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Biosorption and optimization studies on Congo Red dye with fanwort powder using Box Behnken design

Dr. Ch asha Immanuel raju [1], V R Nagalakshmi Nethi[2]

[1](Asst Professor, Chemical Department, AU Engineering College/ Andhra University,INDIA)
[2](Research Schlor (part time) ,AU College of Engineering/ Andhra University, &
Asst professor, Petroleum dept, GCE, Rajahmundry)

Abstract: *Water pollution leads to an imbalance in ecosystem. Most of the industrial effluents today are causing the water pollution in a direct or indirect way. This paper discusses the removal techniques of dyes which are one of the dangerous effluents from industries through the process of biosorption. The capacity of the bio material "fanwort powder" to adsorb the dye (Congo red) has been discussed. The FTIR, XRD, and SEM studies reveal the characterisation of fanwort powder. The parameters considered for the process are agitation time ranging from 1minute to 180minutes, pH ranging from 2 to 8, Initial concentration of Congo red dye ranging from 20mg/L to 200mg/L, dosage of the biosorbent ranging from 10mg/L to 60mg/L and temperature ranging from 283K to 323K. The process issues such as kinetics, isotherms, and thermodynamic studies are also included. BOX BEHNKEN design is used to optimize the process. The optimum time for biosorption is found to be 40min, pH is 5, and adsorbent dosage is 40g/L, while the initial concentration of the dye is 20mg /L. Freundlich isotherm with its elevated correlation factor has gone well with the experiment. The pseudo second order kinetics got the best fit for the process.*

I. Introduction

Water is said to be the best chemical species that man had ever found. In-spite of its polarity it is capable of dissolving most of the substances and considered as the best solvent ever. Water is a neutral compound. As water is a fundamental need for life, every living organism requires it for their metabolism. Due to its wide adaptability water is used for many purposes like household as well as for industrial usage. Water had its importance in a country's economy by the evolution of industries. As the industries increased, the needs of humans too increased along with the increase in pollution that led to environmental and health hazards. The ground water as well as the surface water is contaminated by the industrial effluents posing a serious threat to ecosystems. Constant consumption of this polluted water will lead to damaged genes and carcinogenic diseases. Here comes the need for the treatment techniques of water within the economical and ecological aspects including physical treatments such as filtering and sedimentation, chemical treatments like oxidation, flocculation, agglomeration, and chlorination and biological methods like adsorption on biomaterials, sand filtration etc. From all the above, the process of adsorption using a bio material is stated as a promising technique due its feasibility, ease of operation, and low costs. The experimental procedure involves the treatment of Congo red dye using Fanwort as an adsorbent. The design of Box Behnken is used to carry out the process of optimization of the obtained data.

II. Material And Methods

The following steps are being involved by the materials and the methods.

Equipment and reagents
Preparation of biosorbent
Process of biosorption and equilibrium studies

Reagents and materials

All the reagents utilized in this study were of investigative grade and used directly. The basic Congo red dye solution is prepared by using distilled water. The stock Solution of CR dye is having a concentration of mg per liter. Adding the solutions of 0.1M NaOH and 0.1M HCL, the required pH for the dye solution can be obtained.

Preparation of the Biosorbent:

The algae Fanwort is collected from the River Godavari at Rajahmundry. A thorough water wash facilitates the dust removal as well as the impurities that are soluble in nature. Then the algae are dried in the sunlight till it becomes crispy. The Crispy-dried algae is then powdered and sorted according to their sizes by using sieves that have their mesh size varying in between 300 and 75. The powder of various sizes such as 53µm, 75µm, 105µm, 125µm, and 152µm is separated and stocked up in the bottles that have the facility of double capping which allows the bottles to stay dry and avoid any moisture contact. The stored powder is the biosorbent.

Process of biosorption and equilibrium studies

The process of biosorption gets carried out as a batch process. It starts by adding a measured quantity of biosorbent (Fanwort powder) to a specific volume of aqueous solution. It is then put in the orbital shaker for the pre-fixed interval of time. Various parameters such as pH, dosage of the biosorbent, time taken for the agitation, initial concentrations, and temperature of the aqueous solution are

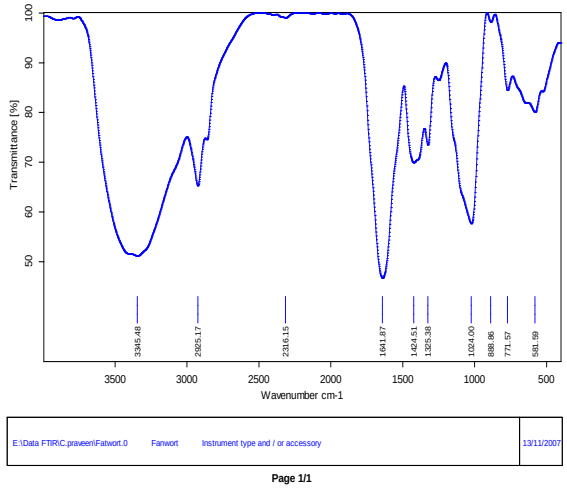
evaluated for their effects on the CR dye biosorption process. The evaluation is made by using optimization process of single step. Furthermore optimizations are carried out by using the design of Box Behnken.

