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Decolourization of aqueous dye solutions by a novel adsorbent: Application of statistical designs and surface plots for the optimization and regression analysis

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Abstract

Adsorption of Neolan Blue 2G (Acid Blue 158) and Basic Methylene Blue (Basic Blue 9) was investigated using a hybrid adsorbent that was prepared by pyrolysing a mixture of carbon and flyash at 1:1 ratio. A 2^4 full factorial central composite design with nine replicates at the center point and thus a total of 31 experiments were successfully employed for batch experimental design and analysis of the results. The combined effect of pH, temperature, particle size and time on the dye adsorption was studied. An empirical model was developed and validated applying ANOVA analysis incorporating interaction effects of all parameters and optimized using response surface methodology. The optimum pH, temperature, particle size and time were found to be 2.20, 27.85 °C, 0.0565 mm, 245 min, respectively, for Acid Blue 158 and those for Basic Blue 9 were 13.40, 28.45 °C, 0.0555 mm and 230 min, respectively. Complete removal (100%) was observed for both the dyes using the hybrid adsorbent.

Keywords: Adsorption; Hybrid adsorbent; Dye removal; Response surface methodology; Statistical analysis

1. Introduction

The presence of dyes in effluents is a major concern due to their adverse effect to many forms of life. Coloured waters are also objectionable on aesthetic grounds for drinking and other municipal and agricultural purposes [1]. Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents. The Treatment of aqueous water containing soluble dyes thus requires complete removal followed by secure disposal [2]. The most commonly used techniques for colour removal include chemical precipitation, ion exchange, reverse osmosis, ozonation and solvent extraction etc. However, these techniques have certain disadvantages such as high capital cost and operational costs or secondary sludge disposal problem [3]. The Adsorption technique has been proved to be an excellent way to treat effluents, offering significant advantages over more conventional process especially from an energetic and environmental point of view [2]. Activated carbon is being used as a potential adsorbent for its high efficiency. However, increase in the price of carbon results in economic difficulties for developing countries like India. Hence, alternate adsorbents with equivalent potential of activated carbon are current thrust area of research.

The adsorption of dyes on various types of materials has been studied in detail. These include: activated carbon [4], peat [5], chitin [6], silica [7], hardwood sawdust [8], hardwood [9], bagasse pith [10], flyash [11,12], mixture of flyash and coal [13], chitosan fiber [14], paddy straw [15], rice husk [16], slag [17], chitosan [18], acid treated spent bleaching earth [19], palm fruit bunch [20] and bone char [21].

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

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Nomenclature

C_0	initial concentration of dye solution (mg/l)
C_t	concentration of dye solution at the desired time, t (mg/l)
Exp.	experimental value
Pred.	predicted value
x_i	dimensionless coded value of the variable, X_i
X_0	value of the X_i at the center point
δX	step change
X_1	time (min)
X_2	pH
X_3	temperature (°C)
X_4	particle size (mm)
Y	predicted response

Greek letters

β_0	offset term
β_i	linear effect
β_{ii}	squared effect
β_{ij}	interaction effect
η	removal efficiency (%)

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) [22]. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing the 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 [23]. 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 [24].

For any batch adsorption process, the main parameters to be considered are pH, temperature, particle size and time [25]. Hence it is necessary to investigate extensively on the relationship between adsorption efficiency and the parameters affecting it. Owing to high cost of activated carbon, an adsorbent that is cheap and easily available would be a better alternative. In the present study, a novel adsorbent consisting of 1:1 mixture of carbon and flyash was investigated for its efficiency to remove two classes of dyes namely Basic Methylene Blue (BB 9) ($C_{14}H_{15}C_{l2}N_3S$) and Neolan Blue 2G (AB 158) ($C_{20}H_{18}CrN_2Na_2O_{11}S_2$) from aqueous solution. Their chemical structures are shown in Figs. 1 and 2. The interaction between the parameters was studied and optimized using response surface methodology.

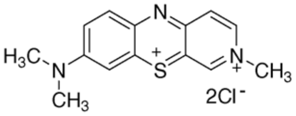

Fig. 1. Structure of Basic Methylene Blue (BB 9).

