SORPTION OF SYNTHETIC CONGO RED DYE USING SARGASSUM VULGARE POWDER AND OPTIMIZATION USING CENTRAL COMPOSITE DESIGN

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Abstract: ***The agile industrial activity during last three decades is greatly contributing to an increased dispersion of toxic elements in natural environments, mainly in aquatic systems. The present study deals with the biosorption of Congo red dye with Sargassum vulgare powder by single step optimization process. The parameters pH (2–8), Agitation time (5–180 min), Size of biosorbent (53–152 µm), Biosorbent dosage (10–80 g/L), Initial CR dye concentration (20–200 mg/L), Temperature (283–323 K) are studied carefully. Under this study the maximum biosorption of CR dye was observed at the optimum conditions of pH 6.0, Agitation time 60 min, Size of biosorbent 53µm, Biosorbent dosage 35 g/L, Initial CR dye concentration 20 mg/L and Temperature 303^{0}C. Lagergren first order kinetics fitted well for CR dye biosorption. The fit of isotherms are in the order of Freundlich , Langmuir and Temkin. 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.***

Index Terms – CR, Sargassum vulgare, 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, ultrafiltration, 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 addressed since agriculture contributes 46% to the gross national product [9]. All these demands a sustainable utilization of water and its resources both effectively and efficiently without resulting into scarcity and degradation in the existing quality of water.

2.0 EXPERIMENTAL PROCEDURE

The experimental procedure consists of the following steps:

2.1 Reagents and Chemicals
2.2 Preparation of the bisorbents
2.3 Characterization of biosorbents
2.4 Preparation of the stock solutions
2.5 Preparations of the 1000 mg/L of CR dye stock solution.
2.6 Studies on Equilibrium Biosorption Process.
2.1 Reagents and Chemicals: CR dye are used as source of dye stock solution.

2.2 PREPARATION OF THE BIOSORBENT

Sargassum vulgare 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.

2.3 Characterization of biosorbents

Biosorption of CR dye using Sargassum vulgare powder has many affecting factors which include characterization (FTIR, XRD, SEM), Biosorbents were characterized by FTIR spectrometry using Spectrum GX of Perkin Elmer, The X-Ray Diffractograms (XRD) of the powder samples are taken using a Rigaku Ultima model IV. XRD patterns are recorded from 3 to 900. For SEM studies, the dried powders and the corresponding CR dye loaded powders were first coated with ultra-thin film of gold by an ion sputter JFC-1100 and then were exposed under a Japanese make electron microscope (JEOL, JXA-8100).

2.4 Preparation of 1000 Mg/L of CR Dye Stock Solution

To prepare 1000 ppm of CR dye stock solution 1.0 g of 99 % CR dye powder was dissolved in 1.0 L of distilled water. From this stock solution synthetic samples of different concentrations of CR dye were prepared by appropriate dilutions. 100 ppm CR dye stock solution was prepared by diluting 100 ml of 1000 ppm CR 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.

2.5 Studies on Equilibrium Biosorption Process

Equilibrium studies agitation time, biosorbent size, pH, initial concentration, biosorbent dosage, temperature. Isotherms (Langmuir, Freundlich, Temkin), Kinetics (Lagergren First Order, Pseudo Second Order), Thermodynamics (Entropy, Enthalpy and Gibb's Free Energy) and Optimization using Central Composite Design.

3.0 RESULTS AND DISCUSSION

Biosorption of CR dye onto Sargassum vulgare powder

Biosorption of CR dye using Sargassum vulgare powder has many affecting factors which include characterization (FTIR, XRD, SEM), equilibrium studies (agitation time, biosorbent size, pH, initial concentration, biosorbent dosage, temperature), Isotherms (Langmuir, Freundlich, Temkin), Kinetics (Lagergren First Order, Pseudo Second Order), Thermodynamics (Entropy, Enthalpy and Gibb's Free Energy) and Optimization using Central Composite Design.

3.1 Characterization of Sargassum vulgare powder

3.1.1 Fourier Transform Infra-Red Spectroscopy (FTIR)

3.1.1(a) FTIR spectrum of untreated CR dye:

FTIR spectrum of untreated Sargassum vulgare powder is presented in fig. 3.1.1 (a). 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.

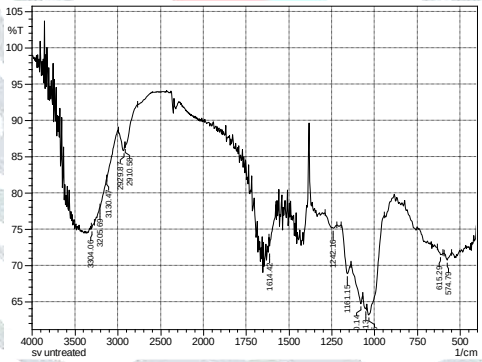

Fig. 3.1.1 (a) FTIR spectrum of CR untreated Sargassum vulgare powder

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.

3.1.1(b) FTIR spectrum of CR treated with Sargassum vulgare powder:

FTIR measurements for CR dye loaded algal biomass are shown in fig. 3.1.1 (b). 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.

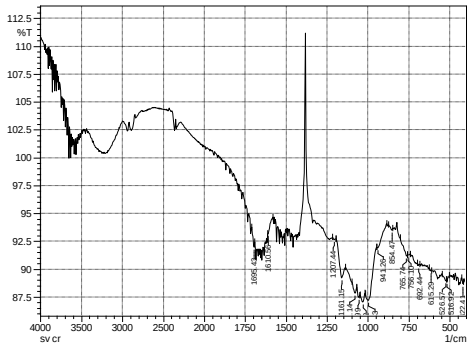

Fig. 3.1.1(b) FTIR spectrum of CR dye treated Sargassum vulgare powder

The sharp peaks of 1010.70 and 1070.49 cm-1 arose suddenly after loading of CR dye 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 patterns of untreated powder are shown in figs. 3.1.2.1 (a) & (b). XRD patterns shown in figs. 5.2(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 6.646.

Fig. 3.1.2.1 (a) XRD pattern of CR dye untreated Sargassum vulgare powder

Fig. 3.1.2.1 (b) XRD pattern of CR dye untreated Sargassum vulgare powder with matching compounds

3.1.2.2 XRD for CR dye treated with Sargassum vulgare 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 Sargassum vulgare powder**

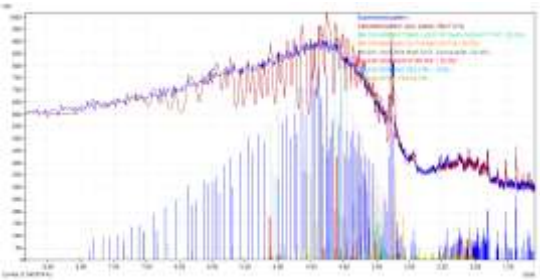

Fig. 3.1.2.2 (b) XRD pattern of CR dye treated Sargassum vulgare powder with matching compounds

3.1.3 Scanning Electron Microscope (SEM):

3.1.3.1 SEM analysis for untreated Sargassum vulgare powder

The SEM pictures of untreated Sargassum vulgare 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.

