



Statistical Analysis and Optimization of Acid Dye Biosorption by Brewery Waste Biomass Using Response Surface Methodology

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Abstract

Biosorption of Acid Yellow (AY 17) and Acid Blue (AB 25) were investigated using a biomass obtained from brewery industrial waste spent brewery grains (SBG). A 2^4 full factorial response surface central composite design with seven replicates at the centre point and thus a total of 31 experiments were employed for experimental design and analysis of the results. The combined effect of time, pH, adsorbent dosage and dye concentration on the dye biosorption was studied and optimized using response surface methodology. The optimum contact time, pH, adsorbent dosage and dye concentration were found to be 45min, 6, 0.5g, 75 mg/L respectively for the maximum decolorization of AY 17(97.2%) and 40 min, 2, 0.4g and 75 mg/L respectively for the maximum decolorization of AB 25(97.9%). A quadratic model was obtained for dye decolorization through this design. The experimental values were in good agreement with predicted values and the model developed was highly significant, the correlation coefficient being 0.89 and 0.905 for AY 17 and AB 25 respectively. Experimental results were analyzed by Analysis of variance (ANOVA) statistical concept.

Keywords: Biosorption, Response surface methodology, Acid dyes, Spent brewery grains, Statistical analysis

1. Introduction

Dyes are intensely coloured substance used for the dyeing of various materials such as textiles, paper, leather, hair, foods, drugs, cosmetics, plastics and many more substances. They are retained on these materials by physical adsorption, salt or metal complex formation, solution mechanical retention, or by the formation of covalent chemical bonds. The colour of the dye is due to electronic transitions between various molecular orbital, the probability of these transitions determining the intensity of the colour. Textile dyes are also designed to be resistant to fading by chemicals and light. They must also be resilient to both high temperatures and enzyme degradation resulting from detergent washing. For these reasons, degradation of dyes is typically a slow process.

The effluents arising out of textile and dyeing industries are the most problematic to be treated not only for their high chemical and biological oxygen demands, suspended solids in toxic compounds but also for colour, which is the first contaminant to be recognized by human eye. Dye wastewater is usually treated by physical or chemical treatment processes for colour removal. These include chemical coagulation/flocculation, precipitation, ozonation, adsorption, oxidation, ion exchange, membrane filtration and photo degradation. These methods for colour removal from effluents have high operating costs and limited applicability (Cooper, 1993). In recent years, biological decolorization method has been considered as an alternative and eco-friendly economical method. This has led many researchers to search for the use of effective, economical and eco-friendly alternative materials such as Chitin (McKay *et al.*, 1983); Silica

(McKay, 1984); the hardwood sawdust (Asfour et al., 1985); Bagasse pith (McKay et al., 1987); Fly ash (Khare et al., 1987); Paddy straw (Deo, 1993); Rice husk (Lee & Low, 1997); Slag (Ramakrishna & Viraraghavan, 1997); Chitosan (Juang et al., 1997); Palm fruit bunch (Nasser, 1997); Bone char (Ko et al., 2000). Thus research is still going on to develop alternative low cost adsorbents to activated carbon which is used mostly in industries. So in the present study spent brewery grains (SBG) which is present in abundant as waste in brewery industry is tried and tested as biosorbent.

Except a few studies in the literature for colour removal only traditional methods of experimentation were followed to study the effects of all variables which are lengthy, random processes and also require large number of experimental combinations to obtain the desired results. In addition, obtaining the optimum conditions i.e., the point at which maximum % colour removal could be achieved is almost beyond the scope. The traditional step-by-step approach, although widely used, involves a large number of independent runs and does not enable us to establish the multiple interacting parameters. This method is also time consuming, material consuming and requires large number of experimental trials to find out the effects, which are unreliable. So, specifically designed experiments to optimize the system with lesser number of experiments are the need of the hour. These limitations of the traditional method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design (Montgomery, 1991).

So, in this present study, experiments were designed by incorporating all important process variables namely time, pH, adsorbent dosage, and initial dye concentration using Statistical Design Software Minitab 14 (USA). Experimental design allows a large number of factors to be screened simultaneously to determine which of them has a significant effect on % colour removal. A polynomial regression response model shows the relationship of each factor towards the response as well as the interactions among the factors. Those factors can be optimized to give the maximum response (% colour removal) with a relatively lower number of experiments. In this context, a new approach using statistically designed experiments for finding optimum conditions for maximum % colour removal was discussed in detail. The corresponding interactions among the variables were studied and optimized using central composite design and response surface and contour plots.

2. Materials and Methods

2.1 Biosorbent and Adsorbate

The Brewery Industry waste Spent Brewery grain was obtained from Mohan breweries and distilleries Limited, Chennai, India and dried at 60°C for 12 hours. Synthetic textile dye acid yellow and acid blue was obtained from Sigma-Aldrich Chemicals Private Ltd., India and was used without further purification their chemical structures are shown in Fig.1 and Fig.2. All chemicals and reagents used for experiments were of analytical grade and supplied by Qualigens fine chemicals.

