Studies on Biosorption of Titan Yellow Dye with Hyptis Suaveolens Powder and Optimization Through Central Composite Design

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Abstract:- Slight colouration of water sources could make them unacceptable to consumers though it may not be toxic to the same degree. The source of such pollution lies in the rapid increase in the use of synthetic dyes. These wastes spoil the natural habitat of the aquatic species, the best practice for the removal of dyes and heavy metals is considered for the present investigation is Biosorption Hyptis Suaveolens powder is used for the removal of Tiatan Yellowdye from aqueous solution. 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**:- Tiatan Yellowdye, Hyptis Suaveolens, RSM, CCD.*

I. INTRODUCTION

Environmental pollution takes place when the environment *cannot* process and neutralize harmful by-products of human activities (for example, poisonous gas emissions) *in due course* without any structural or functional damage to its system. In fact, “the due course” itself may last many years during which the nature will attempt to decompose the pollutants; in one of the worst cases – that of radioactive pollutants – it may take as long as thousands of years for the decomposition of such pollutants to be completed. Pollution in water cause Water-born Disease. Single ounce of polluted water is enough to cause disorders; think of 70% of water covering earth is going to be poisoned. Heavy metal pollution in waters has been the most pervasive environmental issues nowadays. Natural waters can easily be polluted by metal ions as a result of their release by industrial plants or mining activities [1-4]. Lead and mercury ions are among the commonly encountered pollutants in waste discharges and may cause chronic and acute effects on human health [5]. According to the ranking of metal interested priorities referred by Volesky [6], Pb (II) is one of the most interesting heavy metal for removal and recovery considering the combination of environmental risk and reserve depletion. This metal is widely used in many industrial applications, such as storage battery manufacturing, painting pigment, fuels, photographic materials, explosive manufacturing, coating, automobile, aeronautical and steel industries [7-10]. Therefore, the discharges should be free from these pollutants to prevent subsequent possible accumulations in live tissues. On the other hand, recovery of metal ions may offer a worthy input if it can be succeeded in a cost effective way. Removal of heavy metals from waste waters is a major ecological and economical problem. Conventional technologies for the removal and recovery of heavy metals from wastewater include chemical precipitation, ion exchange, membrane separation and adsorption by activated carbon. Most of these methods have some bottlenecks such as high operational costs and need for disposal of resulting sludge, particularly when the unwanted heavy metals are present at low concentrations i.e. <100 mg L−1 [11-13]. In this connection Better and cheaper process required i.e., Biosorption. Although a number of studies using different types of biomass have proved that biosorption is a more effective method for heavy metal removal than the conventional methods, further investigation is still needed to optimize the maximum efficiency of removal, which is expected to lead to its large scale exploitation [14]. Biosorption is a term that describes the removal of heavy metals by the passive binding to nonliving microorganisms (bacteria, fungi and algae) and other biomass (such as peat, rice hull, fruit peel, leave and bark of tree) from an aqueous solution [15-17].Many microorganisms including bacteria, fungi and algae had been investigated in metal adsorption studies [18-20]. Biosorption often referred to as passive uptake and physicochemical binding of chemical species or ions to biomass or biopolymers has been suggested as a potential alternative to the existing physico-chemical technologies for the detoxification and the recovery of toxic and valuable metals from wastewaters [21, 22].On analysis of various cost efficient methods available biosorption is discovered to be a novel low cost route. It has been satisfactory both in terms of efficiency and cost effectiveness to solve the above problem. The present experimentation was carried out in order to evaluate the potential and power of Hyptis Suaveolens powder for the removal of novel dye Tiatan Yellowfor the first time. Apart from cost considerations there are various other limitations such as generation of sludge etc. On analysis of various cost efficient methods available biosorption is discovered to be a novel low cost route. It has been satisfactory both in terms of efficiency and cost effectiveness to solve the above problem. The present experimentation was carried out in order to evaluate the potential and power of Hyptis Suaveolens powder for the removal of novel dye Titan Yellow for the first time.

II. 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:

- Preparation of the bisorbent
- Characterization of biosorbent
- Preparation of the stock solutions
- Studies on Equilibrium Biosorption Process

A. Preparation of the bisorbent

Hyptis Suaveolens 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.

B. Characterization of biosorbent

Biosorption of Titan Yellow dye using Hyptis Suaveolens 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.

C. Preparation of stock solution

The standard stock solution of Titan Yellow dye (1000 mg/L) was prepared by dissolving 1.0 g of 99.9 % analytical grade Phenol 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.

D. Studies on Equilibrium Biosorption Process

The biosorption was carried out in a batch process by adding a pre-weighed amount of the Hyptis Suaveolens 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 Phenol Red dye were evaluated using single step optimization process

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

Table 1. Experimental conditions for biosorption of TY dye

III. RESULTS AND DISCUSSIONS

In the present investigation, the prospectives of two sorbents namely Hypnea musciformis powder and Dulce powder were evaluated to estimate their performance for the decolorization titan yellow (T.Y) dye present in aqueous solutions. The effects of parameters on decolorization of T.Y dye were measured, data consisting of contact time, sorbent size, pH of the solution, initial concentration, sorbent dosage and temperature.

A. Sorption of Titan Yellow dye using Hyptis Suaveolens powder

In the present investigation, the potential of dry *Hyptis* powder as a sorbent for dye decolorization of Tiatan Yellow present in an aqueous solution is investigated. The effects of various parameters on dye decolorization of indigo caramine are studied. The measured data consists of initial and final concentration of Titan Yellow, contact time, sorbent size, sorbent dosage, pH of the aqueous solution and temperature of the aqueous solution. The experimental data are obtained by conducting batch experiments.

B. Equilibrium studies on dye decolorization

From the experimentations on dye decolorization of indigo caramine, the percentage dye decolorization of indigo caramine is found from the relation $= \frac{C_0 - C_e}{C_0} x\ 100$

The amount of indigo caramine biosorbed per unit mass of the sorbent, q_t in mg/g is computed by using the expression:

$$q_t = \frac{C_0 - C_e}{w}$$

The effects of various parameters on dye decolorization of indigo caramine are discussed below.

C. *Effect of contact time*

The Decolourization of Dye Titan yellow TY was studied as a function of contact time at Room temperature. 50 ml of 20 mg/L Dye Solution The rate of adsorption becamegradually slower and reached an exhaust stage, resulting constant value. As a result of the experiment, the highest % Removed for the Dye TY was 52 % atthe time of 40 min. The dye uptake capacities were shown in fig. 3.18. The rapid uptake of the dye indicates that the sorption process could be ionic in nature where the anionic dye molecules bind to the various positively charged organic functional groups present on the surface of the pp-zn-nps. [23-27].

