Studies on Removal of Congo Red Dye Using Pterocladia Lucida Red Algae Powder

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Abstract: The intensification of industrial activity during recent years is greatly contributing to an increasing dispersion of toxic compounds in natural environments, mainly in aquatic systems. The present study deals with the biosorption of CR dye with pterocladia Lucida powder by single step optimization for the removal of Congo red dye. The parameters pH (2–8), Agitation time (5–180 min), Size of biosorbent (53–152 µm), Biosorbent dosage (10–80 g/L), Initial Congo red dye concentration (20–200 mg/L), Temperature (283–323 K) are studied carefully. Under this study the maximum biosorption of Congo red dye was observed at the optimum conditions of pH 4.0, Agitation time 40 min, Size of biosorbent 53µm, Biosorbent dosage 30 g/L, Initial Congo red dye concentration 20mg/L and Temperature 303^0C. first order kinetics fitted well for Congo red dye biosorption. The fit of isotherms are in the order of Langmuir, Temkin and Freundlich. The thermodynamic study was well presented by VantHoff equation and plot. As the ΔH (enthalpy) is positive, the biosorption is endothermic. The negative value of ΔG (Gibbs Free Energy) indicated the spontaneity of biosorption.
IndexTerms – CR, Pterocladia lucida, CCD, RSM.

Introduction

With every drop of water, you drink, every breath you take. Water has been used since antiquity as a symbol by which to express devotion and purity. "Water is needed for almost every aspect of energy production, from digging up fossil fuels to refining oil and generating power and the amount of water consumed by the sector is on track to double within the next 25 years, according to the International Energy Agency. Contrary to the past, our recent developed technological society has become indifferent to this miracle of life. Our natural heritage (rivers, seas and oceans) has been exploited, mistreated and contaminated. In developing nations, however, the search for safe drinking water can be a daily crisis. Within the next few decades, the lack of freshwater in certain areas of the globe will intensify and cause one of the greatest challenges to the world's population. 70.8% from earth's surface is represented by water only 2.7% is freshwater and 0.46% can be directly utilized [1] This domestic water consumption is dwarfed by the demands of agriculture and ecosystems, even in wealthy countries where per capita domestic water consumption greatly exceeds these figures [2]. To cover all these requirements and to avoid water stress, experts generally agree that about 1,000 cubic meters of freshwater precipitate per year is needed [3]. Water pollution due to toxic heavy metals released by industrial activities is a serious environmental and public health issue because they tend to remain indefinitely circulating and eventually accumulating throughout the food chain. [4,5]. Various conventional processes, such as chemical precipitation, membrane filtration, ion exchange, reverse osmosis, evaporation and electrolysis, are usually applied to the treatment of industrial drainage. However, the application of such processes is often limited because of technical or economic constraints. [6] The main disadvantages are the high cost of implantation and operations for concentrations below 100 mg/L.[7] Therefore, new technologies with acceptable costs are necessary for reduction of the heavy metal concentration in industrial drainage.

EXPERIMENTASL PROCEDURE

The experimental procedure consists of the following steps:
2.1 Reagents and materials.
2.2 Preparation of the biosorbent.
2.3 Preparation of the 1000mg/L of CR Dye stock solution.
2.4 Studies on equilibrium biosorption process.

2.1 Reagents and materials:

All the chemicals used in this investigation were of analytical grade and used without further purification. Congo red was used as the source of dye and all the solutions were made with distilled water. The solution of Congo red dye was made from a stock solution containing 1000 mg of CR dye in 1litre. The pH of dye solution was adjusted to the desired value by addition of 0.1M HCL and 0.1M NaOH solutions.

2.2 Preparation of Biosorbent

Pterocladia lucida leaves were available beside at Jodugulla palem beach, near tenneti park, Visakhapatnam, were washed with water to remove dust, micro algae and soluble impurities and dried in sunlight till the leaves became crisp. Then the dried leaves were finely powdered and sized by passing it through a set of sieves ranging from 300 to 75 mesh sizes. The powder of 125 µm fractions was separated & stored and used as biosorbent.

2.3 Preparation of Congo red stock solution:

Congo red dye was used as the source for Congo red dye stock solution. All the required solutions are prepared with analytical reagents and double-distilled water. 1.0 g of 99% Congo red is dissolved in distilled water in 1 L volumetric flask up to the mark to obtain 1000 ppm (mg/L) of Congo red stock solution. Synthetic samples of different concentrations of CR dye are prepared from this stock solution by appropriate dilutions. 50 mg/L of CR stock solution is prepared by diluting 50 mL of 1000 ppm CR dye stock solution with distilled water in 1000 mL volumetric flask up to the mark. Similarly, solutions with different metal concentrations such as (20, 50, 100, 150 and 200 mg/L) are prepared. The pH of aqueous solution is adjusted to the desired value by addition of 0.1 N HNO_3 or 0.1N NaOH solution.

2.4 Studies on equilibrium biosorption:

The biosorption was carried out in batch process by adding a pre-weighed amount of Pterocladia lucida red algae powder to known volume of aqueous solution for a predetermined time interval in an orbital shaker. The procedures adopted to evaluate the various parameters agitation time, pH, initial concentration of CR dye in aqueous solution, biosorbent dosage and temperature

I. RESULTS AND DISCUSSION

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

The parameters are:

3.1 characterization (FTIR, XRD, SEM)

3.2 Effect of Agitation time

3.3 Effect of size of biosorbent.

3.4 Effect of dosage of biosorbent

3.5 Effect of initial concentration of the solution, C0 (mg/L)

3.6 Effect of pH of the solution

3.7 Effect of temperature, T, (K)

Table-1

The range of variables covered is compiled in

Variables	Symbol	Units	Range From	Range to
Agitation time	T	Min	5	180
Size of biosorbent	dp	µm	53	152
Biosorbent dosage	W	G	0.5	4
Initial concentration of the solution	C0	mg/L	20	200
Aqueous solution pH	pH	-	2	8
Temperature	T	K	283	323

3.1 CHARACTERIZATION OF PETROCLADIA LUCIDA POWDER

3.1.1 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FTIR)

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

3.1.1.1 FTIR spectrum of untreated CR dye:

FTIR spectrum of untreated petrocladia lucida powder is presented in fig. 3.1.1.1. The sharp peak at 895.01 cm-1 denotes the involvement and participation of S=O and C–S–O from ester sulphonate in biosorption. The bands at 1039.68 and 1056.07 cm-1 indicates the involvement of C–H bending bonds. The bands at 1153.48 cm-1 assigns the C–O stretching bond.