2.2 Preparation of biomass

Spent Brewery Grains, taken from Mohan breweries and distilleries Limited, Chennai, India, was suspended in 1M sulphuric acid solution (20g of SBG per 100mL of acid solution) for one hour. Then it was filtered and the acid solution was discarded. The biomass was washed with distilled water many times until it is completely free from the acid and dried at 60°C for 24 hours. The dried biomass was ground, sieved to 270 mesh size and stored for further use in the experiments. As seen from the Fig.3 the scanning electron micrograph (SEM) image shows the porous structure of the biosorbent.

2.3 Batch Experiments

Stock solution 1000mg/L of dye (AY 17 and AB 25) were prepared in double distilled water and was diluted as required according to the working concentration. The required pH was adjusted by 0.1N HCl or 0.1N NaOH. pH was measured using a pH meter (Elico, model LI 120, Hyderabad, India). Dye concentration was measured using UV-Vis Spectrophotometer (HITACHI U 2000, spectrophotometer) at a wavelength corresponding to the maximum absorbance of each dye $\lambda_{\max} = 401.5$ nm for AY 17 and $\lambda_{\max} = 600$ nm for AB 25. The dye solution (50 mL) at desired concentration, pH and adsorbent dosage taken in 250 ml Erlenmeyer flasks was contacted. The flasks were kept under agitation in a rotating orbital shaker at 150 rpm for desired time. Experiments were performed according to the central composite design (CCD) matrix given in Table 2. The response was expressed as % color removal calculated as

$$\% \text{ Colour removal} = \left[\frac{C_0 - C_t}{C_0} \right] \times 100 \quad (1)$$

2.4 Factorial experimental design

The parameters contact time, pH, adsorbent dosage and dye concentration were chosen as independent variables and the output response, removal efficiency of dye. Independent variables, experimental range and levels for AY 17 and AB 25 removal are given in Table 1 and Table 2. A 2^4 full-factorial experimental design, with seven 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 are given in Table 3. The analysis focused on how the colour removal efficiency is influenced by independent variables, i.e., time (X_1), pH (X_2), adsorbent dosage (X_3) and dye concentration (X_4). The dependent output variable is maximum removal efficiency. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \left[\frac{X_i - X_0}{\delta X} \right] \quad (2)$$

The behavior of the system was explained by the following quadratic equation

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (3)$$

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

3. Results and Discussion

3.1 Response Surface Methodology (RSM)

The most important parameters, which affect the efficiency of a biosorption process are contact time, pH, adsorbent dosage and dye concentration. 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 main effects of each parameter on dye removal are given in Fig.4 and Fig.5 for AY 17 and AB 25 respectively. From the figure, it was observed that the maximum removal was found to occur at 60 min for AY 17 and 45 min for AB 25. This indicates that higher the contact time between the dye and adsorbent, higher is the equilibrium removal efficiency. Maximum adsorption occurred at acidic pH range for both the acid dyes. This may be due to high electrostatic attraction between the positively charged surface of the SBG and anionic dyes AY 17 and AB 25. Acid dyes are also called as anionic dyes because of the negative electrical structure of the chromophore group. As the initial pH increases, the number of negatively charged sites on the biosorbent surfaces increases and the number of positively charged sites decreases. A negative surface charge does not favor the biosorption of dye anions due to electrostatic repulsion (Namasivayam and Kavitha, 2002). In general, the acidic dye uptakes are much higher in acidic solutions than those in neutral and alkaline conditions.

It was observed that the removal efficiency of both the dyes AY 17 and AB 25 increases as the adsorbent dosage increases. This may be due to the increase in the available active surface area of the adsorbent. It is observed that the removal efficiency of AY 17 decreases with the increase in dye concentration due to unavailability of surface area of the adsorbent to the increasing number of dye molecules and for AB 25 it is increasing in the studied range up to 175 mg/L with increase in initial dye concentration. Using the experimental results, the regression model equation (second order polynomial) relating the removal efficiency and process parameters was developed and is given in Equ. (4). and Equ. (5) for AY 17 and AB 25 respectively.

The regression equation for the determination of output response for AY17 is

$$\eta = (62.7143) + (2.5590X_1) + (-2.6632X_2) + (12.5382X_3) + (-5.4092X_4) + (-0.2117(X_1^2)) + (-4.4617X_2^2) + (0.2883X_3^2) + (1.9609X_4^2) + (0.1823X_1 X_2) + (0.5469X_1 X_3) + (0.8073 X_1 X_4) + (-0.3906 X_2 X_3) + (0.5990 X_2 X_4) + (-0.9115 X_3 X_4) \quad (4)$$

The regression equation for the determination of output response for AB 25 is

$$\eta = (96.8571) + (0.9867X_1) + (-1.8254X_2) + (-0.3079X_3) + (0.5308X_4) + (-2.1964(X_1^2)) + (-0.5897X_2^2) + (0.1089X_3^2) + (0.0909X_4^2) + (-1.5768X_1 X_2) + (0.5658X_1 X_3) + (-0.0163 X_1 X_4) + (-0.0653 X_2 X_3) + (0.4310 X_2 X_4) + (-0.0572 X_3 X_4) \quad (5)$$