The equilibrium time for Hyptis suaveolens powder TY dye system is 40 min, the % removal of time between 5 to 40 min is 16% to 52% and no further removal was occurred bTYond the time from 40 min to180 min. The % removal and dye uptake were 0.32 to 1.04mg/g as follows. Contact time is an important parameter in environmental engineering. For the removal of pollutant it is critical to obtain a contact time that is economical and enough to remove pollutants in a conscionable condition.

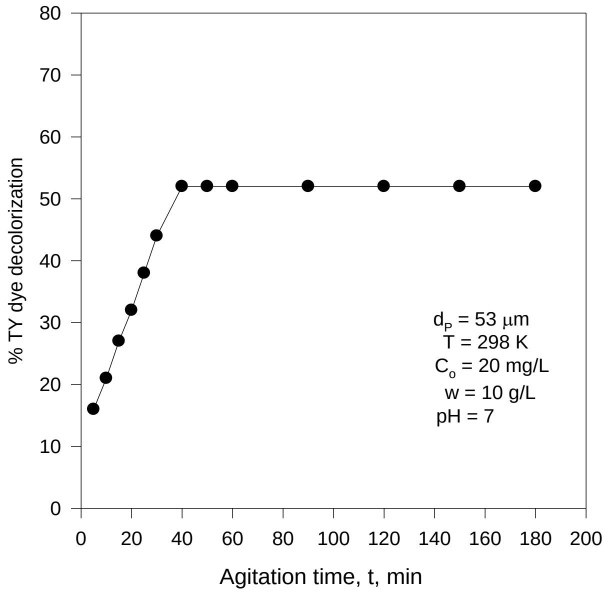


Fig 1:- Effect of agitation time on % removal of TY dye

D. *Effect of size of biosorbent (d_p)*

The effect size of biosorbent on the removal of TY dye onto Hyptis suaveolens powder was studied at dosage of 0.5g/L. A graph was drawn between % removals of dye against size of biosorbent in fig-3.19 and for the fixed initial concentration of solution at 10 mg/L, for the fixed volume of 50 ml of solution at an agitation time of 40 min. The equilibrium time for Hyptis suaveolens powder TY dye system is 53 um, the % removal of TY dye decrease 36 % to 52 % to size of biosorbent increases 152 to 53 um. The % removal and dye uptake were 1.04 to 0.72 mg/g as follows It is cleared from the plots that % removal drops with size of biosorbent. It is due to less surface area available at higher size of biosorbent and uptake also decreasing with size of sorbent [23-27].

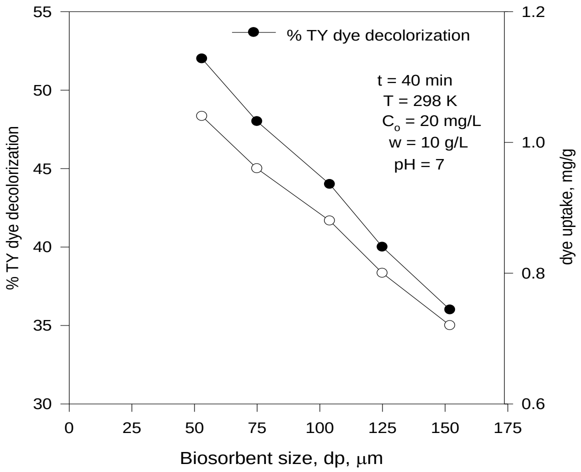


Fig 2:- Effect of size on % removal of TY dye

E. *Effect of pH*

The pH parameter has been identified as one of the most important parameter that is effective on Dye decolourization. In order to find the effect of pH on Dye Decolourization using the Hyptis suaveolens powder TY dye system, experiments have been carried out at various initial pH values and results are given in figure 3.20.The removal was decreased from 40 % to 46 % as pH was increased from 2 to 8, The pH is varied for every dye used with the Hyptis suaveolens powder TY dye system whereas further increase in pH had a negative effect. The maximum % removal was found to be 60 % at pH 6 for TY Dye. the remaining all experiments were carried out at this pH value. The biosorption capacity of the dried cells of A. Under alkaline conditions biosorption capacity significantly decreased ($p<0.05$). The decrease of the biosorption capacity with increase in the medium pH can be explained by the dye binding sites on the biosorbent surface becoming negatively charged, restricting the approach of the dye molecules as a result of repulsive forces. This can be explained that at a lower pH, positive charges of the biomass TY to attraction between the anionic species of the dye and the surface of the biosorbent. The electrostatic attraction force of the dye compound with biosorbent surface is likely to be reduced when the pH value increases. In other words at a lower pH, the biomass cell is positively charged TYing to a decrease in free negatively charged adsorbent sites which are favorable to the adsorption of the negative charged dye.[28-32]

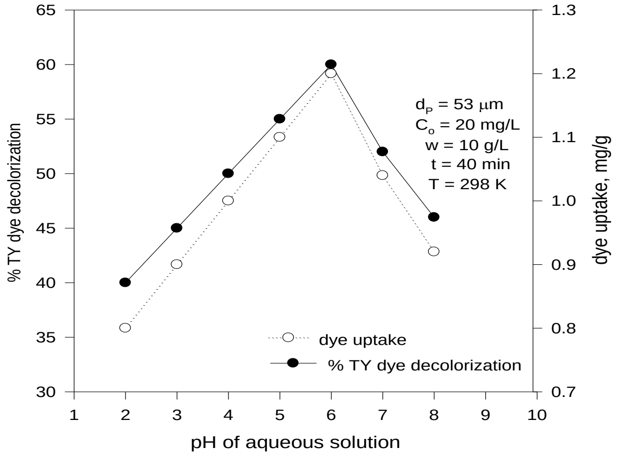


Fig 3:- Effect of pH on % removal of TY dye

F. *Effect of initial concentration of dyes*

The percentage Removal of dyes at various initial concentrations is depicted in Fig. 3.21. At concentration of Dye solution (20 mg/L), maximum %removal is obtained (60 to 48%)and is different for TY Dye using Hyptis suaveolens power and on further increase in concentration (200 mg/L), %removal has been decreased. The capacity of % removal is increased up to concentration 20 mg/L. This is due to higher interaction between Hyptis suaveolens power and the TYDye solution.

At concentration of Dye solution (20 mg/L), maximum %removal is obtained and is different for TY Dye using Hyptis suaveolens power and on further increase in concentration (200 mg/L), %removal has been decreased.

Biosorption capacity increased as a result of increasing initial dye concentration because the initial dye concentration favors a driving force to accomplish the mass transfer resistance between the solid and aqueous phases [33-37].