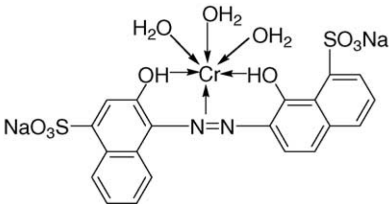

Fig. 2. Structure of Neolan Blue 2G (AB 158).

2. Materials and methods

2.1. Preparation of hybrid adsorbent

Flyash, obtained from Ennore Thermal Power Plant, Chennai, Tamilnadu, was washed with distilled water, dried under sunlight and subsequently in hot air oven at 60 °C. Hybrid adsorbent was prepared by mixing carbon (supplied by SD Fine chemicals) with flyash at 1:1 ratio by pyrolysing in an isothermal reactor powered by an electric furnace. High purity nitrogen was used as the purging gas. The isothermal reactor was heated to the desired temperature of 650 °C at a heating rate of 15 °C/min, and a holding time of 3 h. After pyrolysis, the product was activated at the same temperature for 3 h using CO_2 as oxidizing agent and subsequently used as adsorbent. The scanning electron micrograph (SEM) image (Fig. 3) shows irregular and porous structure of the hybrid adsorbent, owing to their exposure to a combustion environment, which indicates very high surface area. Chemical analysis of the hybrid adsorbent showed that carbon was the major constituent along with small amount of silica, lime and alumina. The origin of carbon constituents could be reasoned by analyzing the process and material used for carbon manufacture. Silica and alumina content were due to the constituents present in the flyash.

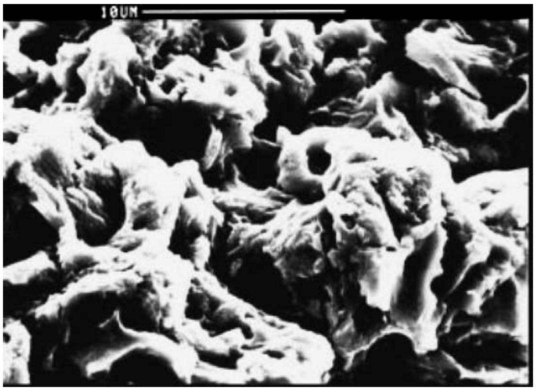

Fig. 3. SEM image of the hybrid adsorbent.

Table 1
Experimental range and levels of independent process variables for AB 158 removal

Independent variable	Range and level				
	$-\alpha$	-1	0	1	α
Time (X_1, min)	5	15	135	320	472
pH	0.5	1	3.5	6	8.5
Temperature (X_3, °C)	18	27	36	45	54
Particle size (X_4, mm)	0.0343	0.0585	0.33825	0.618	0.89775

Table 2
Experimental range and levels of independent process variables for BB 9 removal

Independent variable	Range and level				
	$-\alpha$	-1	0	1	α
Time (X_1, min)	5	15	127.5	285	420
pH	4.75	7.5	10.25	13	14
Temperature (X_3, °C)	18	27	36	45	54
Particle size (X_4, mm)	0.0343	0.0585	0.3349	0.618	0.9011

2.2. Methods

2.2.1. Batch adsorption

Stock solutions of dyes (AB 158 and BB 9) were prepared in deionized water and were diluted according to the working concentration. The required pH was adjusted by 0.1 N HCl or 0.1 N NaOH. Dye concentration was measured using UV–Vis spectrophotometer (Shimadzu UV 1600, Japan) at a wavelength corresponding to the maximum absorbance for each dye, 592 nm ($\lambda_{\max}$ maximum absorbance) for AB 158 dye and 535 nm ($\lambda_{\max}$ maximum absorbance) for BB 9. A 100 ml of the dye solution at desired pH value was contacted with 10 g/l of hybrid adsorbent in a 250 ml Erlenmeyer flask.