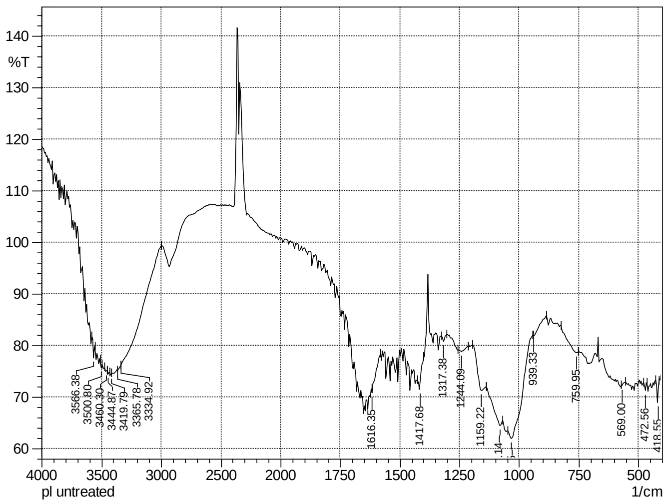


Fig. 3.1.1.1 FTIR spectrum of CR untreated petrocladia lucida powder

The peaks at 1201.70 and 1236.42 cm−1 in native biomass designates the presence of C-O stretching, –SO3 stretching bonds and is not observed after loading CR dye. It indicates the direct involvement of C-O stretching in the ion-exchange process. The bands from 1318.40 to 1373.38 cm-1 denotes the presence of –CH2 bending vibrations. The peaks at 1616.42 and 1623.17 represents the stretching of C=C aromatic rings. The peaks at 1634.74 depict the oleifinic C = C and carbonyl C= O stretching bonds. The peak at 2938.68 cm-1 assigned for CH2 stretching vibrations in is shown in untreated powder. The sharp peak at 3253.09 cm-1 denots the presence of C–H stretching vibrations. Further, the band peaks at 3322.53, 3334.10, 3345.67 and 3355.32 cm-1 are assigned for the bounded –OH and –NH groups and –OH stretching or NH2 stretching bonds. 3334.10, 3345.67 and 3355.32 cm^{-1} are assigned for the bounded –OH and –NH groups and –OH stretching or NH_2 stretching bonds.

3.1.1.2 FTIR spectrum of CR treated with petrocladia lucida powder:

FTIR measurements for CR dye loaded algal biomass are shown in fig. 3.1.1.2. The sharp peak at 1234.50 cm-1 is shifted to 1236.42 cm-1 denoting the involvement and participation of SO3 streching in biosorption. The shifting of band from 1602.91 cm-1 to 1616.42 cm-1 indicates the involvement of streching of C=C aromatic rings. The bands at 3177.86, 3198.11 and 3209.69 cm-1 (assigned for the presence of C–H stretching vibrations respectively) are not shown in untreated biomass. The characteristic of stretching modes of O–H (indicated by the band at 3312.88 cm-1) is also not seen in untreated biomass.

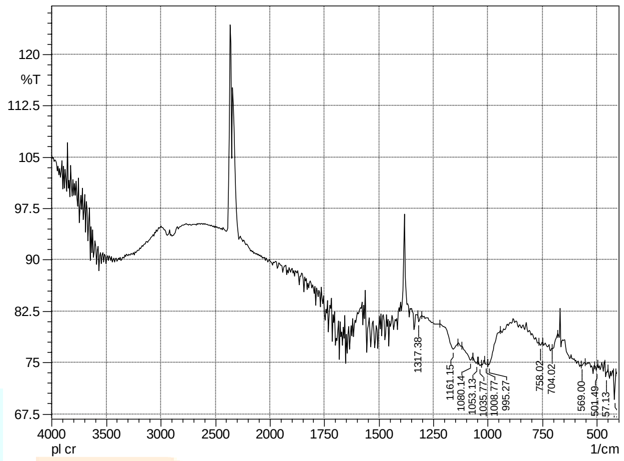


Fig. 3.1.1.2 FTIR spectrum of CR dye treated petrocladia lucida powder

The sharp peaks of 1010.70 and 1070.49 cm^{-1} arose suddenly after loading of CR dye due to the involvement of C–O stretching of alcohols and carboxylic acids and –C–O benzene ring stretching respectively. Further, three additional peaks at 1471.69, 1506.41 and 1521.84 cm^{-1} denoting stretching of C=C aromatic rings and 1568.13 cm^{-1} for amide N-H bending vibrations have suddenly appeared in CR dye treated biomass. The peak appearing at 2343.51 cm^{-1} in CR dye treated powder is denoting phosphate ester group and is not seen in native biomass. The peaks at 3523.95 and 3566.38 cm^{-1} are obtained in treated biomass due to the involvement of the stretching vibration bands of hydroxyl group**.** This may be due to the adjustment of pH and physical disruption of cell walls upon the vigorous shaking.

3.1.2 X-Ray Diffraction:

XRD patterrns of untreated powder are shown in figs.3.1.2.1 (a) & (b). XRD patterns shown in figs. 3.1.2.1(a) & (b) do not indicate sharp peaks, less crystallinity and exhibit little amorphous nature. The peaks at 2θ values of 0.7748, 0.7273, 0.7273, 0.7159 and 0.7035 corroborate the presence of Fe2H474K44, Eu8K16.5O206, As6ClCS3.9, H168K3Li5.5 and C40K13O368 (ICDD files). Their corresponding d-values are 5.5771, 5.1148, 5.8082, 6.4302 and 6.6466.