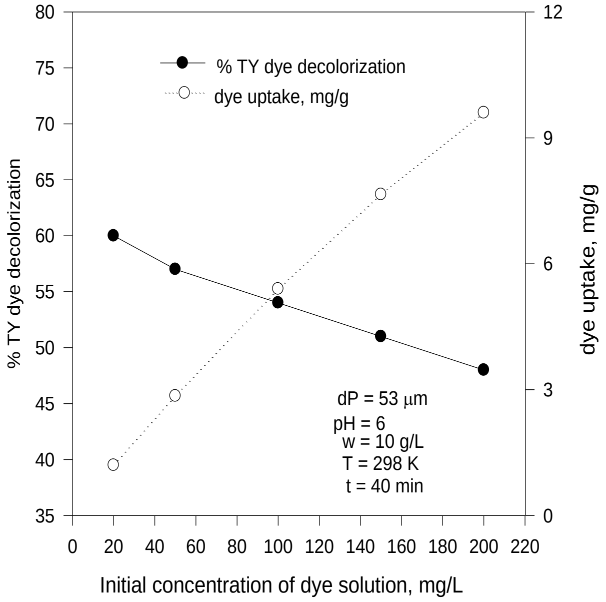


Fig 4:- Effect of initial concentration on % removal of TY dye

G. *Effect of biosorbent dosage*

The variation of % removal of DyeTY was studied using different dosages of the Hyptis suaveolens power. Results from the fig 3.22 showed that % removal of Dye TY increased 60 to 79.5% and uptake decreased 1.2 to 0.318mg/g with increase in dosage 0.5 to 4g/l . The maximum % removal was almost constant at higher dosages. This trend could be explained as a consequence of partial aggregation. Therefore, The maximum % removal of TY dye is 76% at dosage 1.5g/l and dye uptake is 0.5066 mg/g [38-42].

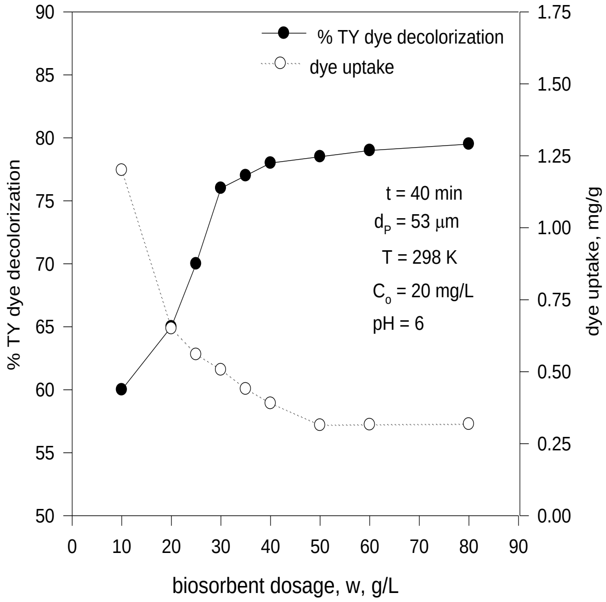


Fig 5:- Effect of dosage on % removal of TY dye

H. *Effect of temperature*

The dependence of temperature on the % removal of dyes is investigated at different temperatures as given in fig. 3.23. Results from fig 3.23 showed that %removal of TY Dye increased from 72% to 79% with increase in temperature from 283 K to 323 K. This indicates that the % removal of Dye using Hyptis suaveolens powerwas controlled by an endothermic process. The increase in removal with temperature may be attributed to either increase in the number of active surface sites available for interaction on the Dyes. This indicates that the % removal of Dye using Hyptis suaveolens powerwas controlled by an endothermic process. The increase in removal with temperature may be attributed to either increase in the number of active surface sites available for interaction on the Dyes.

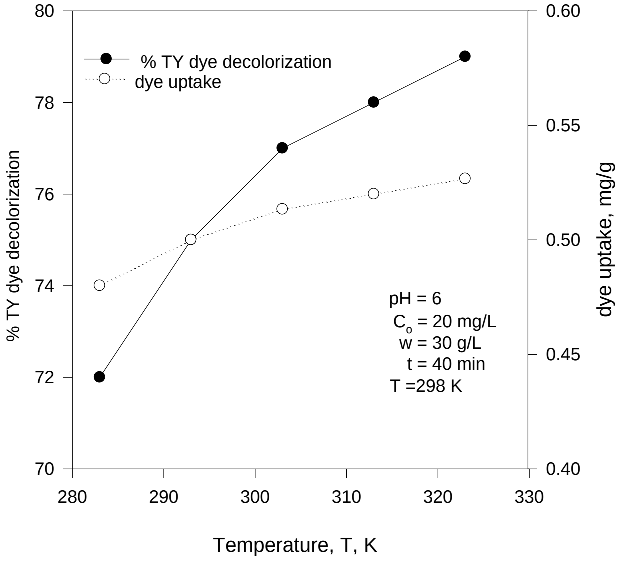


Fig 6:- Effect of Temperature on % removal of TY dye

➢ *Isotherm model*

A. *Langmuir Isotherm model*

In the present study three models were tested and the various isotherms are presented in figs. 3.24 to 3.26 Based on the correlation coefficients, it is found that the biosorption of TY ions on Hyptis suaveolens power was correlated well with three isotherms in the order Freundlich > Langmuir > Temkin. From Langmuir isotherm, the adsorption affinity constant (b) and maximum capacity (q_m) of the TY dye to form a complete monolayer on to the surface of the Hyptis suaveolens power was found to be 0.0064 L/mg and 23.6966 mg/g respectively. The separation factor R_L value (0.9734) lying between 0 and 1 indicate favorable isotherm shape ($0 < R_L < 1$) for biosorption of TYdye on Hyptis suaveolens power [43-47].

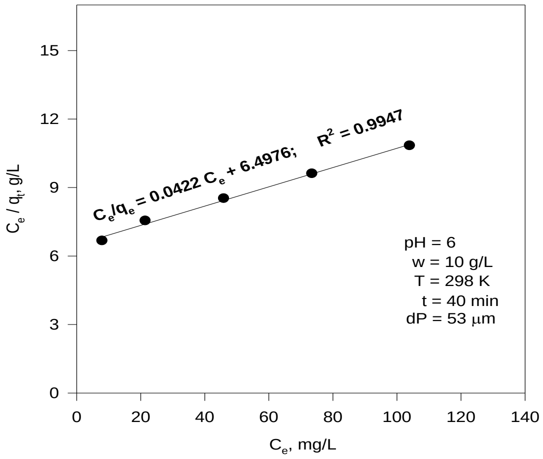


Fig 7:- Langmuir isotherm for biosorption of TY dye

B. *Freundlich isotherm*

For Freundlich isotherm, the constants related to the biosorption coefficients (K_f) and intensity (n) were determined as 0.2263 and 0.8171respectively. A favorable biosorption tends to have Freundlich constant 'n' between 1 and 10 [48-52].