III. Results and discussions

1. Characterization of fanwort powder

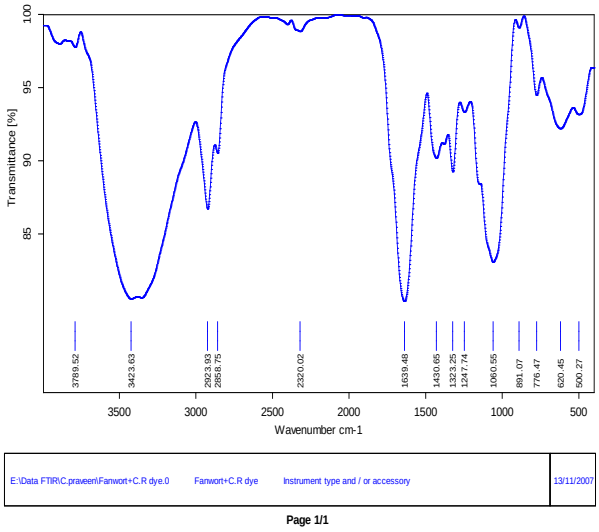
FTIR spectrum of untreated fanwort powder

The figure mentioned below represents the FTIR spectrum of untreated fanwort powder. 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} show the involvement of C–H bending bonds. The bands at 1153.48 cm^{-1} gives the C–O stretching bond. The peaks at 1201.70 and 1236.42 cm^{-1} in native biomass confirm the presence of C-O stretching, $-SO_3$ stretching bonds and is not seen after loading CR dye. It specifies the direct association of C-O stretching in the ion-exchange process. The bands from 1318.40 to 1373.38 cm^{-1} represents the existence of $-CH_2$ bending vibrations. The peaks at 1616.42 and 1623.17 denotes the stretching of C=C aromatic rings. The peaks at 1634.74 portrays the oleifinic C = C and carbonyl C= O stretching bonds. The peak at 2938.68 cm^{-1} consigned for CH_2 stretching vibrations and is shown in untreated fanwort powder. The sharp peak at 3253.09 cm^{-1} indicates the incidence of C–H stretching vibrations. Additionally, the band peaks at 3322.53, 3334.10, 3345.67 and 3355.32 cm^{-1} are allocated for the bounded –OH and –NH groups and –OH stretching or NH_2 stretching bonds.



FTIR spectrum of CR dye treated fanwort powder:

The below mentioned figure shows the FTIR measurements for CR dye treated biosorbent. The sharp peak at 1234.50 cm^{-1} is moved to 1236.42 cm^{-1} showing the association of SO_3 stretching in biosorption. The shifting of band from 1602.91 cm^{-1} to 1616.42 cm^{-1} shows the participation of stretching of C=C aromatic rings. The bands at 3177.86, 3198.11 and 3209.69 cm^{-1} (allocated for the existence of C–H stretching vibrations respectively) are not shown in untreated biosorbent. The characteristic of stretching modes of O–H (portrayed by the band at 3312.88 cm^{-1}) is also not visible in untreated biosorbent. The sharp peaks of 1010.70 and 1070.49 cm^{-1} came up unexpectedly after loading of CR dye due to the contribution of C–O stretching of alcohols and carboxylic acids and –C–O benzene ring stretching respectively. Moreover, three extra peaks at 1471.69, 1506.41 and 1521.84 cm^{-1} signifies the stretching of C=C aromatic rings and 1568.13 cm^{-1} for amide N-H bending vibrations have swiftly emerged in CR dye treated biosorbent. The peak came out at 2343.51 cm^{-1} in CR dye treated powder is showing phosphate ester group and is not observed in native biosorbent. The peaks at 3523.95 and 3566.38 cm^{-1} are attained in treated biosorbent due to the participation of the stretching vibration bands of hydroxyl group. This may be due to the alteration of pH and physical interruptions of cell walls upon the vigorous shaking.

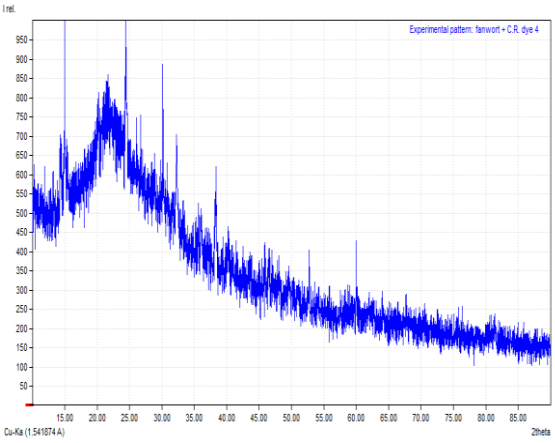


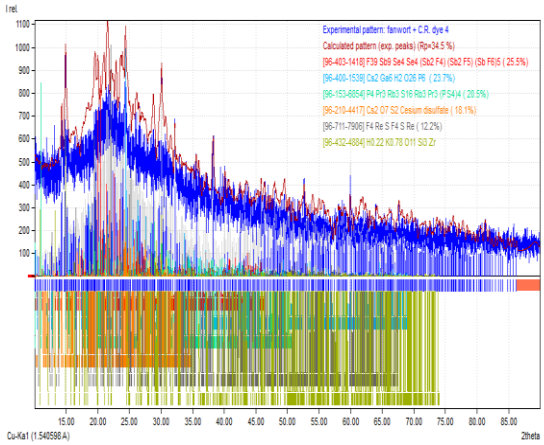
X-Ray Diffraction:

The Rigaku Ultima model IV is used to take the X-Ray Diffractograms (XRD) of the powder samples. At a scan speed of 2^0/min the diffracted X-ray intensities are recorded as a function of 2q by using a copper target (Cu-Ka radiation with wave length, λ= 1.5492 A^0). From 3^0 to 90^0 the patterns of XRD are recorded. 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.

