



# Box–Behnken design optimization for the removal of Direct Violet 51 dye from aqueous solution using lignocellulosic waste

Sana Sadaf<sup>a,\*</sup>, Haq Nawaz Bhatti<sup>a,\*</sup>, Muhammad Arif<sup>b</sup>, Misbah Amin<sup>a</sup>, Farva Nazar<sup>c</sup>, Misbah Sultan<sup>d</sup>

<sup>a</sup>Environmental Chemistry Laboratory, Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan, email: sanasadaf@gmail.com (S. Sadaf), Tel. +92 41 9200161/3319; Fax: +92 41 9200764; emails: hnbhatti2005@yahoo.com, haq\_nawaz@uaf.edu.pk (H.N. Bhatti), chemistry\_mystery2000@yahoo.com (M. Amin)

<sup>b</sup>Department of Mathematics and Statistics, University of Agriculture, Faisalabad 38040, Pakistan, email: arif\_uaf@hotmail.com (M. Arif) <sup>c</sup>College of Statistical and Actuarial Sciences, University of the Punjab, Lahore 54000, Pakistan, email: farva.nazar@gmail.com (F. Nazar) <sup>d</sup>Department of Polymer Engineering, National Textile University, Faisalabad, Pakistan, email: misbahsultan@ymail.com (M. Sultan)

Received 29 January 2014; Accepted 27 August 2014

#### ABSTRACT

The present research work was designed to explore the biosorption efficiency of sugarcane bagasse (SB) biomass for the removal of Direct Violet 51 dye from aqueous solution. The modification of SB biomass was carried out by different physical and chemical treatments. HCl-treated SB biomass depicted maximum biosorption efficiency among all the modified SB biomasses. Box–Behnken experimental design was employed to illustrate the effect of three independent variables (initial dye concentration (A), biosorbent dose (B), and pH (C)) on the dye removal process. Maximum dye removal (63.0 mg g<sup>-1</sup>) was achieved at pH 2 and 0.05 g biosorbent dose. Higher initial dye concentration was found to be favorable for the dye removal process. Desorption study was conducted using NaOH solution of different strengths, and it was observed that 61.58% dye can be desorbed from the loaded biosorbent using 1 M NaOH solution. Characterization of SB biomass was also carried out by FTIR, scanning electron microscope, and TGA analysis. The results indicated that SB biomass can be used as an efficient biosorbent for the treatment of dye containing wastewater.

*Keywords:* Direct Violet 51; Box–Behnken experimental design; FTIR analysis; TGA analysis; Desorption study

### 1. Introduction

The extensive industrial operations have intensified the deterioration of several ecosystems, and this situation is seriously threatening the human health and environment. Water scarcity and contamination of natural water resources has limited the availability of high-quality potable water supplies for public consumption [1]. The water pollution control has become an arduous task for the scientific community today. The scientist and researchers have developed different treatment technologies (sedimentation, precipitation, ion exchange, membrane technologies, biological degradation, adsorption, etc.) for water recycling and scavenging of the industrial effluents. These technologies have different levels of successes [2].

<sup>\*</sup>Corresponding authors.

<sup>1944-3994/1944-3986 © 2014</sup> Balaban Desalination Publications. All rights reserved.

Among the different treatment technologies, the adsorption process has become the focus of intense interest for the researchers and environmentalists [3]. Adsorption is found to be highly efficient, promising, economically viable, and technically feasible technique for the wastewater treatment [4]. Since the past few decades, the agro-based waste materials have found potential applications in the field of adsorption [5]. The abundant availability of agro wastes and presence of different functional groups on their surface has made their use more attractive [6]. Many scientists and researchers have conducted researches on the exploitation of agricultural wastes for the wastewater treatment [7–9]. The exploitation of agricultural waste materials provides twofold advantage with respect to environmental management. One advantage is that the water pollution can be overcome using these waste biomaterials at a reasonable cost, and the second advantage is that large volumes of agricultural byproducts can be reduced by this practice which otherwise may create solid waste problems [10,11].