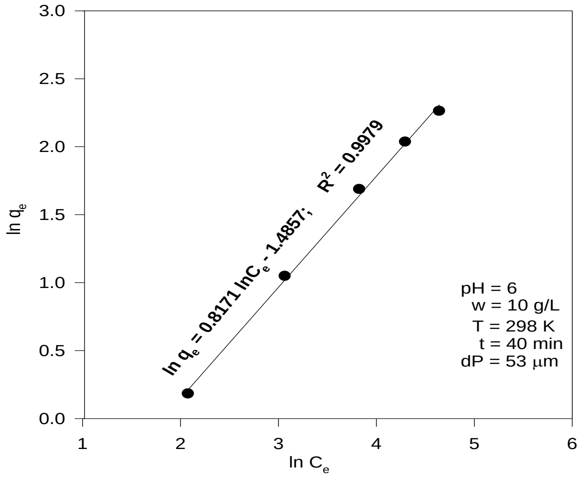


Fig 8:- Freundlich isotherm for biosorption of TY dye

C. *Temkin isotherm*

The Temkin equation produced correlation coefficient (R^2) of 0.9947 indicating favourable conditions for biosorption. Equilibrium binding constant (A_T) and Temkin isotherm constant (b_T) were obtained to be 0.1441 L/mg and 776.9135 J/mol respectively **[53-57].**

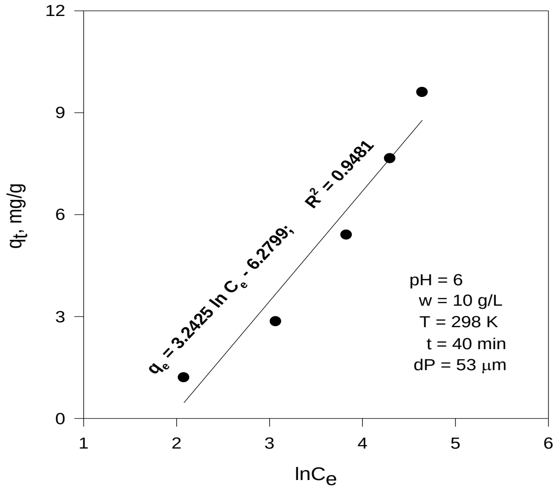


Fig 9:- Temkin isotherm for biosorption of TY dye

The parameters of Freundlich, Langmuir, and Temkin isotherms are given in table 3.10.

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
q_m = 23.6966 mg/g	K_f = 0.2263 mg/g	A_T = 0.1441 L/mg
K_L = 0.9734	n = 0.8171	b_T = 776.9135
R^2 = 0.9949	R^2 = 0.9979	R^2 = 0.9481

Table 2. Freundlich, Langmuir and Temkin isotherm model parameters

➢ *Kinetic studies*

A. *Lagergren-first-order kinetic model*

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 5 min to 180 min. Lagragen plots of log (q_e-q_t) versus agitation time (t) for biosorption of TY the biosorbent size (53 µm) of Hyptis suaveolens power in the interaction time intervals of 5 to 180 min are drawn in figs.3.27& 3.28 [58-62].

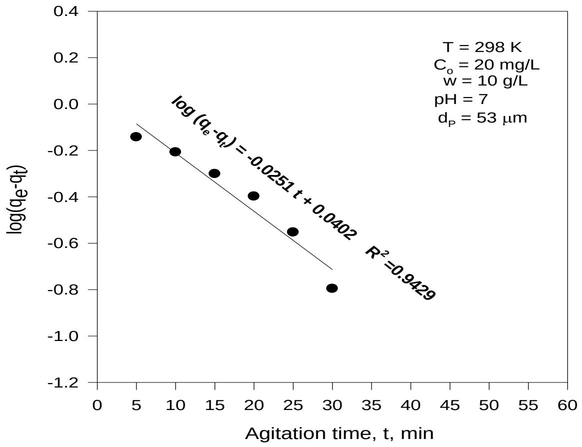


Fig 10:- First order kinetics for biosorption of TY dye

K_1	q_e (mg/g)	R^2
0.0578	1.0418	0.9429

Table 3. Lagergren-first-order-constants

B. *Pseudo-second-order kinetic model*

The pseudo second order model 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 [63-67].

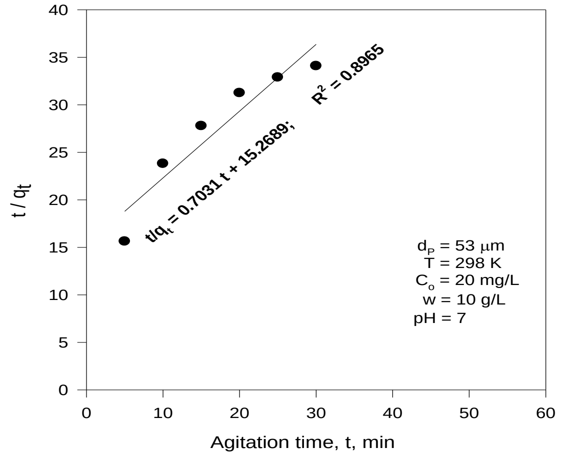


Fig 11:- second order kinetics for biosorption of TY dye

K_2	q_{et} (mg/g)	q_e (mg/g)	R^2
0.0323	2.0223	1.4222	0.8965

Table 4. Pseudo-second-order-constants

C. *Thermodynamic Parameters*

The standard enthalpy (ΔH) and entropy (ΔS) changes of biosorption determined from slope and intercept from Van’t Hoff plot (fig.3.29) of ln (q_e/C_e) as a function of 1/T. The positive value of the ΔH indicates that the biosorption is endothermic in nature while the positive ΔS corresponds to increase in the degree of freedom of sorbed species. The ΔG values decreased with increase in temperature, it indicates that biosorption is spontaneous [68-72].

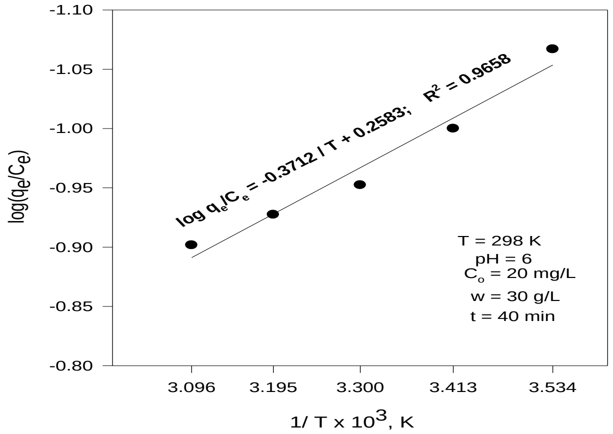


Fig 12:- Vant hoff plot for biosorption of TY dye

Experiments are conducted to understand the biosorption behavior varying the temperature from 283 to 323 K. The plots indicating the effect of temperature on biosorption of TY are shown in fig. 5.29. The Vant Hoff’s plot for the biosorption data obtained results in the following values: ΔG = –1491.44J/mole, ΔH = 7.1074J/mole and ΔS = 4.9457.