XRD patterns of Congo Red with untreated Fanwort powder

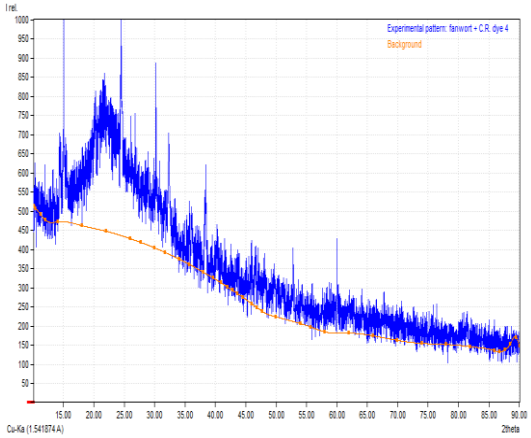
XRD patterns shown in figures do not indicate sharp peaks, less crystallinity and exhibit little amorphous nature. The peaks at 2θ values of 0.7748, 0.7273, 0.7273, 0.7159 and 0.7035 corroborate the presence of $Fe_2H_{474}K_{44}$, $Eu_8K_{16.5}O_{206}$, $As_6ClCS_{3.9}$, $H_{168}K_3Li_{5.5}$ and $C_{40}K_{13}O_{368}$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

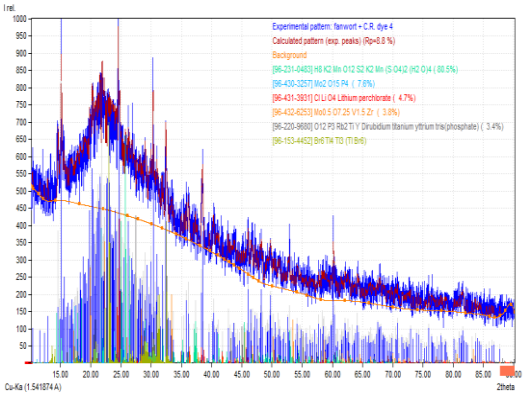




XRD patterns for Congo Red with treated Fanwort powder

XRD patterns revealed in the figures display good crystallinity, more amorphous nature and amplified in surface area and porosity. The peaks at 2θ values of 0.7765, 0.6899, 0.6084, 0.5983 and 0.5397 confirm the existence of $Fe_{39}Sb_9Se_4$, $AS_{14}Cs_4Zn$, O_9P_3Y, F_7RuXe and $Cl_2H_{12}P_4Ru$. Their equivalent d-values are 3.9371, 3.7334, 3.4874, 3.4391 and 3.6449.



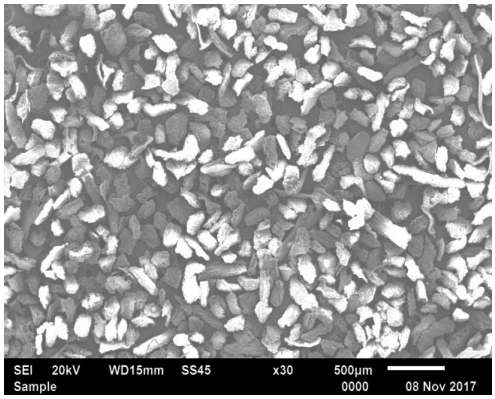


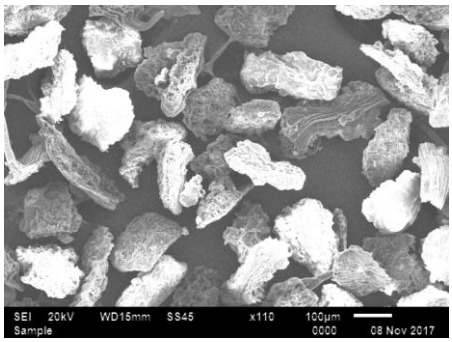
Scanning Electron Microscope

The technique of SEM is very helpful in the studying both the natural sorbent morphology and its modification derived from sorbate interactions. It is an electron microscope that offers images of the sample surface by scanning it with a high energy beam of electrons. When the electron contacts with the atoms of the sample they produce signals that contain information about topography, morphology, and composition of the sample surface**.** The samples on their surface at least must be electrically conductive, for conventional SEM imaging. Nonconductive samples are coated with an ultra-thin layer of electrically conducting material. This coating averts the buildup of static electric charges on the sample surface throughout the electron irradiation. Magnification of the imaging can be controlled over a range of up to 6 orders of magnitude from about ×25 to 250,000 times. SEM-EDAX gives proof for both existence of dyes on the sorbent surface and dye micro precipitation**.** In this investigation, possible mechanisms involved in the sorption of the toxic elements in biomasses and differences due to the application of the adjustments are investigated using SEM.