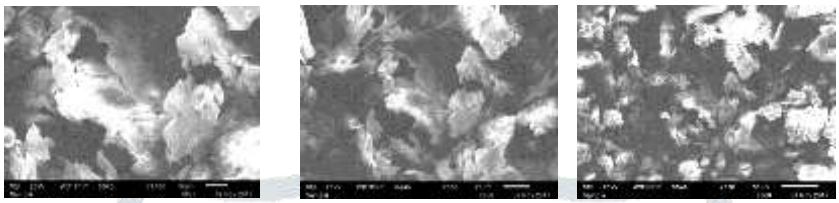

Fig. 3.1.3.1 SEM pattern of CR dye untreated Sargassum vulgare powder

3.1.3.2 SEM analysis for CR dye treated with Sargassum vulgare 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.

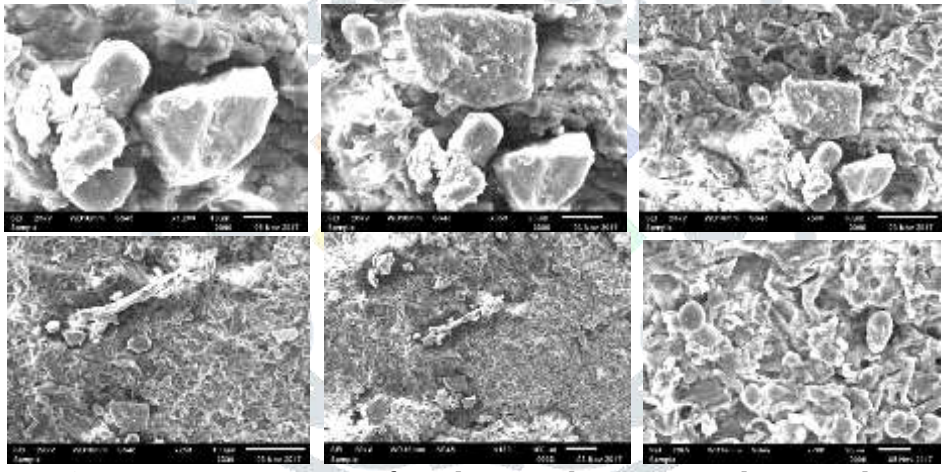

Fig. 3.1.3.2 SEM pattern of CR dye treated Sargassum vulgare powder

3.2 Equilibrium studies on biosorption of CR dye

3.2.1 Effect of agitation time:

For a typical experiment with 50 mL of aqueous solution adding 10 g/L of 53 µm size biosorbent, the % biosorption is increased from 22% to 72% in the agitation time period of 5 to 60 min. The equilibrium time for Sargassum vulgare powder CR dye system is 60 min, and no further removal was occurred beyond the time from 60 min to180 min fig.3.2.1 [10-19].

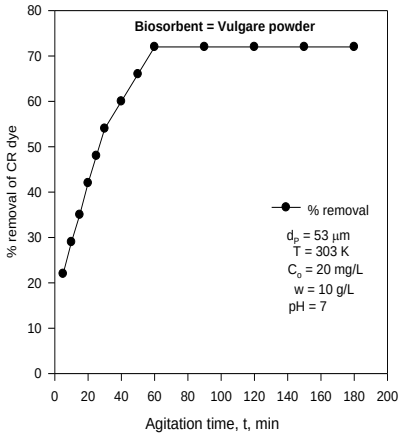

Fig. 3.2.1 Effect of agitation time on % biosorption of CR dye

3.2.2 Effect of biosorbent size:

The variations in % biosorption of CR dye with biosorbent size are drawn in fig. 3.2.2. The percentage biosorption is increased from 72 % to 40 % as the biosorbent size decreases from 152 to 53µm. The % removal and dye uptake were 1.44 to 0.8 mg/g as follows It is cleared from the plots that % removal drops with size of biosorbent. [20-29].

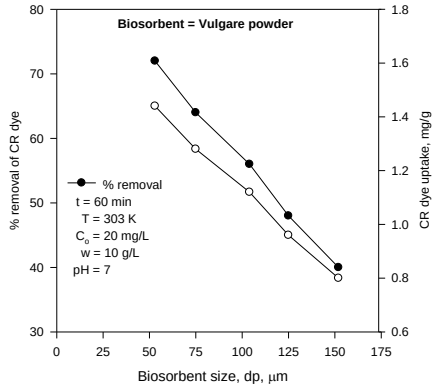

Fig 3.2.2 Effect of biosorbent size on % biosorption

3.2.3 Effect of pH in aqueous solution:

A plot is drawn in fig. 3.2.3 between % biosorption of CR dye and pH of aqueous solution. A significant increase in percentage biosorption of CR dye is observed as pH is increased from 2 to 6 and downward trend of the % biosorption is noted with an increase in pH above 6. the extent of biosorption is increased from 51 % to 78 % in the pH range from 2 to 6 and dye uptake is 1.02 to 1.56 mg/g and beyond the pH value of 6 it was decreased. [30-39].

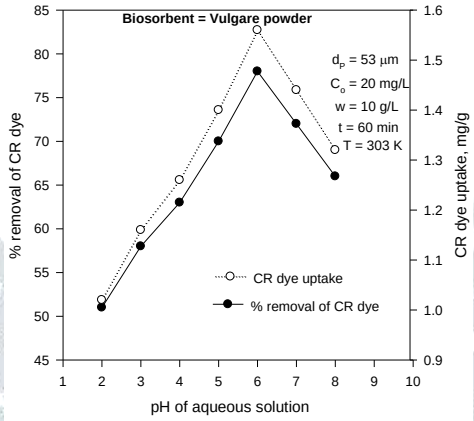

Fig. 3.2.3 Effect of pH on % biosorption

3.2.4 Effect of initial concentration of CR dye:

The effect of initial concentration of CR dye in the aqueous solution on the percentage biosorption at equilibrium agitation time is shown in fig. 3.2.4. The % biosorption is gradually decreased from 50 % to 78 % (10 to 1.56 mg/g) by increasing CR dye Concentration from 20 to 200 mg/L [40-49].

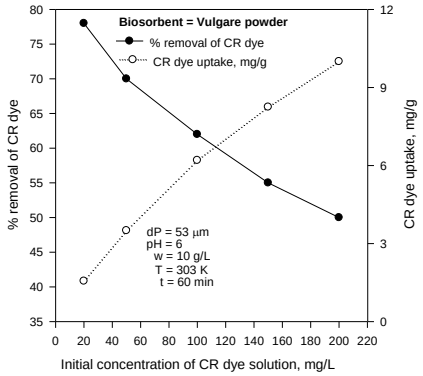

Fig.3.2.4 Effect of initial concentration for the biosorption

3.2.5 Effect of biosorbent dosage:

Fig. 3.2.5 represents the variation in percentage biosorption of CR dye from the aqueous solution with biosorbent dosage. The % biosorption is increased from 78 % to 90% as dosage is increased from 10 to 35 g/L. The increase in % biosorption is not appreciable (90 to 92 %) as dosage is increased from 35 to 80 g/L. Hence all other experiments are conducted at a dosage of 35 g/L [50-59].

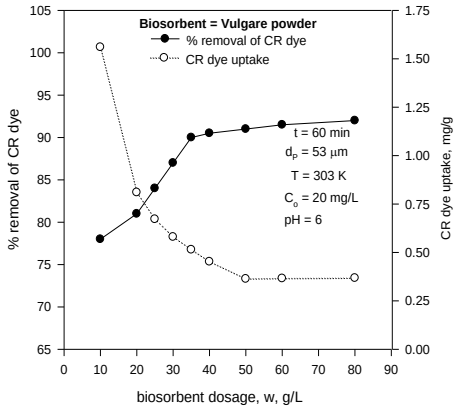

Fig. 3.2.5 Effect of biosorbent dosage on % biosorption

3.2.6 Effect of Temperature:

The effect of changes in the temperature on the CR dye uptake is shown in Fig. 3.2.6. Results indicate that the adsorption capacity of Saragassum vulgare power for the CR dye increased with temperature [60-69].

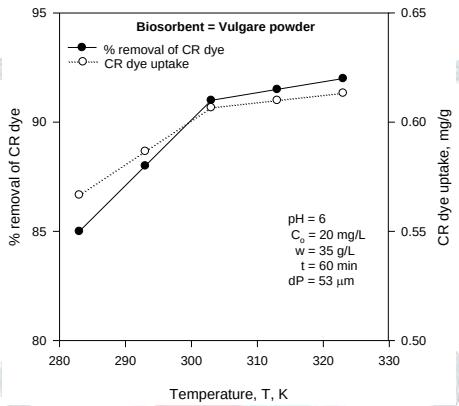

Fig. 3.2.6 Effect of temperature for the biosorption

3.3 Isotherms

3.3.1 Langmuir isotherm:

Langmuir isotherm is drawn between Ce/qe and Ce in fig. 3.3.1 for the present data. The resulting equation is (Ce/qe) = 0.0732 Ce + 2.9900 ------- (1) The (correlation coefficient of 0.9830) confirms strong binding of CR dye ions to the surface of Sargassum vulgare powder [70-79].

