3.14**  
ANOVA of EY dye biosorption for entire quadratic model

Source of variation	SS	df	Mean square(MS)	F-value	P> F
Model	557.023	14	39.7873	35524	0.00000
Error	0.0168	15	0.00112		
Total	557.0398				

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

R<sup>2</sup>=0.99219; R<sup>2</sup> (adj):0.9849;

It is predicted from table-5.14 that 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-5.15

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 EY dye

**Table-3.15**  
**Regression coefficients**

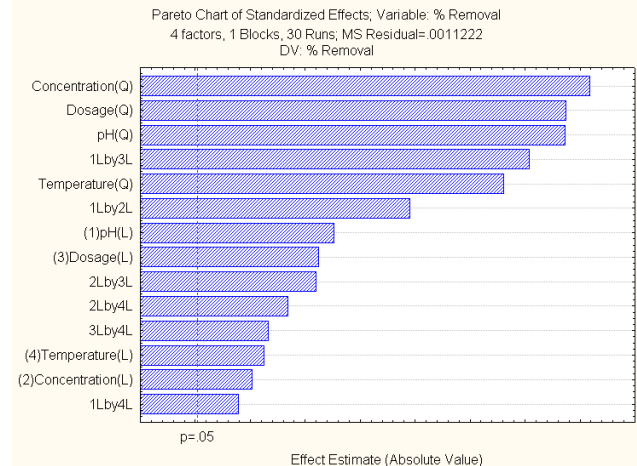
Term	Regression	Standard error
Mean/Intercept	-2056.89	6.719584
Dosage, w, g/L (L)	44.42	0.277733
Dosage, w, g/L (Q)	-2.15	0.006396
Conc, Co, mg/L (L)	2.93	0.054869
Conc, Co, mg/L (Q)	-0.09	0.000256
pH (L)	14.77	0.057042
pH (Q)	-0.09	0.000256
Temperature, T, K (L)	10.94	0.039953
Temperature, T, K (Q)	-0.02	0.000064
1L by 2L	-0.33	0.001675
1L by 3L	-0.51	0.001675
1L by 4L	0.03	0.000837
2L by 3L	-0.04	0.000335
2L by 4L	0.01	0.000167
3L by 4L	-0.01	0.000167

<sup>a</sup>insignificant ( $P \geq 0.05$ )

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

$$Y = -2056.89 + 44.52 X_1 + 2.93 X_2 + 14.77 X_3 + 10.94 X_4 - 2.15 X_1^2 - 0.09 X_2^2 - 0.09 X_3^2 - 0.02 X_4^2 - 0.33 X_1X_2 - 0.51 X_1X_3 + 0.03 X_1X_4 - 0.04 X_2X_3 + 0.01 X_2X_4 - 0.01 X_3X_4 \quad \text{----- (5.18)}$$

The regression coefficient value of 0.99996 indicates that 0.004 % of the total variations are not satisfactorily explained by the model [55-59]. The statistical significance of the ratio of mean square due to regression and mean square due to residual error are tested. It is proved from that table that, the *F*-statistics value for entire model is higher. i.e., % biosorption of EY dye 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-3.14. It is implied from table-5.15 that all the squared terms of the variables are significant compared to the linear terms. Among the interaction terms, all the terms ( $P < 0.05$ ) are highly significant on biosorption capacity.

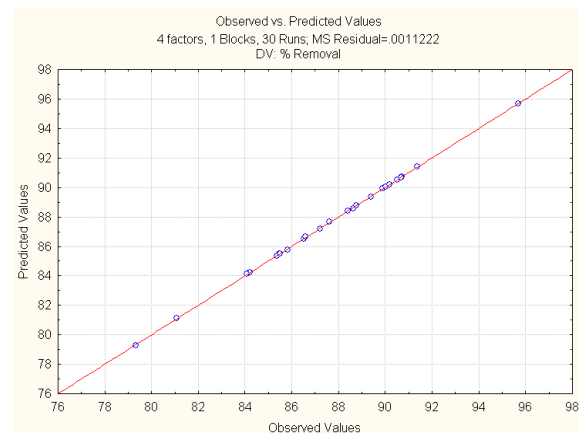


**Fig. 3.13 Pareto Chart**

The optimal set of conditions for maximum percentage biosorption of EY dye is pH = 5.8809, initial EY dye concentration = 20.0533 mg/L, biosorbent dosage = 44.3682 g/L, and temperature = 304.2994 K. The extent of biosorption of EY dye at these optimum conditions was 95.8056 %. 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 EY dye is 93 %, which is closer to the predicted % biosorption.

