Fixed Bed Column Study For The Removal Of Reactive Red 120(Rr120) Dye From Aquatic Environment By Low Cost Adsorbents

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Abstract—**This study described adsorption of Reactive Red120 (RR120) by cotton shell and neem bark in batch and fixed-bed column modes at 293 K. The kinetic and equilibrium of adsorption in batch mode were studied. Nonlinear regressive method was used to obtain relative parameters of adsorption models. The kinetic process was better described by a -first-order kinetic model. The equilibrium adsorption was effectively described by Freundlich and Langmuir adsorption isotherm. The value of C1 from the Langmuir model was 34.375,(RR120 by NB), 33.33,(RR120 by CS),mg/g, Langmuir adsorption intensity Kd had value of 0.2909,(RRNB), 0.25,(RRCS) and the value of Freundlich adsorption capacity Kf is 2.664 (1/n)=0.38(RR120 NB) , 2.691 (1/n)=0.44(RR120 CS) . In fixed-bed column adsorption, the effects of bed height, feed flow rate, and inlet Reactive Red120(RR120) concentration were studied by assessing breakthrough curve. The column data were fitted by the Thomas, Clark and modified dose–response models. The modified dose–response model was best to fit the breakthrough curves at experimental conditions. Box behnken design was successfully employed for experimental design and analysis of the results.The combined effect of pH, temperature and Dye concentatration on the dye adsorption was investigated and optimized using response surface methodology. The optimum pH, temperature, and dye concentration were found to be 6.46,32.22oC and 12.60 for Reactive Red120(RR120) by cotton Shell and the optimum pH, temperature, and dye concentration were found to be 6.37,30.82oC and 11.65 for Reactive Red120(RR120) by neem bark.The results were implied that cotton shell and neem bark may be suitable as an adsorbent material for adsorption of Reactive Red(RR120) from an aqueous solution.**

Key words: Low cost adsorbents (cotton shell and neem bark), freundlich and Langmuir isotherm, Box- Behnken (RSM), Fixed bed column.

I. INTRODUCTION

The release of large quantity of dyes in to water bodies by textile industries poses serious environmental problems due to persistent and recalcitrant nature of some of these dyes. According to one estimate up to 50 % of the dyes may be directly lost in to waterways when using reactive dyes. Untreated or partially treated effluents from other industries namely paper, plastic, leather, cosmetic, food, wooden, and carpet also contributes to the pollution load.

There are four main methods of reducing color in textile effluents streams ; physical methods such as membrane technology (Gholami et al .,2001), Chemical methods such as coagulation (Nabi Bidhendi et al .,2007),photo chemical oxidation (Rezaee et al.,2008), processes biological methods such bas anaerobic /aerobic sequential process (Naimabadi et al.,2009) , and physic chemical processes. Among the physic chemical processes, adsorption technology is considered to be on of the most effective and proven technology having potential application in both water and waste water treatment.(Venkatmohan et al.,2000).Adsorption equilibria information is the most important piece of information in understanding an adsorption process.

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity toxic substances. Adsorption has been used extensively in industrial process for separation and purification. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption processes. At present, there is a growing interest in using low cost, commercially available materials for the adsorption of dyes. Various techniques have been employed in the past for the removal of dyes from waste water. Most of these conventional treatment techniques are rather expensive. But adsorption process has been found to be more effective method for treating dye- containing effluents.The major advantages of an adsorption treatment for the control of

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water pollution are less investment in terms of initial development cost, simple design, easy operation, and free from or less generation of toxic substances. Adsorption on commercial activated carbon has been found to be an effective process for removal of dye from dye wastewater.

The main advantages of using the cotton shell and neem bark are economically viable, ease of availability. Various types of reactive dyes are commercially available. The Freundlich isotherm curves in the opposite way and is exponential in form. It often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction.

Both batch adsorption and fixed-bed adsorption studies are required to obtain key parameters required for the design of fixed-bed adsorber. Batch adsorption studies are performed to obtain the key parameters such as isotherm constants and pore diffusivity. Fixed-bed adsorption is used to determine the experimental breakthrough curve. This study investigated the use of cotton shell and neem bark for reactive red120 (RR120) removal by adsorption.