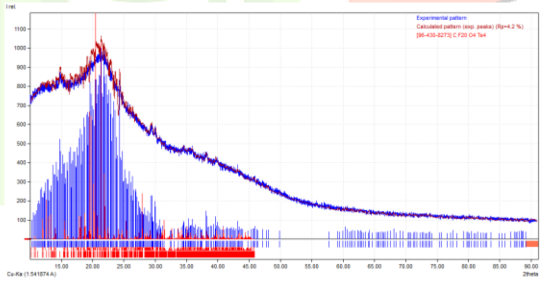


Fig. 3.1.2.1 (a) XRD pattern of CR dye untreated petrocladia Lucida powder

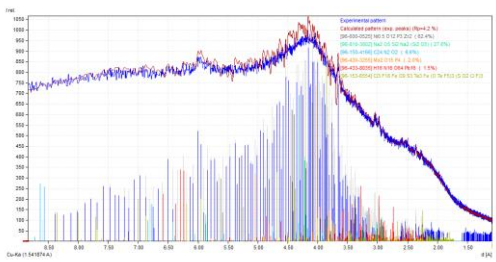


Fig. 3.1.2.2 (b) XRD pattern of CR dye untreated petrocladia lucida powder with matching compounds

3.1.2.2 XRD for CR dye treated with petrocladia lucida powder

XRD patterns for treated powder [Figs.3.1.2.2(a) & 3.1.2.2(b)] exhibit good crystallinity, more amorphous nature and increase in surface area and porosity. The peaks at 2θ values of 0.7765, 0.6899, 0.6084, 0.5983 and 0.5397 corroborate the presence of Fe39Sb9Se4, AS14Cs4Zn, O9P3Y, F7RuXe and Cl2H12P4Ru. Their corresponding d-values are 3.9371, 3.7334, 3.4874, 3.4391 and 3.6449.

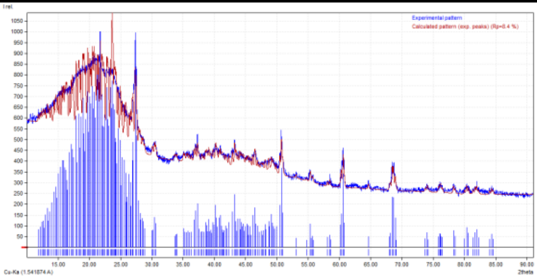


Fig. 3.1.2.2 (a) XRD pattern of CR dye treated petrocladia lucida powder

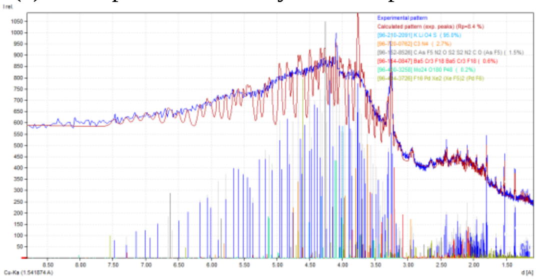


Fig. 3.1.2.2 (b) XRD pattern of CR dye treated petrocladia lucida powder with matching compounds

3.1.3 Scanning Electron Microscope (SEM):

3.1.3.1 SEM analysis for untreated petrocladia lucida powder

. The SEM pictures of untreated petrocladia lucida powder shown in fig. 3.1.3.1 , demonstrates the surface morphology of powder as porous and uneven. From the SEM images, it is clear that the investigated sorbent is porous material due to the presence of pores and cavities.

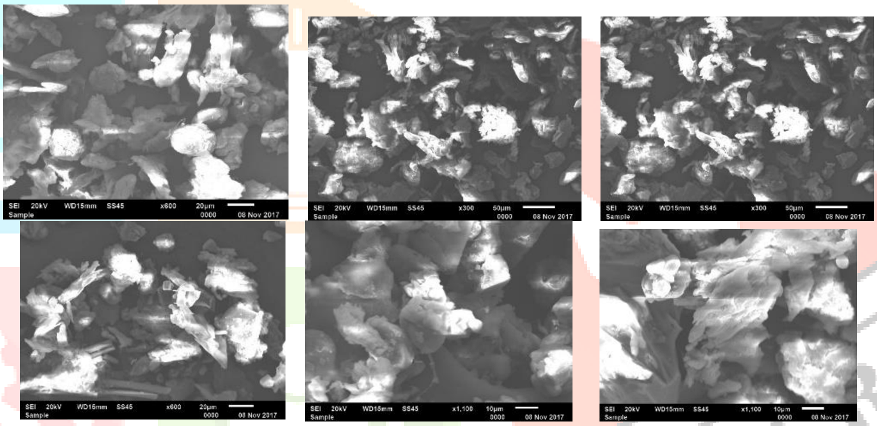


Fig. 3.1.3.1 SEM pattern of CR dye untreated petrocladia Lucida powder

3.1.3.2 SEM analysis for CR dye dye treated with petrocladia Lucida powder

SEM analysis after biosorption in Fig. 3.1.3.2 shows that the surface has irregular texture with globular, elongated grains and shiny particles over the surface of biosorbent which are absent in the fresh biosorbent. These elongated grains show that the CR dye particles are adhered onto the surface of algae. The clustered grains like morphology, on treated biosorbent denote increased active surface area.