Surface modification has found to be an emerging field in the adsorption process. The surface-modified adsorbents exhibit high adsorption capacity for the pollutants [12]. The surface modification technique helps in increasing the number of binding sites and also helps in enhancing their activation on the surface of adsorbents which leads to the enhancement in adsorption potential [13]. Different researchers have worked on the treatment of biosorbents to increase their adsorption potential for the removal of dyes from aqueous solutions [14–16].

No work has been reported for the adsorptive removal of Direct Violet 51 dye using sugarcane bagasse (SB) biomass. Direct Violet 51 is a locally available commercial dye which has been used in textile industries. So, the present work was designed to check out the adsorption potential of SB biomass in its treated form for the removal of Direct Violet 51 dye from aqueous solution. Different physical and chemical treatments were carried out to enhance the adsorption potential of SB biomass for the removal of anionic dye. Box–Behnken experimental design was employed for the optimization of important process variables during adsorption process. Desorption studies were also carried out for the regeneration of adsorbent and adsorbate.

## 2. Materials and methods

#### 2.1. Preparation of biomass

SB was collected from the local market of Faisalabad, Pakistan. The washed and dried biomass

was ground with a food processor (Moulinex, France) and sieved using Octagon sieve (OCT-DIGITAL 4527-01) to a 300 µm mesh size. SB biomass was pretreated physically and chemically. During physical treatments, autoclaving (the SB biomass was autoclaved at 121°C for 15 min) and boiling (5 g of biomass/100 mL of H<sub>2</sub>O and boiled for 30 min) was carried out. In chemical modifications, 1g of the biosorbent was treated with 5% of different acids (HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>, CH<sub>3</sub>COOH), alkali (NaOH), surfactants (CTAB, SDS, and Triton X-100), chelating agents (PEI, EDTA, and glutaraldehyde), and organic solvents (benzene and methanol). The chemical treatments were carried out in orbital shaker at 30°C and 120 rpm shaking speed for 1 h. Then, all the modified biomass was washed with double-distilled water and filtered. The modified biosorbent was dried in oven at 60°C for 24 h and grounded [17].

### 2.2. Preparation of aqueous dye solutions

Direct Violet 51 dye was obtained from Sandal Dyestuff Industries, Faisalabad, Pakistan, and was used without further purification. Stock solution was prepared by dissolving 1 g of dye in 1,000 mL of double-distilled water. The experimental solutions (50 mL) of different concentrations ranging from 10 to 200 mg L<sup>-1</sup> were made by further dilutions. The  $\lambda_{max}$  for Direct Violet 51 dye was found to be 549 nm.

#### 2.3. Characterization of SB biomass

The characterization of biosorbent was carried out by FTIR, scanning electron microscope (SEM), and TGA. The unloaded and dye-loaded HCl-treated SB biomasses were analyzed and interpreted by Bruker Tensor 27 Fourier transform infrared spectrometer with the samples prepared as KBr discs. The surface structure of SB biomass was analyzed by JEOL JMT 300 SEM. The surface area of SB biomass was also determined using surface area analyzer (Quantachrome v2.1 (Nova Station B) by Brunauer, Emmett, and Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. Results were obtained by the adsorption of pure liquid N<sub>2</sub> at 77  $\pm$  0.5 K. Thermal analysis was performed using a SDT Q 600 V 8.2 Build 100 universal instrument.

#### 2.4. Experimental design

Box–Behnken experimental design was employed for this study which has been proved appropriate for fitting the quadratic surface [18]. Three important process variables (initial dye concentration (*A*), biosorbent dose (*B*), and pH (*C*)) were selected for this study. Total 17 experimental runs were generated by Design Expert software (version 7.0.0) using the following formula:

$$N = K^2 + K + CP \tag{1}$$

where *N* represents total number of experiments, *K* is the number of variables, and *CP* is the number of replicate of center points.