The flasks were kept under agitation in a rotatable orbital shaker at 150 rpm for the desired time. Experiments were performed according to central composite design (CCD) matrix given in Table 3. The response was expressed as % of dye removal calculated as:

$$\frac{(C_0 - C_t)}{C_0} \times 100.$$

2.3. Factorial experimental design and optimization of parameters

Temperature, pH, particle size and time were chosen as independent variables and the efficiency of colour removal as dependent output response variable. Independent variables, experimental range and levels for AB 158 and BB 9 removal are given in Tables 1 and 2, respectively. A 2^4 full-factorial experimental design [23], with nine replicates at the center point and thus a total of 31 experiments were employed in this study. The center point replicates were chosen to verify any change in the estimation procedure, as a measure of precision property. Experimental plan showing the coded value of the variables together with dye removal efficiency for AB 158 and BB 9 are given in Table 3. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\delta X} \tag{1}$$

The behaviour of the system was explained by the following quadratic equation:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \tag{2}$$

The results of the experimental design were studied and interpreted by MINITAB 14 (PA, USA) statistical software to estimate the response of the dependent variable.

3. Results and discussion

The most important parameters, which affect the efficiency of an adsorbent are time, pH and temperature of the solution and particle size of the adsorbent. In order to study the combined effect of these factors, experiments were performed at different combinations of the physical parameters using statistically designed experiments. The pH range studied was between 0.5 and 8.5 for AB 158 and between 4.75 and 14 for BB 9. The temperature was between 27 °C and 45 °C, particle size was small (0.0585 mm), medium (0.33825 mm), large (0.618 mm) for both the dyes and the time varied between 5 min and 472 min for AB 158 and between 5 min and 420 min for BB 9.

The main effects of each of the parameter on dye removal are given in Figs. 4 and 5 for AB 158 and BB 9, respectively. From the figures, it was observed that the maximum removal was found to be at 472 and 420 min for AB 158 and BB 9, respectively. This indicates that higher the contact time between dye and adsorbent, higher the removal efficiency till the equilibrium time is reached. The same trend was found to be correct by McKay 1983 [6] for dye removal on chitin. Maximum adsorption of AB 158 and BB 9 occurred at pH 1 and 13, respectively. This is due to the fact that dyes adsorb poorly when they are ionized [26].

When pH is such that dyes are in ionized form, adjacent molecules of the dyes on the hybrid adsorbent surface will repel each other to a significant degree, because of their equal electrical charge. Thus, both the dyes AB 158 and BB 9 that are acidic and basic in nature, respectively, could not get packed very densely on the hybrid adsorbent surface at pH values other than 1 and 13, respectively. The equilibrium amount of the adsorbed solute was only modest. In contrast, when the adsorbing species is not ionized, no such electrical repulsion exists, and thus the packing density on the surface can be much higher. This explains the common observation that non-ionized form of acidic and basic compounds adsorb much better than their ionized counterparts.

Table 3
Full factorial central composite design matrix for AB 158 and BB 9 removal

Observations	Time (X_1, min)	pH	Temperature (X_3, °C)	Particle size (X_4, mm)	Removal efficiency (η, %)			
					AB 158		BB 9	
					Exp.	Pred.	Exp.	Pred.
1	−1	−1	−1	−1	4.7250	3.9850	24.655	23.363
2	1	−1	−1	−1	99.825	98.955	78.265	77.652
3	−1	1	−1	−1	9.2250	8.9550	38.365	37.341
4	1	1	−1	−1	99.900	99.190	99.655	99.128
5	−1	−1	1	−1	10.755	9.9955	12.6	11.355
6	1	−1	1	−1	79.825	78.985	62.325	61.631
7	−1	1	1	−1	3.5500	3.1240	34.76	33.574
8	1	1	1	−1	55.855	54.355	89.925	87.593
9	−1	−1	−1	1	8.9550	8.1500	14.33	13.532
10	1	−1	−1	1	82.820	82.120	62.275	61.514
11	−1	1	−1	1	2.8200	2.1200	32.31	31.521
12	1	1	−1	1	62.730	61.630	90.18	89.524
13	−1	−1	1	1	3.2250	3.1250	8.73	7.4541
14	1	−1	1	1	59.485	58.185	59.295	58.454
15	−1	1	1	1	1.2250	1.8520	19.535	18.545
16	1	1	1	1	8.5200	8.1200	79.76	78.465
17	$-\alpha$	0	0	0	2.1250	1.9850	25.38	24.534
18	α	0	0	0	82.525	81.985	74.265	73.432
19	0	$-\alpha$	0	0	38.515	37.855	6.28	05.432
20	0	α	0	0	4.5250	4.1235	64.455	63.468
21	0	0	$-\alpha$	0	49.325	48.355	21.235	20.424
22	0	0	α	0	14.245	13.655	14.165	13.421
23	0	0	0	$-\alpha$	36.825	35.655	33.855	33.482
24	0	0	0	α	28.525	27.355	21.265	20.421
25	0	0	0	0	36.515	35.985	38.325	37.423
26	0	0	0	0	36.515	35.985	38.325	37.423
27	0	0	0	0	36.515	35.985	38.325	37.423
28	0	0	0	0	36.515	35.985	38.325	37.423
29	0	0	0	0	36.515	35.985	38.325	37.423
30	0	0	0	0	36.515	35.985	38.325	37.423
31	0	0	0	0	36.515	35.985	38.325	37.423

