

# Studies on Biosorption of Titan Yellow Dye with Hypnea Musciformis Powder and Optimization Through Central Composite Design

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## Abstract

The major three resources like Air, Water and Food have been polluted and are seeking a special attention for their originality which has to be reestablished. The present research was investigated using Hypnea musciformis powder as a potential biosorbent for the removal of Titan Yellow. The operating parameters involved are agitation time, biosorbent size, and pH of the solution, initial concentration of solution, dosage of biosorbent and temperature of the solution. The optimization was also incorporated using Central Composite Design (CCD). The optimum size of biosorbent is 53  $\mu$ m, pH was obtained at 6.0 and initial concentration of INDIGO CARAMINE is 20 mg/L were compared using one factor at a time with CCD. The kinetics and isotherm studies are also studied along with thermodynamic study.

**Keywords:** Hypnea musciformis; Titan Yellow; biosorbent; CCD

## I. INTRODUCTION

Water – a priceless gift from the nature to the mankind. It is irreplaceable. The role of water in human life is noteworthy without which tasks such as running water for household activities, to rear cattle and farming, or for the industrial usage remain dormant [1]. There may be various reasons causing the degradation in quality of water day by day which include weathering, dissolution, precipitation, ion exchange, various biological processes, Sewage leakages, high population density, oil spillage, Industrial waste dumps, pollution of ground water through drilling activities, flooding during rainy season which carries waste deposits into our waters, radioisotopes, Heavy metal, Combustion, Toxic waste disposal at sea, Deforestation, Mining, Littering, Pesticides, herbicides and fertilizers, Failing septic system, House hold chemicals, Animal wastes [2]. In the recent years, population increase has been sharp and both the industrial and domestic needs of people increased tremendously [3]. Out of the several uses of water, drinking purpose holds a major role and ground water stands as a major source for drinking needs in most parts of India accounting for about 88% of safe drinking water in rural India For drinking and even 45% irrigation water is supplied from groundwater [4]. There are various techniques in use to treat water that has been polluted such as screening, filtration and centrifugal separation, Sedimentation, gravity separation, coagulation, flotation, Aerobic, Anaerobic, distillation, crystallization, evaporation, solvent extraction, reverse osmosis, ultra filtration, electro dialysis etc [5]. Industrial discharge has been the major chunk of wastewater contributors this has been one of the main causes of irreversible ecosystem degradation [6]. These facts remaining so, water consumption rates are increasing from 313 liters per capita day for the affluent to a mere 16 liters per capita day for the slum dweller [7]. The data obtained on monitoring quality of water exposed the fact that quality of water at most of the monitoring points is poor [8]. On evaluating the water quality for irrigation suggest that the majority of the groundwater samples are not good for irrigation in post monsoon this needs to be addressed since agriculture contributes 46% to the gross national product [9]. All these demand a sustainable utilization of water and its resources both effectively and efficiently without resulting into scarcity and degradation in the existing quality of water.

## II. EXPERIMENTAL PROCEDURE

### A. Preparation of the Biosorbent

Hypnea musciformis algae were collected from Jodugullapalem beach in Visakhapatnam and were washed with water to remove dust and soluble impurities and dried in sun light till the algae became crispy and colorless. By passing it through a set of sieves ranging from 300 to 75 mesh sizes the dried algae were finely powdered and sized. The powder of 53, 75, 105, 125 and 152 micron meters were separated and stored in dry bottles with double cap and used as biosorbent.

### B. Preparation of 1000 Mg/L of Indigo Carmine Dye Stock Solution

To prepare 1000 ppm of indigo carmine dye stock solution 1.0 g of 99 % Indigo Carmine dye powder was dissolved in 1.0 L

of distilled water. From this stock solution synthetic samples of different concentrations of Indigo Carmine dye were prepared by appropriate dilutions. 100 ppm Indigo Carmine dye stock solution was prepared by diluting 100 ml of 1000 ppm Indigo Carmine stock solution with distilled water in 1000 ml volumetric flask up to the mark. Similarly solutions with different dye concentrations such as 20, 50, 100, 150 and 200 ppm were prepared.

### C. Studies on Equilibrium Biosorption Process

The biosorption was carried out in a batch process by adding a pre-weighed amount of the *Hypnea musciformis* algae 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, which include characterization (FTIR, XRD, SEM), 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.

## III. RESULTS AND DISCUSSIONS

In the present investigation, the perspectives of two sorbents namely *Hypnea musciformis* powder and Dulce powder were evaluated to estimate their performance for the decolorization of Indigo carmine (I.C) and titan yellow (T.Y) dyes present in aqueous solutions. The effects of parameters on decolorization of I.C and T.Y dyes 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 *Hypnea musciformis* powder.

#### 1) Effect of Contact Time

Duration of equilibrium dye decolorization is defined as the time required for dyes concentration to reach a constant value during dye decolorization. The equilibrium contact time is determined by plotting the % dye decolorization of Titan yellow against contact time as shown fig. 4.18 for the interaction time intervals between 1 to 180 min. The % sorption is found to increase up to 40 min reaching 60 %.

The rate of sorption is fast in the initial stages because adequate surface area of the sorbent is available for the sorption of TY dye. As time increases more amount of TY dye gets adsorbed onto the surface of the sorbent due to forces of attraction and results in decrease of available surface area. The sorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the sorbent is exhausted. The maximum percentage of sorption is attained at 40 min of contact and becomes constant after 40 min indicating the attainment of the equilibrium with 53  $\mu\text{m}$  size of 10 g/L sorbent dosage mixed in 50ml of aqueous solution ( $C_0=20 \text{ mg/L}$ )[10-14].

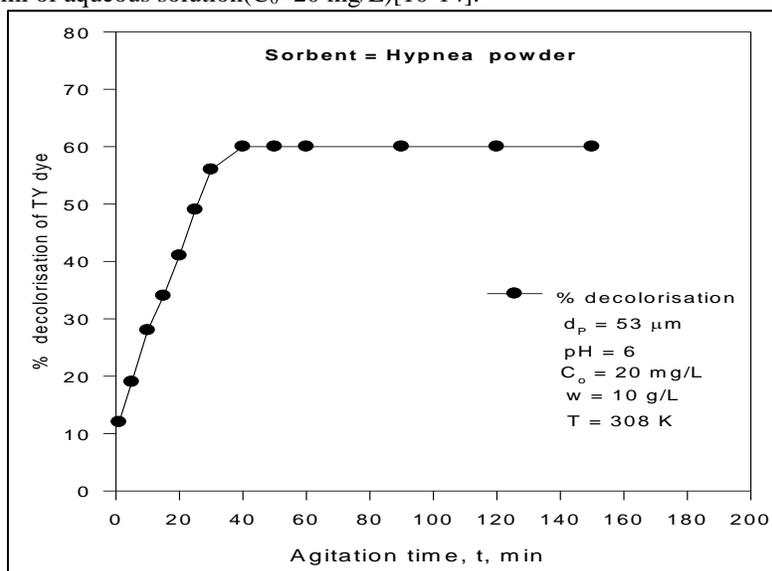


Fig. 4.18: Effect of contact time on % dye decolorization of TY dye

#### 2) Effect of Sorbent Size

The variations in % dye decolorization of TY dye from the aqueous solution with sorbent size are obtained. The results are drawn in fig.3.1 with percentage dye decolorization of TY dye as a function of sorbent size. The percentage sorption is increased from 46 to 60 % as the sorbent size is decreased from 152 to 53  $\mu\text{m}$ . As the size of the particle decreases, surface area of the sorbent enhances and extra number of active sites on the sorbent are available to the sorbate[15-19].