The second-order equation was used to show the relationship between dependent and independent variables, and was given as:

$$y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} A B + \beta_{13} A C + \beta_{23} B C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \varepsilon$$
(2)

where *y*: the response variable;  $\beta_0$ : intercept,  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ : the coefficients of A, B, and C;  $\beta_{12}$ ,  $\beta_{13}$ ,  $\beta_{23}$ : coefficients of cross products;  $\beta_{11}$ ,  $\beta_{22}$ ,  $\beta_{33}$ : coefficients of quadratic terms, and  $\varepsilon$ :  $\varepsilon \sim N(0, \sigma^2)$ .

A positive sign in the equation represents a synergistic effect of the variables, while a negative sign indicates an antagonistic effect of the variables. The optimum values were obtained by solving the regression equation, analyzing the contour plot, and also by setting the constraints for the levels of the variables.

The upper and lower limits of process variables for Direct Violet 51 dye biosorption are presented in Table 1.

## 2.5. Batch experimental program

The batch experiments were conducted as designed by the Box–Behnken experimental design at 120 rpm and 30°C for 1 h of agitation time to check out the effect of initial dye concentration, biosorbent dose, and pH on the removal of Direct Violet 51 dye. Solution pH was adjusted by using 0.1 M NaOH and

Table 1 Experimental ranges and levels of independent variables

	Ranges and levels		
Factors	-1	0	+1
A: Initial dye concentration (mg L <sup>-1</sup> ) B: Biosorbent dose (g) C: pH	10 0.05 2	105 0.17 5.5	200 0.30 9

0.1 M HCl. After 1 h of agitation, the samples were taken out and centrifugation was performed at 5,000 rpm for 20 min, and the concentration of remaining dye solution was determined by using UV-vis spectrophotometer (Schimadzu, Japan). The responses were recorded in the form of biosorption capacity (mg g<sup>-1</sup>).

The equilibrium biosorption uptake,  $q_e$  (mg g<sup>-1</sup>), was calculated using the following relationship:

$$q_e = \frac{(C_0 - C_e)V}{w} \tag{3}$$

where  $C_0$  is the initial dye concentration (mg L<sup>-1</sup>),  $C_e$  is the equilibrium dye concentration (mg L<sup>-1</sup>), V is the volume of the solution (L), and W is the mass of the biosorbent (g).

## 2.6. Desorption study

Desorption study was performed using NaOH (0.2–1.0 M). Sorption procedure was carried out by adding 0.1 g of selected biosorbent in 50 mg L<sup>-1</sup> of dye solution at optimized pH and 30°C for 3 h. The amount of dye adsorbed (mg g<sup>-1</sup>) was calculated. The dye solution was then filtered and the loaded biosorbent was dried in oven at 60°C. Desorption process was studied by shaking the dried, dye-loaded biomass with NaOH. The % age desorption can be estimated by using following equation:

Desorption % = Amount of dye desorbed 
$$(mg/g)/$$
  
Amount of dye adsorbed  $(mg/g) \times 100$   
(4)

#### 3. Results and discussion

## 3.1. Effect of pretreatment

Different chemical and physical treatments were carried out to see their effect on the adsorption potential of SB for the removal of Direct Violet 51 dye. The following order was observed regarding various physical and chemical treatments on the biosorption capacity of SB as compared to its untreated form: CTAB < SDS < NaOH < Triton X-100 < HNO<sub>3</sub> < Native < Glutaraldehyde < Methanol < Boiled < CH<sub>3</sub>COOH < autoclaved < benzene < EDTA < PEI < H<sub>2</sub>SO<sub>4</sub> < HCl (Fig. 1). The results indicated that the treatment of biosorbent with acids, chelating agents, and organic solvents resulted in increase in the biosorption capacity of biomass as compared to its native form. Physical

treatments also resulted in significant improvement in the adsorption potential of biosorbent. Maximum dye removal (24.19 mg g<sup>-1</sup>) among all types of chemically and physically treated biomass was achieved with HCl-treated SB biomass. Acid treatments have been found suitable for enhancing the adsorption capacity of biosorbents. Acid treatments results in the removal of impurities present on the surface of biosorbent results in the increased surface area and number of binding sites of biosorbent leading to the enhanced pollutant removal [19,20]. The treatment of SB with chelating agents also enhanced the biosorption capacity of biomass. Among the three chelating agents (EDTA, PEI, and glutaraldehyde), PEI-treated biomass depicted the highest dye removal. PEI undergoes cross-linking with the biomass and as a result of this cross-linking, large number of amine groups have been introduced on the surface of biomass and some more hydroxyl groups have also been introduced as a result of cross-linking reaction. This results in the increase in electrostatic interaction between dye anions and amine groups which lead to the increased dye



