Optimization, Equilibrium and Kinetic Studies of Basic Red 2 Removal onto Waste *Gossypium hirsutum* Seeds

Sivarajasekar, Natesan*[+]

Department of Biotechnology, Kumaraguru College of Technology, Coimbatore 641049, Tamil Nadu, INDIA

Baskar, Rajoo

Department of Food Technology, Kongu Engineering College, Perundurai, Erode 638052, Tamil Nadu, INDIA

ABSTRACT: *Cationic dye - basic red 2 (BR2) was removed from aqueous solutions by sulfuric acid activated waste* Gossypium hirsutum *seeds (WGSAB). The main and interactive effects of five process variables such as, adsorbent dose (1.25 – 5 g/L), initial dye concentration (100–300 mg/L), contact time (1–3 h), pH (2 – 12) and temperature (20 – 40^{0}C) were investigated via response surface methodology (RSM) based on Box–Behnken statistical design. The optimum values of the key variables were estimated using Derringer's desirability function. The optimal values were found to be at an adsorbent dose 2.41 g, initial dye concentration 150 mg/L, pH 8.69, temperature 33.57^{0}C, and contact time 1.42 h with the maximum desirability of 91%. The equilibrium data obeyed Redlich-Peterson isotherm which showed that the WGSAB was heterogeneous and BR2 was adsorbed in multilayers. The kinetic investigation showed that the BR2 was chemisorbed on WGSAB surface following Avrami fractional order kinetics. The thermodynamic parameters revealed that The BR2 adsorption process was spontaneous and endothermic. Regeneration of exhausted WGSAB found to be possible via acetic acid as elutant.*

KEYWORDS: *Adsorption; Box–Behnken; Derringer's desirability; Gossypium hirsutum seed; equilibrium.*

INTRODUCTION

Industries like paper, textile, plastic, leather, cosmetic, and food employ dyes to color their products. The residual and unspent dyes of those processes are delivered into the water bodies as such [1]. The dye effluents are considered to be extremely toxic to the aquatic biota and disturb the symbiotic process by affecting the natural equilibrium by reducing photosynthetic activity due to the colorization of the water [2]. Among, the major three type of dyes (cationic, anionic and neutral), the cationic dye is more toxic [3]. These dyes have been reported to cause allergy, irritation, cancer and even mutation in humans [4]. Hence, the complete removal of these dyes from effluents before discharge to public water sources is a need of the hour.

Adsorption is an effective technique for the treatment of dye-containing effluents due to cost effectiveness and

* *To whom correspondence should be addressed.*
+ *E-mail: sivarajasekar@gmail.com*
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its versatility to use for a wide variety of dyes. Activated carbon was commonly used in the removal of dyes from effluent, which had a relatively high adsorption capacity for a wide variety of dyes. Commercially available activated carbons are usually obtained from either wood or coal, and hence, are still considered expensive [5]. In recent years, the research has gained momentum towards the preparation of adsorbents from agricultural byproducts and waste materials due to the cost of activated carbon [6-10]. Agricultural by-products or wastes are a rich source of organic matter containing hydroxyl, carboxyl and amine groups which can easily enhance binding of cations such as cationic dyes [11]. India is the third largest country in the world which produces cotton (*Gossypium hirsutum*) approximately 5787 × 10^3 tons per year [12]. After harvest, the cotton seeds separated from cotton fibers are used for oil extraction. The immature cotton seeds unfit for germination and oil extraction are discarded as waste in large quantity, in India. This cheap and renewable waste material can be utilized for adsorbent preparation.

The processing cost of adsorption based effluent treatment is greatly minimized by optimum utilization of commercial activated carbons. The dynamic characteristic of adsorption process is very complex and hence obtaining the optimum process variables become vital to get the optimum pollutant removal efficiency [13]. One of the methodologies for obtaining the optimum results is the Response Surface Methodology (RSM). The classical one variable at a time method is time consuming when a large number of variables is considered [14]. But RSM comprises the reduced number of experiments needed to examine the effect of variables and their interactions [15]. Therefore the application of RSM in adsorption process modeling can result in better profit, reduced inconsistency, and reduced development time and cost [16].

Keeping the above points in mind, an attempt was made to prepare a novel adsorbent from waste *Gossypium hirsutum* seeds for removing basic red (BR2) from aqueous solution. The influence of various operating variables and optimum process conditions for the basic red 2 adsorptions were investigated using Box-Behnken statistical Design (BBD) which is not tried till to the best of our knowledge. The experimental data were analyzed by isotherms, kinetics, and thermodynamic parameters.