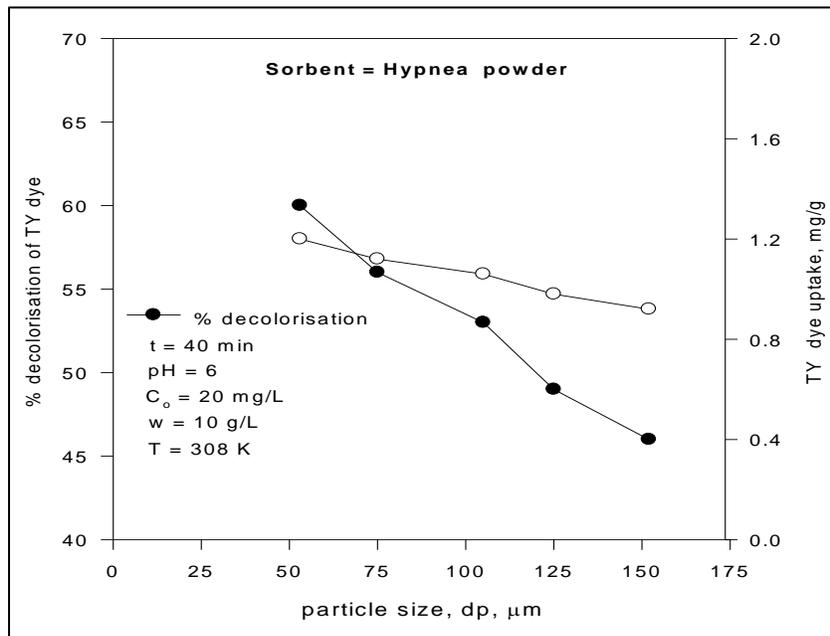


Fig. 3.1: % Dye decolorization of TY dye as a function of sorbent size

### 3) Effect of pH

pH controls dye decolorization by influencing the surface change of the sorbent, the degree of ionization and the species of biosorbate. In the present investigation, TY dye decolorization data are obtained in the pH range of 2 to 8 of the aqueous solution ( $C_0 = 20 \text{ mg/L}$ ) using  $10 \text{ g/L}$  of  $53 \mu\text{m}$  size sorbent. The effect of pH of aqueous solution on % dye decolorization of TY dye is shown in fig.4.20. The percentage sorption is increased from 45 % to 60 % as pH is increased from 2 to 6. The percentage sorption is decreased from 60 % to 46 % as pH increases from 6 to 8. The principal driving force for dye ion sorption is the electrostatic interaction between sorbent and sorbate. Low pH depresses dye decolorization due to competition with  $\text{H}^+$  ions for appropriate sites on the sorbent surface. However, with increasing pH, this competition weakens and TY dye ions replace  $\text{H}^+$  ions bound to the sorbent. The increase in sorption capacity at higher pH may also be attributed to the reduction of  $\text{H}^+$  ions which compete with TY dye lower pH. This is the reason for higher sorption of TY dye in the pH range of 6. At pH higher than 6, precipitation of TY dye occurred and sorption is reduced [20-29].

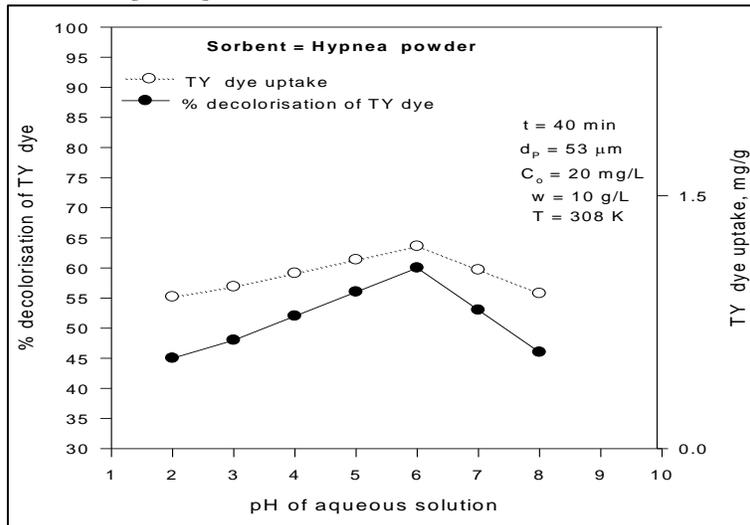


Fig. 3.2: Observation of pH along with % dye decolorization of TY dye

### 4) Effect of Initial Concentration of Titan Yellow Dye

The experiments were carried out using various concentrations of TY dye in the aqueous solution under the optimum size, pH values and equilibrium contact time. The effect of initial concentration of TY dye in the aqueous solution on the percentage dye decolorization of TY dye is shown in fig.3.3. The percentage sorption is decreased from 60 to 44 % as the initial concentration of TY dye increased from  $20 \text{ mg/L}$  to  $200 \text{ mg/L}$ . Such behavior can be attributed to the increase in the amount of sorbate to the uninterrupted number of freely active sites on the sorbent [30-39].

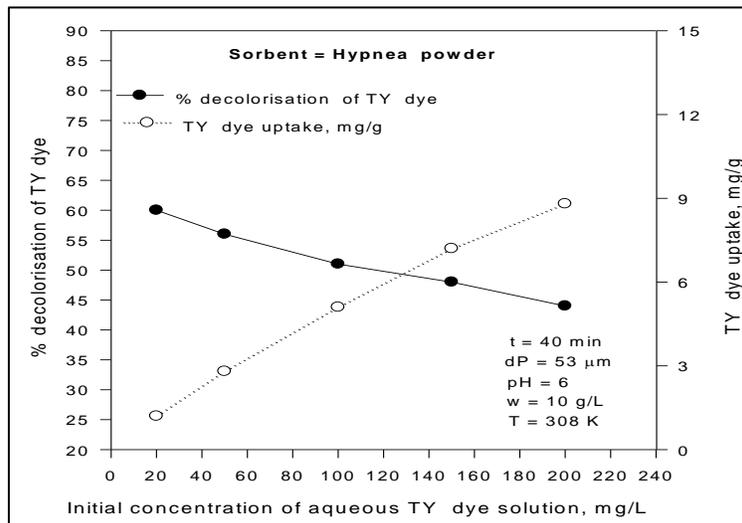


Fig. 3.3: Variation of initial concentration with % dye decolorization of TY dye

### 5) Effect of Sorbent Dosage

The percentage dye decolorization of TY dye is drawn against sorbent dosage for  $53 \mu\text{m}$  size sorbent in fig.3.4. The percentage sorption increased with increase in sorbent dosage. For a sorbent size of  $53 \mu\text{m}$ , percentage dye decolorization increased from 60% to 92%, as dosage is increased from 10 to 40 g/L. Such behavior is obvious because the number of available sites for dye removal would be more as the amount of the sorbent increases [40-59].

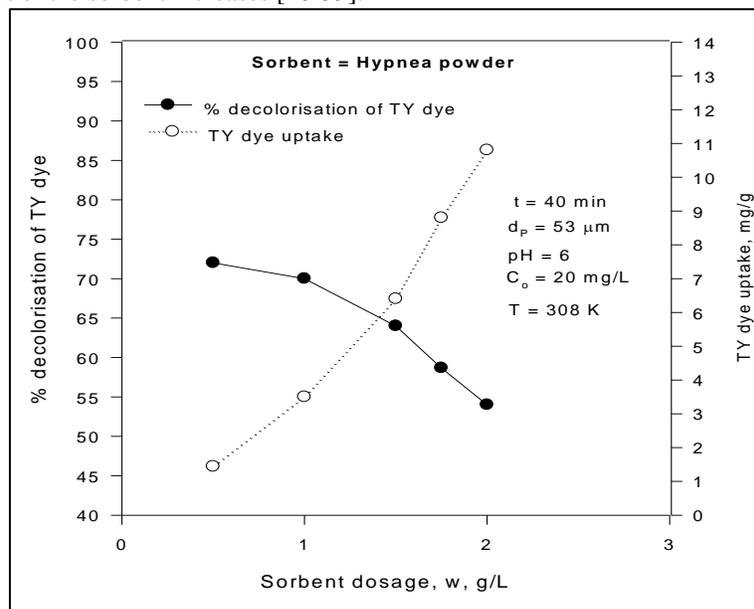


Fig. 3.4: Dependency of % dye decolorization of TY dye on sorbent dosage

### 6) Effect of Temperature

The effect of temperature on the equilibrium dye uptake was significant. The effect of changes in the temperature on the TY dye uptake is shown in Fig.3.5. When temperature was lower than 303 K, TY dye uptake increased with increasing temperature, but when temperature was over 303 K, the results were on the contrary. This response suggested a different interaction between the ligands on the cell wall and the dye. Below 303 K, chemical dye decolorization mechanisms played a dominant role in the whole dye decolorization process, dye decolorization was expected to increase by increase in the temperature [60-79] while at higher temperature, the plant powder were in a nonliving state, and physical dye decolorization became the main process. Physical dye decolorization reactions were normally endothermic, thus the extent of dye decolorization generally is constant with further increasing temperature.

The sorption capacity of dye is increased at higher temperatures, which indicates that sorption of dyes in this system is an endothermic process. This may be attributed to increased penetration of reactive dyes inside micropores at higher temperatures or the creation of new active sites. The formation of more than one molecular layer on the surface of hypnea powder appears to be achieved in the case of TY dye sorption at higher temperatures.