Fig. 1. Effect of pretreatments on the biosorption efficiency of SB for the removal of Direct Violet 51 dye.

Table 2

Box–Behnken design matrix for the real and coded values along with experimental and predicted results for the removal of Direct Violet 51 dye by HCl-treated SB biomass

	Real (coded) values			Biosorption capacity (mg g <sup>-1</sup> )	
Run order	A	В	С	Experimental	Predicted
1	105(0)	0.05(-1)	9(+1)	24.14	25.86
2	10(-1)	0.17(0)	2(-1)	5.8	7.72
3	10(-1)	0.05(-1)	5.5(0)	6.7	6.01
4	105(0)	0.17(0)	5.5(0)	28.78	28.94
5	105 (0)	0.17(0)	5.5(0)	28.99	28.94
6	200(+1)	0.17(0)	9(+1)	22.1	22.18
7	105(0)	0.3(+1)	9(+1)	17.22	18.46
8	10(-1)	0.17(0)	9(+1)	2.39	1.36
9	105(0)	0.17(0)	5.5(0)	29.52	28.94
10	200(+1)	0.3(+1)	5.5(0)	18.9	19.59
11	105(0)	0.17(0)	5.5(0)	28.51	28.94
12	105(0)	0.3(+1)	2(-1)	28.7	26.98
13	200(+1)	0.05(-1)	5.5(0)	56.7	56.9
14	105(0)	0.05(-1)	2(-1)	63	61.76
15	105(0)	0.17(0)	5.5(0)	28.91	28.94
16	10(-1)	0.3(+1)	5.5(0)	1.35	1.15
17	200(+1)	0.17(0)	2(-1)	57.2	58.23

Note: A: initial dye concentration (mg  $L^{-1}$ ), B: biosorbent dose (g), and C: pH.

CV	6.42
Adequate precision	46.64
Predicted R <sup>2</sup>	0.942
$R^{2}_{adj}$	0.991
$R^2$	0.996
inal equations with coded factors	$Y_{\text{DV} 51} = 28.94 + 17.33A - 10.55B - 11.11C - 8.11AB - 7.92AC + 6.85BC - 9.71 A^2 + 1.68B^2 + 2.64C$

Table 3 ANOVA results for response parameters



Fig. 2. Normal probability plot of residuals for Direct Violet 51 dye.

removal [13]. The enhanced biosorption capacity of benzene-treated SB was due to the elimination of lipids and proteins from the surface of biosorbent resulting in the exposure of more active sites [15]. Physical treatments also enhanced the biosorption capacity of SB. This is because of the fact that these physical treatments help in the removal of the organic and mineral molecules from binding sites by dissolving and decomposing them [17].

Treatment of SB with NaOH has resulted in significant reduction in the biosorption capacity of SB. This might be due to the fact that alkali treatment results in the de-protonation of functional groups present on the surface of biomass. The Direct Violet 51 dye is anionic in nature and electrostatic repulsion takes place between negatively charged dye anions and deprotonated functional groups on the surface of biosorbent [21].