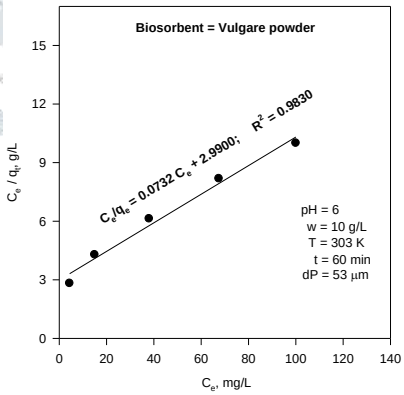

Fig. 3.3.1 Langmuir isotherm for biosorption

3.3.2 Freundlich isotherm:

Freundlich isotherm is drawn between ln Ce and ln qe in fig. 3.3.2, resulted in the following equation

ln qe = 0.5976 ln Ce - 0.4025 ------ (2)

The equation has a correlation coefficient of 0.9965. The 'n' value of 0.78487 indicates favorable biosorption satisfying the condition of 0<n<1 [80-89].

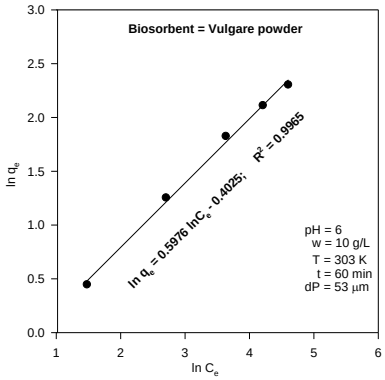

Fig.3.3.2 Freundlich isotherm for biosorption

3.3.3 Temkin isotherm:

Plot between qe and ln Ce is shown in fig. 3.3.3. The equation for Bromo Phenol Blue biosorption is
qe = 2.6829 ln Ce – 3.0291 ------ (3)

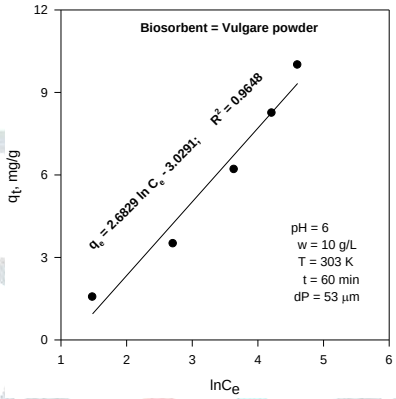

Fig. 3.3.3 Temkin isotherm for biosorption

It is found that biosorption data are well represented by Freundlich isotherm (R2=0.9965), Temkin (R2=0.9648) and Langmuir isotherms (R2=0.9830) [90-99].

3.4 Kinetics

3.4.1 First order kinetics

Lagergren plot and first order kinetics plot for biosorption of CR dye are drawn in figs. 3.4.1. the rate constant values for first order rate equations log (qe-qt) = –0.0202 t – 0.1533 [100-109]. It is noted that both first order rate equations explain the biosorption interactions satisfactorily.

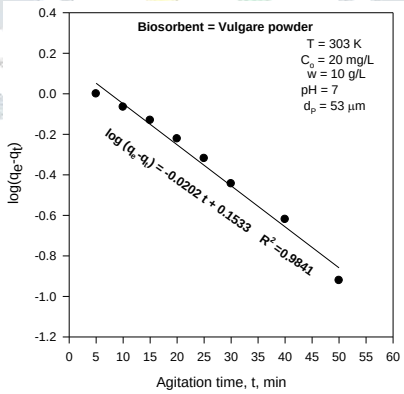

Fig.3.4.1 First order kinetics for biosorption

3.4.2 Second order kinetics

Lagergren plot and second order kinetics plot for biosorption of CR dye are drawn in figs. 3.4.2. the rate constant values for second order rate equations t/qt = 0.5493 t + 11.4696 [110-119]. It is noted that both first order rate equations explain the biosorption interactions satisfactorily.

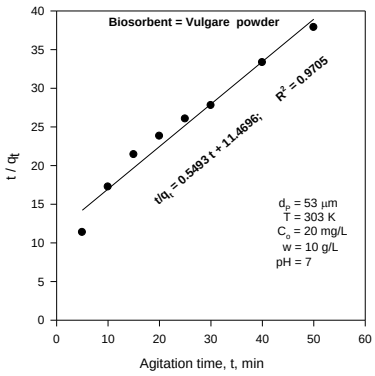

Fig.3.4.2 Second order Kinetics for biosorption

3.5 Thermodynamics :

Van't Hoff's plot is drawn in fig. 3.5. From the data, Gibbs free energy change (ΔG) is calculated to be –10744.1 J/mol for biosorption of CR dye. The ΔH parameter is 13.8242 kJ/mol K. The negative ΔH indicates the endothermic nature of biosorption. ΔS parameter is found to be 35.50455 J/mol K for CR dye biosorption [120-129].

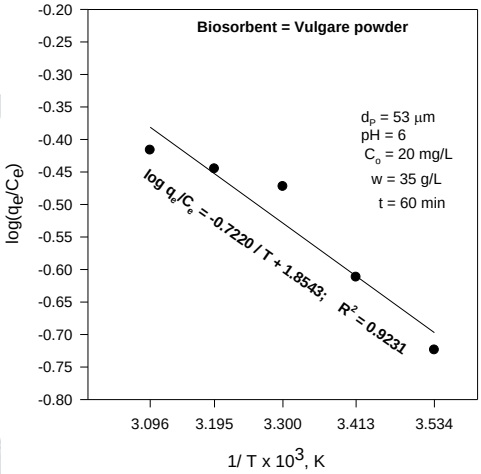

Fig.3.5 Vant Hoff's plot for biosorption

3.6 Optimization using Response Surface Methodology (RSM):

3.6.1 Optimization using CCD

The parameters that have greater influence over the response are to be identified so as to find the optimum condition for the biosorption of CR dye ions. The quadratic model is used in the present study, to relate four independent variables and percentage biosorption of CR dye. The regression equation for is % biosorption of CR dye (Y) is function of pH (X1), Co (X2), w (X3) and T (X4) [130-139].

The variations in the corresponding coded values of four parameters and response are presented in table-1

Table-1

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

Variable	Name	Range and levels				
		-2	-1	0	1	2
X1	pH of aqueous solution	4	5	6	7	8
X2	Initial concentration, Co, mg/L	10	15	20	25	30
X3	Biosorbent dosage, w, g/L	25	30	35	40	45
X4	Temperature, T, K	283	293	303	313	323

The following equation represents multiple regression analysis of the experimental data for the biosorption of CR dye:

$$Y = -1332.06 + 47.14 X1 + 2.75 X2 + 4.37 X3 + 7.73 X4 - 3.73 X12 - 0.08 X22 - 0.07 X32 - 0.01 X42 + 0.03 X1X2 - 0.02 X1X3 - 0.01 X1X4 - 0.00 X2X3 + 0.00 X2X4 + 0.00 X3X4 \quad \text{------ (4)}$$

Table-2

Results from CCD for CR dye biosorption by Sargassum vulgsre powder

Run no.	X1, pH	X2, Co	X3, W	X4, T	% biosorption of CR dye	
					Experimental	Predicted
1	3	15	25	293	82.42000	82.41000
2	3	15	25	313	82.82000	82.81250
3	3	15	35	293	83.62000	83.58917
4	3	15	35	313	84.42000	84.45667

5	3	25	25	293	81.18000	81.22250
6	3	25	25	313	81.92000	81.88000
7	3	25	35	293	81.98000	82.00667
8	3	25	35	313	83.12000	83.12917
9	5	15	25	293	83.52000	83.51917
10	5	15	25	313	83.72000	83.70667
11	5	15	35	293	84.18000	84.23333
12	5	15	35	313	84.92000	84.88583
13	5	25	25	293	83.00000	82.97667
14	5	25	25	313	83.38000	83.41917
15	5	25	35	293	83.28000	83.29583
16	5	25	35	313	84.18000	84.20333
17	2	20	30	303	75.98000	75.97750
18	6	20	30	303	78.18000	78.16083
19	4	10	30	303	84.72000	84.73417
20	4	30	30	303	82.90000	82.86417
21	4	20	20	303	84.20000	84.21750
22	4	20	40	303	86.22000	86.18083
23	4	20	30	283	86.24000	86.21417
24	4	20	30	323	87.52000	87.52417
25	4	20	30	303	92.00000	92.00000
26	4	20	30	303	92.00000	92.00000
27	4	20	30	303	92.00000	92.00000
28	4	20	30	303	92.00000	92.00000
29	4	20	30	303	92.00000	92.00000
30	4	20	30	303	92.00000	92.00000