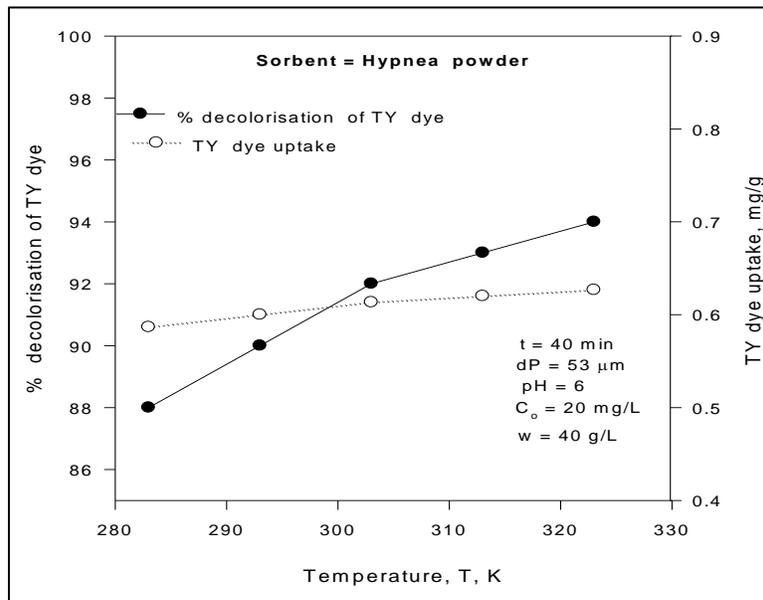


Fig. 3.5: Effect of temperature on % dye decolorization of TY dye

### 7) Equilibrium Isotherm Models

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

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

Each site can hold only one biosorbate specie

All sites are energetically equivalent

There are no interaction between the biosorbate species

The Langmuir relationship is hyperbolic and the equation is:

$$q_e/q_m = bC_e / (1+bC_e) \quad \dots\dots (3.1)$$

Equation (5.1) can be rearranged as

$$(C_e/q_e) = 1/(bq_m) + C_e/q_m \quad \dots\dots (3.2)$$

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

$0 < R_L < 1$  indicates favorable adsorption

$R_L > 1$  indicates unfavorable adsorption

$R_L = 1$  indicates linear adsorption

$R_L = 0$  indicates irrepressible adsorption

Langmuir isotherm, for the present data has yielded the equation

$$(C_e/q_e) = 0.0565 C_e + 6.4975$$

The correlation coefficient value of 0.99017 indicates strong binding of TY dye to the biosorbent.

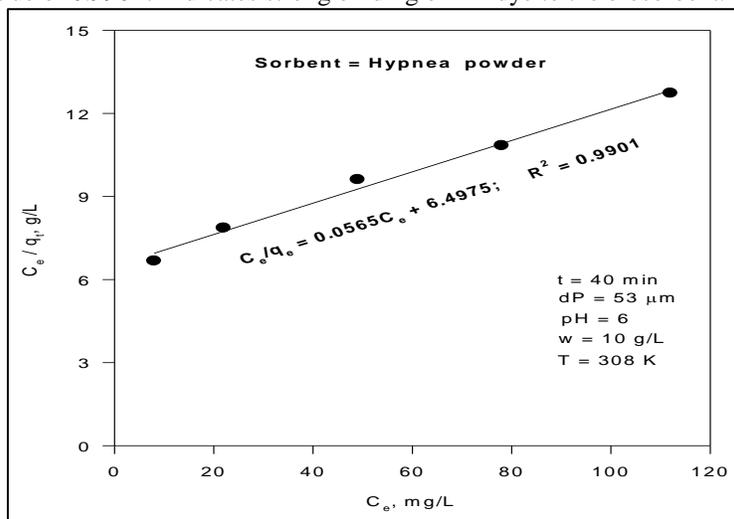


Fig. 3.6: Langmuir isotherm for % dye decolorization of TY dye

a) Freundlich isotherm:

Freundlich presented an empirical dye decolorization isotherm equation that can be applied in case of low and intermediate concentration ranges. It is easier to handle mathematically in more complex calculations.

The Freundlich isotherm is given by

$$q_e = K_f C_e^n$$

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

$$\ln q_e = \ln K_f + n \ln C_e$$

Freundlich isotherm is drawn between  $\ln C_e$  and  $\ln q_e$  in Fig.3.7 for the present data.

Drawn between  $\ln C_e$  and  $\ln q_e$ , has resulted the equation

$$\ln q_e = 0.7614 \ln C_e - 1.3640$$

The equation has a correlation coefficient of 0.99722.

The 'n' value of 0.761411 satisfies the condition of  $0 < n < 1$ , indicating favorable sorption

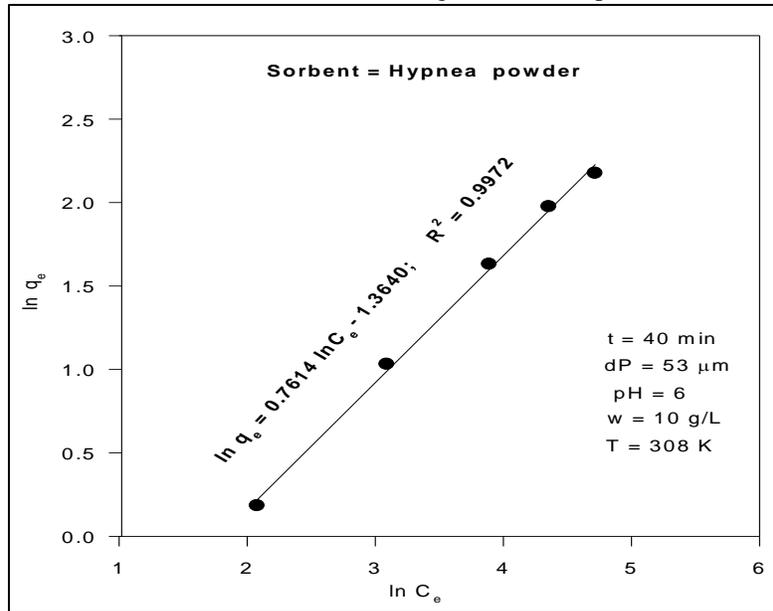


Fig. 3.7: Freundlich isotherm for % dye decolorization TY dye

b) Temkin isotherm:

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

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

The linear form of Temkin isotherm can be expressed as

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

where

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

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

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

$$b = RT / b(1)$$

The present data are analysed according to the linear form of Temkin isotherm and the linear plot is shown in Fig.4.26. The present data are analysed according to the linear form. The equation obtained for TY dye sorption is

$$q_e = 2.8683 \ln C_e - 5.3850$$

The correlation coefficient value is 0.9548.

The best fit model is determined based on the linear regression correlation coefficient (R). From the Figs 3.6,3.7 & 3.8, it is found that dye decolorization data are well explained by Langmuir isotherm (0.99017), Temkin (0.99722) and Freundlich isotherm (0.9548)[80-89].

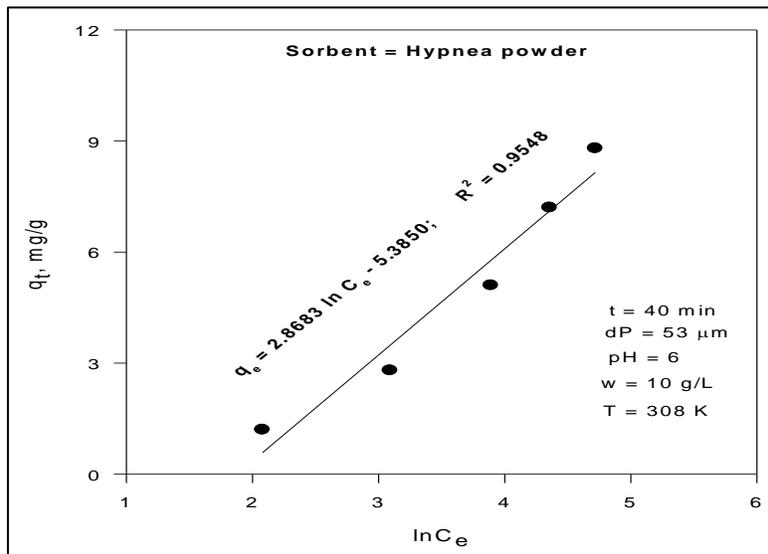


Fig. 3.8: Temkin isotherm for % dye decolorization of TY dye

Table - 4.9  
Isotherm Constants

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
$q_m = 17.69285 \text{ mg/g}$	$K_f = 0.25563 \text{ mg/g}$	$A_T = 0.152984 \text{ L/mg}$
$K_L = 0.008699$	$n = 0.761411$	$b_T = 892.763$
$R^2 = 0.99017$	$R^2 = 0.99722$	$R^2 = 0.9548$