EXPERIMENTAL SECTION

Adsorbent preparation and Characterization

Waste Gossypium hirsutum seeds were obtained from seed producers near Attur, Tamil Nadu, India. The seeds were washed thoroughly and dried at 313 K in an oven for 3 days. The dried biomass was soaked with concentrated sulphuric acid in the weight ratio of 1:4 and was stirred occasionally. The resultant material washed with 0.1N sodium bicarbonate solution, waste Gossypium hirsutum seed activated biomass (WGSAB) was dried, finely ground, sieved to a size of 0.088 cm and stored in an airtight container for subsequent adsorption experiments.

The iodine number and methylene blue numbers of WGSAB were calculated based on the ASTM 4607–86 standards at 298 K [12]. The specific surface area of WGSAB was measured using a surface analyzer (Micromeritics ASAP 2020). Surface morphology was examined by using a scanning electron microscope (SEM: JSM–6390LV–JEOL Ltd., Japan). The functional groups present on the WGSAB surface were determined using Boehm titrations [12].

Box-Behnken Design – Batch Adsorption

BBD was chosen to study the effects of pH, temperature, adsorbent dosage, initial concentration, and contact time on BR2 adsorption. The experimental design was given in Table 1. Batch adsorption experiments were conducted according to BBD explained similarly to elsewhere [17]. Experimental analysis was repeated three times and the results were statistically analyzed. Percentage of dye removal from the bulk dye solution was calculated using the following equation:

$$\%R = \frac{C_i - C_0}{C_i} \times 100 \quad (1)$$

where C_i and C_0 (mg/L) are an initial and final concentration of the dye in the aqueous solution. The dye adsorption capacity q_t (mg/g) at any time t, was determined as

$$q_t = (C_i - C_t) \times \frac{V}{M} \quad (2)$$

Where C_t (mg/L) is a concentration of BV2 at any time t, V (l) is the volume of the dye solution, and M (g) is the amount of WGSAB. Regeneration studies were carried using

Table 1: BBD design Matrix with actual and predicted values.

S.No	A Dosage (g/L)	B Concentration (mg/L)	C Time (h)	D pH	E Temperature (^{0}C)	$\%R_{act}$	$\%R_{pre}$
1	-1(6.25)	-1(50)	0(2)	0(7)	0(30)	58.12	57.83
2	1(25)	-1(50)	0(2)	0(7)	0(30)	57.91	57.71
3	-1(6.25)	1(150)	0(2)	0(7)	0(30)	47.85	47.85
4	1(25)	1(150)	0(2)	0(7)	0(30)	60.87	60.97
5	0(15.63)	0(100)	-1(1)	-1(2)	0(30)	41.57	41.43
6	0(15.63)	0(100)	1(3)	-1(2)	0(30)	43.35	43.29
7	0(15.63)	0(100)	-1(1)	1(12)	0(30)	50.78	50.71
8	0(15.63)	0(100)	1(3)	1(12)	0(30)	51.01	51.01
9	0(15.63)	-1(50)	0(2)	0(7)	-1(20)	56.12	56.55
10	0(15.63)	1(150)	0(2)	0(7)	-1(20)	53.41	53.79
11	0(15.63)	-1(50)	0(2)	0(7)	1(40)	68.57	68.29
12	0(15.63)	1(150)	0(2)	0(7)	1(40)	64.64	64.33
13	-1(6.25)	0(100)	-1(1)	0(7)	0(30)	37.35	37.54
14	1(25)	0(100)	-1(1)	0(7)	0(30)	46.82	46.66
15	-1(6.25)	0(100)	1(3)	0(7)	0(30)	40.9	41.24
16	1(25)	0(100)	1(3)	0(7)	0(30)	45.12	45.12
17	0(15.63)	0(100)	0(2)	-1(2)	-1(20)	40.54	40.23
18	0(15.63)	0(100)	0(2)	1(12)	-1(20)	44.13	44.31
19	0(15.63)	0(100)	0(2)	-1(2)	1(40)	47.13	46.95
20	0(15.63)	0(100)	0(2)	1(12)	1(40)	59.57	59.87
21	0(15.63)	-1(50)	-1(1)	0(7)	0(30)	63.65	63.76
22	0(15.63)	1(150)	-1(1)	0(7)	0(30)	54.31	54.18
23	0(15.63)	-1(50)	1(3)	0(7)	0(30)	58.47	58.62
24	0(15.63)	1(150)	1(3)	0(7)	0(30)	61.57	61.48
25	-1(6.25)	0(100)	0(2)	-1(2)	0(30)	35.92	35.97
26	1(25)	0(100)	0(2)	-1(2)	0(30)	41.75	41.91
27	-1(6.25)	0(100)	0(2)	1(12)	0(30)	44.05	43.91
28	1(25)	0(100)	0(2)	1(12)	0(30)	50.98	50.97
29	0(15.63)	0(100)	-1(1)	0(7)	-1(20)	41.15	41.158
30	0(15.63)	0(100)	1(3)	0(7)	-1(20)	42.51	42.282
31	0(15.63)	0(100)	-1(1)	0(7)	1(40)	52.2	52.342
32	0(15.63)	0(100)	1(3)	0(7)	1(40)	53.47	53.378
33	-1(6.25)	0(100)	0(2)	0(7)	-1(20)	35.47	35.2
34	1(25)	0(100)	0(2)	0(7)	-1(20)	41.58	41.4
35	-1(6.25)	0(100)	0(2)	0(7)	1(40)	45.91	46.04
36	1(25)	0(100)	0(2)	0(7)	1(40)	52.61	52.84
37	0(15.63)	-1(50)	0(2)	-1(2)	0(30)	58.02	58.29
38	0(15.63)	1(150)	0(2)	-1(2)	0(30)	53.11	53.33
39	0(15.63)	-1(50)	0(2)	1(12)	0(30)	65.31	65.19
40	0(15.63)	1(150)	0(2)	1(12)	0(30)	63.61	63.43
41	0(15.63)	0(100)	0(2)	0(7)	0(30)	65.01	65.02
42	0(15.63)	0(100)	0(2)	0(7)	0(30)	64.98	65.02
43	0(15.63)	0(100)	0(2)	0(7)	0(30)	65.02	65.02
44	0(15.63)	0(100)	0(2)	0(7)	0(30)	65.01	65.02
45	0(15.63)	0(100)	0(2)	0(7)	0(30)	65.03	65.02
46	0(15.63)	0(100)	0(2)	0(7)	0(30)	65.05	65.02