Experimental conditions [Coded Values] and observed response values of central composite design with 24 factorial runs, 6- central points and 8- axial points. Agitation time fixed at 20 min and biosorbent size at 53 µm

Table-2 represents the results obtained in CCD. Response obtained from regression in eq.4 in the form of ANOVA is presented. From the Fisher's F-test (Fmodel = 285.1025) and a very low probability value (Pmodel > F=0.000000), it is known from table–3 that the model is highly significant. At 5% level, the computed F-value (F0.05 (14.15) = MSmodel/MSerror = 285.1025) is greater than that of the tabular F-value (F0.05 (14.15) tabulars = 2.42**),** indicating that the treatment differences are significant

Table-3
ANOVA of CR dye biosorption for entire quadratic model

Source of variation	SS	Df	Mean square(MS)	F-value	P > F
Model	501.5007	14	35.8214	29851	0.00000
Error	0.0181	15	0.00120		
Total	501.5188				

df- degree of freedom; SS- sum of squares; F- factor F; P- probability
R2=0.99999; R2 (adj):0.99998:

Table-4
Estimated regression coefficients for the CR dye biosorption onto Sargassum vulgare powder

Terms	Regression coefficient	Standard error of the coefficient	t-value	P-value
Mean/Intercept	-1332.06	6.755569	-197.180	0.000000
Dosage, w, g/L (L)	47.14	0.283772	166.104	0.000000
Dosage, w, g/L (Q)	-3.73	0.006633	-562.771	0.000000
Conc, Co, mg/L (L)	2.75	0.056041	48.986	0.000000

Conc, Co, mg/L (Q)	-0.08	0.000265	-309.105	0.000000
pH (L)	4.37	0.057213	76.429	0.000000
pH (Q)	-0.07	0.000265	-256.336	0.000000
Temperature, T, K (L)	7.73	0.041137	187.941	0.000000
Temperature, T, K (Q)	-0.01	0.000066	-193.391	0.000000
1L by 2L	0.03	0.001737	18.568	0.000000
1L by 3L	-0.02	0.001737	-13.386	0.000000
1L by 4L	-0.01	0.000868	-6.189	0.000017
2L by 3L	-0.00	0.000347	-11.371	0.000000
2L by 4L	0.00	0.000174	7.341	0.000002
3L by 4L	0.00	0.000174	13.386	0.000000

ainsignificant ($P \geq 0.05$)

The larger the value of t and smaller the value of P, the more significant is the corresponding coefficient term. The 't' and 'P' values are analyzed from table-4. It is found that the X1, X2, X3, X4, X12, X22 , X32 , X42 X1X2, X1X3, X2X3 and X2X4 have high significance to explain the individual and interaction effect of independent variables on Bromo Phenol Blue biosorption. The other terms (X1X2, X1X4, X2X3, X2X4 and X3X4) are insignificant and are not required to explain biosorption. The model is reduced to the following form by removing insignificant terms.

$$Y = -1332.06 + 47.14\,X1 + 2.75\,X2 + 4.37\,X3 + 7.73\,X4 - 3.73\,X12 - 0.08\,X22 - 0.07\,X32 - 0.01\,X42 + 0.03\,X1X2 - 0.02\,X1X3 - 0.01\,X1X4 \quad \text{---- (5)}$$

A synergistic effect is indicated by positive sign of the coefficient which means response increases with an increase in effect, while an antagonistic effect is indicated by a negative sign which means response decreases with an increase in effect. In the observed response values, a measure of the models variability is provided by the correlation coefficient (R2). In the present study, the value of the regression coefficient (R2 = 0.9999) for eq.5 indicates that 0.001 % of the total variations are not satisfactorily explained by the model. It is proved from that table that Fstatistics value for entire model is higher. This large value means that % biosorption can be adequately explained by the model equation. Generally P values lower than 0.05 indicates that the model is considered to be statistically significant at 95% confidence level. The % biosorption prediction from the model is shown in table-5.6. It is implied from table-5.7 that all the squared terms of all the variables and the linear terms are significant ($P < 0.05$). Among the interaction terms, all the terms ($P < 0.05$) are insignificant on the biosorption capacity. Fig. 3.6.1 and Fig. 3.6.2 shows pareto chart and normal probability plot (NPP) of residual values. It could be seen that the experimental points are reasonably aligned suggesting normal distribution.

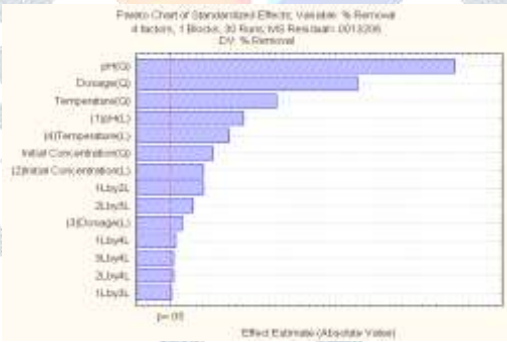

Fig. 3.6.1 Pareto Chart

3.6.2 Interaction effects of biosorption variables:

The three-dimensional view of response surface contour plots [Fig. 3.6.3 (a) to (f)] show % biosorption as a function of for various combinations of independent variables. The plots are represented as a function of two factors at a time **keeping** other factors fixed at zero level.

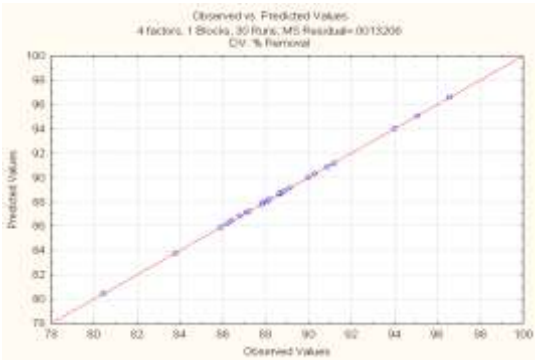

Fig. 3.6.2 Normal probability plot for % biosorption of CR dye

It is found from the response surface plots that the % biosorption is maximal at low and high levels of the input variables. However, there exists a region where neither an increasing nor a decreasing trend in % biosorption is observed. The biosorption variables should be optimum to maximize the % biosorption. The % biosorption of CR dye is strongly influenced by the pH as evident from figs. 3.6.3 (a) & (b).

The predicted optimal set of conditions for percentage biosorption of CR dye is

pH of aqueous solution	= 6.0674
Initial CR dye concentration	= 19.4353 mg/L
Biosorbent dosage	= 35.7489 g/L
Temperature	= 304.3023 K
% biosorption of CR dye	= 92.10288

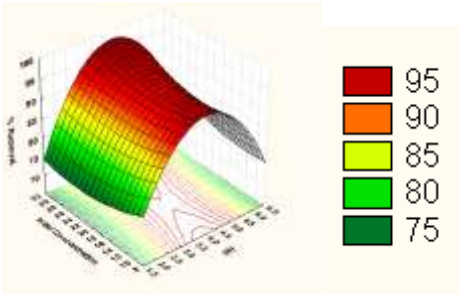

Fig. 3.6.3 (a) Surface contour plot for the effects of pH and initial CR dye concentration on % biosorption

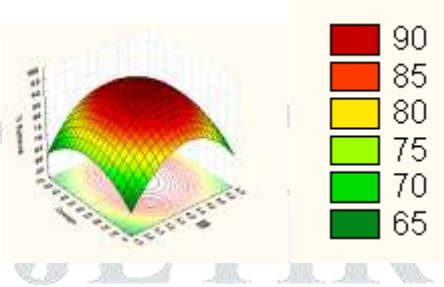

Fig. 3.6.3 (b) Surface contour plot for the effects of pH and dosage on % biosorption of CR dye

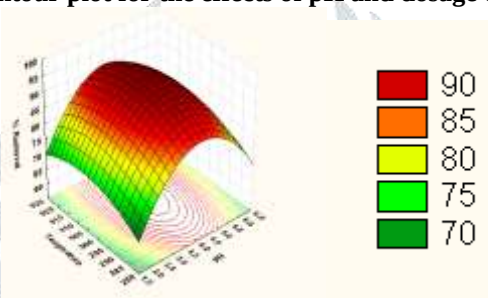

Fig. 3.6.3 (c) Surface contour plot for the effects of pH and Temperature on % biosorption of CR dye