SEM analysis for untreated *fanwort* powder

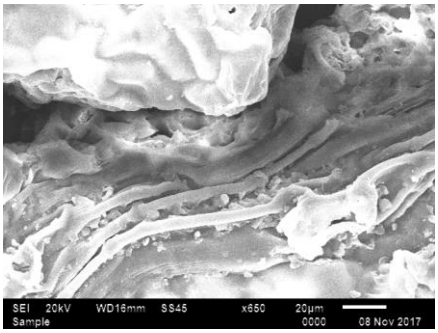
The figure produced below shows the SEM pictures of untreated fanwort powder. It expresses the surface morphology of powder as porous and uneven. From the SEM images, it is clear that the investigated sorbent is porous material due to the existence of pores and cavities.

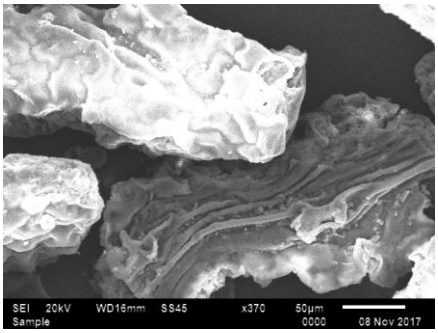




SEM analysis for CR dye treated with *fanwort* powder

The below mentioned figure portrays the SEM analysis after biosorption. This indicates 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 explain that the CR dye particles are adhered onto the surface of algae. The clustered grains like morphology, on treated biosorbent signify increased active surface area.

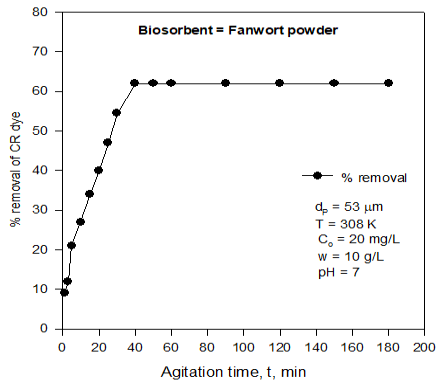




A. Equilibrium studies on biosorption of Congo Red

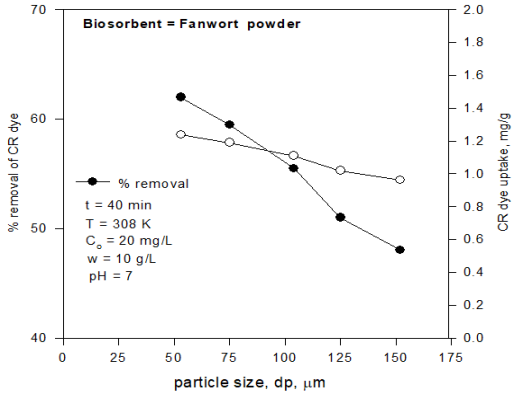
1. Effects of agitation time

The % biosorption of Congo Red is plotted against agitation time. It is found from the plots that the % biosorption gradually increased in the first 40 min of agitation. Outside the agitation time of 40 min, the % biosorption is more or less constant. So the equilibrium agitation time is 40 min. The % biosorption is increased from 9 to 62% in the agitation time period of 1 to 40 min. The rate of percentage biosorption is elevated in the initial stages because sufficient surface area of the biosorbent is accessible for the biosorption of Congo Red.



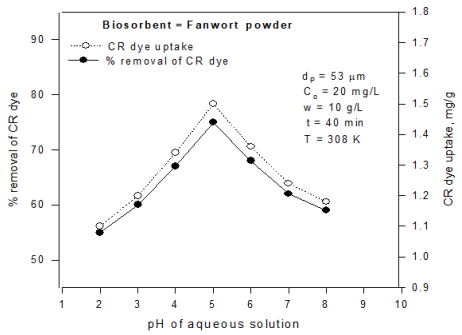
2. Effect of biosorbent size

The deviation in % biosorption of congo red with respect to biosorbent size is plotted. The percentage biosorption is decreased from 62 to 48 % as the biosorbent size decreases from 53 to 152µm. The surface area of the biosorbent increases as the size of the particle decreases and the number of active sites on the biosorbent are better exposed to the biosorbate.



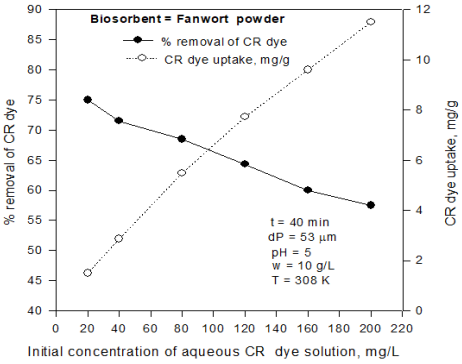
I. Effect of pH

A plot is made between % biosorption of Congo Red and pH of aqueous solution. A significant boost in percentage biosorption of CR is seen as pH is increased from 2 to 5 and downward trend of the % biosorption is noticed with an increase in pH above 5. The percentage biosorption is increased from 55 % to 75 % as pH is increased from 2 to 5. The percentage biosorption is decreased from 75 % to 59 % as pH increases from 5 to 8. With an increase in interaction, the Congo Red dye replace H^+ ions bound to the biosorbent for forming part of the surface functional groups like OH, COOH.