8) Kinetics

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

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

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

The above equation can be presented as

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

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

$$\log (q_e - q_t) = -0.0253 t + 0.04426$$

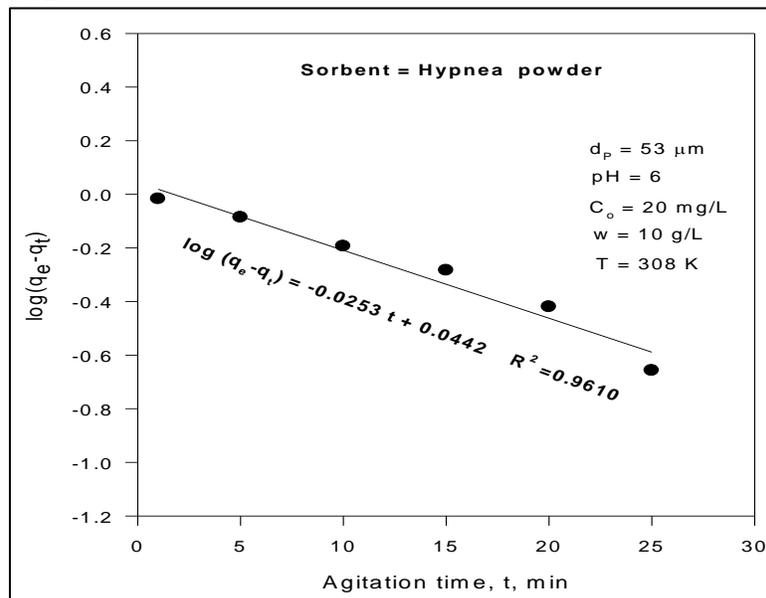


Fig. 3.9: first order kinetics for % dye decolorization of TY dye

Lagergren plot of  $\log (q_e - q_t)$  vs contact time ( $t$ ) and pseudo second order kinetics plot between ' $t$ ' vs ' $t/q_t$ ' for sorption of TY dye.

If the experimental results do not follow the above equation, they differ in two important aspects:

Kad ( $q_e - q_t$ ) does not represent the number of available dye decolorization sites and

$\log q_e$  is not equal to the intercept.

In such cases, pseudo second order kinetic equation:  $(dq_t/dt) = K (q_e - q_t)^2$  is applicable, where

'K' is the second order rate constant.

The other form of the above equation is:  $(dq_t / (q_e - q_t)^2) = K dt$

let  $q_e - q_t = x$

$dq_t = dx$

$1/x = K x + C$

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

Substituting these values in above equation, we obtain:

$1/(q_e - q_t) = Kt + (1/q_e)$

Rearranging the terms, we get the linear form as:

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

$t/q_t = 0.8414 t + 7.1968$

In the present study, the kinetics are investigated with 50 mL of aqueous solution ( $C_0 = 20$  mg/L) at 303 K with the interaction time intervals of 1 min to 180 min. Lagergren plots of  $\log (q_e - q_t)$  versus contact time (t) for dye decolorization of TY dye the sorbent size (53  $\mu\text{m}$ ) of *Hypnea* powder in the interaction time intervals of 1 to 180 min are drawn in figs.4.27 & 4.28.

The following equations and constants are obtained for Lagergren first order and pseudo second order kinetics.

$\log (q_e - q_t) = -0.0253 t + 0.04426$  with a correlation coefficient 0.96107

$t/q_t = 0.8414 t + 7.1968$  with a correlation coefficient 0.89137

Summarize rate constant values for first and second order rate equations. It is noted that both first and second order rate equations explain the sorption interactions. 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.

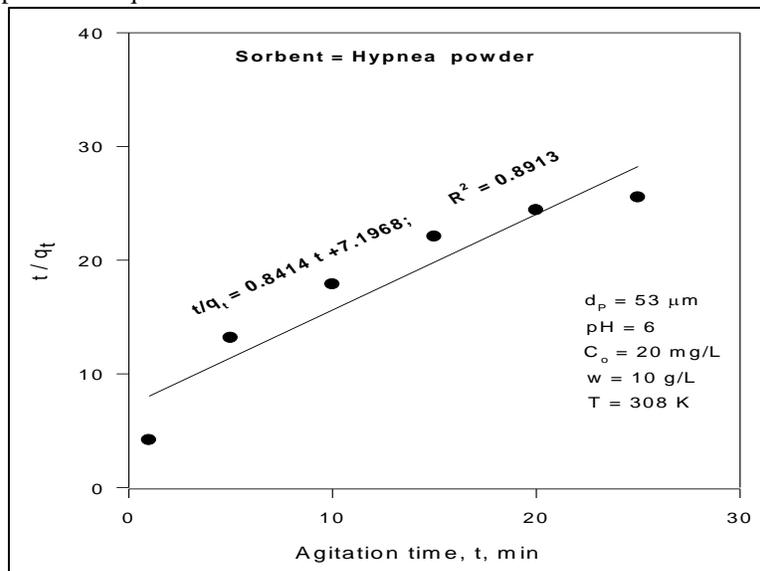


Fig. 3.10: second order kinetics for % dye decolorization of TY dye

The pseudo second order model [90-99] based on above equation, considers the rate-limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the biosorbate and sorbent.

Table - 4.10

Equations and rate constants

Order	Equation	Rate constant	R <sup>2</sup>
Lagergren first order	$\log (q_e - q_t) = -0.0253 t + 0.04426$	$0.058266 \text{ min}^{-1}$	0.96107
Pseudo Second order	$t/q_t = 0.8414 t + 7.1968$	$0.09839 \text{ g/(mg-min)}$	0.89137

### 9) Thermodynamics of Sorption

Dye decolorization is temperature dependant. In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of dye decolorization ( $\Delta H$ ), change in entropy of dye decolorization ( $\Delta S$ ) and change in Gibbs free energy ( $\Delta G$ ).

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

The  $\Delta H$  is related to  $\Delta G$  and  $\Delta S$  as

$$\Delta G = \Delta H - T \Delta S$$

$\Delta S < 1$  indicates that dye decolorization is impossible whereas  $\Delta S > 1$  indicates that the dye decolorization is possible.  $\Delta G < 1$  indicates the feasibility of sorption.

The Vant Hoff's equation is

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

Where  $(q_e / C_e)$  is called the dye decolorization affinity.

If the value of  $\Delta S$  is less than zero, it indicates that the process is highly reversible. If  $\Delta S$  is more than or equal to zero, it indicates the reversibility of process. The negative value for  $\Delta G$  indicates the spontaneity of dye decolorization. Whereas the positive value indicates is non spontaneity of sorption.

Experiments are conducted to understand the dye decolorization behavior varying the temperature from 283 to 323 K. the plots indicating the effect of temperature on dye decolorization of TY dye for different initial dye concentrations are shown in fig.4.29. 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  $-12210.6$  J/mole indicates that sorption of TY dye by hypnea powder could take place spontaneously. Higher temperatures have benefitted sorption and increased the equilibrium sorption capacity[80-89].

Positive  $\Delta H$  of  $14.53268$  J/mole indicates indicates endothermic nature of sorption while positive  $\Delta S = 39.69203$  J/mole-K demonstrates the affinity of hypnea powder to TY dye

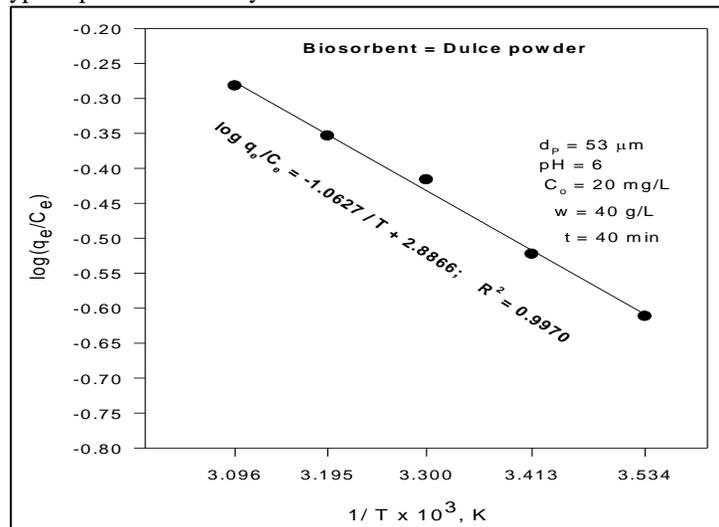


Fig. 3.11: Vantoff's plot for % dye decolorization of TY dye

### 10) Optimization of the Selected Parameters using CCD

In the present study, the levels of four process input variables for % dye decolorization

Based on the results of the preliminary experimental studies, pH, initial TY dye concentration, sorbent dosage and temperature were chosen as the independent input variables and percentage dye decolorization was used as the dependent output variable. A CCD was employed to analyze the interactive effects of these parameters and to arrive for an optimum values. The experiments with different pH values of 3–7, different TY dye concentrations of 10–30 mg/L, different sorbent dosages of 20–40 g/L and different temperatures of 283–323 K were coupled to each other and varied simultaneously to cover the combination of parameters in the CCD. The levels and ranges of the chosen independent parameters used in the experiments for the removal of TY dye were given in Table 3.11.