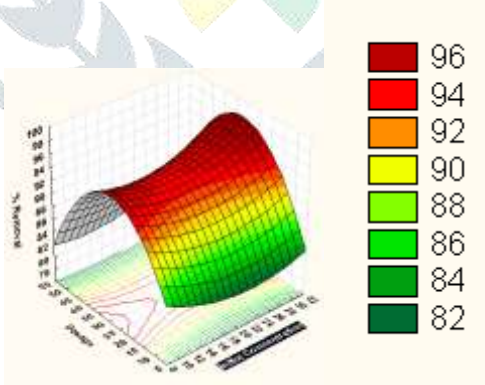

Fig. 3.6.3 (d) Surface contour plot for the effects of initial concentration and dosage on % biosorption of CR dye

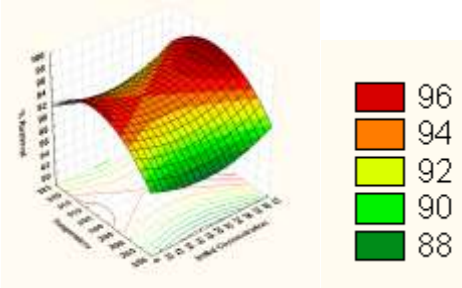

Fig. 3.6.3 (e) Surface contour plot for the effects of initial concentration and Temperature on % biosorption of CR dye

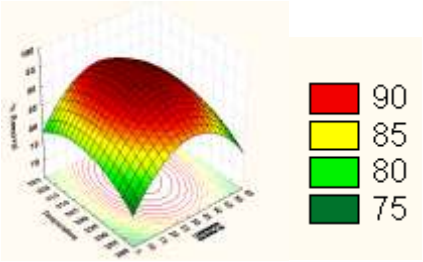

Fig. 3.6.3 (f) Surface contour plot for the effects of Dosage and Temperature on % biosorption of CR dye

Table – 5
Comparison between optimum values from CCD and experimentation

Variable	CCD	Experimental value
pH of aqueous solution	6.0674	4
Initial cobalt concentration, mg/L	19.4353	20
Biosorption dosage, w, g/L	35.7489	30
Temperature, K	304.3023	303
% biosorption	92.10288	95.0

Table – 6
Dyes uptake capacities for different biosorbents

Authors	Biosorbent	qt, mg/g
A. Bennani Karim et al [140]	Moroccan clay	50.25
Barka Noureddine et al [141]	crystalline Hydroxy apatite	243.9
Dong Yanan et al [142]	Activated Carbon	133
Fatih Deniz et al [143]	Paulownia tomentosa Steud. leaf powder	0.57
George Z. Kyzas et al [144]	carbon prepared from rice husk	690
Gonul Akkaya et al [145]	Dicranella varia	2000
Gurusamy Annadurai [146]	Strongly Chelating Polymer chitosan	40
Hema M et al [147]	acid activated low cost carbon	9.5693
Jung-Hyun Kim et al [148]	Polymer Particles	67
M. Santoshkumar et al [149]	native biomass of a new isolate of Penicillium sp	5.88
Present investigation	Sargassum vulgare powder	13.6612

REFERENCES

[1] F. W. Owa et al. "Water pollution: sources, effects, control and management" International Letters of Natural Sciences 3 (2014) 1-6

[2] M. Jeevanandam et al. "Hydrogeochemistry and Groundwater Quality Assessment of Lower Part of the Ponnaiyar River Basin, Cuddalore District, South India" Environ Monit Assess (2007) 132:263–274

[3] C. R . RAMAKRISHNAIAH et al. "Assessment of Water Quality Index for the Groundwater in Tumkur Taluk , Karnataka State, India" E-Journal of Chemistry 2009, 6(2), 523-530

[4] C. K. Jain et al. "Assessment of ground water quality for drinking purpose, District Nainital, Uttarakhand, India " Environ Monit Assess (2010) 166:663–676

[5] Vinod Kumar Gupta et al. "Chemical treatment technologies for waste-water recycling—an overview" | RSC Adv., 2012, 2, 6380–6388

[6] SUNIL KUMAR KARN et al. "Surface Water Pollution in Three Urban Territories of Nepal, India, and Bangladesh "Environmental Management Vol. 28, No. 4, pp. 483–496

[7] PURNAMITA DASGUPTA et al. "Valuing health damages from water pollution in urban Delhi, India: a health production function approach" Environment and Development Economics 9: 83–106 2004

[8] Bishwanath Goldar "Impact of informal regulation of pollution on water quality in rivers in India" Journal of Environmental Management 73 (2004) 117–130

[9] N. Subba Rao et al. "Seasonal variation of groundwater quality in a part of Guntur District, Andhra Pradesh, India" , Environ Geol (2006) 49: 413–429

[10] El-Geundi, Mohammad S. "Colour removal from textile effluents by adsorption techniques." Water Research 25, no. 3 (1991): 271-273.

[11] Namasivayam, C., and N. Kanchana. "Waste banana pith as adsorbent for color removal from wastewaters." Chemosphere25, no. 11 (1992): 1691-1705.

[12] Al-Ghouti, M., M. A. M. Khraisheh, M. N. M. Ahmad, and S. Allen. "Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: a kinetic study." Journal of Colloid and Interface Science 287, no. 1 (2005): 6-13.\

[13] Namasivayam, C., and R. T. Yamuna. "Removal of congo red from aqueous solutions by biogas waste slurry." Journal of Chemical Technology and Biotechnology 53, no. 2 (1992): 153-157.

[14] Namasivayam, C., R. Jeyakumar, and R. T. Yamuna. "Dye removal from wastewater by adsorption on 'waste'Fe (III)/Cr (III) hydroxide." Waste management 14, no. 7 (1994): 643-648.

[15] Namasivayam, C., M. Dinesh Kumar, K. Selvi, R. Ashruffunissa Begum, T. Vanathi, and R. T. Yamuna. "'Waste'coir pith—a potential biomass for the treatment of dyeing wastewaters." Biomass and Bioenergy 21, no. 6 (2001): 477-483.

[16] Namasivayam, C., D. Prabha, and M. Kumutha. "Removal of direct red and acid brilliant blue by adsorption on to banana pith." Bioresource Technology 64, no. 1 (1998): 77-79.

[17] Senthilkumaar, S., P. Kalaamani, K. Porkodi, P. R. Varadarajan, and C. V. Subburaam. "Adsorption of dissolved reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste." Bioresource Technology 97, no. 14 (2006): 1618-1625.

[18] Meshko, V., L. Markovska, M. Mincheva, and A. E. Rodrigues. "Adsorption of basic dyes on granular acivated carbon and natural zeolite." Water research 35, no. 14 (2001): 3357-3366.

[19] Waranusantigul, P., P. Pokethitiyook, M. Kruatrachue, and E. S. Upatham. "Kinetics of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza)."Environmental pollution 125, no. 3 (2003): 385-392.

[20] Poots, V. J. P., G. McKay, and J. J. Healy. "Removal of basic dye from effluent using wood as an adsorbent." Journal (Water Pollution Control Federation) (1978): 926-935.

[21] Khattri, S. D., and M. K. Singh. "Colour removal from synthetic dye wastewater using a bioadsorbent." Water, Air, and Soil Pollution 120, no. 3-4 (2000): 283-294.

[22] Jain, A. K., V. K. Gupta, Amit Bhatnagar, and Suhas. "A comparative study of adsorbents prepared from industrial wastes for removal of dyes." Separation Science and Technology 38, no. 2 (2003): 463-481.

[23] Gong, Renmin, Mei Li, Chao Yang, Yingzhi Sun, and Jian Chen. "Removal of cationic dyes from aqueous solution by adsorption on peanut hull." Journal of Hazardous Materials121, no. 1-3 (2005): 247-250.

[24] Al-Ghouti, M., M. A. M. Khraisheh, M. N. M. Ahmad, and S. Allen. "Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: a kinetic study." Journal of Colloid and Interface Science 287, no. 1 (2005): 6-13.

[25] Gupta, G. S., G. Prasad, and V. N. Singh. "Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal." Water Research 24, no. 1 (1990): 45-50.