**5.21.2 Interpretation of residual graphs:**

Fig. 3.14 shows normal probability plot of residual values. The experimental values are in good agreement with predicted values with minimum error.



**Fig. 3.14 Normal probability plot for % biosorption of EY dye**

**3.9.3 Interaction effects of biosorption variables:**

Figs.3.15(a) to (f) depict the three-dimensional view of response surface plots. The % biosorption of biosorbent is maximal at low and high levels of the variables but there is a region where

increasing/decreasing trend in % biosorption is not observed. The predicted optimum values for percentage biosorption of EY dye are:

- pH = 5.8809,
- Initial EY dye concentration = 20.0533 mg/L
- Biosorbent dosage = 44.3682 g/L,
- Temperature = 304.2994 K
- % EY dye biosorption = 95.8056

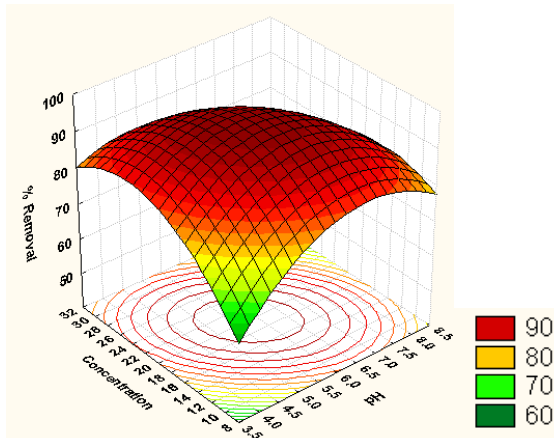


Fig. 3.15 (a) Surface contour plot for the effects of pH and initial concentration of EY dye on % biosorption

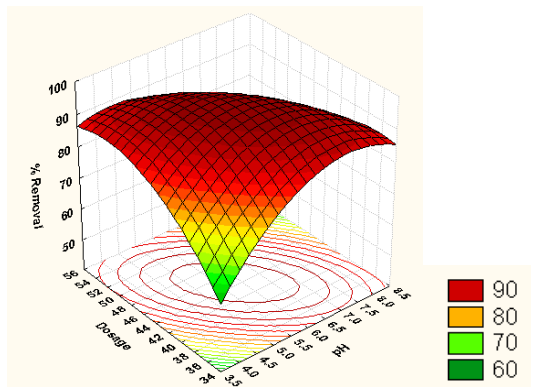


Fig. 3.15 (b) Surface contour plot for the effects of pH and dosage on % biosorption of EY dye

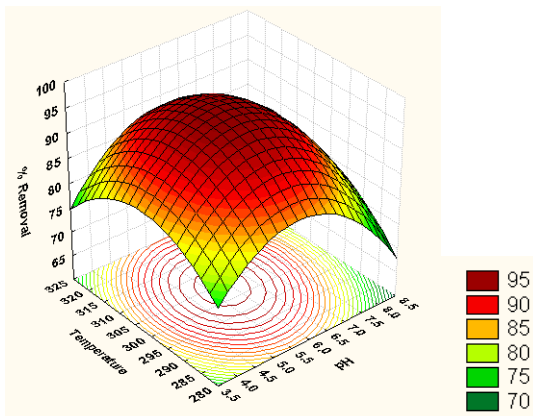


Fig. 3.15 (c) Surface contour plot for the effects of pH and Temperature on % biosorption of EY dye

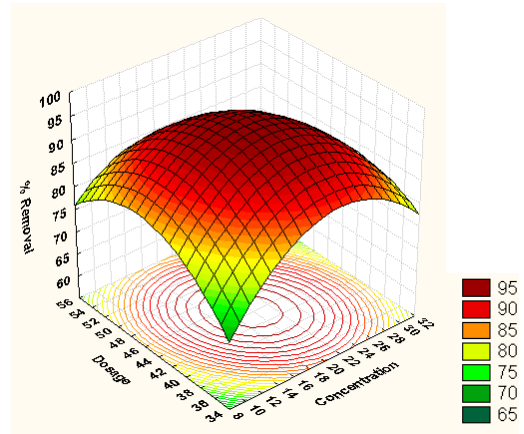


Fig. 3.15 (d) Surface contour plot for the effects of initial concentration and Dosage on % biosorption of EY dye