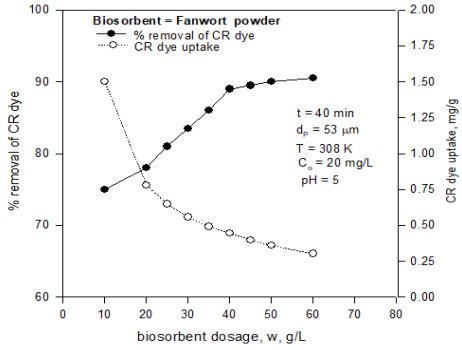
II. Effect of initial concentration of CR dye

The effect of initial concentration of congo red in the aqueous solution on the percentage biosorption is shown at equilibrium agitation time. The % biosorption is gradually decreased from 75 to 57.5 % (1.5 to 11.5 mg/g) by increasing congo red C_o from 20 to 200 mg/L. Lesser percentage of CR is removed for higher concentration of CR in the aqueous solution. This behavior is due to the increase in the amount of biosorbate to the static number of available active sites on the biosorbent.



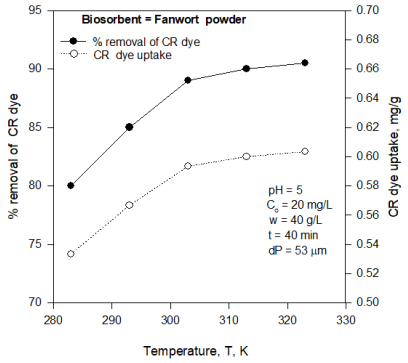
III. Effect of biosorbent dosage

The variation in percentage biosorption of Congo red from the aqueous solution (pH = 5) with biosorbent dosage. The % biosorption is increased from 75 to 89% as dosage is increased from 10 to 40 g/L. The % biosorption from the aqueous phase increases with an increase in the biosorbent amount. The increase in % biosorption is not appreciable (89 to 90.5 %) as w is increased from 40 to 60 g/L. All other experiments are conducted at w = 40 g/L.



B. Effect of temperature

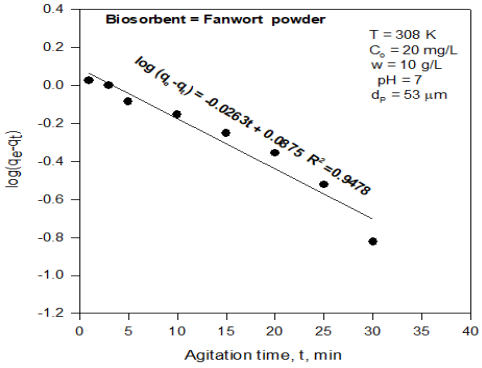
The effects of changes in the temperature on the CR dye uptake are mentioned in the below graph. Results point that the adsorption capacity of Fanwort for the CR red increased with temperature. This may be a result of increase in the mobility of the large dye with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Increasing temperature may produce a swelling effect within the internal structure of the fanwort enabling large dyes to penetrate further.

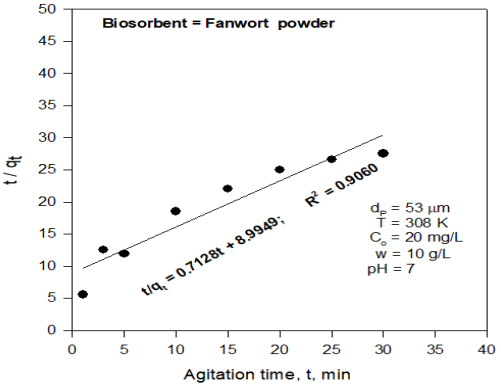


C. Kinetic studies

Lagergren-first-order kinetic model

Lagergren plot and pseudo second order kinetics plot for biosorption of Congo Red are drawn below.





D. Isotherm models

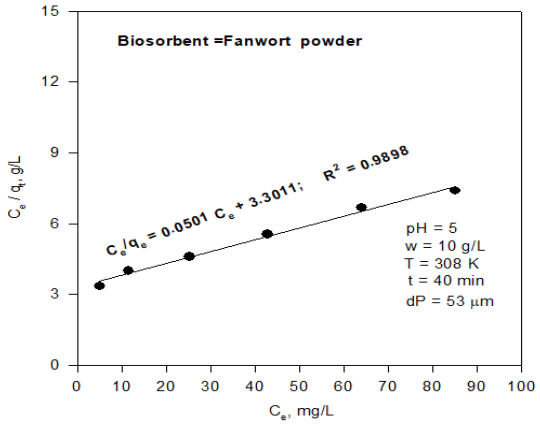
Langmuir model

Langmuir isotherm is the most widely used simple two-parameter equation. The Langmuir relationship is hyperbolic and the equation is
$q_e/q_m = K_L C_e / (1+K_L C_e)$.

This equation can be rearranged as
$(Ce/qe) = 1/(K_L qm) + Ce/qm$.

From the plots between (Ce/qe) and Ce, the slope {1/ (KLqm)} and the intercept (1/qm) can be calculated. The resulting equation is
$(Ce/qe) = 0.0501\ Ce + 3.3011$.