[26] Chuah, T. G., A. Jumasiah, I. Azni, S. Katayon, and SY Thomas Choong. "Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview."Desalination 175, no. 3 (2005): 305-316.

[27] Khraisheh, M. A. M., M. A. Al-Ghouti, S. J. Allen, and M. N. Ahmad. "Effect of OH and silanol groups in the removal of dyes from aqueous solution using diatomite." Water Research39, no. 5 (2005): 922-932.

[28] Khattri, S. D., and M. K. Singh. "Removal of malachite green from dye wastewater using neem sawdust by adsorption."Journal of Hazardous Materials 167, no. 1-3 (2009): 1089-1094.

[29] Mckay, G. B. H. S., H. S. Blair, and J. R. Gardner. "Adsorption of dyes on chitin. I. Equilibrium studies." Journal of applied polymer science 27, no. 8 (1982): 3043-3057.

[30] Kannan, Nagarethinam, and Mariappan Meenakshi Sundaram. "Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study." Dyes and pigments 51, no. 1 (2001): 25-40.

[31] Al-Degs, Y., M. A. M. Khraisheh, S. J. Allen, and M. N. Ahmad. "Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent." Water Research 34, no. 3 (2000): 927-935.

[32] Martin, Maria J., Adriana Artola, M. Dolors Balaguer, and Miquel Rigola. "Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions." Chemical Engineering Journal 94, no. 3 (2003): 231-239.

[33] Demirbas, Ayhan. "Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review." Journal of hazardous materials 167, no. 1-3 (2009): 1-9.

[34] Sivaraj, Rajeshwari, C. Namasivayam, and K. Kadirvelu. "Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions." Waste management 21, no. 1 (2001): 105-110.

[35] Garg, Vinod K., Moirangthem Amita, Rakesh Kumar, and Renuka Gupta. "Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste." Dyes and pigments 63, no. 3 (2004): 243-250.

[36] Namasivayam, C., R. Radhika, and S. Suba. "Uptake of dyes by a promising locally available agricultural solid waste: coir pith." Waste management 21, no. 4 (2001): 381-387.

[37] Qu, Song, Fei Huang, Shaoning Yu, Gang Chen, and Jilie Kong. "Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with Fe2O3 particles."Journal of Hazardous Materials 160, no. 2-3 (2008): 643-647.

[38] Garg, V. K., Rakesh Kumar, and Renuka Gupta. "Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of Prosopis cineraria."Dyes and Pigments 62, no. 1 (2004): 1-10.

[39] Forgacs, Esther, Tibor Cserhati, and Gyula Oros. "Removal of synthetic dyes from wastewaters: a review." Environment international 30, no. 7 (2004): 953-971.

[40] Garg, V. K., Rakesh Kumar, and Renuka Gupta. "Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of Prosopis cineraria."Dyes and Pigments 62, no. 1 (2004): 1-10.

[41] Al-Ghouti, M. A., M. A. M. Khraisheh, S. J. Allen, and M. N. Ahmad. "The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth." Journal of Environmental Management69, no. 3 (2003): 229-238.

[42] Ardejani, F. Doulati, Kh Badii, N. Yousefi Limaee, Seyed Z. Shafaei, and A. R. Mirhabibi. "Adsorption of Direct Red 80 dye from aqueous solution onto almond shells: Effect of pH, initial concentration and shell type." Journal of hazardous materials151, no. 2-3 (2008): 730-737.

[43] Demirbas, Ayhan. "Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review." Journal of hazardous materials 167, no. 1-3 (2009): 1-9.

[44] Namasivayam, C., and Dyes Kavitha. "Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste." Dyes and pigments 54, no. 1 (2002): 47-58.

[45] Gong, Renmin, Mei Li, Chao Yang, Yingzhi Sun, and Jian Chen. "Removal of cationic dyes from aqueous solution by adsorption on peanut hull." Journal of Hazardous Materials121, no. 1-3 (2005): 247-250.

[46] Ho, Y. S., and G. McKay. "The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat." The Canadian Journal of Chemical Engineering 76, no. 4 (1998): 822-827.

[47] Amin, Nevine Kamal. "Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith." Desalination 223, no. 1-3 (2008): 152-161.

[48] Al-Ghouti, M., M. A. M. Khraisheh, M. N. M. Ahmad, and S. Allen. "Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: a kinetic study." Journal of Colloid and Interface Science 287, no. 1 (2005): 6-13.

[49] Daneshvar, N., M. Ayazloo, A. R. Khataee, and M. Pourhassan. "Biological decolorization of dye solution containing Malachite Green by microalgae Cosmarium sp."Bioresource technology 98, no. 6 (2007): 1176-1182.

[50] Yagub, Mustafa T., Tushar Kanti Sen, Sharmeen Afroze, and Ha Ming Ang. "Dye and its removal from aqueous solution by adsorption: a review." Advances in colloid and interface science 209 (2014): 172-184.

[51] Namasivayam, C., R. Radhika, and S. Suba. "Uptake of dyes by a promising locally available agricultural solid waste: coir pith." Waste management 21, no. 4 (2001): 381-387.

[52] Sivaraj, Rajeshwari, C. Namasivayam, and K. Kadirvelu. "Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions." Waste management 21, no. 1 (2001): 105-110.

[53] Mall, Indra D., Vimal C. Srivastava, and Nitin K. Agarwal. "Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash—kinetic study and equilibrium isotherm analyses." Dyes and pigments 69, no. 3 (2006): 210-223.

[54] Gong, Renmin, Mei Li, Chao Yang, Yingzhi Sun, and Jian Chen. "Removal of cationic dyes from aqueous solution by adsorption on peanut hull." Journal of Hazardous Materials121, no. 1-3 (2005): 247-250.

[55] Gao, Bao-Yu, Qin-Yan Yue, Yan Wang, and Wei-Zhi Zhou. "Color removal from dye-containing wastewater by magnesium chloride." Journal of Environmental Management 82, no. 2 (2007): 167-172.

[56] Amin, Nevine Kamal. "Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith." Desalination 223, no. 1-3 (2008): 152-161.

[57] Papić, Sanja, Natalija Koprivanac, Ana Lončarić Božić, and Azra Meteš. "Removal of some reactive dyes from synthetic wastewater by combined Al (III) coagulation/carbon adsorption process." Dyes and pigments 62, no. 3 (2004): 291-298.

[58] Lata, Hem, V. K. Garg, and R. K. Gupta. "Removal of a basic dye from aqueous solution by adsorption using Parthenium hysterophorus: an agricultural waste." Dyes and pigments 74, no. 3 (2007): 653-658.

[59] Moussavi, Gholamreza, and Maryam Mahmoudi. "Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles." Journal of Hazardous Materials 168, no. 2-3 (2009): 806-812.

[60] Khattri, S. D., and M. K. Singh. "Colour removal from synthetic dye wastewater using a bioadsorbent." Water, Air, and Soil Pollution 120, no. 3-4 (2000): 283-294.

[61] Gupta, G. S., G. Prasad, and V. N. Singh. "Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal." Water Research 24, no. 1 (1990): 45-50.

[62] Bhatnagar, Amit, and A. K. Jain. "A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water." Journal of Colloid and Interface Science 281, no. 1 (2005): 49-55.

[63] Mohan, Dinesh, Kunwar P. Singh, Gurdeep Singh, and Kundan Kumar. "Removal of dyes from wastewater using flyash, a low-cost adsorbent." Industrial & engineering chemistry research 41, no. 15 (2002): 3688-3695.

[64] Kuo, W. G. "Decolorizing dye wastewater with Fenton's reagent." Water Research 26, no. 7 (1992): 881-886.

[65] Khattri, S. D., and M. K. Singh. "Removal of malachite green from dye wastewater using neem sawdust by adsorption."Journal of Hazardous Materials 167, no. 1-3 (2009): 1089-1094.

[66] Wang, Shaobin, Huiting Li, and Longya Xu. "Application of zeolite MCM-22 for basic dye removal from wastewater."Journal of colloid and interface science 295, no. 1 (2006): 71-78.

[67] Gupta, V. K., I. Ali, and Dinesh Mohan. "Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents." Journal of colloid and interface science 265, no. 2 (2003): 257-264.