The objective of this work was to carry out the batch and fixed-bed adsorption studies. Batch adsorption studies are performed to kinetic and equilibrium processes. Fixed-bed adsorption studies are performed to the effect of bed height initial reactive red120 (RR120) concentration and flow rate on adsorption with the purpose of possible industrial application.

Conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved. This method is also time consuming and requires large number of experiments to determine optimum levels, which are unreliable. These limitations of a classical method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as Response Surface Methodology (RSM). RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions.

The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications. The application of statistical experimental design techniques in adsorption process development can result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs.

For any batch adsorption process, the main parameters to be considered are pH, temperature, dye concentration and time. Hence it is necessary to investigate extensively on the relationship between adsorption efficiency and the parameters affecting it. In the present study, low cost adsorbents was investigated for its efficiency to remove Reactive Red (RR120) from aqueous solution.

II. MATERIALS AND METHODS

A. 1. Preparation of Neem bark

Neem bark collected from a number of neem trees were mixed together and washed repeatedly with water to remove dust and other impurities .The barks were dried at room temperature in a shade and then in an air oven at 333K to 343K for 30hr till the barks could be crushed in to fine powder .The powder was sieved and the 53 to 74 µm were preserved. This neem bark powder is make in to a slurry with 4N formic acid and keep it for one hour .After one hour thoroughly wash it with distilled water for 4-5 times filter it. These is then dried in a hot air oven at a temperature 333K to 343K for 3hr, cool it and keep the neem bark powder in glass bottle and preserved as an adsorbent.

2. Preparation of cotton shell

Cotton shell collected from ginning mill were mixed together and washed repeatedly with water to remove dust and other impurities .The shell were dried at room temperature in a shade and then in an air oven at 333K to 343K for 30hr till the barks could be crushed in to fine powder .The powder was sieved and the 53 to 74 µm were preserved. This shell powder is make in to a slurry with 4N formic acid and keep it for one hour .After one hour thoroughly wash it with distilled water for 4-5 times filter it. These is then dried in a hot air oven at a temperature 333K to 343K for 3hr, cool it and keep the cotton shell powder in glass bottle and preserved as an adsorbent.

B. Preparation of Reactive Red120 (RR120) solution

The dye used in this study was Reactive Red 120 (RR120) obtained from a local textile company (Common Effluent Treatment Plant, Erode) and used without further purification. Its chemical structure is shown in Fig1 .A stock solution (1g /l) of RR120 was prepared by dissolving an accurate quantity of dye in bidistilled water and other concentrations varying between 10 mg/lit to 30 mg/lit were obtained by dilution.Fresh dilutions were used for each adsorption expertiment.The pH of the working solutions was adjusted to the required values by addition of a few drops of dilute HNO3 or NaOH.

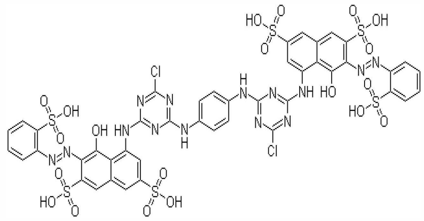

Fig1:Structure of Reactive Red(RR120)

4,4'-[1,4-phenylenebis[imino(6-chloro-1,3,5-triazine-4,2-diyl)imino]]bis[5-hydroxy-6-[(2-sulphophenyl)azo]naphthalene-2,7-disulphonic acid

C. Kinetic and equilibrium studies

The adsorption experiments were carried out in a batch process by using aqueous solutions of reactive red (RR120) .The other variable parameters were adsorbent amount, agitation tile ,temperature, PH of the medium .In each experiment an accurately weighed amount of Neem bark was added to 100 ml of the RR120 solution in a 250ml conical flask and the mixture was agitated in a thermostatic mechanical shaker for a given length of time at variable temperature. If necessary the PH was adjusted by addition of a few drops of dilute HNO_3 or NaOH. The mixture was centrifuged and RR120 remaining unabsorbed (λmax=663-667nm) was determined spectrophotometrically (ELICO BLI50). Experiments were performed according to box-behnken design of experiments.The response was expressed as % of dye removal calculated as

= ((Co-Cf)/Co)*100.Equilibrium experiments were performed with different initial dye concentration .The agitated time was 2.5 hr to reach equilibrium ,the amount of dye adsorbed on to the unit weight of the adsorbent was calculated using the following equations:

$$Q = {V(Co - Cf)}/{m} \quad \text{................(1)}$$

Where V is the solution volume in liter,

Co is the initial concentration in mg/lit

Cf is the final concentration in mg/lit, and

m is the dry weight of adsorbent in gram.