Table – 3.11

Levels of different process variables in coded and un-coded form for % dye decolorization of Titan yellow dye using Hypnea powder

Variable	Name	Range and levels				
		-2	-1	0	1	+2
$X_1$	pH of aqueous solution	3	4	5	6	7
$X_2$	Initial TY dye concentration, $C_o$ , mg/L	10	15	20	25	30
$X_3$	Sorbent dosage, w, g/L	20	25	30	35	40
$X_4$	Temperature, K	283	293	303	313	323

The percentage % decolorization of TY dye (Y) is a function of pH ( $X_1$ ),  $C_o$  ( $X_2$ ), w ( $X_3$ ), and T ( $X_4$ ). The variations in the corresponding coded values of four parameters and response are presented depending on experimental runs and predicted values proposed by CCD design. The following equation represents multiple regression analysis of the experimental data

$$Y = -1484.84 + 51.19 X_1 + 4.35 X_2 + 1.35 X_3 + 8.92 X_4 - 4.64 X_1^2 - 0.07 X_2^2 - 0.02 X_3^2 - 0.01 X_4^2 - 0.06 X_1 X_2 - 0.01 X_1 X_3 - 0.02 X_1 X_4 - 0.000 X_2 X_3 - 0.000 X_2 X_4 + 0.000 X_3 X_4$$

From the Fisher’s F-test and a very low probability value ( $P_{\text{model}} > F = 0.000000$ ), the ANOVA of the model clearly explains that the model is highly significant. It shows that the treatment differences are significant.

The ‘t’ and ‘P’ values are analyzed to predict the response.

It is found that  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_1^2$ ,  $X_2^2$ ,  $X_3^2$ ,  $X_4^2$ ,  $X_1X_2$ ,  $X_1X_3$ ,  $X_1X_4$  have high significance to explain the individual and interaction effects of input variables on sorption of TY dye. The regression coefficient value of 0.9994 indicates that 0.006 % of the total variations are not satisfactorily explained by the model [100-114].

Table – 3.12

Results from CCD for Titan Yellow dye decolorization by *Hypnea musciformis* algae powder

Run no.	$X_1(\text{pH})$	$X_2(\text{Co})$	$X_3(\text{w})$	$X_4(\text{T})$	% dye decolorization of Titan yellow dye	
					Experimental	Predicted
1	5	15	30	293	86.68	86.73792
2	5	15	30	313	87.52	87.57917
3	5	15	50	293	87.32	87.40250
4	5	15	50	313	88.52	88.41125
5	5	25	30	293	86.91	86.64417
6	5	25	30	313	86.62	86.65292
7	5	25	50	293	86.62	86.63625
8	5	25	50	313	86.72	86.81250
9	7	15	30	293	86.52	86.56917
10	7	15	30	313	88.19	88.10792
11	7	15	50	293	87.68	87.58125
12	7	15	50	313	88.88	89.28750
13	7	25	30	293	85.22	85.26292
14	7	25	30	313	85.91	85.96917
15	7	25	50	293	85.52	85.60250
16	7	25	50	313	86.6	86.47625
17	4	20	40	303	78.22	78.27458
18	8	20	40	303	77.9	77.76958
19	6	10	40	303	91.36	91.21458
20	6	30	40	303	88.24	88.30958
21	6	20	20	303	88.79	88.85125
22	6	20	60	303	90.16	90.02292
23	6	20	40	283	89.8	89.85458
24	6	20	40	323	91.7	91.56958
25	6	20	40	303	96.6	96.60000
26	6	20	40	303	96.6	96.60000
27	6	20	40	303	96.6	96.60000
28	6	20	40	303	96.6	96.60000
29	6	20	40	303	96.6	96.60000
30	6	20	40	303	96.6	96.60000

Table – 3.13

Estimated regression coefficients for the TY dye decolorization onto *Hypnea musciformis* algae powder

Terms	Regression coefficient	Standard error of the coefficient	t-value	P-value
Constant	-1484.84	30.99640	-47.904	0.000000
$X_1$	51.19	1.32467	38.643	0.000000
$X_2$	-4.64	0.03145	-147.670	0.000000
$X_3$	4.35	0.26150	16.633	0.000000
$X_4$	-0.07	0.00126	-54.352	0.000000
$X_1 * X_1$	1.35	0.13075	10.326	0.000000
$X_2 * X_2$	-0.02	0.00031	-56.936	0.000000
$X_3 * X_3$	8.92	0.19363	46.093	0.000000
$X_4 * X_4$	-0.01	0.00031	-46.801	0.000000
$X_1 * X_2$	-0.06	0.00824	-7.361	0.000002
$X_1 * X_3$	0.01	0.00412	2.110	0.052101*
$X_1 * X_4$	0.02	0.00412	4.234	0.000721
$X_2 * X_3$	-0.00	0.00082	-4.083	0.000980
$X_2 * X_4$	-0.00	0.00082	-5.054	0.000143
$X_3 * X_4$	0.00	0.00041	1.017	0.325335*

Fischer’s ‘F-statistics’ value is defined as ( $=MS_{\text{model}}/MS_{\text{error}}$ ), where MS (mean square). Fischer’s ‘F-statistics’ value, having a low probability ‘p’ value, indicates high significance. The ANOVA of the regression model is sufficiently great, as proven from the Fisher’s F-test ( $F_{\text{model}} = 1797.08$ ) and has a very low probability value ( $P_{\text{model}} > F = 0.000000$ ). Besides, the computed F-value [ $F_{0.05(14,15)} = MS_{\text{model}}/MS_{\text{error}} = 1797.08$ ] is much higher compared to F-value ( $F_{0.05(14,15)} \text{ tabulars} = 2.42$ ) at 5% level, suggesting that the treatment differences are sufficiently great.

Measure of the models variability to the responses indicated is presented by correlation coefficient ( $R^2$ ). As  $R^2 \rightarrow 1$  inviolable is the model and response is estimated better. In our study,  $R^2 = 0.9896$  suggests that 1.2 % of the total variations are not adequately explained by the model. Statistical relevance of the ratio of mean due to regression and mean square due to residual error is tested with the help of ANOVA. From table-3.14, it is clear that, F statistics value for entire model is quite evident. This value implicates that % dye decolorization can be sufficiently explained by the model equation whereas P values lower than 0.05 refers that the model is considered to be statistically significant at the 95 % confidence level.

Table – 3.14

Analysis of variance (ANOVA) of Titan yellow dye decolorization for entire quadratic model

Source of variation	SS	Df	Mean square(MS)	F-value	P> F
Model	682.5681	14	48.7548	1797.08	0.00000
Error	0.4070	15	0.02713		
Total	682.9751				

a) Interpretation of Residual Graphs:

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

Normal probability plot (NPP) is a graphical technique used for analyzing whether or not data set is normally distributed to greater extent. This NPP plot is used to check normality of data obtained. The difference between the observed and the predicted values from the regression is termed as residual. Fig. 3.12 exhibits normal probability plot for the present data. It is evident that the experimental data are reasonably aligned implying normal distribution.