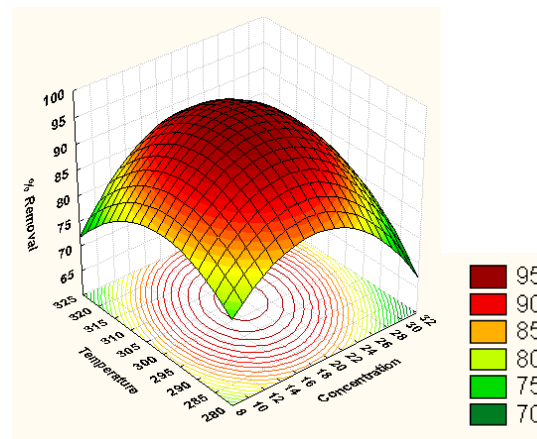


Fig. 3.15 (e) Surface contour plot for the effects of initial concentration and Temperature on % biosorption of EY dye

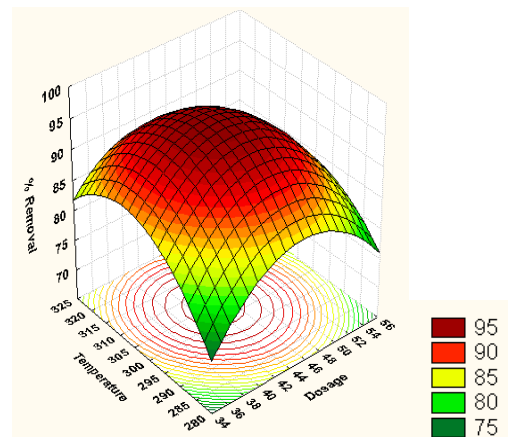


Fig. 3.15 (f) Surface contour plot for the effects of Dosage and Temperature on % biosorption of EY dye



**Table – 3.16**  
**Comparison between optimum values from CCD and experimentation**

Variable	CCD	Experimental value
pH of aqueous solution	5.8809	5
Initial EY dye concentration, mg/L	20.0533	20
Biosorption dosage, w, g/L	44.3682	30
Temperature, K	304.2994	303
% biosorption	95.8056	94.9

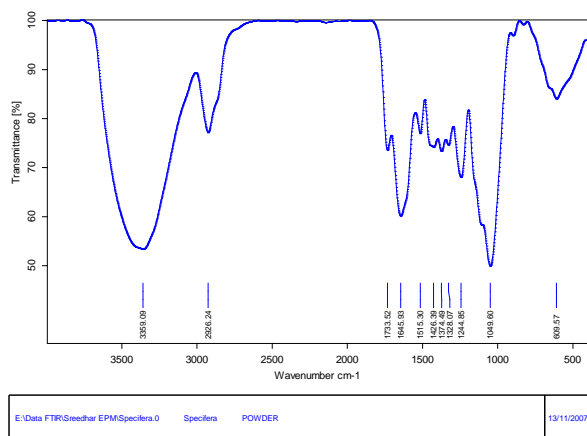
The present EY dye biosorption uptake capacities are compiled in table–5.17 with those of other biosorbents.

### 3.10 Characterization of spicifera powder

#### 3.10.1 FTIR spectrum

##### 3.10.1.1 FTIR spectrum of EY dye untreated spicifera powder:

FTIR measurements for untreated spicifera powder are shown in fig. 3.16 (a). FTIR spectra of EY dyeloaded spicifera powder biomass is shown in fig. 3.16 (b). These two figures indicate that the band at 609.36 cm<sup>-1</sup> is shifted to the 609.57 cm<sup>-1</sup> due to the dye interaction with the 2,4 benzene deformation out of phase. This indicates the slight involvement of functional group in biosorption. The band at 1048.53 cm<sup>-1</sup> is also shifted to 1049.60 cm<sup>-1</sup> due to the slight participation in EY dye loading by overlapping of C–H bending vibrations. The band peak at 1244.42 cm<sup>-1</sup> is shifted to 1244.85 cm<sup>-1</sup> respectively after treatment due to -SO<sub>3</sub> stretching [60-64].