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 interactions 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 (Montgomery, 1991). The regression coefficient, t and P values for all the linear, quadratic and interaction effects of the parameter are given in Table 4 and Table 5 for AY 17 and AB 25. It was observed that the coefficients for the linear effect of adsorbent dosage, dye concentration ($P=0.000, 0.001$) was highly significant and coefficient for the linear effect of time was the least significant for AY 17 and pH, time ($P = 0.000, 0.004$, respectively) was highly significant and coefficient for the linear effect of adsorbent dosage was the least significant for AB 25. The coefficient of the quadratic effect of pH and dye concentration ($P = 0.002, 0.130$) was highly significant and the coefficient of the quadratic terms of time ($P = 0.865$) was least significant for AY 17. The coefficient of the quadratic effect of time and pH ($P = 0.000, 0.042$) was highly significant and the coefficient of the quadratic terms of dye concentration ($P = 0.737$) was least significant for AB 25.

The coefficients of the interactive effects of AY 17 among the variables did not appear to be very significant in comparison to the interactive effects of AB 25. However, the interaction effect between time and pH ($P = 0.000$) and time and adsorbent dosage ($P = 0.131$) were found to be significant for AB 25. The significance of these interaction effects between the variables would have been lost if the experiments were carried out by conventional methods.

The optimum values of the process variables for the maximum removal efficiency for both the dyes AY 17 and AB 25 are shown in Table 6. These results are in close agreement 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, only a few attempts has been made to optimize them using statistical optimization methods. The predicted values (using the model equation) were compared with experimental result and the data are shown in Table 3.

3.2 Analysis of Variance (ANOVA)

The statistical significance of the ratio of mean square due to regression and mean square due to 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 hypothesis on the parameters of the model (Seguro et al., 1999). According to the ANOVA Table 7 and Table 8 for AY 17 and AB 25, 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 $F_{\text{statistics}}$ value of 9.24 is greater than tabulated $F_{14, 16}$ (2.38) which indicates that the second order polynomial equation (4) is highly significant and adequate to represent the actual relationship between the response and the variables with a high value of coefficient of determination ($R = 0.9433$; $R^2 = 0.89$) for AY 17. The $F_{\text{statistics}}$ value of 10.9 is greater than tabulated $F_{14, 16}$ (3.14) which indicates that the second order polynomial equation (5) is highly significant and adequate to represent the actual relationship between the response and the variables with a high value of coefficient of determination ($R = 0.9513$; $R^2 = 0.905$) for AB 25.

The associated P -value is used to judge whether F Statistics is large enough to indicate statistical significance. A P -value lower than 0.05 indicates that the model is considered to be statistically significant (Kim et al., 2003). The P -values for almost all of the regressions for both the acid dyes AY 17 and AB 25 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 response surface and contour plots to estimate the removal efficiency over independent variables adsorbent dosage, pH and pH, dye concentration for the dyes are shown in Fig.6 and 7 for AY 17 and Fig.8 and 9 for AB 25 respectively. The contour plots given in figures show the relative effects of any two variables when concentration of the remaining variables is kept constant. The maximum predicted yield is indicated by the surface confined in the smallest curve of the contour diagram (Gopal et al., 2002).

Figs. 10 - 13 depict the experimental and model predicted removal efficiencies. The predictive capacity of the models was also evaluated in terms of the relative deviations $(RE_{\text{Exp}} - RE_{\text{Pred}}) / RE_{\text{Exp}}$ for the model. With a few exceptions, the values of the variables showed a good agreement (within 3% error) with the experimental data shown in Table 3.

4. Conclusions

The present investigation clearly demonstrated the applicability of SBG as biosorbent for AY 17 and AB 25 dye removal from aqueous solutions. Experiments were carried out covering a wide range of operating conditions. The influence of time, pH, adsorbent dosage and initial dye concentration was critically examined. It was observed from this investigation that the percentage removal efficiency is significantly influenced by time, pH, adsorbent dosage and initial dye concentration. A 2^4 Full factorial central composite experimental design was applied. The experimental data were analyzed using response surface methodology and the individual and combined parameter effects on colour removal efficiency were analyzed. Regression equations were developed for removal efficiency using experimental data and solved using the statistical software Minitab 14. It was observed that model predictions are in good agreement with experimental observations. Under optimal values of process parameters around 97.2% and 97.9% colour removal was achieved for AY 17 and AB 25 dye respectively using the SBG. 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.

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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)
RE_{Exp}	Removal Efficiency experimental value
RE_{Pred}	Removal Efficiency predicted value
RE	Removal Efficiency
x_i	dimensionless coded value of the variable, X_i
X_0	value of the X_i at the center point
X_1	time (min)
X_2	pH
X_3	adsorbent dosage(g)
X_4	dye concentration (mg/L)
δX	step change
Y	predicted response
<i>Greek letters</i>	
β_0	offset term
β_i	linear effect
β_{ii}	squared effect
β_{ij}	interaction effect
η	removal efficiency

Table 1. Experimental range and levels of independent process variables for AY 17 removal

Independent variable	Range and level				
	$-\alpha$	-1	0	+1	$+\alpha$
Time(X_1 ,min)	15	30	45	60	75
pH(X_2)	4	6	8	10	12
Adsorbent dosage(X_3 ,g)	0.125	0.25	0.375	0.5	0.625
Dye concentration(X_4 ,mg/L)	75	100	125	150	175