Acid species thus adsorb better at low pH and basic species adsorb much better at higher pH. Hence, the effect of solution pH is extremely important when the adsorbing species is capable of ionizing in response to the prevailing pH. Normal atmospheric temperature (∼27 °C) was found to be better for maximum adsorption of both the dyes and adsorption efficiency decreased with increase in temperature.

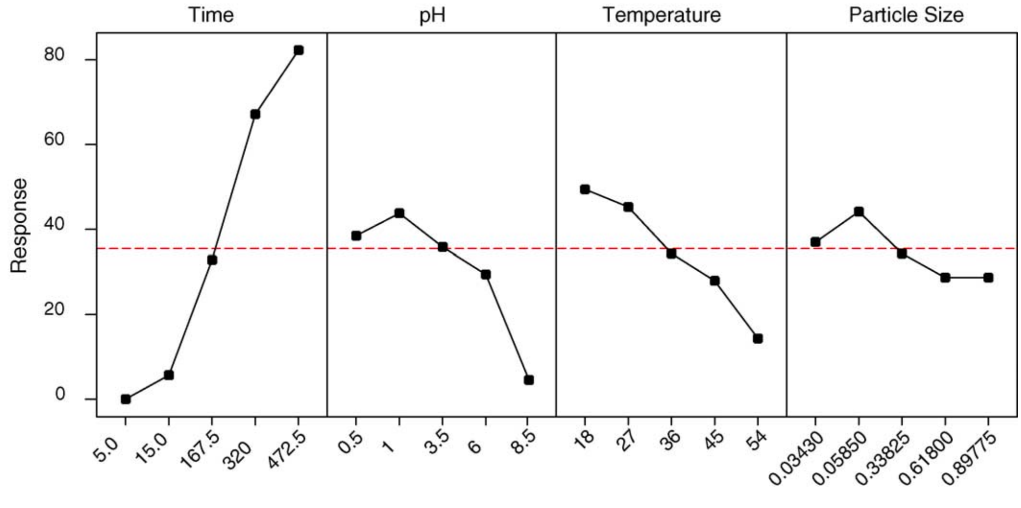

Fig. 4. Main effects plot of parameters for AB 158 removal.