different solvents like hot water, acetone, diluted HCl and diluted acetic acid.

A second order polynomial equation correlating the effect of variables in terms of linear, quadratic and cross product terms was employed to predict the percentage removal of BR2. The general equation is of the form:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{j=1}^{k}\beta_{ji} X_i^2 + \sum_{i=1}^{k}\sum_{j<i=1}^{k}\beta_{ji} X_i X_j + \in \quad (3)$$

Where Y is the response, k is the number of the patterns, i and j are the index numbers for the pattern, β_0 is the free or offset term called intercept term, X_1, X_2... X_k are the coded independent variables, β_i is the first–order (linear) main effect, β_{ii} is the quadratic (squared) effect, β_{ij} is the interaction effect, and ε is the random error which allows for discrepancies or uncertainties between predicted and measured values. Experimental design data were analyzed using the statistical software Design Expert 8.0.7.1 (Stat-Ease Minneapolis, USA).

Isotherms and kinetics

The batch equilibrium data obtained for five different initial concentrations (100, 150, 200, 250 and 300 mg/L) at pH 12, temperature 313 K and contact time 180 min was fitted to isotherms such as Langmuir [18], Freundlich [19] and Redlich–Peterson [20]. Batch experiments were carried out for differential concentrations (100, 150, 200, 250 and 300 mg/L) at pH 12, temperature 313K and contact time 180 min to investigate the adsorption kinetics. Kinetic equations including *Ho* [18], and *Avrami* [19] were employed for testing the batch kinetic data.

The isotherm and kinetic parameters were determined using the MATLAB® non-linear curve fitting tool. The statistical parameters such correlation coefficient (R^2) and Root Mean Square Error (RMSE) were considered for examining the correlations. The R^2 close to unity and smaller RMSE is the index to select the suitable correlation.

Thermodynamics

Batch experiments were carried out for differential temperatures (293K, 303K, 313K, and 323K) at pH 12, initial concentration of 150 mg l^{-1} and contact time 180 min to examine the adsorption thermodynamics. The thermodynamic parameters were calculated from the following equations [21]:

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

$$\Delta H_{is} = \frac{d\left(\ln C_e\right)}{d(1/T)} \quad (6)$$

Where R is gas constant (8.314 J/mol K) and T is the absolute temperature (K).