The (correlation coefficient of 0.9898) verifies strong binding of CR dye to the surface of fanwort powder.



Freundlich isotherm

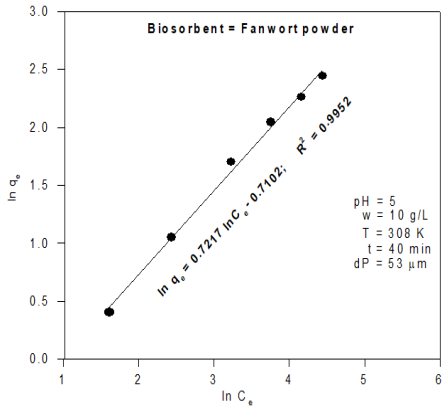
Freundlich presented an empirical adsorption isotherm equation that can be applied in case of low and intermediate concentration ranges. The Freundlich isotherm is given by

$q_e = K_f C_e^n$
Taking ln on both sides, we get
$\ln q_e = \ln K_f + n \ln C_e$

Freundlich isotherm, drawn between $\ln C_e$ and $\ln q_e$ has resulted in the following equation

$\ln q_e = 0.7271 \ln C_e - 0.7102$

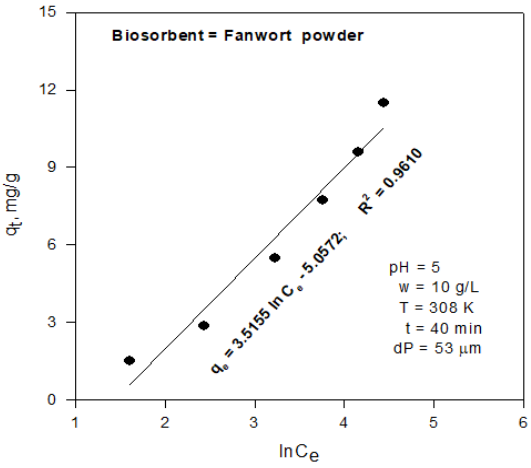
The equation has a correlation coefficient of 0.9952. The 'n' value of 0.7271 indicates favorable biosorption satisfying the condition of 0<n<1.



Temkin isotherm

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

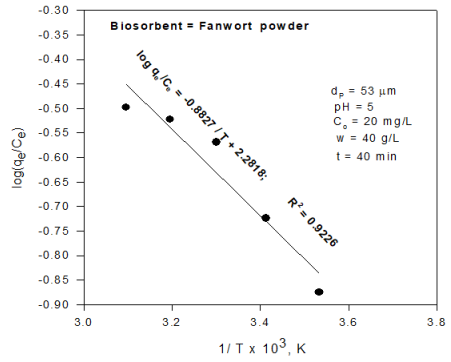
$q_e = RT \ln(A_T C_e)/b_T$
The linear form of Temkin isotherm is
$q_e = (RT/ b_T) \ln(A_T) + (RT/b_T) \ln(C_e)$
Plot between q_e and $\ln C_e$
$q_e = 3.5155 \ln C_e - 5.0572$



E. Thermodynamics

Vanthoff's plot:

Van't Hoff's plot is drawn in the following figure. For the biosrption of Congo Red, Gibbs free energy change (ΔG) is calculated to be –13221.2 J/mol from the data. The '-ve' value of ΔG shows thermodynamically possible and spontaneous nature of biosorption. The value of ΔH is found to be 16.9011 kJ/mol.K. The '+ve' ΔH shows the nature of biosorption is endothermic. The value of ΔS is found to be 43.6899 J/mol K for the biosorption of Congo Red. The '+ve' ΔS value implies an increase in the randomness at the interface of solid /solution during biosorption.



F. Optimization using Response Surface Methodology (RSM):

Optimization of the selected parameters using BBD

The identification of parameters that have greater control over the response is mandatory so as to know the optimum condition for Congo Red biosorption. For relating the percentage of biosorption and the four independent variables, the quadratic model is used in the present study. The regression equation for the percentage of biosorption is a function of pH (X_1), w (X_2), C_o (X_3), and T (X_4). The differences in the equivalent coded values of four parameters and response are presented in the following table.

Variable	Name	Range and levels		
		-1	0	+1
X_1	pH of aqueous solution	4	5	6
X_2	Initial concentration, C_o, mg/L	10	20	30
X_3	Biosorbent dosage, w, g/L	1	2	3
X_4	Temperature, T, K	293	303	313

The following equation represents multiple regression analysis of the experimental data for the biosorption of Congo Red:

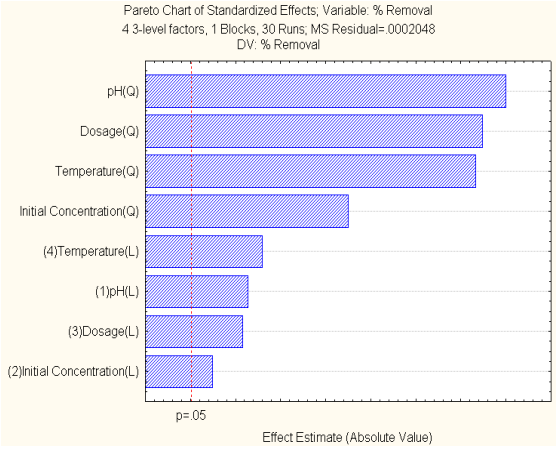
$$Y = -1364.39 + 37.32\,X_1 + 2.39\,X_2 + 4.23\,X_3 + 8.49\,X_4 - 4.53\,X_1^2 - 0.06\,X_2^2 - 0.07\,X_3^2 - 0.01\,X_4^2 + 0.00\,X_1X_2 - 0.01\,X_1X_3 - 0.00\,X_1X_4 + 0.00\,X_2X_3 - 0.00\,X_2X_4 + 0.00\,X_3X_4 \quad \text{---- (10)}$$