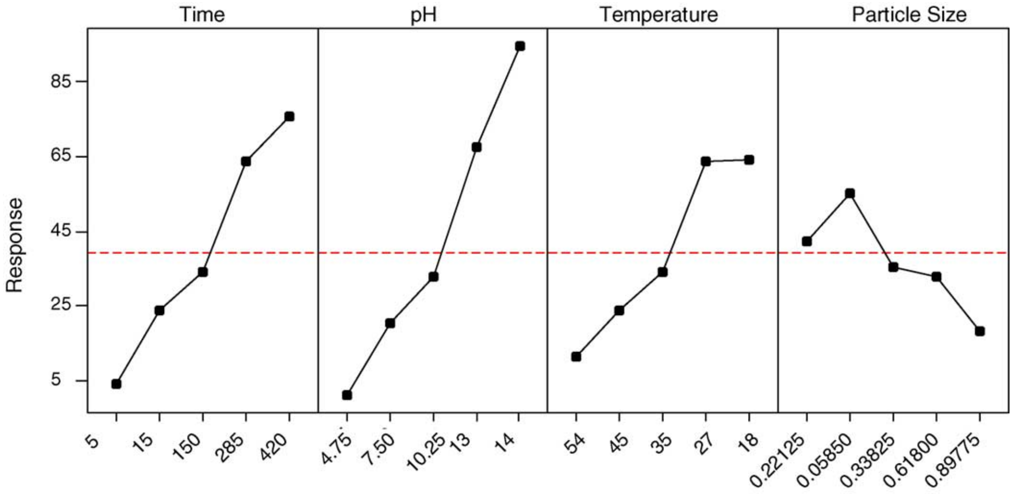

Fig. 5. Main effects plot of parameters for BB 9 removal.

This indicates the exothermic nature of the process and is due to the enhanced magnitude of the reverse step in the mechanism as the temperature increases. Similar temperature effects on the adsorption of reactive dye on chitosan beads had also been observed by Chion, 2002 [27]. The present study reveals the fact that in general increasing of the temperature leads to decrease of adsorption.

The adsorbed molecules have greater vibrational energies and therefore are more likely to desorb from the surface at higher temperature and hence adsorption will be lower if a system is run at higher temperature. Higher removal efficiency was found in particles of smaller size (0.0585 mm) for both the dyes. This relative increase in adsorption with particles of smaller sizes may be attributed to the fact that they have large surface area. Small particles will have a shorter diffusion path, thus allowing the adsorbate to penetrate deeper into the adsorbent particle more quickly, resulting in a higher rate of adsorption. In 2000, McKay had also observed similar results for the metal ions adsorption on bone char [21]. In case of large particles, the internal diffusion path is increased and therefore the greater is the probability of encountering smaller pores. Consequently, the dye uptake decreases with increasing particle diameter. Using the experimental results, the regression model equations (second order polynomial) relating the removal efficiency and process parameters were developed and are given in Eqs. (3) and (4) for AB 158 and BB 9, respectively.

Apart from the linear effect of the parameter for the dye removal, the RSM also gives an insight into the quadratic and interaction effect of the parameters. These analyses were done by means of Fisher's *F*-test and Student's *t*-test. The Student's *t*-test was used to determine the significance of the regression coefficients of the parameters. The *P*-values were used as a tool to check the significance of each of the interaction among the variables, which in turn may indicate the patterns of the interactions among the variables.

In general, larger the magnitude of *t* and smaller the value of *P*, the more significant is the corresponding coefficient term [28]. The regression coefficient, *t*- and *P*-value for all the linear, quadratic and interaction effect of the parameter are given in Tables 4 and 5 for AB 158 and BB 9, respectively.

Regression equation for AB 158

$$\begin{aligned}\eta = {} & -26.265966 + (0.514114 \times X_1) + (8.986224 \times X_2) \\ & +(0.800743 \times X_3) + (33.553273 \times X_4) \\ & +(-0.000056 \times X_1^2) + (-0.502439 \times X_2^2) \\ & +(-0.001837 \times X_3^2) + (25.029409 \times X_4^2) \\ & +(-0.011294 \times X_1 \times X_2) + (-0.005787 \times X_1 \times X_3) \\ & +(-0.135961 \times X_1 \times X_4) + (-0.141869 \times X_2 \times X_3) \\ & +(-4.568285 \times X_2 \times X_4) + (-1.234756 \times X_3 \times X_4)\end{aligned} \tag{3}$$

Table 4
Estimated regression co-efficient and corresponding *t*- and *P*-value for AB 158

Term	Co-efficient	Standard deviation	*t*	*P*
Constant	−26.265966	22.1160	−1.228	0.237
X_1	0.514114	0.0495	10.654	0.000
X_2	8.986224	3.1293	2.704	0.016
X_3	0.800743	1.0397	0.659	0.519
X_4	33.553273	27.3763	0.399	0.695
$X_1 \times X_1$	−0.000056	0.0001	−1.036	0.315
$X_2 \times X_2$	−0.502439	0.2266	−1.547	0.142
$X_3 \times X_3$	−0.001837	0.0135	0.075	0.941
$X_4 \times X_4$	25.029409	18.4055	2.223	0.041
$X_1 \times X_2$	−0.011294	0.0039	−3.991	0.001
$X_1 \times X_3$	−0.005787	0.0011	−5.282	0.000
$X_1 \times X_4$	−0.135961	0.0346	−4.227	0.001
$X_2 \times X_3$	−0.141869	0.0656	−2.226	0.041
$X_2 \times X_4$	−4.568285	2.1102	−1.803	0.090
$X_3 \times X_4$	−1.234756	0.5862	−1.321	0.205