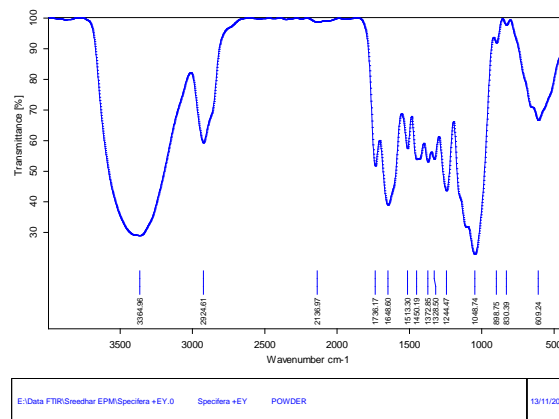


**Fig. 3.16 (a) FTIR spectrum of EY dye untreated with spicifera powder**

##### 3.10.1.2 FTIR spectrum of EY dye treated spicifera powder

The new peaks are observed after biosorption at 1737.91, 2925.14 and 3359.17 cm<sup>-1</sup> due to the

involvement of the Assymmetric stretching vibration of C = O and –OH stretching or –NH<sub>2</sub> stretching functional groups respectively in the ion-exchange process. After biosorption of EY dye ions on the surface of the biomass, several peaks have disappeared indicating that the direct and predominant involvement of the functional groups in the ion-exchange process.



**Fig. 3.16 (b) FTIR spectrum of EY dye treated spicifera powder**

Further, the peaks at 3359.17 cm<sup>-1</sup>, attributed to –OH stretching or –NH<sub>2</sub> stretching modes and are not seen in untreated biomass. This may be due to direct and predominant involvement in biosorption of EY dye. The shifts in peaks are presented in table-3.18.

**Table – 5.18**  
**Shift of FTIR peaks for untreated and treated spicifera powder with EY dye**

##### Shift of FTIR peaks for untreated and spicifera powder treated EY dye

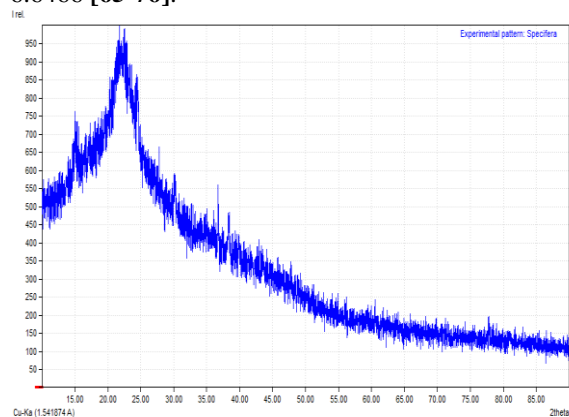
S. No.	Peaks in untreated powder, cm <sup>-1</sup>	Peaks in treated powder, cm <sup>-1</sup>	Description
1	---	609.24	2,4 benzene deformation out of phase
2	609.57	---	2,4 benzene deformation out of phase
3	---	830.39	S = O and C–S–O bands from ester sulphonate
4	---	898.75	S = O and C–S–O bands from ester sulphonate
5	---	1048.74	C–H bending vibrations
6	1049.60	---	C–H bending vibrations
7	---	1244.47	-SO <sub>3</sub> stretching
8	1244.85	---	-SO <sub>3</sub> stretching
9	1328.07	---	–CH <sub>2</sub> bending vibrations
10	---	1328.50	–CH <sub>2</sub> bending

			vibrations
11	---	1372.85	-CH <sub>2</sub> bending vibrations
12	1374.49	---	-CH <sub>2</sub> bending vibrations
13	1426.39	---	C-N stretching
14	---	1450.19	C-N stretching
15	---	1513.30	Amide N-H bending vibrations
16	1515.30	---	Amide N-H bending vibrations
17	1645.93	---	Oleifinic C = C and Carbonyl C = O stretching
18	---	1648.60	Oleifinic C = C and Carbonyl C = O stretching
19	1733.52	---	Assymmetric stretching vibration of C = O
20	---	1736.17	Assymmetric stretching vibration of C = O
21	---	2136.97	C ≡ N in the polyacrylnitrile
22	---	2924.61	CH <sub>2</sub> stretching vibrations
23	2926.24	---	CH <sub>2</sub> stretching vibrations
	3359.09	---	-OH stretching or -NH <sub>2</sub> stretching
	---	3364.96	Hydroxyl stretching or amine stretching