Run no.	X_1 pH	X_2 C_o	X_3, W	X_4 T	% removal of CR dye	
					Experimental	Predicted
1	4	10	2	303	86.38000	86.42
2	6	10	2	303	87.48000	87.48
3	4	30	2	303	86.02000	86.01
4	6	30	2	303	87.06000	87.07
5	5	20	1	293	84.34000	84.34
6	5	20	3	293	85.30000	85.31
7	5	20	1	313	85.66000	85.66
8	5	20	3	313	86.62000	86.63
9	5	20	2	303	92.48000	92.48
10	4	20	2	293	84.02000	84.01
11	6	20	2	293	85.06000	85.07
12	4	20	2	313	85.32000	85.33
13	6	20	2	313	86.42000	86.39
14	5	10	1	303	86.76000	86.75
15	5	30	1	303	86.34000	86.34
16	5	10	3	303	87.72000	87.71
17	5	30	3	303	87.32000	87.30
18	5	20	2	303	92.48000	92.48
19	4	20	1	303	84.12000	84.11
20	6	20	1	303	85.16000	85.17
21	4	20	3	303	85.08000	85.07
22	6	20	3	303	86.12000	86.13
23	5	10	2	293	86.66000	86.65
24	5	30	2	293	86.24000	86.24
25	5	10	2	313	87.98000	87.97
26	5	30	2	313	87.54000	87.56
27	5	20	2	303	92.48000	92.48
28	5	20	2	303	92.48000	92.48
29	5	20	2	303	92.48000	92.48

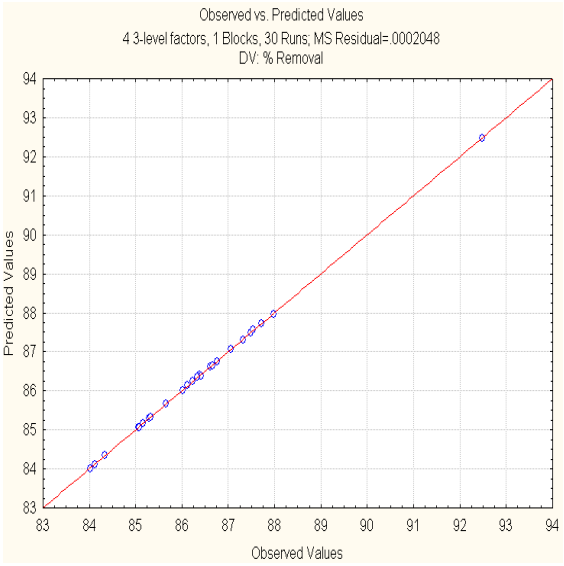
ANNOVA RESULTS:

Source of variation	SS	Df	Mean square(MS)	F-value	P>F
Model	224.18	14	16.0128	55858	0.00000
Error	0.0043	15	0.000286		
Total	224.1843				

Terms	Regression coefficient	Standard error of the coefficient	t-value	P-value
Mean/Interc.	-3223.17	5.043150	-639.119	0.00
(1)pH (L)	38.76	0.054801	707.344	0.00
pH (Q)	-3.82	0.005465	-699.663	0.00
(2)Initial Concentration(L)	0.75	0.002225	335.281	0.00
Initial Concentration(Q)	-0.02	0.000055	-350.594	0.00
(3)Dosage (L)		0.022245	657.450	0.00
Dosage (Q)	-3.54	0.005465	-647.051	0.00
(4)Temperature(L)	21.02	0.033118	634.813	0.00
Temperature(Q)	-0.03	0.000055	-632.869	0.00