### 3.2. Response surface methodology

Batch experiments were conducted as designed by Box-Behnken experimental design to check out the effect of three important process variables (initial dye concentration (A), biosorbent dose (B), and pH (C)) for the removal of Direct Violet 51 dve using HCl-treated SB biomass. The experimental results clearly indicated that these three variables significantly affect the biosorption process. The experimental and predicted biosorption capacity (mg g<sup>-1</sup>) of HCl-treated SB biomass for Direct Violet 51 dye is presented in Table 2. The results revealed that maximum dye removal  $(63.0 \text{ mg g}^{-1})$  was achieved at pH 2 with the biosorbent dose of 0.05 g using initial dye concentration of  $105 \text{ mg L}^{-1}$  (Run 14). The results indicated a close agreement between experimental and predicted adsorption capacities of SB for the removal of Direct Violet 51 dye. This close correlation between the experimental and predicted adsorption capacities was also shown by the values of  $R^2$  (0.996) and adjusted  $R^2$ (0.991) which are found to be closer to one (Table 3). For a model with good prediction efficiency, the value of  $R^2$  should be close to 1.0 [22]. The prediction of maximum adsorption potential was carried out by using second-order quadratic equation. The value of predicted  $R^2$  was also found to be in agreement to the  $R^2$  and adjusted  $R^2$  values. The value of adequate precision was found to be 46.64 which shows high signalto-noise ratio, and signal-to-noise ratio above 4 is desirable.

The model suitability can also be checked by the residual graphs. The difference between the actual and predicted values is called residual, and visual inspection of residual graph gives valuable information [23]. The plot of normal % probability vs. studentized residuals is presented in Fig. 2. The normality assumption was satisfied as the residual plot approximated along a straight line.

Source	Coefficient estimate	Standard error	<i>F</i> -value	<i>p</i> -value (probability > <i>F</i> )	
Intercept	28.94	0.76			
$X_1$	17.33	0.60	837.24	< 0.0001	
$X_2$	-10.55	0.60	309.97	< 0.0001	
$\overline{X_3}$	-11.11	0.60	343.77	< 0.0001	
$X_1X_2$	-8.11	0.85	91.71	< 0.0001	
$X_1 X_3$	-7.92	0.85	87.46	< 0.0001	
$X_2X_3$	6.85	0.85	65.29	< 0.0001	
$X_{1}^{2}$	-9.71	0.83	138.33	< 0.0001	
$X_2^2$	1.68	0.83	4.15	0.0811	
$X_2^{3}$	2.64	0.83	10.23	0.0151	

Table 4 ANOVA results for the removal of Direct Violet 51 dye



Fig. 3. Counter plots showing the interaction effect of (a) Initial dye conc. and biosorbent dose (b) initial dye conc. and pH, and (c) biosorbent dose and pH on the removal of Direct Violet 51 dye.

The results were also analyzed by the analysis of variance (ANOVA). The application of ANOVA is found to be the most reliable way for the evaluation of the quality of the fitted model [18]. By using ANOVA, one can compare the variation due to the treatment (change in the combination of variable levels) with the variation due to random errors inherent to the measurements of the generated responses. Linear coefficient of quadratic, interaction effects, and *p*-values are shown in ANOVA table (Table 4). The larger *F*-values and the smaller *p*-values indicate a greater significance of the corresponding coefficients.

In RSM, the regression model can be visualized using two-dimensional plots (contour plots) which are found to be helpful in understanding the nature of response at different factor levels. Fig. 3(a) represents the effect of initial dye concentration and biosorbent dose on the removal of Direct Violet 51 dye by keeping the pH constant at 5.5. Both the factors have played a very significant role in the biosorption process. The results indicated an increase in biosorption capacity of HCl-treated SB with the increase in initial dye concentration from 10 to 200 mg  $L^{-1}$ , and reverse order was observed with regard to the effect of biosorbent dose. The increase in biosorbent dose resulted in decreased biosorption capacity of SB biomass. The high concentration of dye solution acts as a driving force to transfer dye molecules from bulk solution to the biomass surface; hence, it overcomes the mass transfer resistance between the aqueous and solid phases [24,25]. Different researchers have investigated the effect of initial dye concentration on the biosorption of dyes and found similar trend. Reddy et al. [11] performed experiments to check out the effect of initial dye concentration on the removal of Congo red dye using Indian jujuba seeds biomass [11]. The results depicted that with the increase in Congo red concentration from 25 to 100 mg  $L^{-1}$ , the dye removal increased from 10.4 to 34.6 mg  $g^{-1}$ . The higher biosorption capacity of biosorbent at lower biosorbent dose was due to the overlapping or aggregation of active sites resulting in the decrease of the total biosorbent surface area available for the attachment of dye molecules and an increase in diffusion path length [26]. This fact can also be explained as at high biosorbent dose, the available dye molecules are insufficient to completely cover the available binding sites on the biosorbent surface, which usually results in low solute uptake [27]. Dawood and Sen [20] also investigated the effect of biosorbent dose on the removal of Congo red dye using pine cone biomass [20], and found a decrease in adsorption of dye from 13.44 to  $6.28 \text{ mg g}^{-1}$  with the increase in biosorbent dose from 0.01 to 0.03 g.