Table 5
Estimated regression co-efficient and corresponding *t*- and *P*-value for BB 9

Term	Co-efficient	Standard deviation	*t*	*P*
Constant	−80.78657	43.8002	−1.831	0.016
X_1	−0.258661	0.0904	−2.568	0.001
X_2	12.126848	6.2932	3.011	0.008
X_3	2.2364827	2.5081	1.169	0.130
X_4	−20.86923	39.1306	−0.588	0.621
$X_1 \times X_1$	0.0036191	0.0032	12.289	0.000
$X_2 \times X_2$	−0.235969	0.4932	−3.505	0.003
$X_3 \times X_3$	−0.024866	0.125	−2.841	0.011
$X_4 \times X_4$	19.896331	20.1655	1.067	0.023
$X_1 \times X_2$	0.0089619	0.0190	0.076	0.140
$X_1 \times X_3$	0.00924545	0.0293	0.699	0.124
$X_1 \times X_4$	−0.0003648	0.1910	0.192	0.151
$X_2 \times X_3$	−0.0894115	0.252	1.045	0.501
$X_2 \times X_4$	0.0894641	4.841	−0.062	0.512
$X_3 \times X_4$	−0.4214156	0.958	0.270	0.123

Table 6
Optimum values of the process parameter for maximum efficiency

Parameter	Optimum value	
	AB 158	BB 9
η (efficiency, %)	100	100
X_1 (time, min)	245	230
X_2 (pH)	2.20	13.40
X_3 (temperature, °C)	27.85	28.45
X_4 (particle size, mm)	0.0565	0.0555

Regression equation for BB 9

$$\begin{aligned}\eta = {} & -80.78657+(-0.2586619 \times X_1)+(12.126848 \times X_2)\\ & +(2.2364827 \times X_3)+(-20.8692328 \times X_4)\\ & +(0.0036191 \times X_1^2)+(-0.235969411 \times X_2^2)\\ & +(-0.02486695 \times X_3^2)+(19.896331 \times X_4^2)\\ & +(0.0089619 \times X_1 \times X_2)+(0.0092454 \times X_1 \times X_3)\\ & +(-0.000364827 \times X_1 \times X_4)+(-0.08941158 \times X_2\\ & \times X_3)+(0.0894641 \times X_2 \times X_4)+(-0.42141562\\ & \times X_3 \times X_4)\end{aligned} \tag{4}$$

It was observed that the coefficients for the linear effect of time, pH ($P = 0.000$, 0.016, respectively) for AB 158 and ($P = 0.001$, 0.008, respectively) for BB 9 was highly significant and coefficient for the linear effect of remaining two parameters, i.e., temperature and particle size for both the dyes were the least significant.

The coefficient of the quadratic effect of time ($P = 0.000$), pH ($P = 0.003$) for BB 9 was highly significant and quadratic effect coefficients did not seem to be significant for AB 158.

The coefficients of the interactive effects of BB 9 among the variables did not appear to be very significant in comparison to the interactive effects of AB 158. However, the interaction effect between time and pH ($P = 0.001$), time and temperature ($P = 0.000$), time and particle size ($P = 0.001$) and pH and particle size ($P = 0.090$) were found to be significant. The significance of these interaction effects between the variables would have been lost if the experiments were carried out by conventional methods.

The model equations (3) and (4) were optimized using multistage Monte-Carlo optimization technique [29]. The optimal values of the process parameters were first obtained in coded units and then converted to uncoded units by using Eq. (1). The optimum values of the process variables for the maximum removal efficiency are shown in Table 6. These results closely agree with those obtained from the response surface analysis, confirming that the RSM could be effectively used to optimize the process parameters in complex processes using the statistical design of experiments.