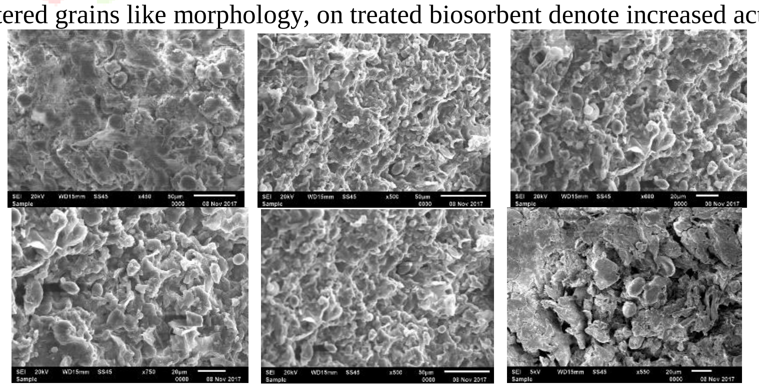


Fig. 3.1.3.2 SEM pattern of CR dye treated petrocladia Lucida powder

3.2 Effect of agitation time (t):

The effect of agitation time on the removal of CR dye onto pterocladia lucida (red algae) powder was studied at dosage of 0.5g/L. And are shown in figs.3.2. The equilibrium time for pterocladia lucida (red algae) powder CR dye system is 40 min, the % removal of time between 5 to 40 min is 15% to 60%. and no further removal was occurred beyond the time from 40 min to180 min. The % removal and dye uptake were 1.2 mg/g as follows at 40min[8-17].

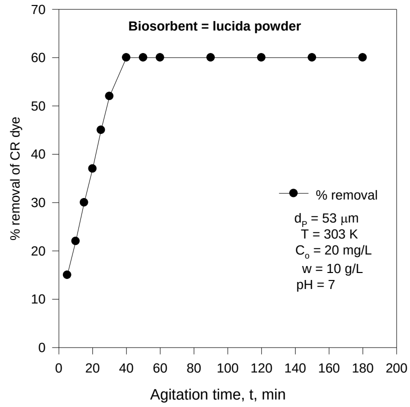


Fig .3.2 Effect of agitation time on % removal of CR dye

3.3 Effect of size of biosorbent (dp):

The equilibrium time for pterocladia lucida (red algae) powder CR dye system is 53 um, the % removal of CR dye decrease 29 % to 60 % to size of biosorbent increases 152 to 53 um. (Fig. 3.3). The % removal and dye uptake were 1.2 to 0.58 mg/g as follows It is cleared from the plots that % removal drops with size of biosorbent. [18-27].

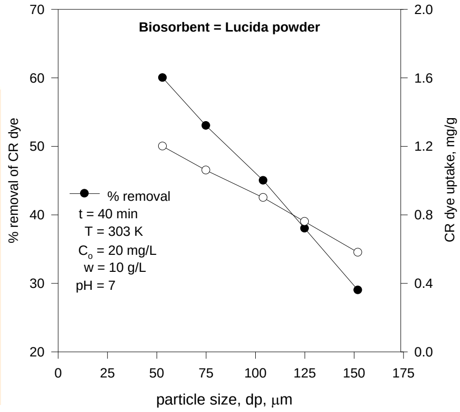


Fig .3.3 Effect of biosorbent size on %removal of CR dye

3.4 Effect of biosorbent dosage:

The equilibrium time for pterocladia lucida (red algae) powder CR dye system is 1.5 g, the 89% removal of biosorbent dosage increase to 0.5 to 1.5 g is 80% to 89%.(fig 3.4) and no further removal was occurred beyond the biosorbent dosage from 1.5 to 4 g. The % removal and dye uptake was 0.5933 mg/g biosorbent dosage 1.5 as follows [28-37].

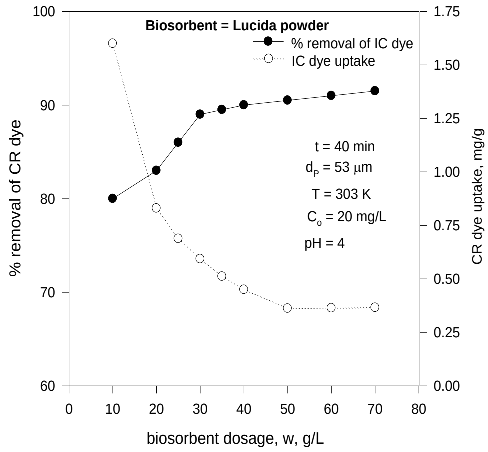


Fig .3.4 . Effect of biosorbent dosage on % removal of CR dye

3.5 Effect of initial concentration of aqueous dye solution (C0, mg/L):

The variation of % dye removal and dye uptake with initial dye concentration are presented in Fig-3.5. However, the percentage removal of by CR dye onto pterocladia lucida powder was decreased from 80 to 52% for CR dye. Though an increase in dye up take was 1.6 to 10.4 mg/g observed, the decrease in percentage removal may be attributed to lack of sufficient surface area to accommodate much more dye available in the solution. [38-47].

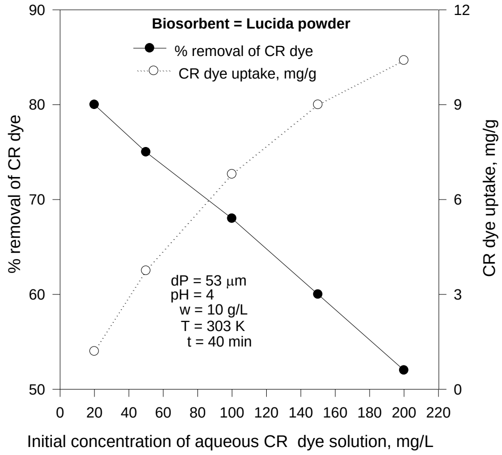


Fig. 3.5 Effect of initial concentration on % removal of CR dye

3.6. Effect of pH:

In the present study CR dye biosorption data were obtained in the pH range of 2 to 8 of the aqueous solution (C0=10 mg/L) using 1.5g/l of 53 µm size biosorbent. The effect of pH of aqueous solution on % biosorption of CR dye is shown in fig.3.6. The % biosorption of CR dye was increased from 64 to 74 % as pH increased from 2 to 4 and dye uptake is 1.28 to 1.6 mg/g and beyond the pH value of 4 it was decreased. [48-57].