D. Column Studies

Column adsorption experiments in a fixed column were conducted in a glass column (2 cm ID and 55 cm height) packed with a known quantity of cotton shell and neem bark .A known concentration of Reactive Red120 (RR120) solutions was pumped in up flow mode at desired flow rates using a peristaltic pump .Samples were collected at regular intervals .The effects of the following column parameters,on Reactive Red120(RR120)adsorption were investigated.(i)Effect of bed height :Bed height was varied between 10 cm (2g) ,20 cm(4g),30 cm(6 g),keeping flow rate and initial Reactive Dyes(RR120) concentration constant at 8 ml/min and 10 mg/lit respectively.

(ii)Effect of flow rate: Flow rate was varied between 8 and 12ml/min, while bed height and inlet Reactive Red (RR120) concentration were held constant at 10 cm and 10 mg/lit. (iii)Effect of inlet Reactive Red (RR120) concentration: Inlet Reactive Red120 (RR120) concentration was varied between 10, 20, 30 mg/lit at 10 cm bed height and 8 ml/min flow rate.

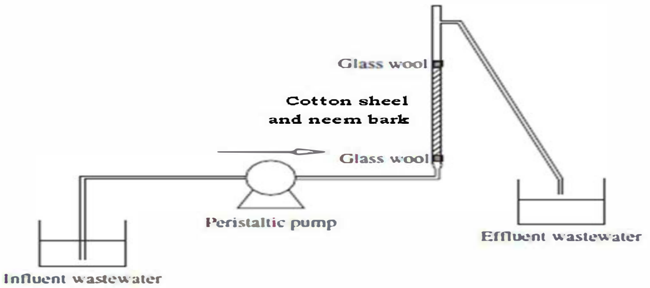

Fig2.Schematic Diagram for Fixed Bed Column

E. Experimental design by RSM (Response Surface Methodology)

RSM is a empirical statistical technique employed multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multi variable equations simultaneously. A statistical program package design Expert 8.0.4.1 was used for regression analysis of the data obtained and to estimate the co efficient of the regreesion equation.The equation were validated by the statistical tests called the ANOVA analysis. The significance of each term in the equation is to estimate the goodness of fit in each case. Response surfaces were drawn to determine the individual and interactive effects of the test variable on the % removal of reactive red120 (RR120) .The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units.

III. RESULTS AND DISCUSSIONS

The study of Reactive Red120(RR120) adsorption using cotton shell and neem bark consists of two parts: batch studies and fixed column studies .In batch studies the process was performed by kinetic and equilibrium studies .In fixed bed column studies ,the breakthrough curves were studied at different operating conditions.

A. Batch studies

1. Kinetic Studies

The kinetics of the adsorption processes was studied by carrying out a separate set of experiments with constant temperature ,neem bark and cotton shell amount and adsorbate concentration using the pseudo first order lagergren equation .The differential rate equation is of the form

$$dq/_{dt} = K1(qe - qt) \quad \text{......................(2)}$$

where qe and qt are the amount adsorbed per unit mass of the adsorbent (mg/g) at equilibrium time t and

k1 is the pseudo first order rate constants (min-1). Integrating the above equation for the boundary conditions t=0 to t=t and qt=0 at t=0, gives

$$log(qe - qt) = {}^{\log\,(qe - k1 \times t)}/_{2.303}$$

……(3)

A linear plot of log (qe-qt) vs t verifies the first order kinetics with the slope yielding the value of the rate constant.The kinetics of reactive red120(RR120) adsorption on cotton shell and neem bark was studied with respect to different amounts of adsorbent.The extent of adsorption varied in a narrow range from 85 % (CS=2g/lit and NB=2 g/lit ,agitation time=4 hr) 88 %. Interactions appeared to attain equilibrium rapidly after about 1.5 hr of agitation. Assuming pseudo first order kinetics for the adsorption process ,log(qe-qt) was plotted against t and the linearity of the lagergren plots(fig 3 and 4) confirmed the same . The first order rate constants evaluated from these plot was 0.1151min-1(RR120 CS),0.0541 min-1 (RR120 NB), for 2 g/lit of the adsorbents. In the present work the intercepts of the lagergren plots not equal to the theoretical log qe values and therefore the kinetics of reactive red120(RR120) on cotton shell and neem bark could be considered as almost pseudo first order in nature .