Table 2. Experimental range and levels of independent process variables for AB 25 removal

Independent variable	Range and level				
	$-\alpha$	-1	0	+1	$+\alpha$
Time(X_1 ,min)	15	30	45	60	75
pH(X_2)	2	4	6	8	10
Adsorbent dosage(X_3 ,g)	0.2	0.4	0.6	0.8	1.0
Dye concentration(X_4 ,mg/L)	75	100	125	150	175

Table 3. Full factorial central composite design matrix for AY 17 and AB 25 removal

Observations	Time (X_1 ,min)	pH (X_2)	Adsorbent dosage (X_3 ,g)	Dye concentration (X_4 ,mg/L)	Removal Efficiency (η , %)			
					AY 17		AB 25	
					RE _{Exp.}	RE _{Pred.}	RE _{Exp.}	RE _{Pred.}
1	-1	-1	-1	-1	53.75	54.10	97.94	98.19
2	1	-1	-1	-1	57.50	56.14	94.55	92.93
3	-1	1	-1	-1	53.75	47.99	96.07	94.51
4	1	1	-1	-1	57.50	50.77	94.11	93.01
5	-1	-1	1	-1	80.00	80.69	93.52	92.66
6	1	-1	1	-1	82.50	84.92	96.47	96.85
7	-1	1	1	-1	78.75	73.02	98.62	98.47
8	1	1	1	-1	80.00	77.98	91.50	90.04
9	-1	-1	-1	1	44.17	42.29	98.58	98.14
10	1	-1	-1	1	46.67	47.57	97.94	98.95
11	-1	1	-1	1	45.83	38.58	98.23	99.00
12	1	1	-1	1	49.17	44.58	90.44	91.15
13	-1	-1	1	1	63.33	65.23	90.29	90.65
14	1	-1	1	1	70.83	72.69	96.23	96.85
15	-1	1	1	1	62.50	59.96	96.23	96.85
16	1	1	1	1	73.33	68.15	97.52	96.67
17	$-\alpha$	0	0	0	51.00	56.75	93.13	92.93
18	α	0	0	0	64.00	66.99	89.41	90.84
19	0	$-\alpha$	0	0	57.00	50.19	83.64	86.09
20	0	α	0	0	24.00	39.54	96.17	95.01
21	0	0	$-\alpha$	0	30.00	38.79	97.52	96.85
22	0	0	α	0	89.00	88.94	97.52	96.85
23	0	0	0	$-\alpha$	76.67	81.38	91.17	91.17
24	0	0	0	α	55.71	59.74	96.47	96.85
25	0	0	0	0	61.00	62.71	92.64	92.66
26	0	0	0	0	63.00	62.71	96.06	97.90
27	0	0	0	0	63.00	62.71	96.38	98.28
28	0	0	0	0	63.00	62.71	97.52	96.85
29	0	0	0	0	63.00	62.71	94.11	94.16
30	0	0	0	0	63.00	62.71	97.05	96.15
31	0	0	0	0	63.00	62.71	93.30	92.78

Table 4. Estimated Regression Coefficients and corresponding T- and P- values for AY 17

Term	Coefficient	Standard error	T	P
Constant	62.7143	2.484	25.247	0.000
X₁	2.5590	1.342	1.908	0.075
X₂	-2.6632	1.342	-1.985	0.065
X₃	12.5382	1.342	9.346	0.000
X₄	-5.4092	1.342	-4.032	0.001
X₁X₁	-0.2117	1.229	-0.172	0.865
X₂X₂	-4.4617	1.229	-3.630	0.002
X₃X₃	0.2883	1.229	0.235	0.817
X₄X₄	1.9609	1.229	1.596	0.130
X₁X₂	0.1823	1.643	0.111	0.913
X₁X₃	0.5469	1.643	0.333	0.744
X₁X₄	0.8073	1.643	0.491	0.630
X₂X₃	-0.3906	1.643	-0.238	0.815
X₂X₄	0.5990	1.643	0.365	0.720
X₃X₄	-0.9115	1.643	-0.555	0.587

Table 5. Estimated Regression Coefficients and corresponding T- and P- values for AB 25

Term	Coefficient	Standard error	T	P
Constant	96.8571	0.5380	180.027	0.000
X₁	0.9867	0.2906	3.396	0.004
X₂	-1.8254	0.2906	-6.282	0.000
X₃	-0.3079	0.2906	-1.060	0.305
X₄	0.5308	0.2906	1.827	0.086
X₁X₁	-2.1964	0.2662	-8.251	0.000
X₂X₂	-0.5897	0.2662	-2.215	0.042
X₃X₃	0.1089	0.2662	0.409	0.688
X₄X₄	0.0909	0.2662	0.342	0.737
X₁X₂	-1.5768	0.3559	-4.431	0.000
X₁X₃	0.5658	0.3559	1.590	0.131
X₁X₄	-0.0163	0.3559	-0.046	0.964
X₂X₃	-0.0653	0.3559	-0.184	0.857
X₂X₄	0.4310	0.3559	1.211	0.243
X₃X₄	-0.0572	0.3559	-0.161	0.874