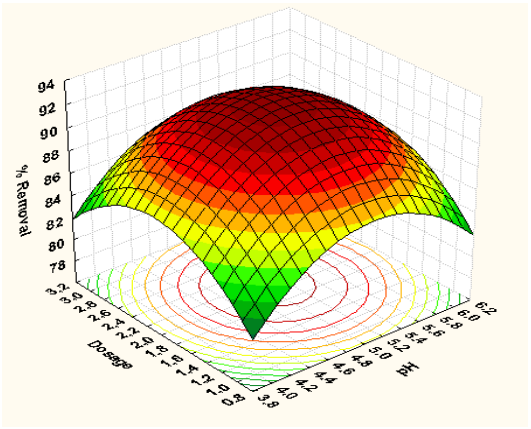


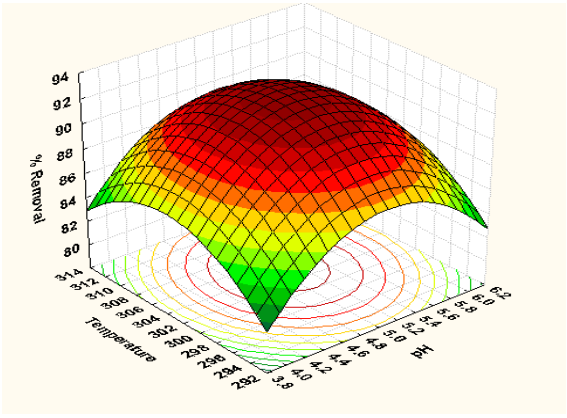
Pareto chart

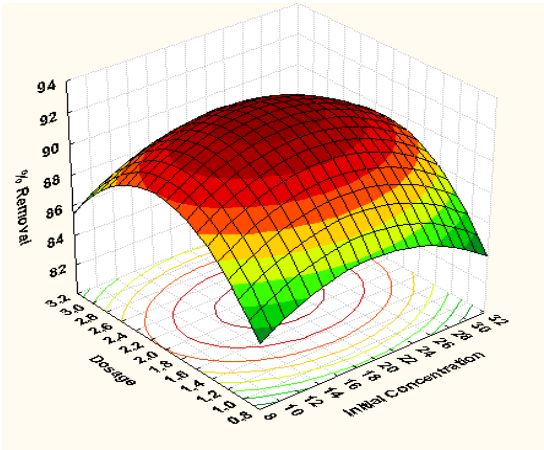


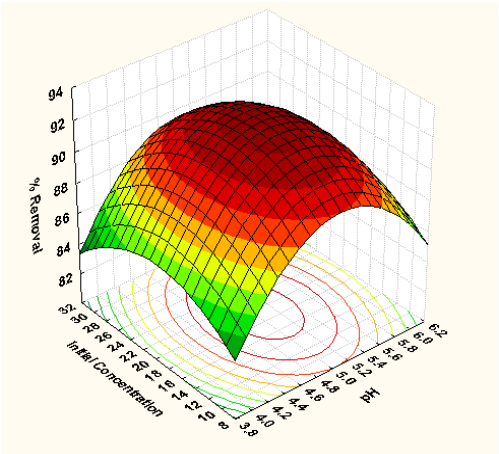
normal probability %biosorption of CR

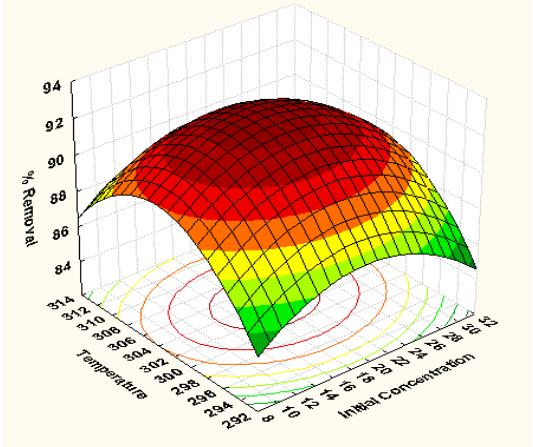
Interaction effects of biosorption variables

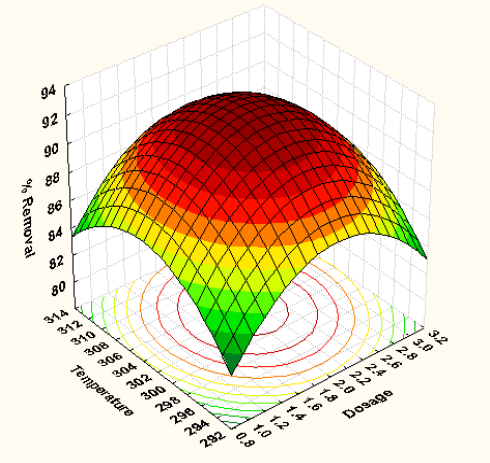












Surface contour plot for the effects of dosage, initial concentration, pH, Temperature on % biosorption of congo red.

Conclusions

Comparison between optimum values from BBD and experimentation CR with fanwort

The equilibrium agitation time is 40 minutes for the biosorption of CR dye. Congo Red dye's Percentage biosorption from the aqueous solution increases drastically with increase in pH from 2 (55 %) to 5 (75 %). The optimum dosage for Congo Red biosorption is 40 g/L (0.445 mg/g). The maximum uptake capacity of 19.96 mg/g is obtained at a temperature of 303 K. The maximum biosorption of CR dye (92.55174 %) onto Fanwort powder is viewed when the processing parameters are set as: pH = 5.0693, w = 2.0681 g, Co = 19.465 mg/L and T = 303.9542 K using CCD. The thermodynamic data show that % biosorption of CR dye is increased with increase in temperature. The investigation also reveals the endothermic nature of biosorption as ΔH is '+ve' (16.9011), irreversible nature of biosorption as ΔS is '+ve' (43.6899) and impulsiveness of biosorption as indicated by '–ve' ΔG (ΔG = –13221.2 J/mole).

Variable	BBD	Experimental value
pH of aqueous solution	5.0693	5
Initial CR concentration, mg/L	19.465	20
Biosorption dosage, w, g/L	2.0681	2
Temperature, K	303.9542	303
% biosorption	92.55174	89

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