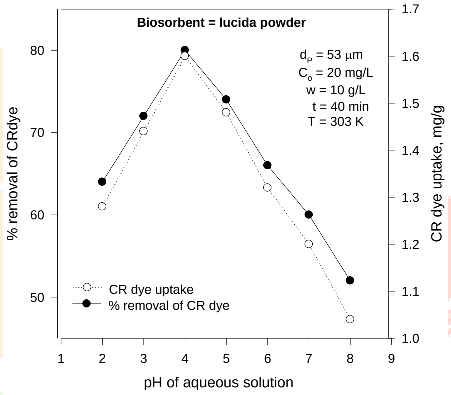
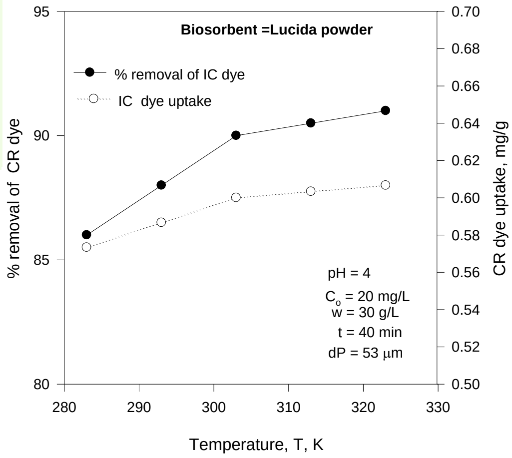


Fig .3.6. Effect of pH on % removal of CR dye

3.7. Effect of Temperature (T, K);

The effect of change in the temperature on the CR dye uptake is shown in fig.3.7. The effect of temperature was investigated from batch experiments carried out at five constant temperatures 283, 293,303.313 and 323 K. [58-67].



3.7 Effect of temperature on % removal of CR dye

3.8 Isotherms

3.8.1: Langmuir Isotherm:

The correlation coefficient is R2=0.999 and Langmuir equation obtained for the present study is: [68-77].

(Ceq/qeq) =0.07208Ce+2.339, R2=0.999 -------(1)

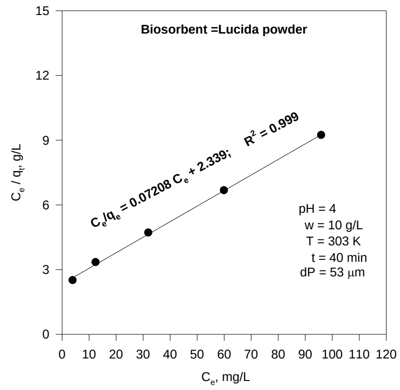


Fig 3.8.1 Langmuir isotherm for %removal of CR dye.

3.8.2: Freundlich isotherm

Freundlich isotherm is derived assuming heterogeneity surface. Fig 3.8.2 is plot of ln [Ceq] versus ln [qeq), which is a straight line with a slope of n and an intercept of ln (Kf) [78-87].

ln(qeq)= 0.5969ln(Ce)-0.26503 ---------(2)

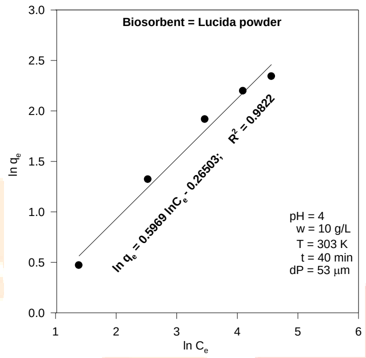


Fig 3.8.2. Freundlich isotherm for % biosorption of CR dye

3.8.3 Temkin Isotherm:

Fig.3.8.3 is the plot of ln Ce versus qe, which is a straight line with slope of RT/bT and the intercept of RT/bT ln (AT). The Temkin equation obtained for the present study is [88-97].

qe= 2.839ln Ce- 2.7955, R2=0.9858. --------(3)

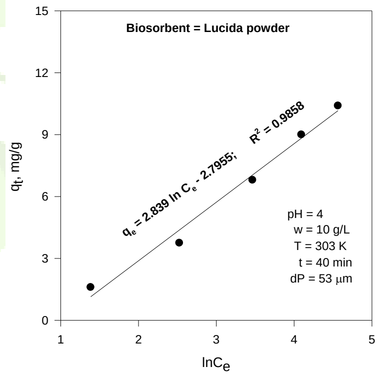


Fig 3.8.3. Temkin Isotherm for biosorption of CR dye

3.9. Biosorption kinetics:

3.9.1 first order kinetic equation

The Plot is drawn between the time (t) versus log (qe-q) (Fig.3.9.1) gives straight line for first order kinetics the computation of biosorption first order rate constant (K) [98-107].

Log(qe-qt) = 0.16723-0.029 t, R2 =0.9428 ------------(4)

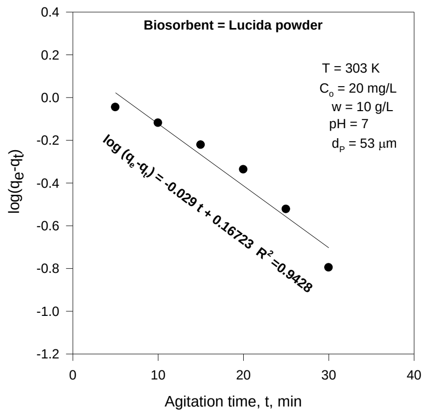


Fig 3.9.1. First order kinetics for % biosorption of CR dye.