Table 6. Optimum values of the process parameter for maximum efficiency for AY 17 and AB 25

Parameter	Optimum Values	
	AY 17	AB 25
η (Removal Efficiency, %)	97.2	97.9
X₁ (Time, min)	45	45.00
X₂ (pH)	6	2.00
X₃ (Adsorbent Dosage, g)	0.5	0.4
X₄ (Dye Concentration, mg/L)	75	75

Table 7. ANOVA of removal efficiency for AY 17: Effect of time, pH, adsorbent dosage and Dye concentration

Source	Degree of freedom	Sum of Squares	Mean of Squares	F _{statistics}	P
Model	14	5588.78	399.2	9.24	0.000
Linear	4	4802.57	1200.64	27.8	0.000
Square	4	748.99	187.25	4.34	0.015
Interaction	6	37.22	6.20	0.14	0.988
Residual Error	16	691.08	43.19	-	-
Lack of fit	10	687.65	68.77	120.34	0.000
Pure Error	6	3.43	0.57	-	-
Total	30	6279.86	-	-	-

Table 8. ANOVA of removal efficiency for AB 25: Effect of time, pH, adsorbent dosage and Dye concentration

Source	Degree of freedom	Sum of Squares	Mean of Squares	F _{statistics}	P
Model	14	309.256	22.0897	10.90	0.000
Linear	4	112.373	28.0933	13.86	0.000
Square	4	148.881	37.2203	18.37	0.000
Interaction	6	48.002	8.0003	3.95	0.013
Residual Error	16	32.420	2.0262	-	-
Lack of fit	10	29.992	2.9992	7.41	0.012
Pure Error	6	2.428	0.4047	-	-
Total	30	341.676	-	-	-