2. *Equilibrium study*

The well known freundlich isotherm eq (5) is widely used to describe adsorption on a surface having heterogeneous energy distribution.The Langmuir isotherm eq(5) on the other hand is strictly applicable to monolayer chemisorptions. The experimental data are tested with respect to both these isotherms .

Freundlich isotherm

$$qe = Kf \times Ce^{n}$$

……....……………….................(4)

Langmuir isotherm

$$Ce/_{qe} = \left({}^{1}/_{Kd \times c1}\right) + \left({}^{1}/_{C1 \times Co}\right)$$

…………(5)

Where qe is the amount of dye adsorbed at equilibrium in unit mass of adsorbent

Ce is the concentration of the dye in aqueous phase at equilibrium

n and Kf are freundlich co efficient

C1 and Kd are Langmuir co efficients

The linear Freundlich and Langmuir plots were obtained by plotting

(1) log qe vs log Ce and

(2) Ce/qe vs Ce

(3) The adsorbtion co efficients were computed from the slopes and the intercepts.Another important parameter RL known as the separation factor could be obtained from the relation.

$$Rl = {}^{1}/_{(1 + Kd \times Ce)}$$

………………………… (6)

Where

Ce is any equilibrium liquid phase concentration of the solute.

The experimental data yielded good linear plots with both Freundlich isotherm (fig 5 and 6) and Langmuir isotherm (fig 7 and 8) .The freundlich co efficient n which should have value in the range of 0 to 10 for favourable adsoption.freundlich adsorption capacity Kf is 2.664 (1/n)=0.38(RR120 NB) , Kf is 2.691 (1/n)=0.44(RR120 CS).The Langmuir mono layer adsorption capacity C1 was large with value 34.375,(RRNB), 33.33,(RRCS). The Langmuir adsorption intensity Kd had value of 0.2909,(RRNB), 0.25,(RRCS).

3. *Effect of pH*

The pH of the medium shows the significant effect on uptake of Reactive Red120 by both Cotton Shell and Neem Bark(fig 9 and 10). pH of the medium varying from 4.9 to 7.0, the adsorption of the dyes oscillated between 75%and 80%. However, the adsorption remained constant within the range of pH 6.5 and 6.3 for Cotton Shell and Neem Bark respectively.

4. *Effect of contact time*

The percentage of the dye removal as a function of time is shown in(fig 11and 12)with an initial 10 mg/lit ,20 mg/lit concentration of dye and 30 mg/lit at varioustemperatures like 30,40,50 oC of dye and adsorbent dosage 2g for 100 ml of dye solution. The uptake of dye by adsorbents occurs at a faster rate,corresponding to 79% RR120 removal by cotton shell at an equilibrium time 30 min and 85% removal by neem bark at an equilibrium time 35 min. The relative increase in the removal of dye after contact time for both adsorbent not significant and hence it is fixed as the optimum contact time

5. *Effect of adsorbent dose on dye adsorption*

It is readily understood that the number of available adsorption sites and the surface area increase by increasing the adsorbent dose and it ,therefore ,results in the increase of amount of adsorbed dye. Although percent adsorption increases with increase in adsorbent dose ,amount adsorbed per unit mass decreases.This statement can be supported from the results as the adsorption is 85 to 88% at the dose of 4g of adsorbent respectively but on further increase the dose % of adsorption remains same.

6. *Effect of Temperature*

Batch adsorption experiments were carried out at the desired temperature (30,40,50 oC) using particle size of 53 to 74 µm and each used a range of initial dye concentrations from 10 to 30 mg/lit.