D. *Optimization of the selected parameters using CCD*

From the results of preliminary experimental runs, the four parameters (pH, initial TY dye concentration, biosorbent dosage and temperature) have been identified as the potential parameters for the percentage biosorption of TY dye. A summary of the independent parameters and their range and levels was presented in table 3.13.

Parameter	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	10	20	30	40	50
X_4	Temperature, T, K	293	298	303	313	323

Table 5. Experimental range and levels of the independent parameters

A 2^4 – factorial central composite experimental design, with eight axial points ($\alpha=\sqrt{4}$) and six replications at the center points (n_o= 6) TYing to a total number of 30 experiments (table 5.14) was employed for the optimization of the parameters.

The calculated regression equation for the optimization of medium constituents showed that percentage removal of TY dye (Y) was function of the pH (X_1), initial TY dye concentration (X_2), biosorption dosage (X_3) and temperature (X_4).

Multiple regression analysis of the experimental data resulted in the following equation for the biosorption of TY dye:

$$Y = -4270.62 + 76.09\,X_1 + 6.79\,X_2 + 2.76\,X_3 + 26.51\,X_4 - 6.42\,X_1^2 - 0.19\,X_2^2 - 0.05\,X_3^2 - 0.04\,X_4^2 + 0.07\,X_1X_2 - 0.00\,X_1X_3 - 0.00\,X_1X_4 - 0.00\,X_2X_3 + 0.00\,X_2X_4 + 0.00\,X_3X_4 \text{-------} \quad (5.17)$$

Run no.	% biosorption of TY dye	
	Experimental	Predicted
1	65.30000	65.31417
2	65.70000	65.68083
3	66.12000	66.06750
4	66.82000	66.82417
5	63.92000	63.92083
6	64.48000	64.46750
7	64.12000	64.08417
8	65.02000	65.02083
9	63.62000	63.60417
10	63.82000	63.84083
11	64.28000	64.27750
12	64.92000	64.90417
13	63.62000	63.60083
14	63.98000	64.01750
15	63.68000	63.68417
16	64.52000	64.49083
17	60.42000	60.45500
18	58.22000	58.21500
19	67.18000	67.19833
20	65.38000	65.39167
21	64.72000	64.70167
22	65.88000	65.92833
23	66.88000	66.91833
24	68.10000	68.09167
25	85.00000	85.00000
26	85.00000	85.00000
27	85.00000	85.00000
28	85.00000	85.00000
29	85.00000	85.00000
30	85.00000	85.00000

Table 6. CCD matrix showing coded and real values along with the experimental values for percentage biosorption of TY dye

The coefficients of the regression model were calculated and listed in table-5.15. TY contain one block term, four linear, four quadratic and six interaction terms. The significance of each coefficient was determined by student's t-test and p-values and listed in table 3.15. The larger the magnitude of the t-value and smaller the p-value, the more significant was the corresponding coefficient. All the interaction effects of pH, initial concentration, biosorbent dosage and temperature were found to be insignificant. All the quadratic and linear terms were found to be significant ($p<0.05$) which were also presented in table 3.15 [73-77].

The predicted percentage biosorption of TY dye resulted from equation (3.18) are in close agreement with the experimental values as evident from last column of table 3.14, and hence the above equation was deemed to be adequate in representing the percentage biosorption of TY dye under the specified range of experiments. For quadratic models, the optimum point can be characterized as maximum, minimum, or saddle. It is possible to calculate the coordinates of the optimum point through the first derivate of the mathematical function, which describes the response surface and equates it to zero.

Table 7. Coefficients, t-statistics and significance probability of the model

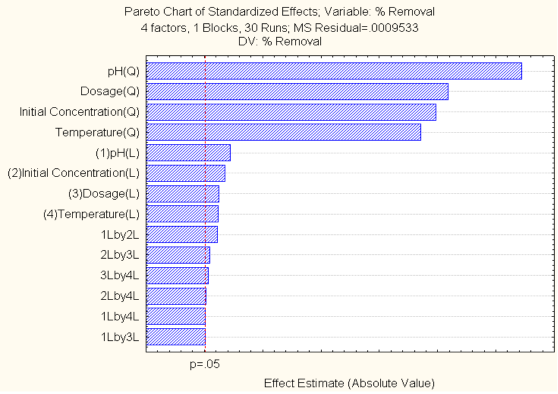


Fig 13:- Pareto chart biosorption of TY Dye

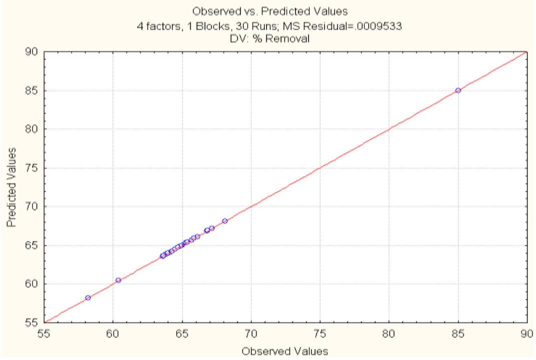


Fig 14:- Parity plot showing the distribution of experimental vs predicted values of percentage biosorption of TY dye

The parity plot (fig. 3.31) showed a satisfactory correlation between the experimental and predicted values of percentage removal of TY indicating good agreement of model data with the experimental data.

The results of the second order response surface model, fitting in the form of ANOVA were shown in table 5.16. The Fisher variance ratio, the F-value ($= S^2_r / S^2_e$), is a statistically valid measure to test the significance and adequacy of the model. The greater the F-value above unity, it is more certain that the factors adequately explain the variation in the data about its mean, and the estimated factor effects are real. The ANOVA of the regression model demonstrated that the model was highly significant, as is evident from the Fisher's F-test (F_{model} = 7944.258) and a very low probability value (P_{model}> F= 0.00000). More ever, the computed F-value ($F_{0.01(14.15)}$ = S^2_r/S^2_e =7944.258) was greater than the tabular F-value ($F_{0.01(14.15)tabular}$s = 2.42) at the 1% level, indicating that the treatment differences were significant.

Source of variation	Sum of squares (SS)	Degree of freedom (DF)	Mean squares (MS)
Model	2093.439	14	149.5313
Error	0.014	15	0.00093
Total	2093.453		

Table 8:- ANOVA for entire quadratic model

The correlation coefficient (R^2) provides a measure of the models variability in the observed response values. The closer the R^2 value to 1, the stronger the model is and it predicts the response better. In this present study, the value of the correlation coefficient indicated that 99.987 % of the variability in the response could be explained by the model. In addition, the value of the adjusted correlation coefficient (adj R^2 = 0.9974) was also very high to advocate for a high significance of the model. A higher value of the correlation coefficient justified an excellent correlation between the independent parameters.

The response surface contour plots of percentage biosorption of TY versus the interactive effect of pH, initial TY concentration, biosorbent dosage and temperature were shown in the figs 3.32 (a-f). Each contour plot represents a number of combinations of two test parameters with the other parameter maintained at zero levels. The maximum percentage biosorption of TY is indicated by the surface confined in the smallest curve (circular or elliptical) of the contour plot.