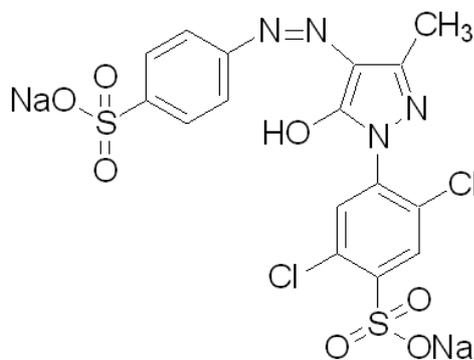


Figure 1. The chemical structure of AY 17 dye

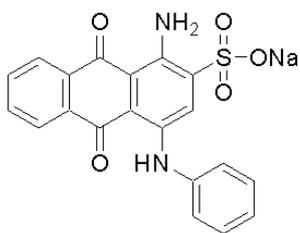


Figure 2. The chemical structure of AB 25 dye

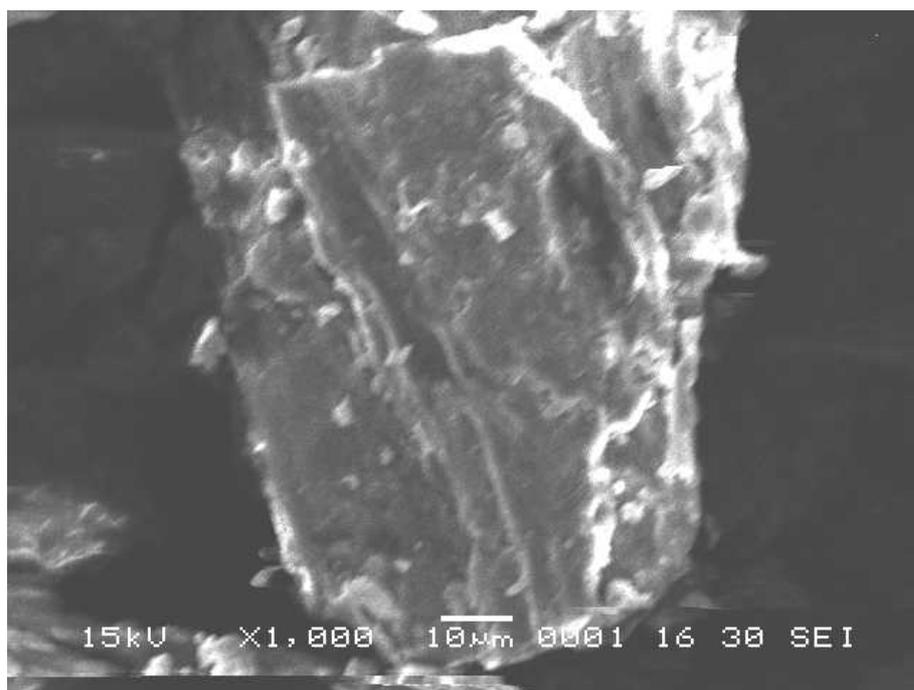


Figure 3. SEM image of the biomass SBG

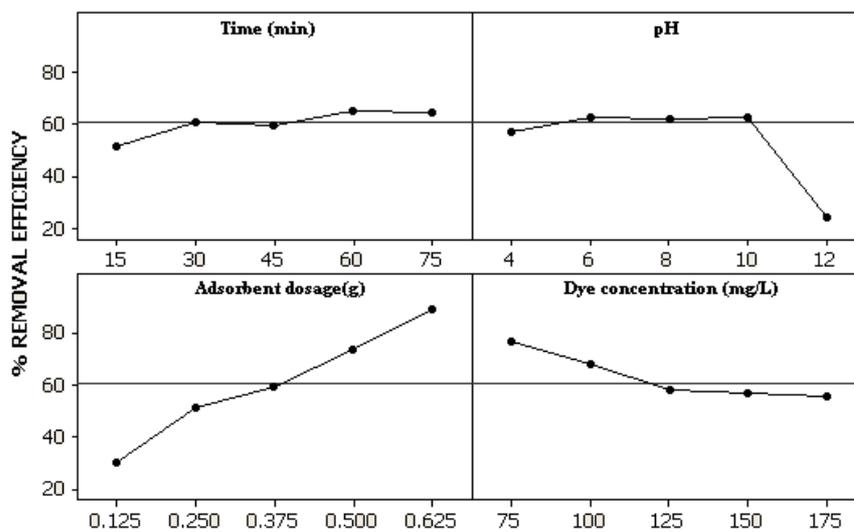


Figure 4. Main effects plot of parameters for AY 17 removal

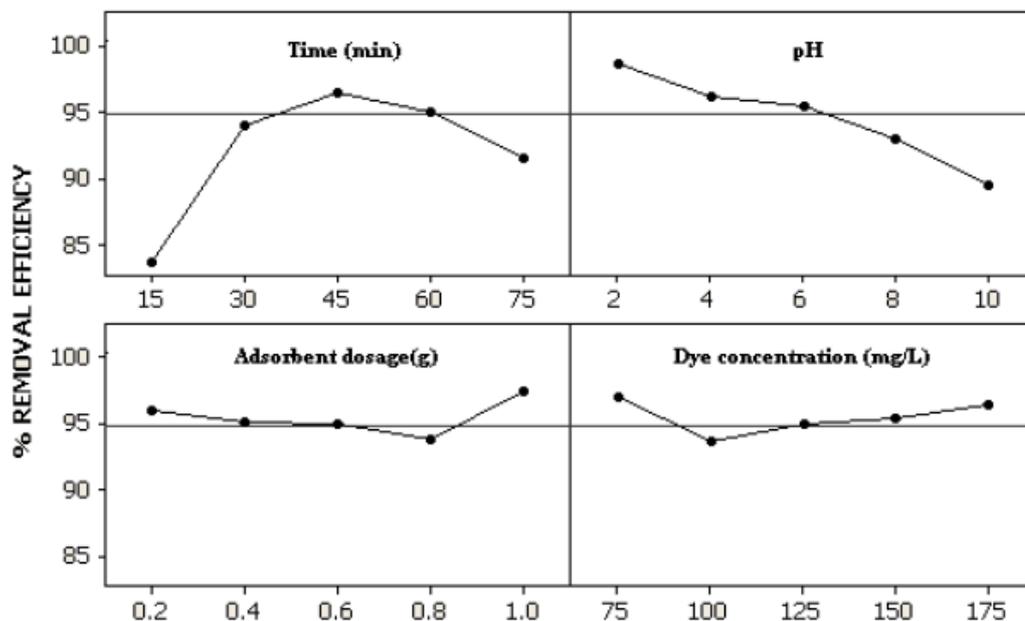


Figure 5. Main effects plot of parameters for AB 25 removal

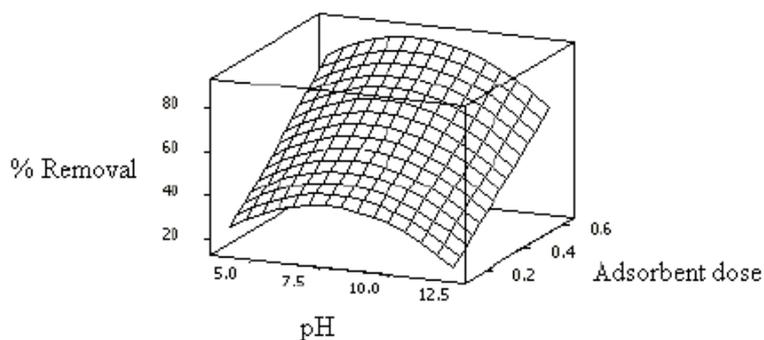


Figure 6. Response surface plot of AY 17 dye removal (%) showing interactive effect of adsorbent dose and pH

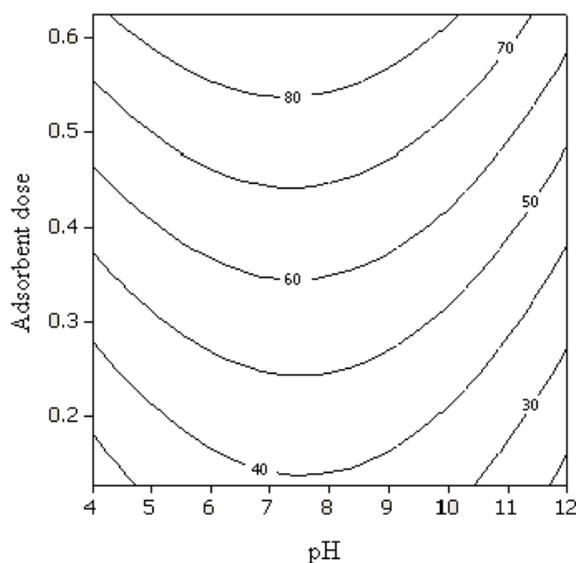


Figure 7. Response contour plot of AY 17 dye removal (%) showing interactive effect of adsorbent dose and pH.