7. *Intraparticle Diffusion*

The variation in the extent of adsorbtion with time at different initial dye concentrations was possessed for evaluating the role of diffusion in the adsorbtion system. Adsorbtion is a multi step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion in to the interior of the pores .The intra particle diffusion equation

$$Qt = Ki \times t^{0.5} \quad \text{.................................... (7)}$$

Where

Ki is the intra particle diffusion rate constant (mg/g min0.5)

The Ki values were calculated from the slopes of the linear plots of qt vs t0.5The plots of qt vs t0.5 (fig 15) were found to be linear with regression co efficients of reactive red120(RR120) ,0.9126(RR120 by NB),0.9401(RR120 by CS).The intra particle diffusion rate constant Ki was 0.06(RR120 by NB),0.04(RR120 by CS) min-1 .The linearity of the plots demonstrated that intra particle diffusion played a significant role in the uptake of the dye by NB and CS powder.

B. *Experimental design and fitting of quadratic model*

Sample No	Dye concentration(A) milligram/litre	pH (B)	Temperature (C) Degree Celsius	% adsorption
1	0	1	-1	68.4
2	-1	-1	0	28.2
3	0	0	0	60.2
4	0	0	0	60.2
5	-1	1	0	68.9
6	1	0	-1	62.2
7	1	-1	0	22.5
8	1	1	0	47.1
9	0	-1	1	20.8
10	0	-1	-1	30.8
11	-1	0	-1	77.5
12	1	0	1	45.6
13	-1	0	1	56.7
14	0	1	1	53.2
15	0	0	0	60.2

TABLE 1 : LEVELS OF DIFFERENT PROCESS VARIABLES IN CODED FORM FOR ADSORPTION OF REACTIVE RED120(RR120) BY COTTON SHELL

Source	Co-efficient estimate	F Value	p-value Prob>F
Intercept	60.2		
Model		114.0342	< 0.0001
A-Dye concent ation	-6.7375	84.38509	0.0003
B-pH	16.9125	531.721	< 0.0001
C-Temperature	-7.825	113.8248	0.0001
AB	-4.025	15.05809	0.0116
AC	1.05	1.024747	0.3578
BC	-1.3	1.570814	0.2655
A^2	-0.6625	0.376572	0.5663
B^2	-17.8625	273.7541	< 0.0001
C^2	0.9625	0.794836	0.4135
Residual	21.52		
Lack of Fit	21.52		
Std. Dev	2.07		
R^2	0.9952		
Mean	50.83		
Adjusted R^2	0.9864		
C.V	4.08%		
Predicted R^2	0.9224		

TABLE 2: ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE QUADRATIC MODEL RR120 BY COTTON SHELL

The results were analyzed by using ANOVA(Table 2). The ANOVA of the quadratic regression model indicate the model to be significant. The model F-Value of 114.03 implies that the model is significant. The smaller the magnitude of the P, the more significant is the corresponding co-efficient. Values of P less than 0.05 indicate the model term is significant.From the P-values, it was found that among the test variables used in the study AB, BC, AC, A2, B2, C2 are significant model.The predicted R2 of 0.9224 is in reasonable agreement with theadjusted R2 of 0,9864 . the fit of the model was also expressed by the co-efficient of regression R2 which was found to be 0.9952 indicating that 99.52% of the variability in the response could be explained by the model. This implies that the prediction of experimental data is quite satisfactory.

Sample No	Dye concentration(A) milligram/litre	pH (B)	Temperature(C) Degree Celsius	% adsorption
1	0	-1	1	58.2
2	1	0	-1	71.8
3	-1	0	-1	34.3
4	-1	1	0	23.7
5	0	0	0	62.5
6	0	0	0	62.5
7	0	-1	-1	83.8
8	0	0	0	62.5
9	0	1	1	52.4
10	-1	-1	0	32.3
11	0	1	-1	63.8
12	-1	0	1	21.4
13	1	0	1	53.5
14	1	-1	0	67.6
15	1	1	0	53.6