The optimal set of conditions for maximum percentage biosorption of TY dye is

pH	= 5.9549
Initial TY dye concentration	= 19.7484mg/L
Biosorbent dosage	= 30.3234g/L
Temperature	= 303.3380K.
The extent of % biosorption of TY dye	= 85.03392%.

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 TY dye is 90 %, which is closer to the predicted % biosorption.

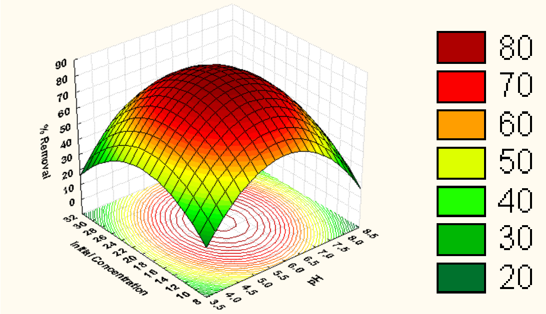


Fig 15:- Surface contour plot effect of pH and concentration on the % biosorption of TY dye

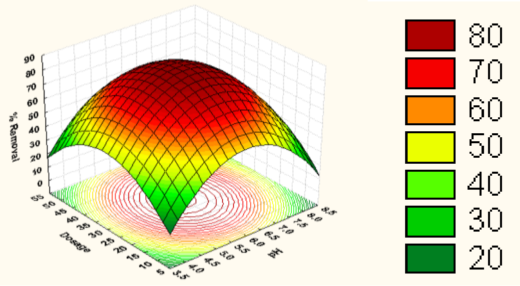


Fig 16:- Surface contour plot effect of pH and dosage on the %biosorption of TY dye

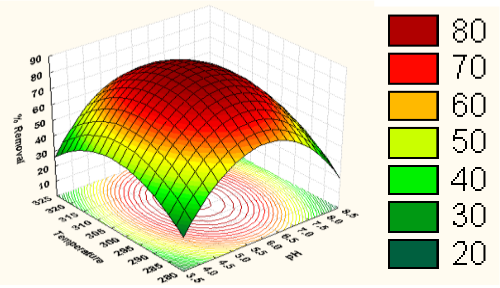


Fig 17:- Surface contour plot effect of pH and temperature on the % biosorption of TY dye

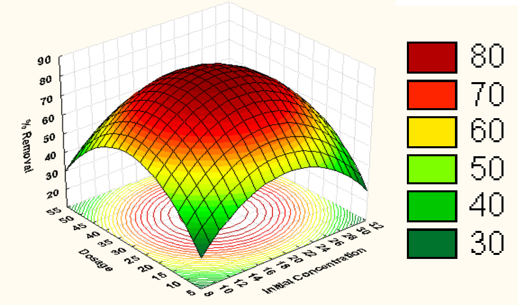


Fig 18:- Surface contour plot effect of concentration and dosage on the % biosorption of TY dye

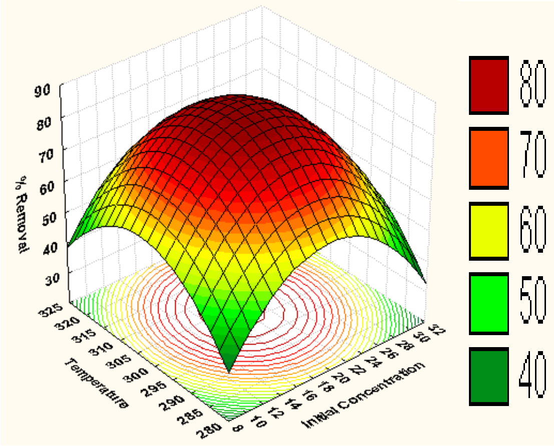


Fig 19:- Surface contour plot effect of concentration and temperature on the % biosorption of TY dye

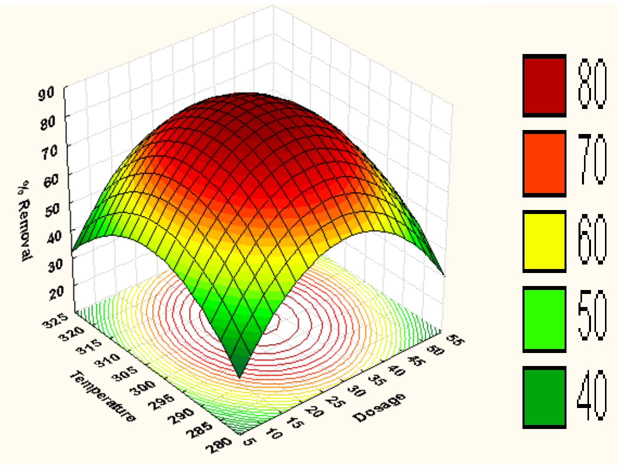


Fig 20:- Surface contour plot effect of dosage and temperature on the % biosorption of TY dye

The experimental and predicted % biosorption of TY at the optimum levels of process parameters were determined in table-3.17.

Parameters	Experimental	CCD
pH (X_1)	6	5.9549
Initial concentration(X_2), mg/L	20	19.7484
Biosorption dosage(X_3), w, g/L	40	30.3234
Temperature(X_4), K	303	303.3380
% biosorption of TY	90	85.03392

Table 9. Optimum values of experimental and predicted % biosorption

Author	Biosorbent	qt, mg/g
Aseel M. Aljeboree et al	coconut shell activated carbon	58.5
Sheikha S. Ashour	steam-activated carbons developed from date pits	42.1
N. Rajamohan	activated water hyacinth roots	13.46
P. N. Palanisamy et al	Activated carbon from Euphorbia tirucalli L wood	181.81
N. Rajamohan et al	activated plant biomass	112.34
G.Vijayakumar et al	natural adsorbent perlite	60.976
Present investigation	hyptis suaveolens	23.6933

Table 10:- Dye uptakes for different biosorbents

- *Characterization of hyptis suaveolens powder*

A. 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 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 [78-82].

- *FTIR spectrum of untreated TY dye*

FTIR spectrum of untreated hyptis suaveolens powder is presented in fig. 3.33 (a). The sharp peak at 897.29 cm^{-1} denotes the involvement and participation of S=O and C–S–O from ester sulphonate in biosorption. The bands at 1048.28 and 1047.14 cm^{-1} indicates the involvement of C–H bending bonds. The bands at 1645.53 cm^{-1} assigns the C–O stretching bond.