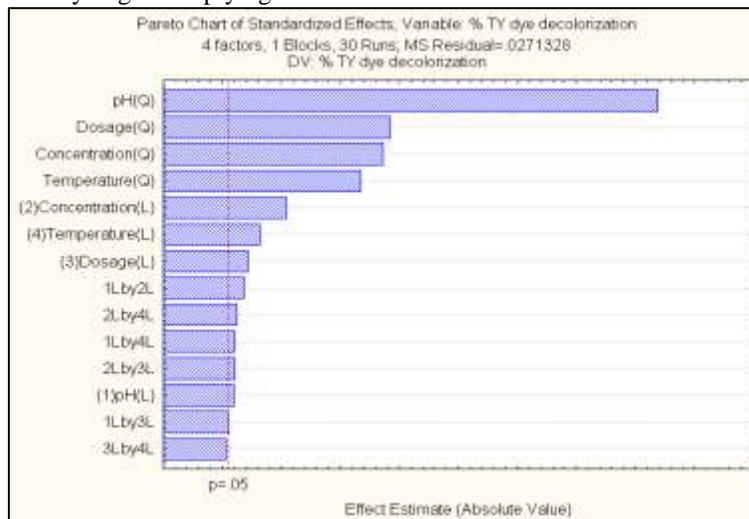


Fig. 3.12: Pareto Chart

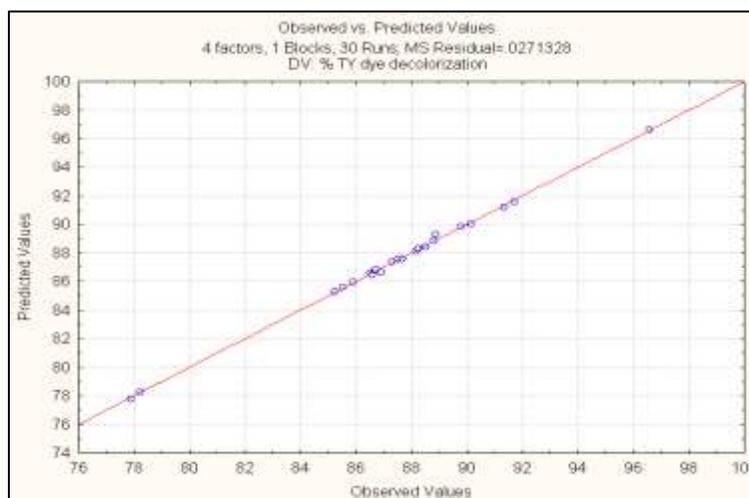


Fig. 3.13: Normal probability plot for % dye decolorization of Titan yellow dye

11) Interaction effects of dye decolorization variables:

The three-dimensional view of response surface plots.

The % sorption of sorbent is maximal at low and high levels of the variables but there is a region where increasing/decreasing trend in % sorption is not observed. The predicted optimum values for percentage sorption of TY dye are Three-dimensional view

of response surface plots [Fig. 3.14 (a) to 3.14 (f)] exhibit % dye decolorization of the Titan yellow dye using *Hypnea musciformis* algae powder for different combinations of independent variables. All the plots are delineated as a function of two factors at a time, imposing other factors fixed at zero level. It is evident from response surface plots that the % dye decolorization of Titan yellow dye is maximal at low and high levels of the variables. But a dead region prevails where increasing or decreasing trend in % TY dye decolorization is not found. This behavior conforms that there is a presence of optimum for the TY dye decolorization variables in order to maximize % TY dye decolorization. The role played by all the variables is so vital in % dye decolorization of Titan yellow dye and seen clearly from the plots.

The predicted optimal set of conditions for maximum percentage dye decolorization of Titan yellow dye is:

pH of aqueous solution = 5.9977,

Initial Indigo caramine dye ion concentration = 18.8661 mg/L

Dye decolorization dosage = 40.9428 g/L and

Temperature = 304.6288 K.

The extent of dye decolorization of Indigo caramine dye at these optimum conditions is 96.73 %.

It is evident that experimental values of % TY dye decolorization 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 percentage dye decolorization of Titan yellow dye is 96.73 %, which is closer to the predicted % dye decolorization. The experimental optimum values are compared with optimum values predicted by CCD in table-3.15.

Table – 3.15

Comparison between optimum values from CCD and Experimentation

Variable	CCD	Experimental value
pH of aqueous solution	5.9977	6.0
Titan yellow dye concentration, mg/L	18.8661	20
Sorbent dosage, w, g/L	40.9428	40
Temperature, K	304.6288	303
% TY dye decolorization	96.73	92

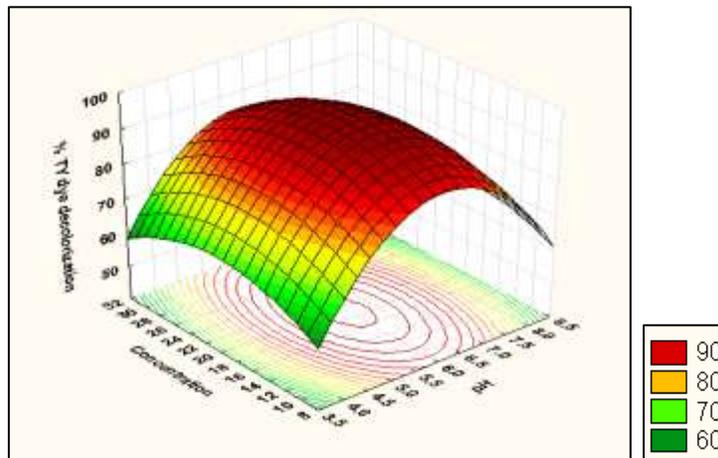


Fig. 3.14: (a). Surface contour plot effect of pH and concentration on the % TY dye decolorization

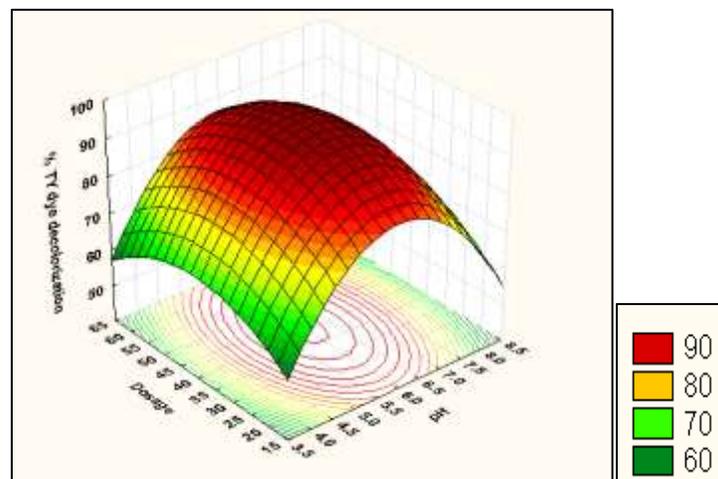


Fig. 3.14: (b). Surface contour plot effect of pH and dosage on the % TY dye decolorization

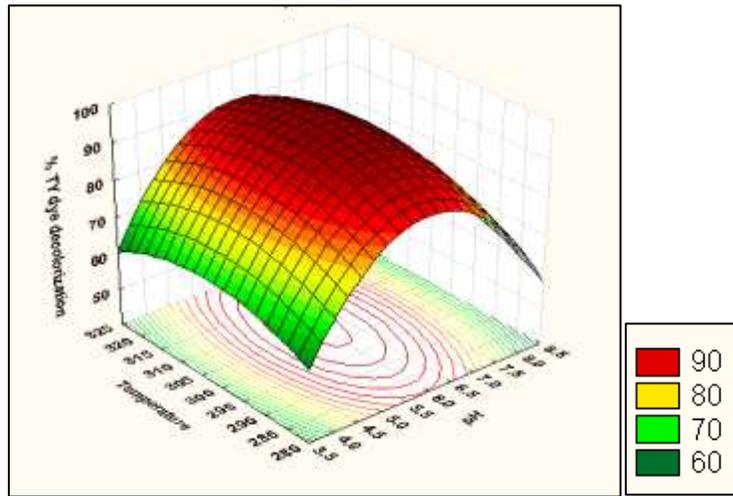


Fig. 3.14: (c). Surface contour plot effect of pH and temperature on the % TY dye decolorization

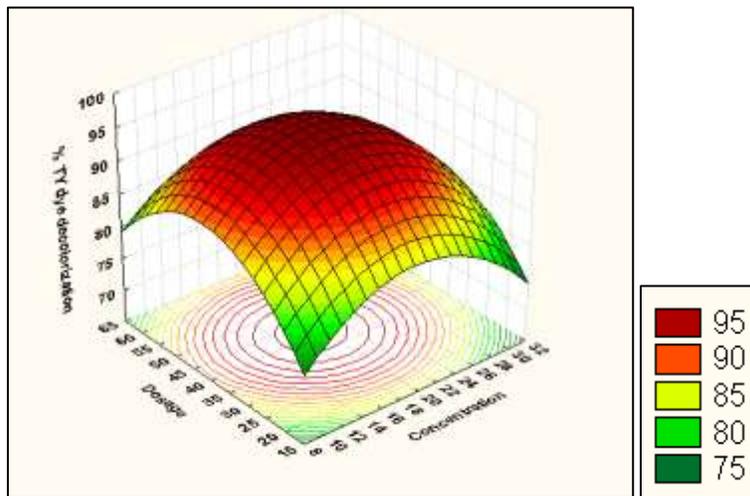


Fig. 3.14: (d). Surface contour plot effect of conc and dosage on the % TY dye decolorization