TABLE 3 : LEVELS OF DIFFERENT PROCESS VARIABLES IN CODED FORM FOR ADSORPTION OF REACTIVE RED120 (RR120) BY NEEM BARK

Source	Co-efficient estimate	F Value	p-value Prob>F
Intercept	62.5		
Model		319.9581	< 0.0001
A-Dye Conc.	16.85	1436.673	< 0.0001
B-pH	-6.05	185.2119	< 0.0001
Temperature	-8.525	367.7451	< 0.0001
AB	-1.35	4.611006	0.0845
AC	-1.35	4.611006	0.0845
BC	3.55	31.88488	0.0024
A^2	-18.75	821.048	< 0.0001
B^2	0.55	0.706466	0.4390
C^2	1.5	5.254707	0.0704
Residual	7.91		
Lack of Fit	7.91		
Std. Dev	1.26		
R^2	0.9983		
Mean	53.59		
Adjusted R^2	0.9951		
C.V	2.35%,		
Predicted R^2	0.9723		

TABLE 4 : ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE QUADRATIC MODEL RR120 BY NEEM BARK

found to be 0.9983 indicating that 99.83% of the variability in the response could be explained by the model. This implies that the prediction of experimental data is quite satisfactory.

indicate the model term is significant.From the P-values, it was found that among the test variables used in the study AB, BC, AC, A2, B2, C2 are significant model.The predicted R2 of 0.9723 is in reasonable agreement with theadjusted R2 of 0,9951 . the fit of the model was also expressed by the co-efficient of regression R2 which was found to be 0.9983 indicating that 99.83% of the variability in the response could be explained by the model. This implies that the prediction of experimental data is quite satisfactory.

C. Response surface estimation for maximium % adsorption:

1. Reactive Red120 (RR120)by cotton shell

Response surface plot as a function of process variable at a time maintaining all other variables at fixed level are more helpful in understanding both the main and the interaction effect of these three factors. The response surface curves are plotted to understand the interaction of the variable and to determine the optimum level of each variable for their response. The response curves for % adsorption as shown in figures 3,4,5.The magnitude of P and F value in table gives the maximum positive contribution of temperature, pH,Dye concentration on the % adsorption .dye concentration and pH, pH and temperature have negative effects whereas the interaction of temperature and dye concentration have positive effect on % adsorption.(Table 2)

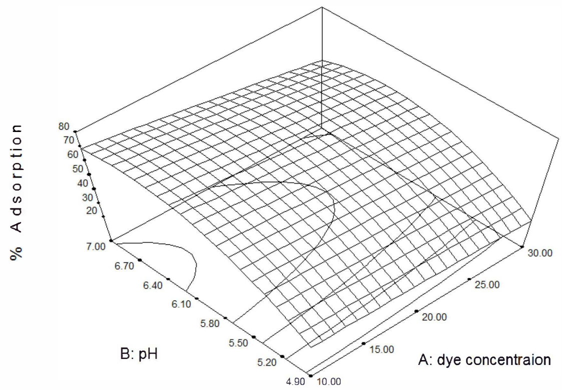

Fig 3. Response surface plot of the combined effects of dye concentration pH on the % adsorption of reactive red120 (RR120) by cotton shell

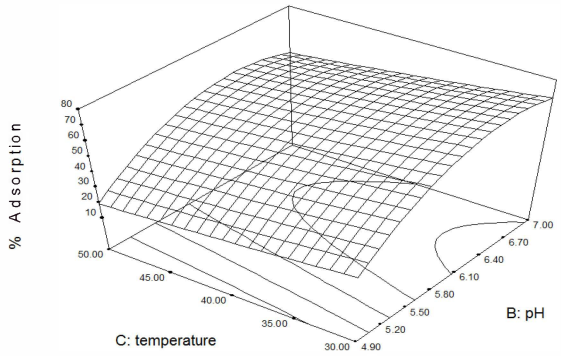

Fig 4. Response surface plot of the combined effects of dye concentration and Temperature on the % adsorption of reactive red120(RR120) by cotton shell

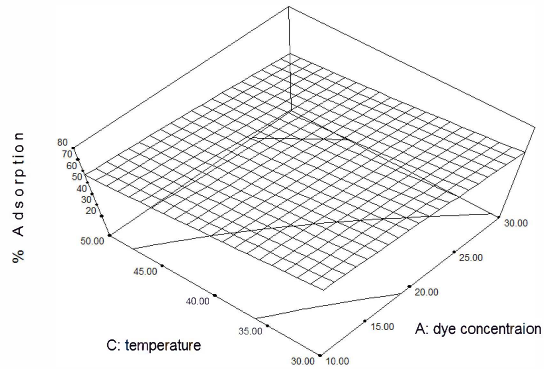

Fig5. Response surface plot of the combined effects of dye concentration and Temperature on the % adsorption of reactive red120(RR120) by cotton shell