Fig. 4. Surface plots showing the interaction effect of (a) initial dye conc. and biosorbent dose (b) initial dye conc. and pH, and (c) biosorbent dose and pH on the removal of Direct Violet 51 dye.





Fig. 5. Overlay perturbation plot of all the independent variables for biosorption of Direct Violet 51.

The effect of pH and initial dye concentration on the removal of Direct Violet 51 dye is shown in Fig. 3(b). The results revealed that maximum dye removal is favorable at lower pH and higher initial dye concentration. pH seems to affect the solution chemistry of dyes and functional groups of biosorbents [28]. It monitors the magnitude of electrostatic charges on adsorbent and adsorbate. Hence, pH exerts a pronounced effect on the biosorption of dyes [29]. Maximum dye removal (63.0 mg g<sup>-1</sup>) was achieved at pH 2. Acidic pH was found to be favorable for the removal of anionic dyes from aqueous solutions. The maximum dye removal at acidic range of pH might be due to the fact that at lower pH, protonation of functional groups takes place on the surface of biosorbents. The positively charged surface of biosorbent facilitates the attachment of dye anions to the biosorbent [30]. At higher pH levels, the concentration of OH<sup>-</sup> ions increase in the solution which compete to the negatively charged dye anions for attachment to the biosorbent surface. Hence, the biosorption of anionic dyes decreases at higher pH levels [31,32].

Fig. 3(c) indicates the effect of biosorbent dose and pH on the Direct Violet 51 dye removal by using HCltreated SB biomass while keeping the initial dye concentration constant ( $105 \text{ mg L}^{-1}$ ), and the results depicted that lower biosorbent dose and lower pH were most favorable conditions for maximum dye removal. The same criteria have been shown by surface plots (Fig. 4).

The perturbation plot is shown in Fig. 5 to check out the simultaneous effect of all the three independent

variables on dye removal. The perturbation plot shows how the response changes as each factor moves from the chosen reference point, with all other factors held constant at the coded zero level of each factor. It is clearly depicted from the perturbation plot that all the three independent variables viz, initial dve conc. (A), biosorbent dose (B), and pH (C) are playing significant role in the dve removal process. The removal of Direct Violet 51 dye was found to be more dependent on the variation in initial dye concentration parameter as shown by the sharp curvature for this parameter as compared to the biosorbent dose and pH.

## 3.3. Desorption study

Desorption study was conducted to check out the possibility of adsorbent and adsorbate recovery after the adsorption process. For desorption study, NaOH was used as eluant in different concentrations (0.2–1.0 M). As the anionic dyes show strong adsorption at acidic pH, a base can be used as a good desorbing agent. The results indicated that with increasing the concentration of NaOH, the desorption of Direct Violet 51 dye from HCl-treated SB increased. Maximum desorption (61.58%) was achieved using 1 M NaOH. This is due to the fact that in the presence of NaOH, the biosorbent surface acquires negative charge and electrostatic repulsion between sorbed dye molecules, and negatively charged biosorbent surface leads to the detachment of dye molecules [28]. Patel and Suresh [33] also conducted the desorption study for the recovery of reactive black 5 dye from dyeloaded Aspergillus foetidus biomass [33]. NaOH was used as eluant in different concentration (0.1-1 M). Maximum desorption of reactive dye was found to be 90% with higher concentration of NaOH solution.