RESULTS AND DISCUSSION

Characterization of WGSAB

The number of micropores (1.0–2.8 nm) and mesopores (around 1.5 nm) are calculated via iodine and methylene blue number [22]. The Iodine number and methylene blue number of WGSAB were measured to be 510 mg/g and 42 mg/g, respectively. Comparison of SEM micrographs (Fig. 1) also revealed the formation of a good number of pores. The BET surface area was found to be 496 m^2/g and after BR2 adsorption the BET surface area was reduced to 85 m^2/g. This conferred the excellent development of pores and their contribution in the BR2 adsorption. Boehm titration provides evidence for the existence of surface functional groups such as carboxylic, lactonic, phenolic and carbonyl contributing to surface acidity [23]. The strength of each functional group determined via Boehm titrations were carboxylic (1.62 mmol/g), lactonic (0.86 mmol/g), phenolic (1.51 mmol/g) and carbonyl (0.38 mmol/g). Besides, total basicity of WGSAB (1.24 mmol/g) surface was smaller compared to surface acidity (5.37 mmol/g) which indicated that WGSAB surface is capable to adsorb the cationic dye. From Table 2, it's obvious from the FTIR spectra that functional groups such as alcoholic, amine, carboxylic and sulfonate groups are the major contributing functional groups for BR2 adsorption.

Box-Behnken Design

Experiments were carried out according to the BBD matrix, in order to study the combined effects of the selected variables on percentage dye removal. Table 1 displays the BBD matrix, experimental and predicted percentage dye removal values. To decide about the adequacy of models among various models to percentage dye removal, two different tests namely the sequential

Table 2: FT-IR peaks before and after BR2 adsorption.

Functional group/parameter	Before adsorption	After adsorption
O-H stretch (Alcohol)	3419 cm^{-1}	3408 cm^{-1}
C=O stretch (carboxylic)	1704 and 1625 cm^{-1}	1689 and 1612 cm^{-1}
S=O stretch (Sulfonate)	1380 cm^{-1}	1343 cm^{-1}
N-H bend (Amine)	793 cm^{-1}	762 cm^{-1}

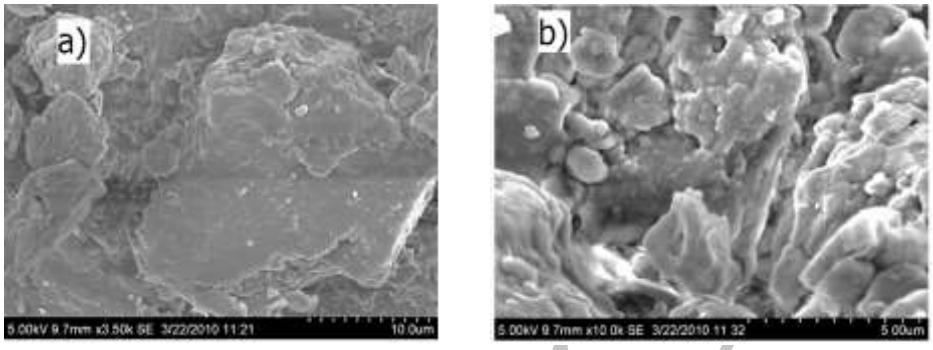

Fig. 1: SEM micrographs of Waste Gossypium hirsutum seeds before (a) and after (b) activation.

the model sum of squares and model summary statistics were carried out and the results are given in Table 3 (a) and (b), respectively. The fit summary of the output indicates that the quadratic model is statistically highly significant and the p-value was lower than 0.0001. This means that at least one of the terms in the regression model has a significant correlation with percentage dye removal. The cubic model was found to be aliased. Model summary statistics showed that the excluding cubic model which was aliased, the quadratic model was found to have maximum adjusted R^2 values. Therefore, the quadratic model was chosen for further analysis.

Model fitting and its adequacy

A quadratic model expressed by a second-order polynomial equation with interaction terms was fitted between the experimental values obtained on the basis of BBD. The final equation obtained in terms of coded factors is given below:

$$\%R = +65.02 + 3.25A - 1.68B + 0.54C + 4.25D + 5.57E + 3.31AB - 1.31AC\ 0.28AD + 0.15AE + 3.11BC + 0.80BD - 0.30BE - 0.39CD - 0.022CE + 2.21DE - 12.90A^2 + 3.97\ B^2 - 9.48C^2 - 8.93D^2 - 8.25E^2$$

Pareto analysis of variance (ANOVA was used to analyze the experimental data and the results are listed in Table 3(b). The higher model F-value (3207.27) and the associated lower p-value ($p < 0.0001$) demonstrated the significance of the developed models and also indicates that most of the variation in the responses could be explained by the developed regression equation [24]. The high value of R^2(0.9996), r_{adj}^2 (0.9993) and R_{pre}^2 (0.9984) demonstrated that the form of the model chosen to represent the actual relationship between the percentage of dye removal and selected variables is well correlated and accurate. The low value of the coefficient of the coefficient of variance (0.48) displayed the high degree of precision and good reliability of the conducted experiments [25]. In this study, the adequate precision (signal to noise ratio) was found to be 192.0.9 (greater than 4), which indicates the best fitness of the developed quadratic second order polynomial model.