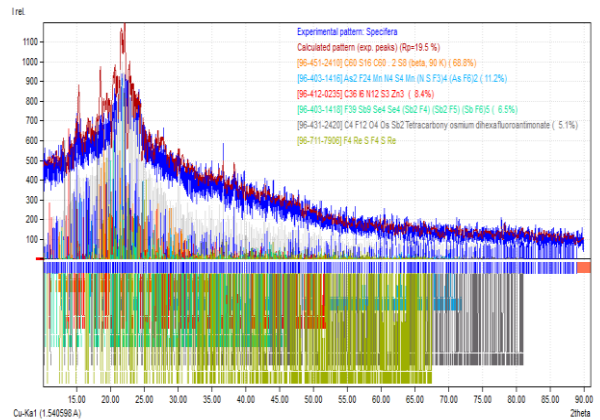
**3.10.2 X-Ray Diffraction:**

**3.10.2.1 XRD pattern of EY dye untreated spicifera powder**

XRD patterns shown in figs 5.34 (a) & (b) for untreated powder do not show very keen or pointed and distinct peaks and exhibits roughly amorphous nature. The peaks at 2θ values of 0.7748, 0.7273, 0.7273, 0.7159 and 0.7035 corroborate the presence of Fe<sub>3</sub>H<sub>47</sub>K<sub>44</sub>, Eu<sub>8</sub>K<sub>16.5</sub>O<sub>206</sub>, As<sub>6</sub>ClCS<sub>3.9</sub>, H<sub>168</sub>K<sub>3</sub>Li<sub>5.5</sub> and C<sub>40</sub>K<sub>13</sub>O<sub>368</sub>(ICDD files). Their corresponding d-values are 5.5771, 5.1148, 5.8082, 6.4302 and 6.6466 [65-76].



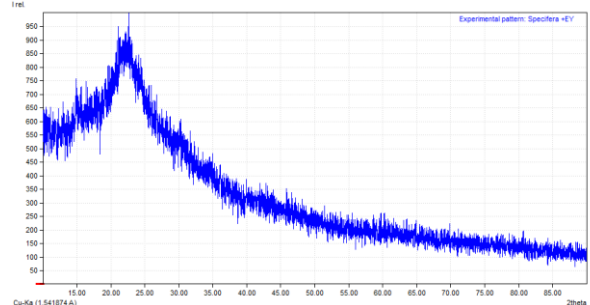
**Fig. 3.17 (a) XRD pattern of EY dye untreated spicifera powder**



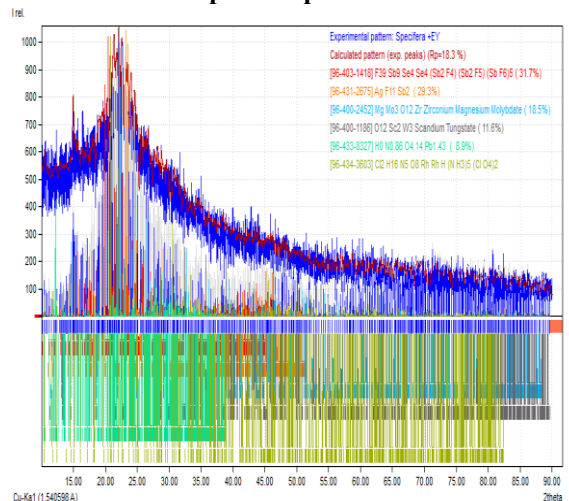
**Fig. 3.17 (b) XRD pattern of EY dye untreated spicifera powder with matching compounds**

**3.10.2.2 XRD Pattern of EY dye treated spicifera powder**

XRD patterns of treated EY dye, shown in figs 5.34 (c) & (d), show very violent and intense and well defined peaks and exhibits precisely amorphous nature. The peaks at 2θ values of 0.8662, 0.8333, 0.7447, 0.7717 and 0.7310 corroborate the presence of Ba<sub>8</sub>S<sub>15</sub>Sn<sub>4</sub>, Fe<sub>39</sub>Sb<sub>9</sub>Se<sub>4</sub>, As<sub>14</sub>Cs<sub>4</sub>Zn, Cs<sub>2</sub>O<sub>7</sub>S<sub>2</sub> and Br<sub>10</sub>Te<sub>8</sub>U<sub>2</sub>. Their corresponding d-values are 3.5370, 3.1420, 4.1371, 3.8977 and 3.7049 respectively.



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



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

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### CONCLUSIONS

1. The equilibrium agitation time for EY dye biosorption is 60 minutes.
2. The optimum dosage for biosorption is 45 g/L.
3. Maximum extent of biosorption is noted at pH = 5.
4. From the predicted values of RSM results, maximum biosorption of EY dye (95.8056 %) is observed when the processing parameters are set as pH = 5.8809, w = 44.3682 g/L, C<sub>0</sub> = 20.0533 mg/L and T = 304.2994 K.
5. The investigation also reveals the:
  - endothermic nature of biosorption as  $\Delta H$  is positive (12.96262J/mole)
  - spontaneity of the biosorption as  $\Delta G$  is negative (-10275J/mole)
  - irreversible nature of biosorption as  $\Delta S$  is positive (33.95363)

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