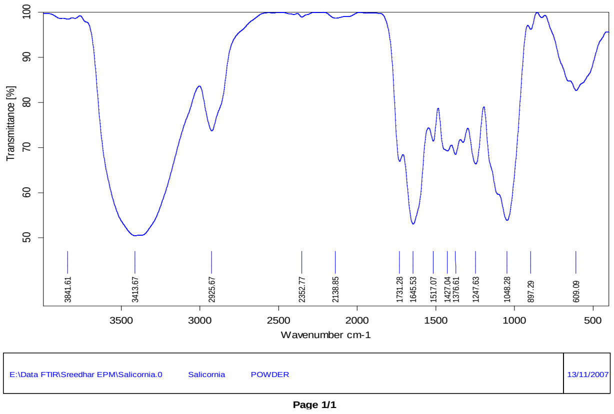


Fig 21:- FTIR spectrum of TY dye untreated hyptis suaveolens powder

FTIR spectrum for untreated powder is shown in fig 5.33 (a). a broad band at 609.09 cm^{-1} is due to the presence of 2,4 benzene deformation out of phase from bands. The broad absorption peaks at around 897.29 cm^{-1} indicates the presence of S = O and C–S–O bands from ester sulphonategroup. The band at 1048.28 cm^{-1} are due to the C–H bending vibrationsbond. The band at 1247.63 cm^{-1} denotes the presence of -SO 3 stretchingband. The band at 1517.08 cm^{-1} aredue to the presence of Amide N–H bending vibrationsbond. The band at 1645.53 cm^{-1} suggests the presence of Oleifinic C = C and Carbonyl C = O stretching bond. Similarly the bands at 1731.28 cm^{-1} are due to the presence of Assymetric stretching vibration of C = O.

- *FTIR spectrum of TY dye treated with hyptis suaveolens powder*

FTIR measurements for TY dye loaded algal biomass are shown in fig. 3.33 (b). The sharp peak at 1247.63 cm^{-1} is shifted to 1247.01 cm^{-1} denoting the involvement and participation of SO_3 streching in biosorption. The shifting of band from 1645.53 cm^{-1} to 1648.00 cm^{-1} indicates the involvement of streching of C=C aromatic rings. The characteristic of stretching modes of O–H (indicated by the band at 3413.67 cm^{-1}) is also not seen in untreated biomass.

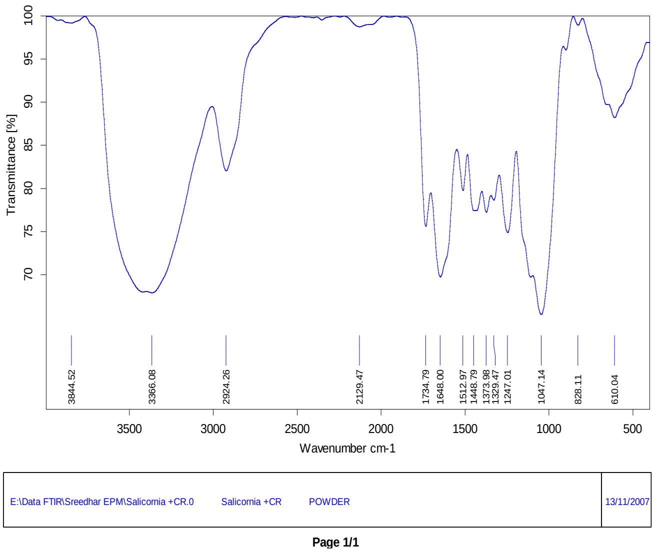


Fig 22:- FTIR spectrum of TY dye treated hyptis suaveolens powder

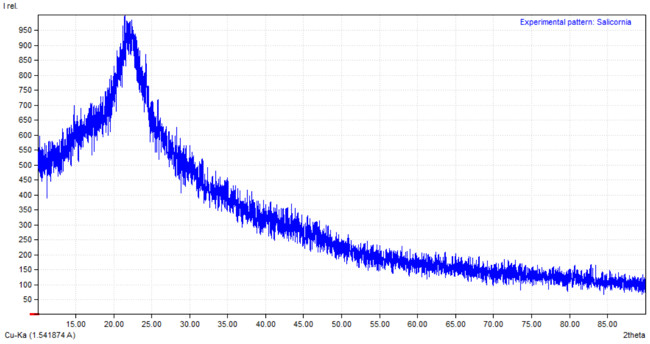
S. No.	Peaks in untreated powder, cm^{-1}	Peaks in treated powder, cm^{-1}	Description
1	609.09	---	2,4 benzene deformation out of phase
2	---	610.44	2,4 benzene deformation out of phase
3	---	828.11	S = O and C–S–O bands from ester sulphonate
4	897.29	---	S = O and C–S–O bands from ester sulphonate
5	---	1047.14	C–H bending vibrations
6	1048.28	---	C–H bending vibrations
7	---	1247.01	-SO 3 stretching
8	1247.63	---	-SO 3 stretching
9	---	1329.47	–CH 2 bending vibrations
10	---	1373.98	–CH 2 bending vibrations
11	1376.61	---	–CH 2 bending vibrations
12	1427.04	---	C–N stretching
13	---	1448.79	C–N stretching
14	---	1512.97	Amide N–H bending vibrations
15	1517.07	---	Amide N–H bending vibrations
16	1645.53	---	Oleificnic C = C and Carbonyl C = O stretching
17	---	1648.00	Oleifinic C = C and Carbonyl C = O stretching
18	1731.28	---	Assymetric stretching vibration of C = O
19	---	1734.39	Assymetric stretching vibration of C = O
20	---	2129.47	Assymetric stretching vibration of C = O
21	2138.85	---	Assymetric stretching vibration of C = O
22	2352.77	---	CH 2 stretching vibrations
23	---	2924.26	CH 2 stretching vibrations
24	2925.67	---	CH 2 stretching vibrations
25	3413.67	--	–OH stretching or –NH 2 stretching
26	---	3366.08	–OH stretching or –NH 2 stretching
27	3841.61	---	–OH stretching or –NH 2 stretching
28	---	3844.52	–OH stretching or –NH 2 stretching

Table 11. Shift of FTIR peaks for untreated and hyptis suaveolens powder treated TY dye

FTIR spectrum for treated powder is shown in fig 3.33 (b). A broad band at 610.44 cm^{-1} suggests the presence of 2,4 benzene deformation out of phase band. The band at 828.11 cm^{-1} is characteristic of S = O and C–S–O bands from ester sulphonate bond. The band at 1047.14 cm^{-1} is due to the presence of C–H bending vibrations group **[231-235]**. The bands at 1247.01, cm^{-1} are the indication for the presence of **-** SO 3 stretching bond. The bands at 1734.39, 2129.47 cm^{-1} contain Assymetric stretching vibration of C = O bond. The peaks at 3366.08, 3844.52 cm^{-1} represents –OH stretching or –NH 2 stretching bonds. The shifts in FTIR peaks are shown in table-3.19 and in turn confirm that bisorption was achieved.