Data were also analyzed to check the normality of the residuals. Normal probability plots of the residuals are shown in Fig. 2(a). The data points on this plot lie reasonably close to a straight line and show the developed model is accurate. The parity plot which relates actual

Table 3 (a): Adequacy of models tested for adsorption of BR2 onto WGSAB.

Source	R^2	R^2_{adj}	R^2_{pre}	PRESS	F Value	p-value Prob > F	Remarks
Linear	0.2410	0.1461	0.0298	4048.21	165529.62	< 0.0001	
2FI	0.2680	-0.0980	-0.6363	6827.90	223483.55	< 0.0001	
Quadratic	0.9996	0.9993	0.9984	6.50	148.43	< 0.0001	Suggested
Cubic	1.0000	0.9999	0.9981	7.77	44.42	0.0004	Aliased

Table 3 (b): ANOVA and statistical values for batch adsorption of BR2 onto WGSAB.

Coefficient				
Source	Estimate	Standard Error	F Value	p-value Prob > F
Model	65.02	0.10	3207.27	< 0.0001
A	3.25	0.06	2606.01	< 0.0001
B	-1.68	0.06	690.35	< 0.0001
C	0.54	0.06	70.59	< 0.0001
D	4.25	0.06	4450.99	< 0.0001
E	5.57	0.06	7645.98	< 0.0001
AB	3.31	0.13	672.95	< 0.0001
AC	-1.31	0.13	105.97	< 0.0001
AD	0.28	0.13	4.65	0.0408
AE	0.15	0.13	1.34	0.2583
BC	3.11	0.13	594.98	< 0.0001
BD	0.80	0.13	39.62	< 0.0001
BE	-0.31	0.13	5.72	0.0246
CD	-0.39	0.13	9.24	0.0055
CE	-0.02	0.13	0.03	0.8613
DE	2.21	0.13	301.13	< 0.0001
A^2	-12.90	0.09	22318.04	< 0.0001
B^2	3.97	0.09	2110.68	< 0.0001
C^2	-9.48	0.09	12053.96	< 0.0001
D^2	-8.93	0.09	10695.43	< 0.0001
E^2	-8.25	0.09	9124.36	< 0.0001
Lack of fit	-	-	14.84	0.0051
C.V%	0.48			
Adequate precision	192.09			

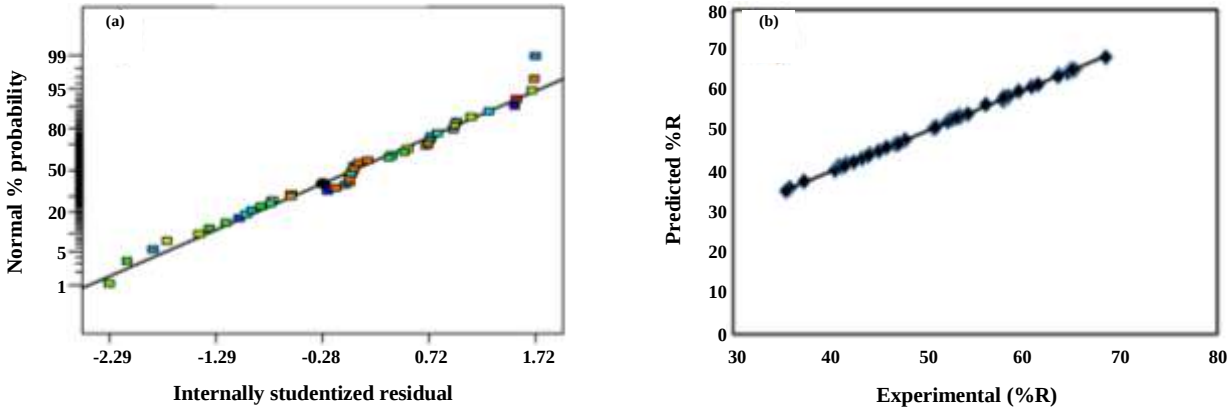

Fig. 2: (a) Normal Probability plot and (b) Parity plot

and the predicted value is shown in Fig. 2 (b). The straight line fit of this plot also indicates the adequacy of the developed model to navigate the design surface.