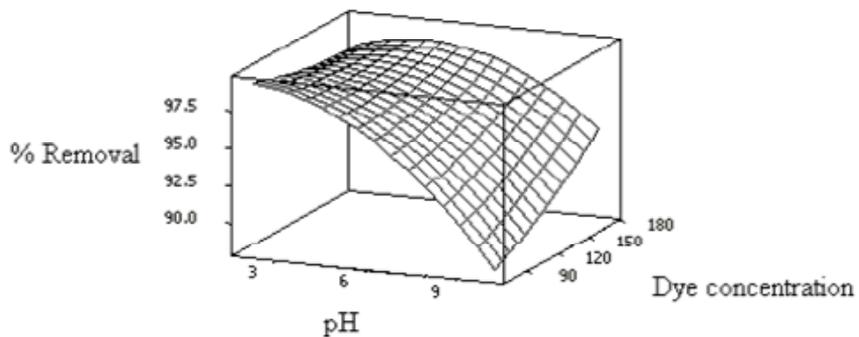


Figure 8. Response surface plot of AB 25 dye removal (%) showing interactive effect of pH and dye concentration

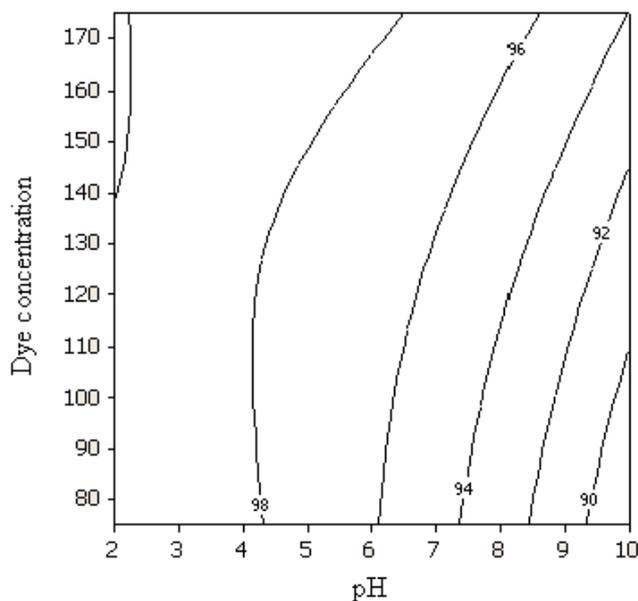


Figure 9. Response contour plot of AB 25 dye removal (%) showing interactive effect of pH and dye concentration