[68] Daneshvar, N., M. Ayazloo, A. R. Khataee, and M. Pourhassan. "Biological decolorization of dye solution containing Malachite Green by microalgae Cosmarium sp."Bioresource technology 98, no. 6 (2007): 1176-1182.

[69] Amin, Nevine Kamal. "Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics."Journal of hazardous materials 165, no. 1-3 (2009): 52-62.

[70] Ho, Yuh-Shan, and Gordon McKay. "Sorption of dye from aqueous solution by peat." Chemical engineering journal70, no. 2 (1998): 115-124.
[71] Al-Ghouti, M. A., M. A. M. Khraisheh, S. J. Allen, and M. N. Ahmad. "The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth." Journal of Environmental Management 69, no. 3 (2003): 229-238.
[72] Khraisheh, M. A. M., M. A. Al-Ghouti, S. J. Allen, and M. N. Ahmad. "Effect of OH and silanol groups in the removal of dyes from aqueous solution using diatomite." Water Research 39, no. 5 (2005): 922-932.
[73] Namasivayam, C., R. Radhika, and S. Suba. "Uptake of dyes by a promising locally available agricultural solid waste: coir pith." Waste management 21, no. 4 (2001): 381-387.
[74] Ramakrishna, Konduru R., and T. Viraraghavan. "Dye removal using low cost adsorbents." Water Science and Technology 36, no. 2-3 (1997): 189-196.
[75] Özacar, Mahmut, and İ. Ayhan Şengil. "Adsorption of metal complex dyes from aqueous solutions by pine sawdust."Bioresource technology 96, no. 7 (2005): 791-795.
[76] Malik, P. Kumar. "Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36." Dyes and pigments 56, no. 3 (2003): 239-249.
[77] Demirbas, Ayhan. "Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review."Journal of hazardous materials 167, no. 1-3 (2009): 1-9.
[78] Mall, Indra Deo, Vimal Chandra Srivastava, Nitin Kumar Agarwal, and Indra Mani Mishra. "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses."Chemosphere 61, no. 4 (2005): 492-501.
[79] Mall, Indra Deo, Vimal Chandra Srivastava, Nitin Kumar Agarwal, and Indra Mani Mishra. "Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses." Colloids and Surfaces A: Physicochemical and Engineering Aspects 264, no. 1-3 (2005): 17-28.
[80] Al-Ghouti, M. A., M. A. M. Khraisheh, S. J. Allen, and M. N. Ahmad. "The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth." Journal of Environmental Management 69, no. 3 (2003): 229-238.
[81] Ho, Yuh-Shan, and Gordon McKay. "Sorption of dye from aqueous solution by peat." Chemical engineering journal70, no. 2 (1998): 115-124.
[82] Khraisheh, M. A. M., M. A. Al-Ghouti, S. J. Allen, and M. N. Ahmad. "Effect of OH and silanol groups in the removal of dyes from aqueous solution using diatomite." Water Research 39, no. 5 (2005): 922-932.
[83] Mall, Indra Deo, Vimal Chandra Srivastava, Nitin Kumar Agarwal, and Indra Mani Mishra. "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses."Chemosphere 61, no. 4 (2005): 492-501.
[84] Ramakrishna, Konduru R., and T. Viraraghavan. "Dye removal using low cost adsorbents." Water Science and Technology 36, no. 2-3 (1997): 189-196.
[85] Namasivayam, C., R. Radhika, and S. Suba. "Uptake of dyes by a promising locally available agricultural solid waste: coir pith." Waste management 21, no. 4 (2001): 381-387.
[86] Malik, P. Kumar. "Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36." Dyes and pigments 56, no. 3 (2003): 239-249.
[87] Demirbas, Ayhan. "Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review."Journal of hazardous materials 167, no. 1-3 (2009): 1-9.
[88] Namasivayam, C., and D. J. S. E. Arasi. "Removal of congo red from wastewater by adsorption onto waste red mud."Chemosphere 34, no. 2 (1997): 401-417.
[89] Özacar, Mahmut, and İ. Ayhan Şengil. "Adsorption of metal complex dyes from aqueous solutions by pine sawdust."Bioresource technology 96, no. 7 (2005): 791-795.
[90] Hameed, B. H. "Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue." Journal of Hazardous materials 162, no. 2-3 (2009): 939-944.
[91] Mall, I. D., V. C. Srivastava, G. V. A. Kumar, and I. M. Mishra. "Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution." Colloids and Surfaces A: Physicochemical and Engineering Aspects 278, no. 1-3 (2006): 175-187.
[92] Tan, I. A. W., B. H. Hameed, and A. L. Ahmad. "Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon." Chemical Engineering Journal 127, no. 1-3 (2007): 111-119.
[93] El-Sayed, Gamal Owes. "Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber."Desalination 272, no. 1-3 (2011): 225-232.
[94] Safa, Yusra, and Haq Nawaz Bhatti. "Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk."Desalination 272, no. 1-3 (2011): 313-322.
[95] Ahmad, Mohd Azmier, and Rasyidah Alrozi. "Removal of malachite green dye from aqueous solution using rambutan peel-based activated carbon: Equilibrium, kinetic and thermodynamic studies." Chemical Engineering Journal 171, no. 2 (2011): 510-516.
[96] Mishra, Ashish Kumar, T. Arockiadoss, and S. Ramaprabhu. "Study of removal of azo dye by functionalized multi walled carbon nanotubes." Chemical Engineering Journal 162, no. 3 (2010): 1026-1034.
[97] Mane, Venkat S., Indra Deo Mall, and Vimal Chandra Srivastava. "Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution." Dyes and Pigments 73, no. 3 (2007): 269-278.
[98] Ahmad, Rais. "Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP)."Journal of hazardous materials 171, no. 1-3 (2009): 767-773.
[99] Başar, Canan Akmil. "Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot." Journal of Hazardous Materials 135, no. 1-3 (2006): 232-241.

[100] Mall, Indra Deo, Vimal Chandra Srivastava, Nitin Kumar Agarwal, and Indra Mani Mishra. "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses."Chemosphere 61, no. 4 (2005): 492-501.

[101] Crini, Grégorio, Harmel Ndongo Peindy, Frédéric Gimbert, and Capucine Robert. "Removal of CI Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies." Separation and Purification Technology 53, no. 1 (2007): 97-110.

[102] Konstantinou, Ioannis K., and Triantafyllos A. Albanis. "TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review."Applied Catalysis B: Environmental 49, no. 1 (2004): 1-14.

[103] Hameed, B. H., D. K. Mahmoud, and A. L. Ahmad. "Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste." Journal of Hazardous Materials 158, no. 1 (2008): 65-72.

[104] Gong, Renmin, Yi Ding, Mei Li, Chao Yang, Huijun Liu, and Yingzhi Sun. "Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution." Dyes and Pigments 64, no. 3 (2005): 187-192.

[105] Vadivelan, V., and K. Vasanth Kumar. "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk." Journal of colloid and interface science286, no. 1 (2005): 90-100.

[106] Garg, V. K., Rakesh Kumar, and Renuka Gupta. "Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of Prosopis cineraria."Dyes and Pigments 62, no. 1 (2004): 1-10.

[107] Doğan, Mehmet, Mahir Alkan, Aydın Türkyilmaz, and Yasemin Özdemir. "Kinetics and mechanism of removal of methylene blue by adsorption onto perlite." Journal of hazardous materials 109, no. 1-3 (2004): 141-148.

[108] Amin, Nevine Kamal. "Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith." Desalination 223, no. 1-3 (2008): 152-161.

[109] Yuh-Shan, Ho. "Citation review of Lagergren kinetic rate equation on adsorption reactions." Scientometrics 59, no. 1 (2004): 171-177.

[110] Mall, Indra Deo, Vimal Chandra Srivastava, Nitin Kumar Agarwal, and Indra Mani Mishra. "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses." Chemosphere 61, no. 4 (2005): 492-501.

[111] Vadivelan, V., and K. Vasanth Kumar. "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk." Journal of colloid and interface science286, no. 1 (2005): 90-100.

[112] Crini, Grégorio, Harmel Ndongo Peindy, Frédéric Gimbert, and Capucine Robert. "Removal of CI Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies." Separation and Purification Technology 53, no. 1 (2007): 97-110.