Although few studies on the effects of parameters on adsorption have been reported in the literature, no attempt has been made to optimize them using statistical optimization methods. The predicted values (using the model equations) were compared with experimental results for both dyes and the data are shown in Table 3. The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using analysis of variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [30]. According to the ANOVA, which is shown in Tables 7 and 8 for AB 158 and BB 9, respectively, the $F_{\text{Statistics}}$ values for all regressions were higher.

The large value of F indicates that most of the variation in the response can be explained by the regression model equation. The associated P-value is used to estimate whether $F_{\text{Statistics}}$ is large enough to indicate statistical significance. A P-value lower than 0.01 (i.e., $\alpha = 0.01$, or 99% confidence) indicates that the model is considered to be statistically significant [31].

The P-values for all of the regressions were lower than 0.01. This means that at least one of the terms in the regression equation has a significant correlation with the response variable. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct. The $F_{\text{Statistics}}$ values of 52.48 for AB 158 and 59.55 for BB 9 are greater than tabulated $F_{14,16}$, indicate that the fitted model exhibits lack of fit (0.00001 for both AB 158 and BB 9) at the confidence level. ANOVA for AB 158 and BB 9, respectively indicated that the second-order polynomial model (Eqs. (3) and (4)) was highly significant and adequate to represent the actual relationship between the response (percent removal efficiency) and the variables, with very small P-value (0.00001 for AB 158 and 0.00001 for BB 9) and a high value of coefficient of determination ($R^2 = 0.991$

Table 7
ANOVA of removal efficiency for AB 158: effect of temperature, pH, time and particle size

Source	Degree of freedom (d.f.)	Sum of squares (SS)	Mean square (MS)	$F_{\text{Statistics}}$	P
Model	14	25603.0	1828.78	52.48	0.000
Linear	4	22837.5	1052.33	30.20	0.000
Square	4	268.6	67.15	1.93	0.155
Interaction	6	2496.8	416.14	11.94	0.000
Residual error	16	557.6	34.85		
Lack of fit	10	557.6	55.76		
Pure error	6				
Total	30	26160.6			

$R = 0.9954$; $R^2 = 0.991$.

Table 8
ANOVA of removal efficiency for BB 9: effect of temperature, pH, time and particle size

Source	Degree of freedom (d.f.)	Sum of squares (SS)	Mean square (MS)	$F_{\text{Statistics}}$	P
Model	14	22800.0	1628.57	59.55	0.00001
Linear	4	17215.7	125.72	7.45	0.0015
Square	4	5534.30	1383.58	49.58	0.00001
Interaction	6	49.9	8.32	0.69	0.36
Residual Error	16	469.4	29.34		
Lack of fit	10	469.4	29.34		
Pure Error	6				
Total	30	23269.4			

$R = 0.9944$; $R^2 = 0.9896$.

for AB 158 and $R^2 = 0.9896$ for BB 9). This implies that 98.96 and 99.1% of the sample variation for BB 9 and AB 158 are explained by the independent variables and this also means that the model did not explain only about 1.04 and 0.09% of sample variation for BB 9 and AB 158, respectively. The response surface plots and contour plots to estimate the removal efficiency surface over independent variables pH and temperature for AB 158 and temperature and particle size for BB 9 are shown in Figs. 6–9, respectively.

The surface and contour plots given in Figs. 6 and 7 show the relative effects of any two variables when the remaining variables are kept constant. The surface and contour plot for AB 158 in Fig. 6 show the interactive effect of temperature and pH by keeping time and particle size constant. Similarly by keeping pH and temperature constant, the surface and contour plot show the interactive effect of time and particle size.