2. Reactive Red120 by neem bark

Response surface plot as a function of process variable at a time maintaining all other variables at fixed level are more helpful in understanding both the main and the interaction effect of these three factors. The response surface curves are plotted to understand the interaction of the variable and to determine the optimum level of each variable for their response. The response curves for % adsorption as shown in figures6,7,8.The magnitude of P and F value in table gives the maximum positive contribution of temperature, pH,Dye concentration on the % adsorption .dye concentration and pH,dye concentration and temperature have negative effects whereas the interaction of temperature and pH have positive effect on % adsorption.(Table 4).

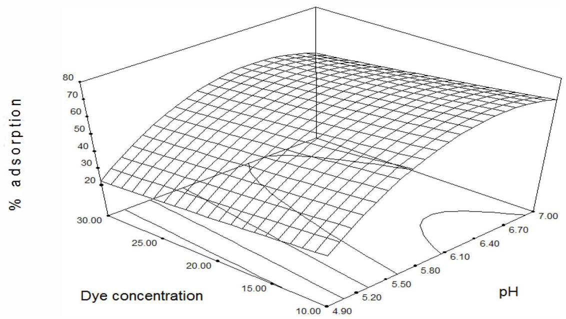

Fig6 .Response surface plot of the combined effects of dye concentration and pH on the % adsorption of reactive red by neem bark.

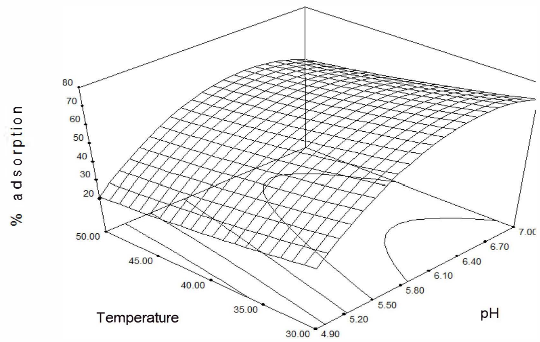

Fig7.Response surface plot of the combined effects of pH and temperature on the % adsorption of reactive red by neem bark.

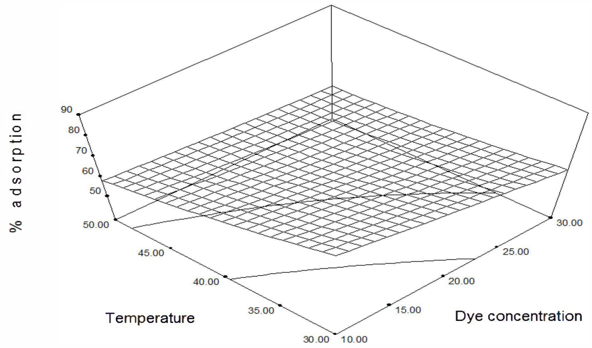

Fig.8 Response surface plot of the combined effects of dye concentration and temperature on the % adsorption of reactive red by neem bark.

E. Optimization:

1. Reactive Red120(RR120) by cotton shell

Desired function methodology was used to optimize the variables with the help of statistical software stat ease Design Expert 8.0.4.1.Response surface methodology was used to carry out the experiments according to do Box-Behnken experimental design with three factors with three levels with respect to all properties. The experiments were done in triplicates. Desired function methodology was used to optimize the parameters of % adsorption. The optimum values obtained by substituting the respective coded values of variables are temperature : 32.22 , Dye concentration: 12.60, pH: 6.46. At this condition the maximum values of % adsorption is 78.02.

2. Reactive Red120(RR120) by neem bark

Desired function methodology was used to optimize the variables with the help of stastical software stat ease Design Expert 8.0.4.1.Response surface methodology was used to carry out the experiments according to do Box-Behnken experimental design with three factors with three levels with respect to all properties. The experiments were done in triplicates. Desired function methodology was used to optimize the parameters of % adsorption. The optimum values obtained by substituting the respective coded values of variables are temperature : 30.82 , Dye concentration: 11.65, pH: 6.37. At this condition the maximum values of %adsorption is 84.44.