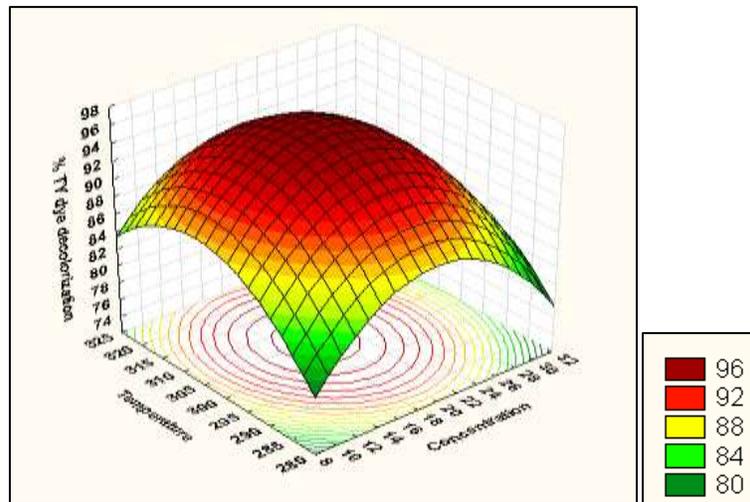


Fig. 3.14: (e). Surface contour plot effect of conc and temperature on the % TY dye decolorization

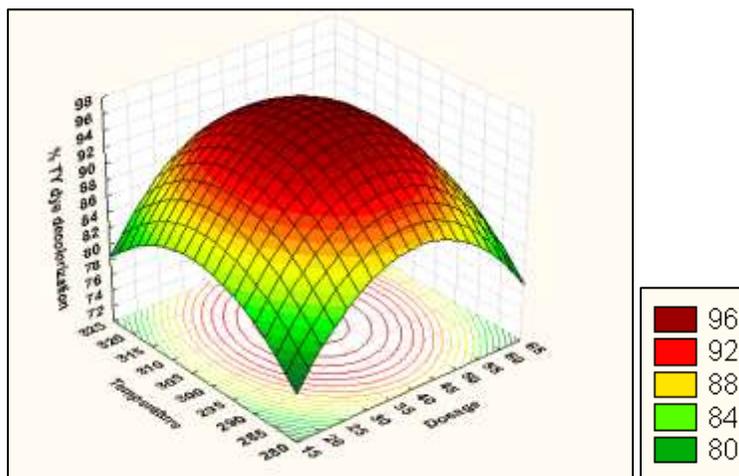


Fig. 3.14: (f). Surface contour plot effect of dosage and temperature on the % TYdye decolorization

### 12) Characterization of *Hypnea musciformis*algae powder

a) FTIR spectrum of untreated *Hypnea musciformis*algae powder

FTIR spectrum for treated powder is shown in fig 3.15(a). A broad band at  $617.66\text{ cm}^{-1}$  is due to the presence of 2, 4 benzene deformations out of phase. The broad absorption peaks at around  $1055.96\text{ cm}^{-1}$  indicates the presence of C–H bending vibrations. The band at  $1382.22\text{ cm}^{-1}$  due to  $-\text{CH}_2$  bending vibrations. The band at  $1650.87\text{ cm}^{-1}$  denotes presence of Oleifinic C = C and Carbonyl C = O stretching. The band at  $1537.84\text{ cm}^{-1}$  due to the presence of Amide N–H bending vibrations. The band at  $2861.78\text{ cm}^{-1}$  suggests the presence of C–H-stretching. The band at  $2927.54\text{ cm}^{-1}$  due to the presence of  $\text{CH}_2$  stretching vibrations. The band at  $1449.24\text{ cm}^{-1}$  indicates the presence of C–N stretching. The band at  $1250.05\text{ cm}^{-1}$  due to the presence of  $-\text{SO}_3$  stretching. The band at  $3348.84\text{ cm}^{-1}$  due to  $-\text{OH}$  stretching or  $-\text{NH}_2$  stretching. The shifts in FTIR peaks are shown in table-4.16.

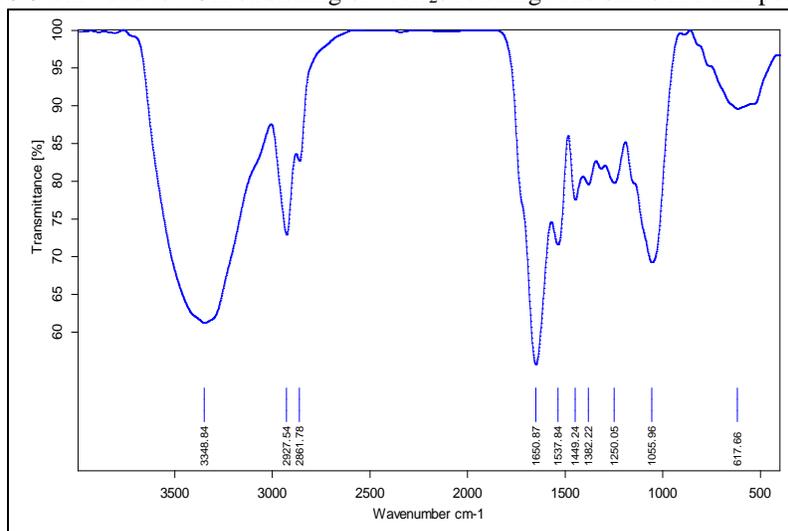


Fig. 3.15: (a) FTIR spectrum of untreated *Hypnea musciformis*algae powder

b) FTIR spectrum of treated *Hypnea musciformis*algae powderwith TY dye

FTIR spectrum for treated powder is shown in fig 4.33(b). A broad band at  $619.97\text{ cm}^{-1}$  due to the presence of 2,4 benzene deformation out of phase. The bond at  $1052.84\text{ cm}^{-1}$  is suggests the presence of C–H bending vibrations. The band at  $1251.28\text{ cm}^{-1}$  is characteristic of  $-\text{SO}_3$  stretching. The band at  $1378.90\text{ cm}^{-1}$  due to the presence of  $-\text{CH}_2$  bending vibrations. The band at  $1450.04\text{ cm}^{-1}$  is indicates the presence of C–N stretching. The band at  $1533.30\text{ cm}^{-1}$  due to the presence of Amide N–H bending vibrations. The band at  $1650.60\text{ cm}^{-1}$  denotes the presence of Oleifinic C = C and Carbonyl C = O stretching. The band at  $2861.19\text{ cm}^{-1}$  suggests the presence of C–H-stretching. The band at  $2927.71\text{ cm}^{-1}$  is characteristics of  $\text{CH}_2$  stretching vibrations. The band at  $3355.20\text{ cm}^{-1}$  due to the presence of  $-\text{OH}$  stretching or  $-\text{NH}_2$  was stretching [115-129]. The shifts in FTIR peaks are shown in table-4.16.

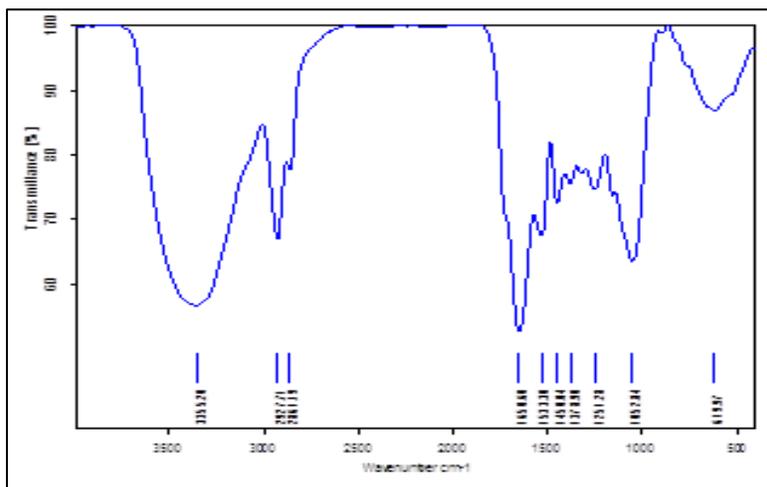
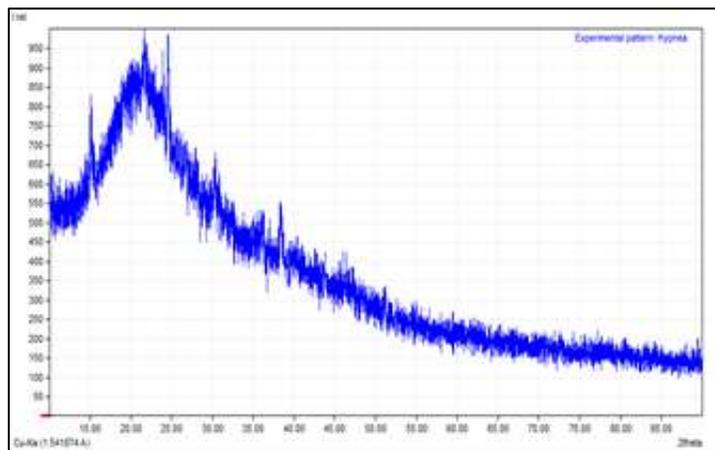