Response surface analysis

Three dimensional (3D) response surface plots and their corresponding contour plots are more helpful in understanding both the main and the interaction effects of the variables on the responses [26]. Therefore, 3D response surface plots Fig. 3 (a to i) for percentage dye removal were formed based on the quadratic polynomial model developed (Eq. (13)). Since the regression model has five independent variables, three factors were held constant at the center level for each plot, hence, a total of ten response 3D plots and ten corresponding contour plots were produced. The nonlinear nature of all 3D response surfaces and the respective contour plots demonstrated that there were reasonable interactions between each of the independent factors and the percentage dye removal. The individual effects of process factors on percentage dye removal were discussed below:

Effect of temperature

The combined effects of temperature with other variables were shown in Fig. 3 (d), (g), (i), and (j) respectively. The temperature displayed a positive linear and quadratic effect on the percentage dye removal (Table 3 (b)). When the temperature increased from 20^0C to 40^0C, the percentage of dye removal was increased which indicated that the BR2 adsorption was favorable at elevated temperatures. This was owing to the increased surface activity and kinetic energy of the dye molecules [2-4, 7-11].

Effect of pH

Fig. 3 (c), (f), (h), and (j) illustrates the effects of pH on percentage dye removal while keeping other three factors at the center level. At larger pH, the negative charge density on the WGSAB surface increased due to the reduction of hydrogen ions concentration on the sorption sites and that enabled the electrostatic attraction of the BR2 cations. But at low pH, the competition between hydrogen and BR2 cations on the sorption sites led to the high density of hydrogen ions which did not favor the dye cationic adsorption. Similar results were also reported in literature for different biomass systems [2-4, 15-17, 27].

Effect of dosage

The combined effects of GHSAC dosage correspond with initial concentration, WGSAB dosage, pH and temperature were shown in Fig. 3(a), (e), (f), and (g) respectively. From the figures, it can be seen that the dosage had a positive effect on the percentage removal while its value increased from low value (1.25 g/L) to high value (5 g/L). An increase in dosage of WGSAB increased the surface area and therefore more availability of active sites to BR2 molecules that caused an improvement in dye removal [2-4, 7-11, 27].

Effect of initial dye concentration

The combined effects of initial dye concentration on percentage dye removal are denoted by Fig. 3(a), (e), (h), and (i) response surface plots. The percentage of dye removal decreased with an increase in initial concentration. The unavailability of active sites to dye molecules on WGSAB particles due to higher concentrations was the reason for it [2-4, 15-17] .