D. Breakthrough curves

The process engineering advantages of a fixed bed adsorption column with cotton shell and neem bark offer easy continuous operation and scale up is a n important process. Fixed bed column studies include the effect of bed height, flow rate and initial dye concentration on Reactive Red120(RR120) .The break through curves at different conditions about Cf/Co vs. t were shown if fig (22 and 23). It was observed from that figures the breakthrough curves became steeper as the flow rate increased. Breakthrough time reaching saturation was increased at lower flow rates. Although Reactive red120 (RR120) adsorption was a fast process,diffusion effects were lower due to the insufficient residence time of dyes in the column at higher flow rates . Hence lower flow rates were desirable for the effective removal of Reactive Red120(RR120) in column mode.At high initial dye concentrations a sharper breakthrough curve indicated shortened mass transfer zone and higher adsorption rates.Therfore when quick dye uptake is desired, which is often the case ,operating with high initial dye concentrations appears to be favorable .The change of concentration gradient affected the saturation rate and breakthrough time. The higher bed column resulted in a decrease in the solute concentration in the effluent at the same time. The slope of the breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone.

E. Modelling of Experimental data in column data

Modelling of data available from column studies facilitates scale –up potential.To describe the column breakthrough curves obtained at different bed heights,flow rates and inlet concentrations of dye,three models were used.These included the Thomas ,clark, Modified - dose response models.

Thomas Model:

$$\frac{Cf}{Co} = \frac{1}{1+exp\left(\left(Kth\,qo\,X/_V\right)-(Kth\,Co\,t)\right)} \qquad \text{......................(8)}$$

Clark Model:

$$\frac{Cf}{Co} = \left[\left(\frac{1}{(1+Ae^{-rt})}\right)\right]^{\frac{1}{(n-1)}} \qquad \text{......................................(9)}$$

Modified dose-response model:

$$\frac{Cf}{Co} = 1-\left(\frac{1}{1+\frac{vt^{a}}{b}}\right) \qquad \text{...(10)}$$

From the value of b,the value of qo can be estimated using following equation

Qo=bCo/x

Where kth is the Thomas rate constant(ml/min mg), qo is the equilibrium Reactive Red120 (RR120) uptake per g of the adsorbent(mg/g).x is the amount of the adsorbent in the column(g),and v is the flow rate of the solution passing through the column (ml/min).The value of t is the flow time (min).A and r are the clark parameters and n is the freundlich parameter .Parameters of a and b are from the modified dose –response model.These models predict the service time for a given dye concentration .experimental data obtained from column study from column studies were fitted to the three models described here. The parameters and values of R2 and X2 according to nonlinear regressive analysis were listed in (table 5 to 10) respectively.At all conditions, the predicted breakthrough curves from the modified dose response model showed good agreement with the experimental curves .So it was concluded that the modified dose response model shows better fit than the other two and the Thomas Model and clark model are reasonable to fit the breakthrough curves. Several researchers studied the metal removal by adsorption in column mode, and found that column kinetics could be described more adequately by the modified dose response model than by the Thomas model.My study about dye removal in column adsorption had similar results.

IV. CONCLUSION

The adsorption of Reactive Red120(RR120) was investigated using cotton shell and neem bark in batch and continuous mode. The kinetic, equilibrium and breakthrough curves were analyzed and it is found that it behaves the pseudo first order process. Experimental results was effectively described by the Freundlich and Langmuir isotherm models. The value of adsorption capacity (C1)from the Langmuir model was 34.375,(RRNB), 33.33,(RRCS) mg/g. The breakthrough curves were significantly affected by flow rate, initial dye concentration and bed height .The column data were fitted by the Thomas, Clark, Modified dose-response models. The modified dose response model was best to fit the breakthrough curves at experimental conditions using nonlinear regressive analysis. Under optimal values of process parameters, removal was found for both the dyes using both adsorbents. This study clearly showed that response surface methodology was one of the suitable methods to optimize the best operating conditions to maximize the dye removal .Box Behnken design of experiments was successfully employed for experimental design and analysis of results.

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