B. 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.[83-87].



- *XRD for TY dye untreated with hyptis suaveolens powder*

XRD patterns of untreated powder are shown in figs.3.34 (a) & (b). XRD patterns shown in figs. 3.34(a) & (b) do not indicate sharp peaks, less crystallinity and exhibit little amorphous nature. The peaks at 2θ values of 11.62,12.12,14.53,17.78,20.39corroborate the presence of $F_{39}Sb_9Se_4$, Ho $N_{0.86}O_{4.14}Pb_{1.43}$, $C_{16}AgAlF_{36}O_4P_8$, $F_{11}K_2O_{27}Tc_9$, $C_{60}S_{16}$Theircorrespondingd-valuesare 0.9362,0.9259,0.9188,0.8972,0.8757 [88-93].

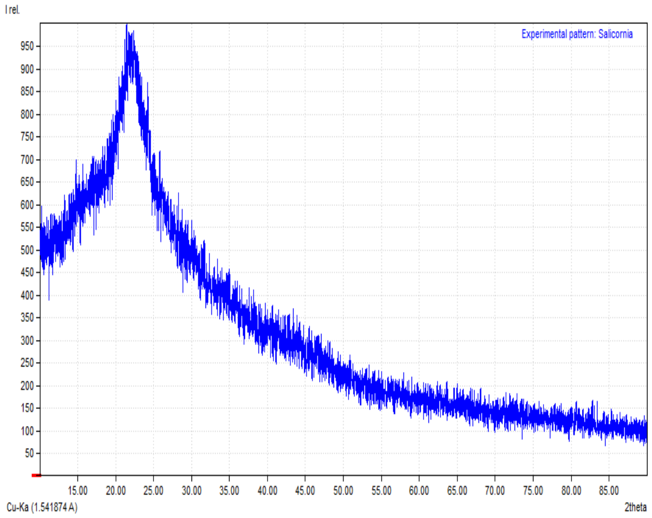


Fig 23:- XRD pattern of TY dye untreated hyptis suaveolens powder

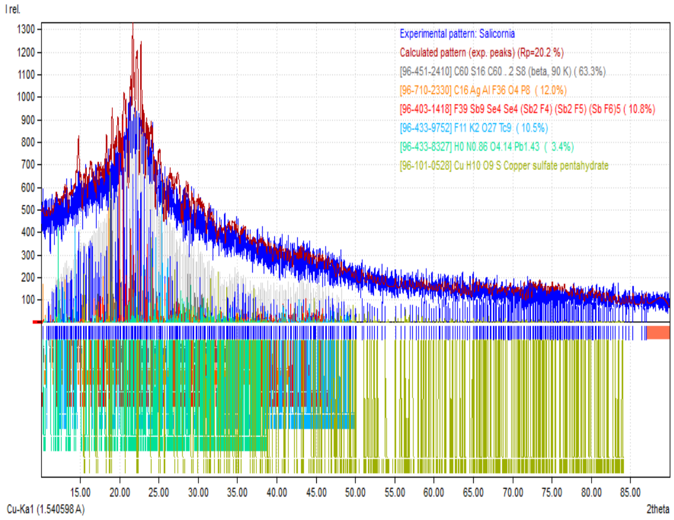


Fig 24:- XRD pattern ofTY dye untreated hyptis suaveolens powder with matching compounds

- *XRD for TY dye treated with hyptis suaveolens powder*

XRD patterns for treated powder [Figs.3.34 (c) & 3.34 (d)] exhibit good crystallinity, more amorphous nature and increase in surface area and porosity. The peaks at 2θ values of 14.39,15.60,15.46,13.79,15.46 corroborate the presence of $C_{36}I_{7.58}N_2Zn_3$, $F_{39}Sb_9Se_4$, $C_{60}S_{16}$, F_4ReS, $Co_2H_{33}N_{10}O_{18}S_4$and their corresponding d-values are 0.9388,0.9196,0.9083,0.8936,0.8944 [94--96].

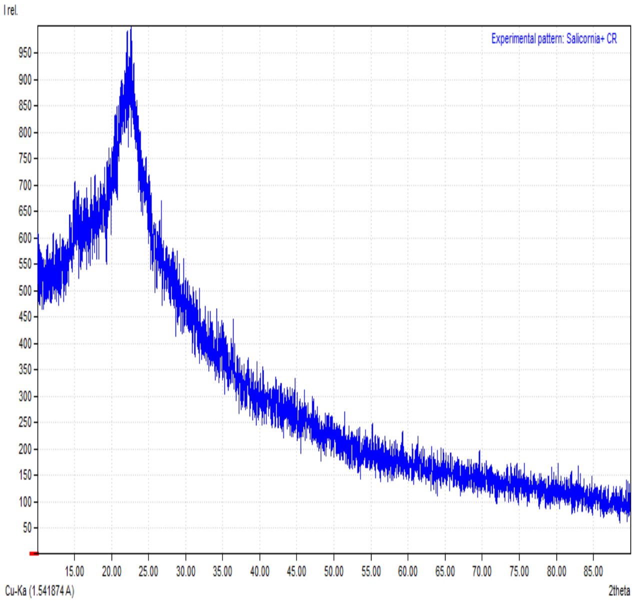


Fig 25:- XRD pattern of TY dye treated hyptis suaveolens powder

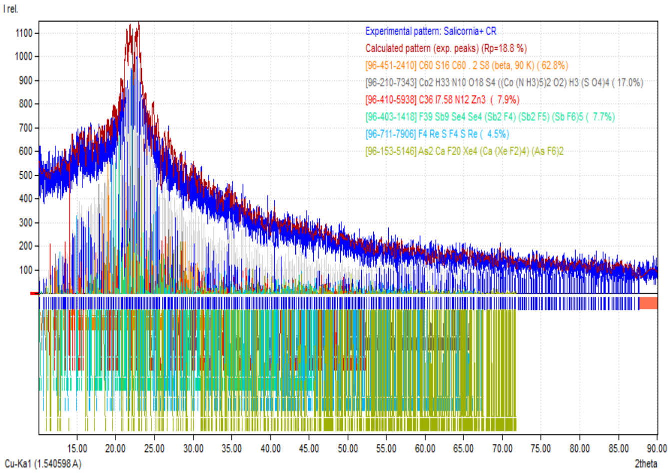


Fig 26:- XRD pattern of TY dye treated hyptis suaveolens powder with matching compounds

IV. CONCLUSIONS

- The equilibrium agitation time for TY dye biosorption is 40 minutes.
- The optimum dosage for biosorption is 35 g/L.
- Maximum extent of biosorption is noted at pH = 6.
- From the predicted values of RSM results, maximum biosorption of TY dye (85.03392 %) is observed when the processing parameters are set as pH = 5.9549, w = 30.3234 g/L, C_o = 19.7484 mg/L and T = 303.3380 K.
- The investigation also reveals the:
- endothermic nature of biosorption as ΔH is positive (7.1074 J/mole)

- spontaneity of the biosorption as ΔG is negative (–1491.44 J/mole)
- irreversible nature of biosorption as ΔS is positive (4.9457)

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