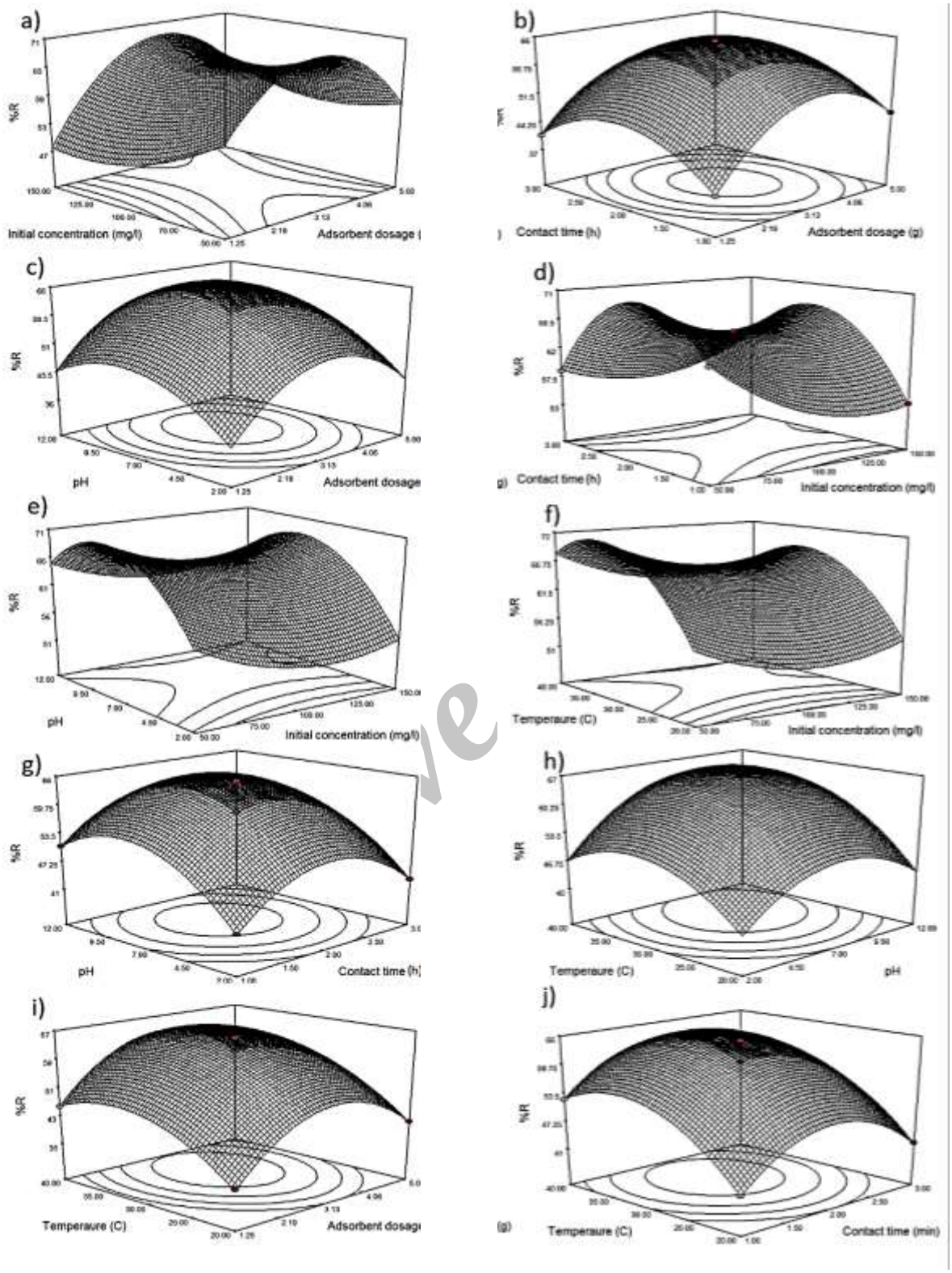

Fig. 3: 3D Response surfaces and contour plots of BR2-WGSAB batch adsorption system.

Table 4: Isotherm parameters.

S.No	Isotherm	Parameters	Values
1.	Langmuir:	Q_{mL} (mg/g)	50.310
	$q_e = \frac{q_{mL} b_L C_e}{1 + b_L C_e}$	b_L (l/mg)	0.126
		R_L	0.033
		R^2	0.991
		RMSE	1.780
2.	Freundlich	K_F (l/g)	8.688
	$q_e = K_F C_e^{1/n_F}$	n_F	2.231
		R^2	0.970
		RMSE	3.199
3.	Redlich-Peterson	K_{RP1} (l/g)	7.871
	$q_e = \frac{K_{RP1} C_e}{1 + K_{RP2} C_e \beta_{RP}}$	K_{RP2} (l/mg)	0.271
		β_{RP}	0.857
		R^2	0.996
		RMSE	1.088

Effect of contact time

The 3D response surface plots such as Fig. 3(b), (e), (h), and (i) depicted the combined effects of contact time with other variables. Increase in percentage removal noted while contact time increased but there was sluggishness in the dye adsorption seen after a short period of time (< 30 min) owing to the chemisorption nature of the adsorption [2-4, 7-11, 27].

Optimization using Derringer's desirability function

The Derringer's desirability function method [28-30] was employed to optimize the process variables. By seeking from 29 starting points in the response surface changes, the best local maximum was found to be at an adsorbent dose 2.41 g, initial dye concentration 150 mg/L, pH 8.69, temperature 33.57^{0}C, and contact time 1.42 h with the maximum desirability of 91%. Confirmatory experiments were conducted using the optimized variables and the obtained percentage dye removal (59.11%) were closely related with the data (59.26%) obtained from optimization analysis. This indicates BBD combined with Derringer's desirability function could be effectively used to optimize the batch adsorption process variables for the percentage removal of BR2.

Isotherms and kinetics

The equilibrium data analysis values are presented in Table 4. Redlich and Peterson's equation includes the characteristics of both Langmuir and Freundlich isotherms into a single equation to represent adsorption equilibrium over a wide range of concentrations. The Redlich–Peterson model exponent (β_{RP}) value tends to zero when this isotherm approaches Freundlich isotherm and tends to unity while this isotherm approaches Langmuir isotherm. By comparing statistical parameters, Langmuir and Freundlich's isotherms seemed to fit the equilibrium data poorly. The low values of RMSE (1.088) and high value of R^2 (0.996) indicated that Redlich-Peterson isotherm properly correlated the equilibrium data. This implied that the WGAB was heterogeneous in the liquid phase and BR2 removal was a multilayer adsorption process. The near unity value of β_{RP} (0.857) is also confirmed this fact. The data presented in Table 5 compares the maximum monolayer adsorption capacity of the different types of adsorbents used for the removal of BR2. The value of (Q_m) in this study is comparable with those in the previous work.