3.9.2 Pseudo second order kinetic equation

If the pseudo second order kinetics are investigated with 50 ml of aqueous solution (C0=10 mg/L) in the agitation time intervals of 5 to 40 min. Pseudo second order plot of time 't' versus (t/q) shown in fig 3.9.2. The second order kinetics obtained for the present study is [108-117].

t/qt=0.4461+16.8665 t, R2 =0.8657 ---------(5)

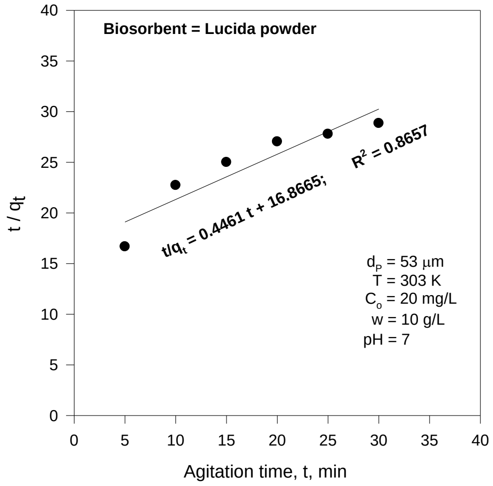


Fig 3.9.2 Second order kinetics for % bisorption of CR dye.

3.10. Thermodynamics studies:

The ΔG, ΔS, and ΔH values of CR dye ions at different temperatures and different concentrations are shown given fig 3.10.Thermodynamic parameters for the biosorption process of CR dye are computed from graph of a log (qe/Ce) versus 1/T. The values of ΔS=21.2246, ΔG=-6421.4 and ΔH=9.65207 obtained in present investigating for different initial concentrations of dye [118-127].

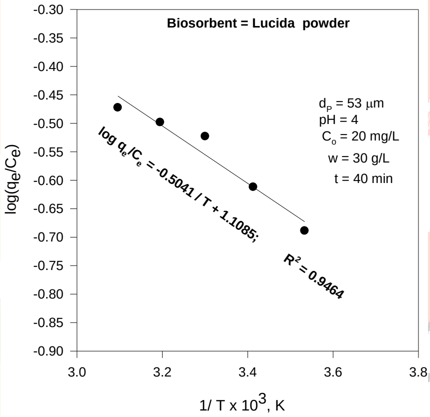


Fig 3.10. Effect of Temperature on % biosorption of CR dye (van't Hoff plot)

4.1 Optimization using Response Surface Methodology (RSM):

4.1.1 Optimization of biosorption conditions using CCD

The effects of four independent variables (pH, initial concentration of CR dye in aqueous solution, biosorbent dosage and temperature) on CR dye biosorption are analyzed using Central Composite Design (CCD). The optimum conditions for the four independent variables on the extent of CR dye biosorption are formed within the quadratic model. Levels of different process variables for percentage biosorption are shown in table–2.

Table-2

Levels of different process variables in coded and un-coded form for % biosorption of CR dye using petrocladia lucida powder

Variable	Name	Range and levels				
		-2	-1	0	1	2
X1	pH of aqueous solution	2	3	4	5	6
X2	Initial concentration, Co, mg/L	10	15	20	25	30
X3	Biosorbent dosage, w, g/L	10	20	30	40	50
X4	Temperature, T, K	283	293	303	313	323

Regression equation for the optimization of biosorption is:

% biosorption of CR dye (Y) is function of pH of aqueous solution (X1), initial concentration (X2), dosage (X3), and Temperature of aqueous solution (X4).

The multiple regression analysis of the experimental data has yield the following equation:

$$Y = 6.650867 + 0.284559\ X1 + 0.056912\ X2 + 0.02830\ X3 + 3.132\ X4 + 0.006939\ X12 + 0.000278X22 + 0.000069X32 + 0.000069\ X42 + 0.001817\ X1X2 + 0.000908\ X1X3 + 0.000908\ X1X4 + 0.000182\ X2X3 + 0.000182\ X2X4 + 0.000091X3X4 \quad \text{----- (8)}$$

Table-6.5 represents the results obtained in CCD. The response obtained in the form of analysis of variance (ANOVA) from regression eq.8 is put together in table–3. Fischer's 'F-statistics' value is defined as MSmodel/MSerror, where MS is mean square. Fischer's 'F-statistics' value, having a low probability 'p' value, indicates high significance.

Table–3
Results from CCD for CR dye biosorption by *petrocladia lucida* powder

Run No.	X_1, pH	X_2, C_o	X_3, w	X_4, T	% biosorption of CR dye	
					Experimental	Predicted
1	5	15	20	293	87.11000	87.10958
2	5	15	20	313	88.62000	88.62208
3	5	15	30	293	86.79000	86.80542
4	5	15	30	313	88.12000	88.09292
5	5	25	20	293	86.22000	86.19875
6	5	25	20	313	87.88000	87.92125
7	5	25	30	293	87.22000	87.18958
8	5	25	30	313	88.72000	88.68708
9	7	15	20	293	87.90000	87.94875
10	7	15	20	313	89.12000	89.13125
11	7	15	30	293	87.82000	87.75958
12	7	15	30	313	88.68000	88.71708
13	7	25	20	293	88.88000	88.88792
14	7	25	20	313	90.28000	90.28042
15	7	25	30	293	89.98000	89.99375
16	7	25	30	313	91.18000	91.16125
17	4	20	25	303	80.42000	80.44500
18	8	20	25	303	83.78000	83.75833
19	6	10	25	303	95.08000	95.06500
20	6	30	25	303	96.58000	96.59833
21	6	20	15	303	85.92000	85.87333
22	6	20	35	303	86.40000	86.45000
23	6	20	25	283	88.18000	88.19167
24	6	20	25	323	90.88000	90.87167
25	6	20	25	303	94.00000	94.00000
26	6	20	25	303	94.00000	94.00000
27	6	20	25	303	94.00000	94.00000
28	6	20	25	303	94.00000	94.00000
29	6	20	25	303	94.00000	94.00000
30	6	20	25	303	94.00000	94.00000

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

Table–4
ANOVA of CR dye biosorption for entire quadratic model

Source of variation	SS	df	Mean square(MS)	F-value	*P* > F
Model	389.1509	14	27.7964	21057	0.00000
Error	0.0198	15	0.00132		
Total	389.1509				