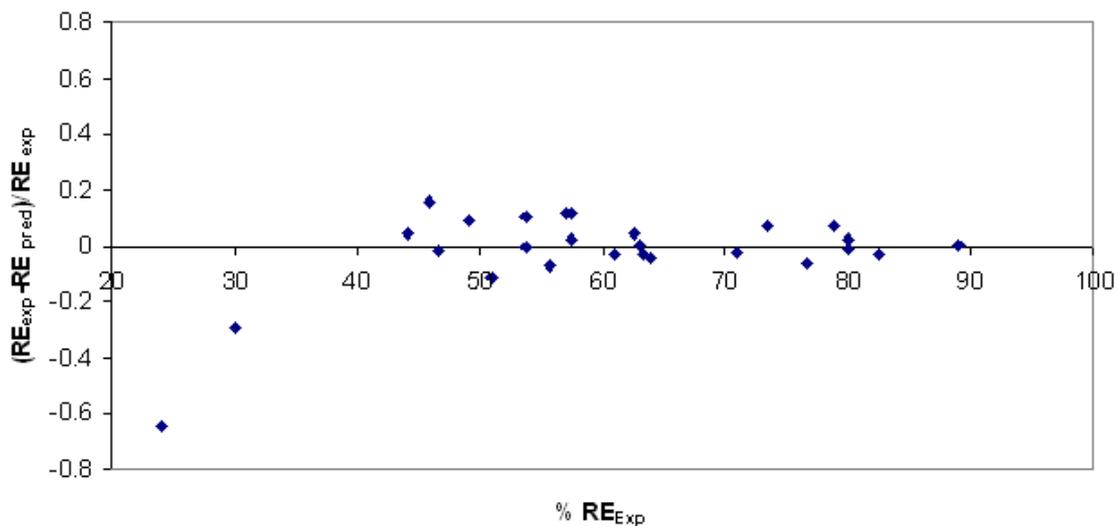


Figure 10. Comparison of experimental and predicted removal efficiency for AY 17

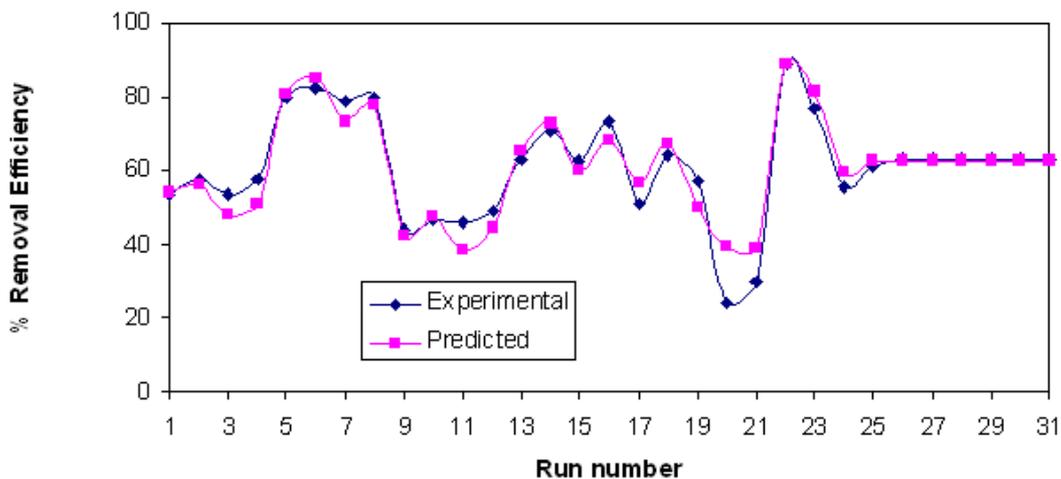


Figure 11. Relative deviation between experimental and predicted removal efficiency for AY 17

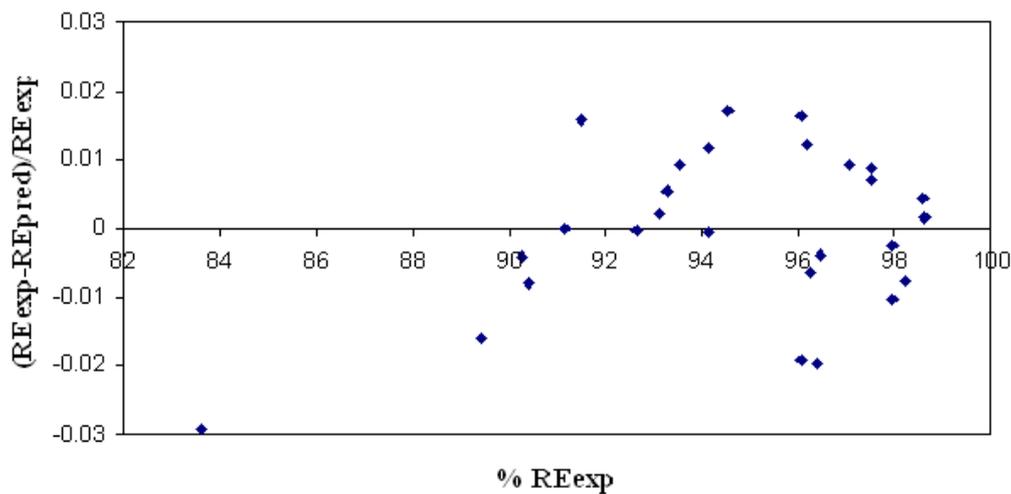


Figure 12. Comparison of experimental and predicted removal efficiency for AB 25

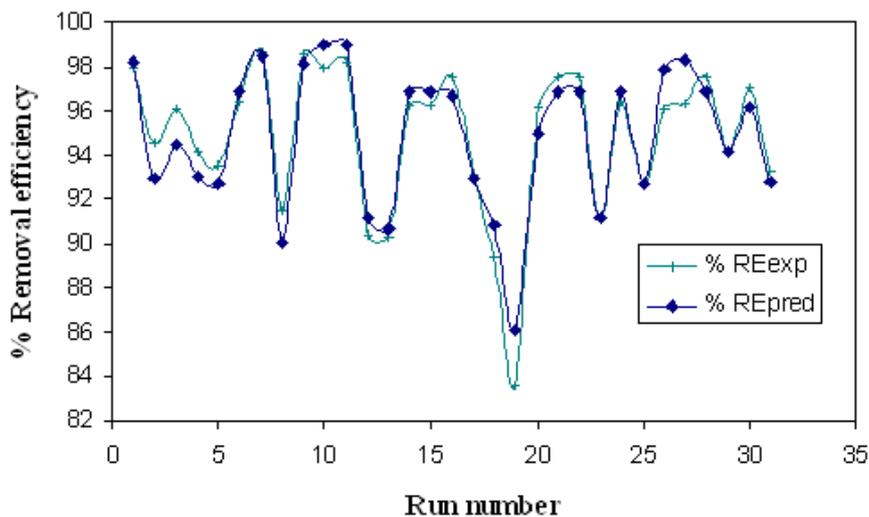


Figure 13. Relative deviation between experimental and predicted removal efficiency for AB 25