[113] Hameed, B. H., D. K. Mahmoud, and A. L. Ahmad. "Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste." Journal of Hazardous Materials 158, no. 1 (2008): 65-72.

[114] Wang, Shaobin, Huiting Li, and Longya Xu. "Application of zeolite MCM-22 for basic dye removal from wastewater." Journal of colloid and interface science 295, no. 1 (2006): 71-78.

[115] Amin, Nevine Kamal. "Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith." Desalination 223, no. 1-3 (2008): 152-161.

[116] Malik, P_K. "Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics." Journal of Hazardous Materials 113, no. 1-3 (2004): 81-88.

[117] Ho, Yuh-Shan, and G. McKay. "Kinetic models for the sorption of dye from aqueous solution by wood." Process Safety and Environmental Protection 76, no. 2 (1998): 183-191.

[118] Kavitha, D., and C. Namasivayam. "Experimental and kinetic studies on methylene blue adsorption by coir pith carbon." Bioresource Technology 98, no. 1 (2007): 14-21.

[119] Tan, I. A. W., A. L. Ahmad, and B. H. Hameed. "Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies." Journal of hazardous materials 154, no. 1-3 (2008): 337-346.

[120] Ahmad, Mohd Azmier, and Rasyidah Alrozi. "Removal of malachite green dye from aqueous solution using rambutan peel-based activated carbon: Equilibrium, kinetic and thermodynamic studies." Chemical Engineering Journal 171, no. 2 (2011): 510-516.

[121] Kumar, P. Senthil, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, and S. Sivanesan. "Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions." Desalination 261, no. 1-2 (2010): 52-60.

[122] Wang, Shaobin, Y. Boyjoo, A. Choueib, and Z. H. Zhu. "Removal of dyes from aqueous solution using fly ash and red mud." Water research 39, no. 1 (2005): 129-138.

[123] Dawood, Sara, and Tushar Kanti Sen. "Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design." Water research 46, no. 6 (2012): 1933-1946.

[124] Yagub, Mustafa T., Tushar Kanti Sen, Sharmeen Afroze, and Ha Ming Ang. "Dye and its removal from aqueous solution by adsorption: a review." Advances in colloid and interface science 209 (2014): 172-184.

[125] Hema, M., and S. Arivoli. "Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon." International Journal of Physical Sciences 2, no. 1 (2007): 10-17.

[126] Kuo, Chao-Yin, Chung-Hsin Wu, and Jane-Yii Wu. "Adsorption of direct dyes from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetics and thermodynamics parameters." Journal of Colloid and Interface Science 327, no. 2 (2008): 308-315.

[127] Kyzas, George Z., Nikolaos K. Lazaridis, and Athanassios Ch Mitropoulos. "Removal of dyes from aqueous solutions with untreated coffee residues as potential low-cost adsorbents: Equilibrium, reuse and thermodynamic approach." Chemical engineering journal 189 (2012): 148-159.

[128] Chowdhury, Shamik, and Papita Saha. "Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, kinetic and thermodynamic studies." Chemical Engineering Journal 164, no. 1 (2010): 168-177.

[129] Demirbas, Ayhan. "Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review." Journal of hazardous materials 167, no. 1-3 (2009): 1-9.

[130] Sharma, Shweta, Anushree Malik, and Santosh Satya. "Application of response surface methodology (RSM) for optimization of nutrient supplementation for Cr (VI) removal by Aspergillus lentulus AML05." Journal of Hazardous Materials164, no. 2-3 (2009): 1198-1204.

[131] Gönen, Ferda, and Zümriye Aksu. "Single and binary dye and heavy metal bioaccumulation properties of Candida tropicalis: Use of response surface methodology (RSM) for the estimation of removal yields." Journal of hazardous materials172, no. 2-3 (2009): 1512-1519.

[132] Ravikumar, K., B. Deebika, and K. Balu. "Decolourization of aqueous dye solutions by a novel adsorbent: application of statistical designs and surface plots for the optimization and regression analysis." Journal of hazardous materials 122, no. 1-2 (2005): 75-83.

[133] Taheri, M., MR Alavi Moghaddam, and M. Arami. "Techno-economical optimization of Reactive Blue 19 removal by combined electrocoagulation/coagulation process through MOPSO using RSM and ANFIS models." Journal of environmental management 128 (2013): 798-806.

[134] Vepsäläinen, Mikko, Mohammad Ghiasvand, Jukka Selin, Jorma Pienimaa, Eveliina Repo, Martti Pulliainen, and Mika Sillanpää. "Investigations of the effects of temperature and initial sample pH on natural organic matter (NOM) removal with electrocoagulation using response surface method (RSM)." Separation and Purification Technology 69, no. 3 (2009): 255-261.

[135] Chen, Dan, Yang Li, Jia Zhang, Wenhui Li, Jizhi Zhou, Li Shao, and Guangren Qian. "Efficient removal of dyes by a novel magnetic Fe3O4/ZnCr-layered double hydroxide adsorbent from heavy metal wastewater." Journal of hazardous materials 243 (2012): 152-160.

[136] Tanyildizi, M. Şaban. "Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull." Chemical Engineering Journal 168, no. 3 (2011): 1234-1240.

[137] Hameed, B. H., I. A. W. Tan, and A. L. Ahmad. "Optimization of basic dye removal by oil palm fibre-based activated carbon using response surface methodology." Journal of hazardous materials 158, no. 2-3 (2008): 324-332.

[138] Zuorro, Antonio, Marcello Fidaleo, and Roberto Lavecchia. "Response surface methodology (RSM) analysis of photodegradation of sulfonated diazo dye Reactive Green 19 by UV/H2O2 process." Journal of environmental management127 (2013): 28-35.

[139] Santos, Sílvia CR, and Rui AR Boaventura. "Adsorption modelling of textile dyes by sepiolite." Applied Clay Science42, no. 1-2 (2008): 137-145.

[140] Bennani Karim , B. Mounir, M. Hachkar, M. Bakasse and A.Yaacoubi, "Adsorption of Malachite Green dye onto raw Moroccan clay in batch and dynamic system", Canadian Journal on Environmental, Construction and Civil Engineering Vol. 2, No. 2, February 2011

[141] Barka Noureddine, Qourzal Samir, Assabbane Ali, Nounah Abederrahman and Ait-ichou Yhya, "Adsorption of Disperse Blue SBL dye by synthesized poorly crystalline Hydroxyapatite", Journal of Environmental Sciences 20(2008) 1268–1272

[142] Dong Yanan , Su Yanle, Chen Wenjuan , Peng Jinming , Zhang Yan and Jiang Zhongyi, "Ultrafiltration Enhanced with Activated Carbon Adsorption for Efficient Dye Removal from Aqueous Solution", Chinese Journal of Chemical Engineering, 19(5) 863—869 (2011)

[143] Fatih Deniz and Saadet D. Saygideger, "Equilibrium, kinetic and thermodynamic studies of Acid Orange 52 dye biosorption by Paulownia tomentosa Steud. leaf powder as a low-cost natural biosorbent", Bioresource Technology 101 (2010) 5137–5143

[144] George Z. Kyzas , Jie Fu and Kostas A. Matis, "The Change from Past to Future for Adsorbent Materials in Treatment of Dyeing Wastewaters", Materials 2013, 6, 5131-5158

[145] Gonul Akkaya and Ayla Ozer, "Biosorption of Acid Red 274 (AR 274) on Dicranella varia:Determination of equilibrium and kinetic model parameters", Process Biochemistry 40 (2005) 3559–3568

[146] Gurusamy Annadurai , "Adsorption of Basic Dye on Strongly Chelating Polymer: Batch Kinetics Studies", Iranian PolynterJourual / Volume II Number 4 (2002)

[147] Hema M and Arivoli S., "Adsorption kinetics and thermodynamics of malachite green dye unto acid activated low cost carbon", J. Appl. Sci. Environ. Manage. March, 2008 ,Vol. 12(1) 43 – 51

[148] Jung-Hyun Kim and Jeong-Yeol Yoon, "Protein Adsorption on Polymer Particles",

[149] M. Santoshkumar, O. Anjaneya, S. Nayak Anand and T.B. Karegoudar, "Biosorption of acid violet dye from aqueous solutions using native biomass of a new isolate of Penicillium sp.", International Biodeterioration & Biodegradation 63 (2009) 782–787