## 3.4. Characterization of biomass

FTIR spectra give important information about the functional groups involved in the adsorption process [34]. FTIR analysis of unloaded HCl-treated SB biomass and Direct Violet 51 dye loaded biomass were carried out in the range of  $400-4,000 \text{ cm}^{-1}$  (Fig. 6). The different major peaks on the surface of unloaded HCl-treated SB biomass were (i) 3,757.33 cm<sup>-1</sup> which indicates the presence of N–H group, (ii) 3,344.57 cm<sup>-1</sup> which confirms the presence of O-H group (carboxylic acid, phenol, and alcohol), (iii) 2,904.80 cm<sup>-1</sup> which might be due to the stretching vibrations of C-H and reveals the presence of -CH and CH groups, (iv) 2,378.23 cm<sup>-1</sup> which is due to the C=C stretching vibration, and (v) 1,701.22 cm<sup>-1</sup> which confirms the



Fig. 6. FTIR spectra of unloaded and Direct Violet 51 dye-loaded HCl-treated SB biomass.

presence of C=O group. A change in the FTIR spectrum was observed after the loading of biomass with Direct Violet 51 dye. The peak present on 3,757.33 cm<sup>-1</sup> has been disappeared after the biosorption process. The involvement of all the above mentioned functional groups in the biosorption process is confirmed due to the vanishing or disappearance of these groups at lower frequencies in the dye-loaded biomass (Fig. 6).

The surface features of SB biomass were analyzed by SEM and surface area studies. The results revealed that the BET-specific surface area of SB biomass was 89.49 m<sup>2</sup> g<sup>-1</sup>, BJH pore volume was 0.69 cc g<sup>-1</sup>, and the total pore diameter was found to be 133.24 Å. The results revealed that in the structure of SB biomass, the major contribution is of mesopores (IUPAC Classification 20 Å < d < 500 Å) which is favorable for the adsorption process [35]. The surface morphology of unloaded and dye-loaded biomass are shown in SEM images (Fig. 7(a) and (b), respectively). These photographs indicated the porous structure of SB biomass which is helpful in biosorption process.



Fig. 7. (a) SEM analysis of unloaded SB biomass and (b) SEM analysis of Direct Violet 51 dye-loaded SB biomass.



Fig. 8. TGA analysis of SB biomass.

The TGA analysis of SB biomass was carried out to study the change in weight loss of the biosorbent as a function of temperature (Fig. 8). The TGA analysis showed that at about 211°C temperature, there was almost 9% loss in the weight of biosorbent. This short weight loss phase can be suggested as a drying phase in which water is liberated from the biosorbent leading to the low loss in biosorbent weight. With the increase in temperature, significant weight loss was observed. At about 400°C, almost 96% reduction in biosorbent weight was observed which was due to liberation of hydrocarbons coming from the decomposition of cellulose, hemicellulose, and lignin present in the structure of SB biomass [36]. A continuous weight loss has also been observed even above the 500°C. This might be due to the decomposition of some heavier lignin compound which remained stable at lower temperatures. 2436

## 4. Conclusion

The present investigation focused on the utilization of SB biomass for the adsorptive removal of Direct Violet 51 dye from synthetic wastewater. HCl-treated SB depicted enhanced removal efficiency for Direct Violet 51 dye as compared to the other different physically and chemically treated SB biomasses. Maximum removal of Direct Violet 51 dye (63.0 mg g<sup>-1</sup>) was achieved at pH 2 and 0.05 g biosorbent dose. Maximum desorption from dye-loaded biomass was achieved by using 1 M NaOH solution. The results indicated that HCl-treated SB can be used as an efficient biosorbent for the removal of Direct Violet 51 dye from aqueous solutions.

## Acknowledgments

The authors are thankful to the Higher Education Commission (HEC) of Pakistan for financial assistance under project No. 20-159/R7D/09/1841 and Indigenous PhD Fellowship Program.