Fig. 3.15: (b) FTIR spectrum of treated Hypnea musciformis powder with TY dye

Table - 3.16  
Shift of FTIR peaks for untreated and treated Hypnea musciformis powder

S No	Before sorption Untreated Hypnea	After sorption TY treated Hypnea	Band
1	617.66		2,4 benzene deformation out of phase
2		619.97	2,4 benzene deformation out of phase
3	1055.96		C-H bending vibrations
4		1052.84	C-H bending vibrations
5	1250.05		-SO <sub>3</sub> stretching
6		1251.28	-SO <sub>3</sub> stretching
7	1382.22		-CH <sub>2</sub> bending vibrations
8		1378.90	-CH <sub>2</sub> bending vibrations
9	1449.24		C-N stretching
10		1450.04	C-N stretching
11	1537.84		Amide N-H bending vibrations
12		1533.30	Amide N-H bending vibrations
13	1650.87		Olefinic C = C and Carbonyl C = O stretching
14		1650.60	Olefinic C = C and Carbonyl C = O stretching
15	2861.78		C-H-stretching
16		2861.19	C-H-stretching
17	2927.54		CH <sub>2</sub> stretching vibrations
18		2927.71	CH <sub>2</sub> stretching vibrations
19	3348.84		-OH stretching or -NH <sub>2</sub> stretching
20		3355.20	-OH stretching or -NH <sub>2</sub> stretching

c) XRD pattern spectrum of untreated Hypnea musciformis powder  
XRD patterns did not indicate sharp peaks, less crystallinity and exhibit little amorphous nature. The peaks at 2θ values of 14.87, 18.35, 15.02, 16.16 and 19.63 corroborate the presence of C<sub>36</sub>17.58N<sub>12</sub>Zn<sub>3</sub>CS<sub>3</sub>S<sub>67</sub>Se<sub>4</sub>(Sb<sub>2</sub>F<sub>4</sub>)(Sb<sub>2</sub>F<sub>5</sub>)(S<sub>6</sub>F<sub>6</sub>)<sub>5</sub>, A<sub>12</sub>CaH<sub>10</sub>O<sub>21</sub>Si<sub>6</sub>F<sub>4</sub>MoS (ICDD files). Their corresponding d-values are 0.9348, 0.9262, 0.9181, 0.9001 and 0.9081



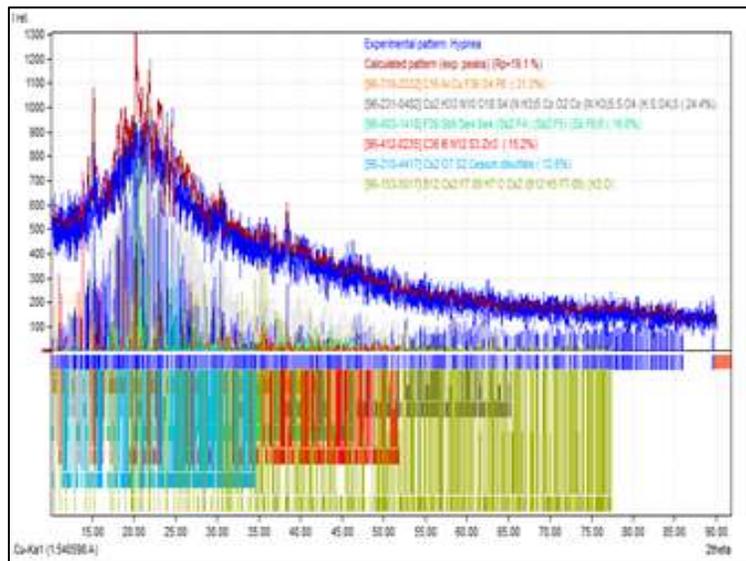


Fig. 3.16: (a) XRD spectrum of untreated *Hypnea musciformis* powder

d) XRD pattern spectrum of treated *Hypnea musciformis* powder

XRD patterns of *hypnea* treated TY dye, show very violent and intense and well defined peaks and exhibits precisely amorphous nature. The peaks at  $2\theta$  values of 17.47, 33.36, 35.63, 14.62 and 35.63 corroborate the presence of  $A_{8.55}S_{22}Sb_{4.45}Ti_5$ ,  $CS_2O_7$ ,  $CD_7Cl_8O_{17}T_7$ ,  $H_2MO_2O_{11}Rb_2U$  and  $Cd_7Cl_8O_{17}T_7$ . Their corresponding d-values are 0.9383, 0.9316, 0.9175 0.9163 and 0.9130 respectively [130-139].

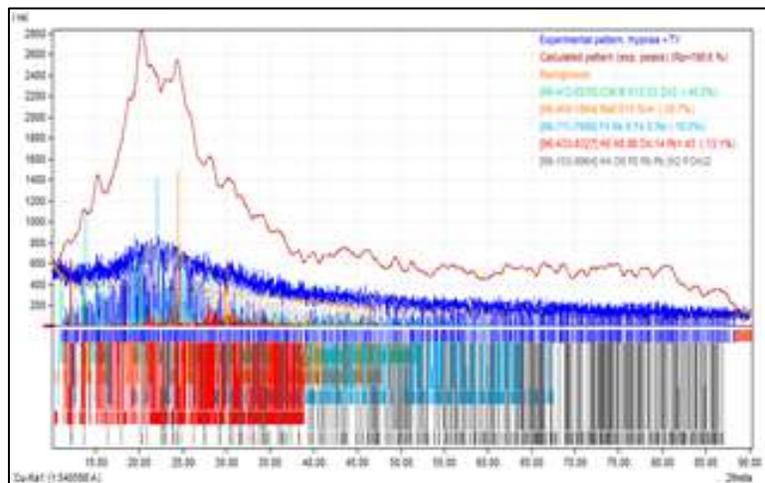
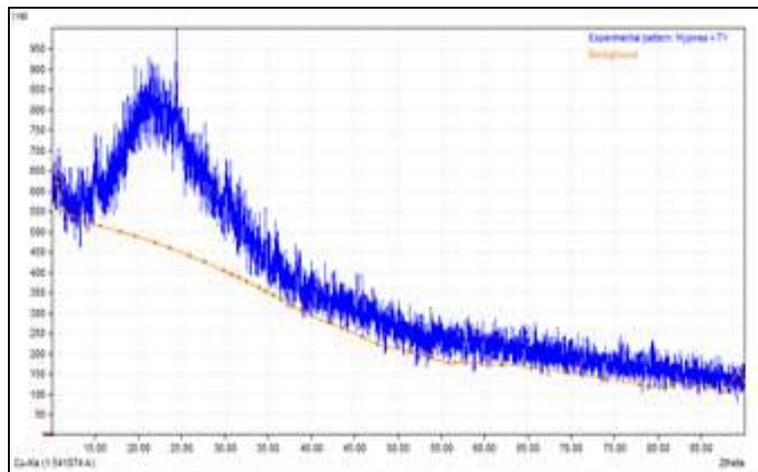


Fig. 3.16: (b) XRD spectrum of treated *Hypnea musciformis* powder with TY dye

#### IV. CONCLUSIONS

- 1) The equilibrium agitation time for TY dye sorption is 40 minutes.
- 2) The optimum dosage for sorption is 53 g/L.
- 3) Maximum extent of sorption is noted at pH = 6.
- 4) From the predicted values of RSM results, maximum sorption of TY dye (96.73121 %) is observed when the processing parameters are set as pH = 5.9977, w = 40.9428 g/L, Co = 18.8661 mg/L and T = 304.6288 K.
- 5) The investigation also reveals the: endothermic nature of sorption as  $\Delta H$  is positive (1453268 J/mole) spontaneity of the sorption as  $\Delta G$  is negative (12210.6 J/mole) irreversible nature of sorption as  $\Delta S$  is positive (39.69203)

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