In order to investigate the specific rate constant of the present adsorption reactions, the kinetic data

Table 5: Comparison for maximum adsorption capacity of different adsorbents for BR2 adsorption.

Adsorbent	Q_{mL} (mg/g)	Reference
Chemically modified olive stone	526.30	[31]
spent bleaching earth	194.80	[32]
Natural zeolite	0.06	[33]
Treated waste cotton seed	50.31	This study

Table 6: Kinetic parameters at various concentrations.

Model	Parameter	100 (mg/L)	150 (mg/L)	200 (mg/L)	250 (mg/L)	300 (mg/L)
Ho $q_t = \frac{q_{e,Ho}^2 k_{Ho} t}{1 + k_{Ho} q_e t}$	K_{Ho}(g/mg min)	0.011	0.004	0.002	0.002	0.001
	Q_{eHo} (mg/g)	10.799	20.671	31.108	40.710	49.557
	h	1.297	1.868	2.349	2.582	2.856
	R^2	0.963	0.990	0.975	0.963	0.955
	RMSE	1.322	1.292	3.075	4.911	6.595
Avrami $q_t = q_{e,A}\left[1+\exp\left(-k_A t\right)^{n_A}\right]$	K_A(min^{-1})	0.287	0.269	0.252	1.000	0.235
	n_A	0.287	0.269	0.252	0.240	0.235
	Q_{eA} (mg/g)	9.808	18.246	27.187	35.043	42.185
	R^2	0.981	0.993	0.992	0.984	0.982
	RMSE	0.932	1.064	1.733	3.226	4.118

Table 7: Thermodynamic parameters for BR2 adsorption onto WGSAB.

T (K)	ΔG^0 (J/mol)	ΔH^0 (J/mol)	ΔS^0 (J/mol K)
293	-45216	678.04	156.64
303	-46783		
313	-48349		
323	-49915		

have been analyzed by Ho and Avrami kinetic models and the calculated parameters are presented in Table 6. While comparing the selected models, the higher values of R^2 and smaller values of RMSE over the selected concentration range shows the Avrami model correlated the kinetic data better than Ho model. It is also seen from Table 6 that, when the concentration increased the rate constant (K_A) values subsequently decreased and uptake capacity ($q_{e,A}$) increased. Further, the fractional order (n_A) and rate constant (K_A) values are almost similar for every concentration in both the dyes. This meant that the higher concentration favored the uptake of both the dyes but led unavailability of active sites to the dye molecules [34,35].

Thermodynamics

Variations of standard thermodynamic parameters during the adsorption process were evaluated and are presented in Table 7. As seen, the adsorption of BR2 by WGSAB was spontaneous with the negative values of ΔG^0 [36]. The value of ΔH^0 was positive which described that the dyes adsorption was endothermic and chemisorptive [37]. The positive ΔS^0 indicated that some structural changes in the WGSAB particles as well as BR2 during the adsorption process [38].

Regeneration studies

The cost of WGSAB can be reduced if it could be regenerated for further use. From Fig. 4, acetic acid

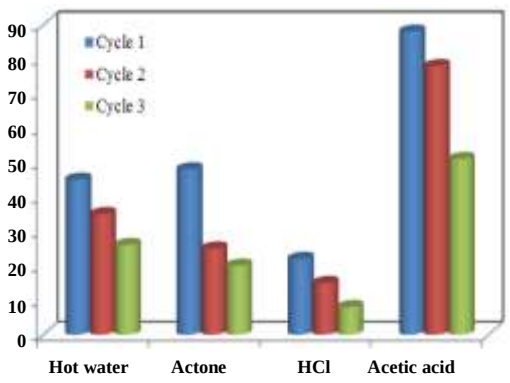

Fig. 4: Comparison of different solvents for regeneration studies.

was found to be efficient to elute BR2 comparatively than other solvents. It was noticed from laboratory batch experiments that BR2 adsorbed WGSAB could be regenerated twice efficiently for further use using acetic acid.

CONCLUSIONS

Sulfuric acid activated waste Gossypium hirsutum seed was utilized as an adsorbent for the batch adsorption of basic red 2. The main and interactive effects of five process variables like adsorbent dose, initial dye concentration, contact time, pH and temperature were investigated using Box–Behnken statistical design. The simultaneous optimization by Derringer's desirability function indicated that 59.26% removal of BR2 could be possible at the optimal conditions. Isotherm studies indicated that BR2 adsorption on to WGSAB was a multilayer adsorption. The kinetic investigation showed that the BR2 adsorption on WGSAB surface following Avrami fractional order kinetics. The thermodynamic studies revealed that the adsorption process was spontaneous and endothermic.

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