Df- degree of freedom; SS- sum of squares; F- factor F; *P*- probability.
R^2=0.99996; R^2 (adj):0.99992

Table-5
Estimated regression coefficients for the CR dye biosorption onto *petrocladia lucida* powder

Terms	Regression coefficient	Standard error of the coefficient	t-value	*P*-value
Mean/Intercept	6.650867	-152.188	0.000000	6.650867
Dosage, w, g/L (L)	0.284559	88.518	0.000000	0.284559
Dosage, w, g/L (Q)	0.006939	-428.696	0.000000	0.006939
Conc, Co, mg/L (L)	0.056912	-27.031	0.000000	0.056912
Conc, Co, mg/L (Q)	0.000278	65.995	0.000000	0.000278
pH (L)	0.028320	43.065	0.000000	0.028320
pH (Q)	0.000069	-282.415	0.000000	0.000069
Temperature, T, K (L)	0.042455	161.709	0.000000	0.042455
Temperature, T, K (Q)	0.000069	-160.994	0.000000	0.000069
1L by 2L	0.001817	50.909	0.000000	0.001817
1L by 3L	0.000908	3.165	0.006412	0.000908
1L by 4L	0.000908	-9.081	0.000000	0.000908
2L by 3L	0.000182	35.636	0.000000	0.000182
2L by 4L	0.000182	5.779	0.000036	0.000182
3L by 4L	0.000091	-6.192	0.000017	0.000091

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

The ANOVA of the regression model is sufficiently great, as proven from the Fisher's F-test and has a very low probability value (Pmodel > F=0.000000). Besides, the computed F-value is much higher compared to F-value (F0.05 (14.15) tabulars = 2.42) at 5% level, suggesting that the treatment differences are sufficiently great. Student's t-test can implicate regression coefficient of the parameter, while pattern of interactions amidst all the factors can be entailed by 'p' values. It is noted from table-4 that more significant corresponding coefficient term can be possessed by having high't' value and low 'P' value. By analyzing't' and 'p' values from table-4, all the variables have high importance to explain the individual and interaction effects of independent variables on biosorption of CR dye to anticipate the response. The model is reduced to the following form by excluding undistinguished terms in eq.8.

Y = 6.650867 +0.284559 X1 + 0.056912 X2 +0.02830 X3 + 3.132 X4 + 0.006939 X12 +0.000278X22 +0.000069X32 +0.000069 X42 + 0.001817 X1X2 + 0.000908 X1X3 + 0.000908 X1X4 + 0.000182 X2X3 +0.000182 X2X4 + 0.000091X3X4 ------- (9)

A positive sign of the coefficient represents an interactive effect i.e., response (% biosorption of CR dye) steps up with increase in effect, whereas a negative sign implies an incompatible effect that means response lowers with an increase in effect.

Measure of the model's variability to the responses indicated is presented by correlation coefficient (R2). As R2 —> 1, model is inviolable and the response is estimated better. In our study, R2 = 0.99996 suggests that 0.004 % of the total variations are not adequately explained by the model. Statistical relevance of the ratio of mean due to regression and mean square due to residual error is tested with the help of ANOVA. F-values implicate that % biosorption can be sufficiently explained by the model equation. If 'P' value is lower than 0.05, the model is considered to be statistically significant at the 95 % confidence level. **[128-135]**

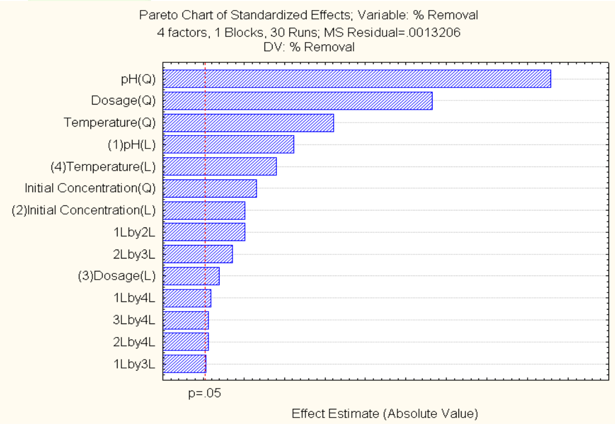


Fig. 4.1 Pareto Chart

4.2.1 Interpretation of residual graphs:

Normal probability plot (NPP) is a graphical technique used for analyzing whether or not a data set is normally distributed to greater extent. The difference between the observed and predicted values from the regression is termed as residual. Fig. 4.2.1 exhibits normal probability plot for the present data. It is evident that the experimental data are reasonably aligned implying normal distribution.

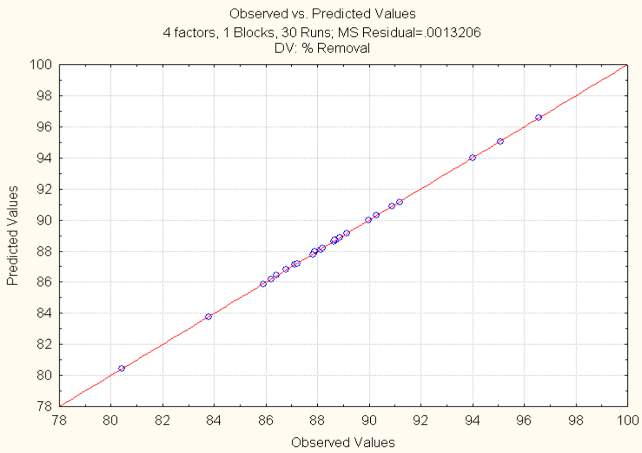


Fig. 4.2.1 Normal probability plot for % biosorption of CR

4.2.2 Interaction effects of biosorption variables:

Three-dimensional view of response surface contour plots [Fig. 4.2.2 (a) to 4.2.2 (f)] exhibit % biosorption of the CR dye using petrocladia lucida powder for different combinations of dependent variables. All the plots are delineated as a function of two factors at a time, imposing other factors fixed at zero level. It is evident from response surface contour plots that the % biosorption is minimal at low and high levels of the variables. This behavior confirms that there is a presence of optimum for the input variables in order to maximize % biosorption. The role played by all the variables is so vital in % biosorption of CR dye and seen clearly from the plots. The predicted optimal set of conditions for maximum % biosorption of CR dye is:

pH of aqueous solution = 4.0978
Initial CR dye concentration = 17.5899 mg/L
Biosorbent dosage = 29.9359 g/L
Temperature = 305.8511 K
% biosorption of CR =94.04316

The experimental optimum values are compared with those predicted by CCD in table-6. The experimental values are in close agreement with those from CCD.