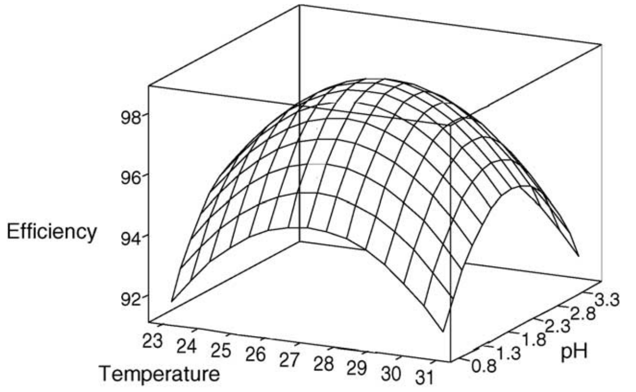

Fig. 6. Response surface plot of AB 158 dye removal (%) showing interactive effect of temperature and pH.

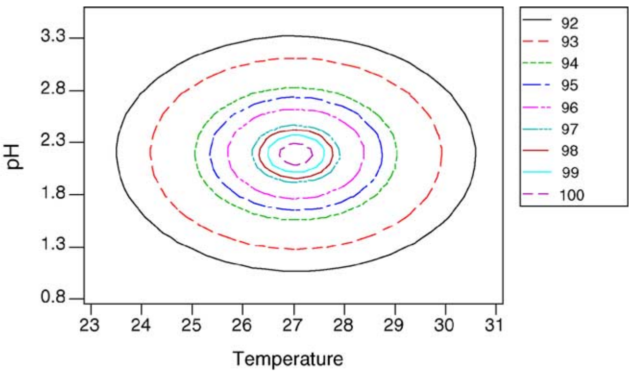

Fig. 7. Response surface contour plot of AB 158 dye removal (%) showing interactive effect of temperature and pH.

The response surfaces of mutual interactions between the variables were found to be elliptical. A similar type of trends was observed for heavy metal removal using biosorbent by Gopal, 2002 [32].

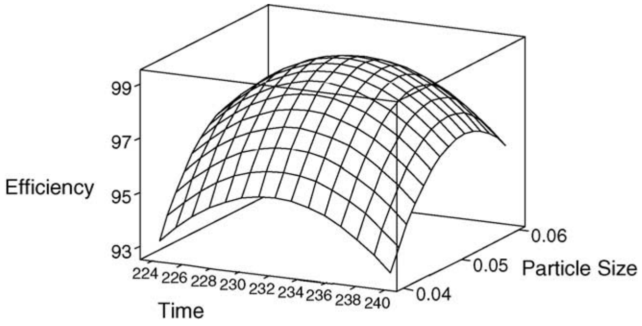

Fig. 8. Response surface plot of BB 9 dye removal (%) showing interactive effect of time and particle size.

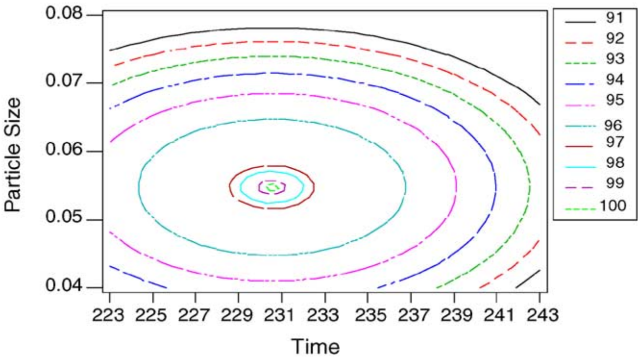

Fig. 9. Response contour plot of BB 9 dye removal (%) showing interactive effect of time and particle size.

The stationary point or central point is the point at which the slope of the contour is zero in all directions. The coordinates of the central point within the highest contour levels in each of these figures will correspond to the optimum values of the respective constituents. The maximum predicted yield is indicated by the surface confined in the smallest curve of the contour diagram [32]. The optimum values drawn from these figures are in close agreement with those obtained by optimizing the regression model Eqs. (3) and (4).

4. Conclusion

The present study clearly demonstrated the applicability of a hybrid adsorbent containing carbon and fly ash in equal proportion for dye removal. Under optimal values of process parameters, complete removal (100%) was achieved for both the dyes using the hybrid adsorbent. 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. A 2^4 full factorial central composite design was successfully employed for experimental design and analysis of results. Satisfactory empirical model equations were developed for both the dyes using RSM to optimize the parameters. Graphical response surface and contour plot was used to locate the optimum point.

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