Table-6

Comparison between optimum values from CCD and experimentation

Variable	CCD	Experimental
pH of aqueous solution	4.0978	4.0
Initial CR dye concentration, mg/L	17.5899	20
Biosorbent dosage, w, g/L	29.9359	30
Temperature, K	305.8511	303
% biosorption	94.04316	90

Table – 7

Dye uptake capacities for different biosorbents

Authors	Biosorbent	q_t, mg/g
Gupta et al. **[136]**	Spirogyra sp.	140.84
Flavio et al. **[137]**	Ponkan peel	112.1
Ruhan et al. **[138]**	Lactarius scrobiculatus	56.2
Matheickal et al. **[139]**	Powder activated carbon	20.7
Lijuan Wang et al **[140]**	Crofton weed stalk	28
Present investigation	***Pterocladia Lucida* powder**	**13.8734**

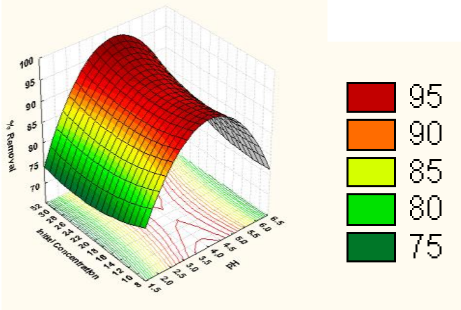


Fig. 4.2.2 (a) Surface contour plot for the effects of pH and initial concentration of CR on % biosorption

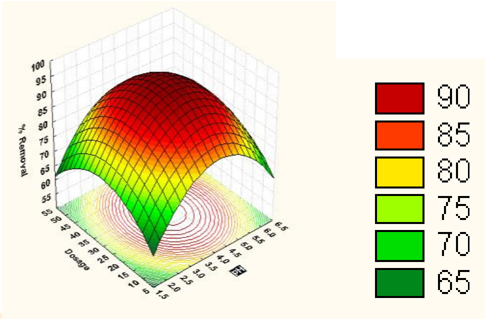


Fig. 4.2.2 (b) Surface contour plot for the effects of pH and Dosage of CR in aqueous solution on % biosorption

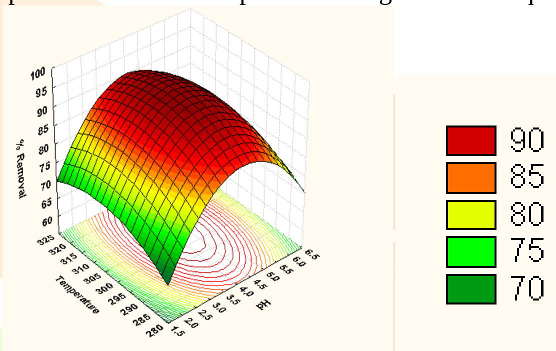


Fig. 4.2.2 (c) Surface contour plot for the effects of pH and temperature of CR dye in aqueous solution on the % biosorption

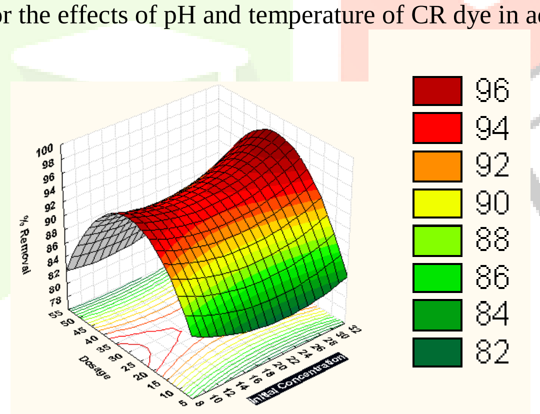


Fig. 4.2.2 (d) Surface contour plot for the effects of concentration and dosage on % biosorption of CR dye

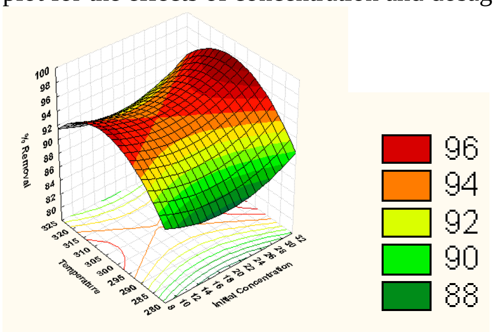


Fig. 4.2.2 (e) Surface contour plot for the effects of concentration and temperature on % biosorption of CR dye

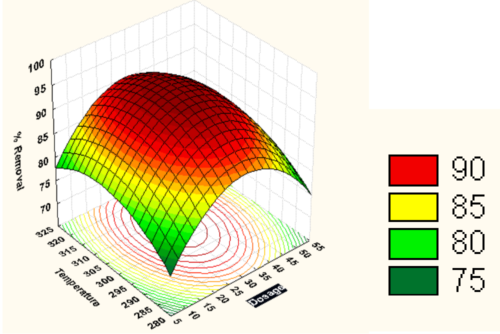


Fig. 4.2.2 (f) Surface contour plot for the effects of Dosage and temperature on % biosorption of CR dye

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