## References

- I. Ghodbane, L. Nouri, O. Hamdaoui, M. Chiha, Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark, J. Hazard. Mater. 152 (2008) 148–158.
- [2] A.L. Ahmad, S. Sumathi, B.H. Hameed, Residual oil and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon: A comparative study, Chem. Eng. J. 108 (2005) 179–185.
- [3] K.Y. Foo, B.H. Hameed, Utilization of rice husk ash as novel adsorbent: A judicious recycling of the colloidal agricultural waste, Adv. Colloid Interface Sci. 152 (2009) 39–47.
- [4] A. Mittal, J. Mittal, A. Malviya, V.K. Gupta, Adsorptive removal of hazardous anionic dye "Congo red" from wastewater using waste materials and recovery by desorption, J. Colloid Interface Sci. 340 (2009) 16–26.
- [5] H.N. Bhatti, Y. Safa, Removal of anionic dyes by rice milling waste from synthetic effluents: Equilibrium and thermodynamic studies, Desalin. Water Treat. 48 (2012) 267–277.
- [6] M.A.M. Salleh, D.K. Mahmoud, W.A. Karim, A. Idris, Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review, Desalination 280 (2011) 1–13.
- [7] R. Gong, X. Zhang, H. Liu, Y. Sun, B. Liu, Uptake of cationic dyes from aqueous solution by biosorption onto granular kohlrabi peel, Bioresour. Technol. 98 (2007) 1319–1323.
- [8] F. Deniz, S.D. Saygideger, Removal of a hazardous azo dye (Basic Red 46) from aqueous solution by princess tree leaf, Desalination 268 (2011) 6–11.
- [9] A. Saeed, M. Sharif, M. Iqbal, Application potential of grapefruit peel as dye sorbent: Kinetics, equilibrium and mechanism of crystal violet adsorption, J. Hazard. Mater. 179 (2010) 564–572.

- [10] A.S. Raymundo, R. Zanarotto, M. Belisário, M.G. Pereira, J.N. Ribeiro, A.V.F.N. Ribeiro, Evaluation of sugar-cane bagasse as bioadsorbent in the textile wastewater treatment contaminated with carcinogenic congo red dye, Braz. Arch. Biol. Technol. 53 (2010) 931–938.
- [11] D.H.K. Reddy, K. Seshaiah, A.V.R. Reddy, S.M. Lee, Optimization of Cd(II), Cu(II) and Ni(II) biosorption by chemically modified *Moringa oleifera* leaves powder, Carbohydr. Polym. 88 (2012) 1077–1086.
- [12] N.M. Mahmoodi, F. Najafi, Preparation of surface modified zinc oxide nanoparticle with high capacity dye removal ability, Mater. Res. Bull. 47 (2012) 1800–1809.
- [13] J. Mao, S.W. Won, K. Vijayaraghavan, Y.-S. Yun, Surface modification of *Corynebacterium glutamicum* for enhanced Reactive Red 4 biosorption, Bioresour. Technol. 100 (2009) 1463–1466.
- [14] T. Akar, E. Ozkara, S. Celik, S. Turkyilmaz, S.T. Akar, Chemical modification of a plant origin biomass using cationic surfactant ABDAC and the biosorptive decolorization of RR45 containing solutions, Colloids Surf., B 101 (2013) 307–314.
- [15] M. Asgher, H.N. Bhatti, Evaluation of thermodynamics and effect of chemical treatments on sorption potential of Citrus waste biomass for removal of anionic dyes from aqueous solutions, Ecol. Eng. 38 (2012) 79–85.
- [16] W. Zhang, H. Li, X. Kan, L. Dong, H. Yan, Z. Jiang, H. Yang, A. Li, R. Cheng, Adsorption of anionic dyes from aqueous solutions using chemically modified straw, Bioresour. Technol. 117 (2012) 40–47.
- [17] H.N. Bhatti, R. Khalid, M.A. Hanif, Dynamic biosorption of Zn (II) and Cu (II) using pretreated *Rosa gruss* an teplitz (red rose) distillation sludge, Chem. Eng. J. 148 (2009) 434–443.
- [18] M. Kousha, E. Daneshvar, H. Dopeikar, D. Taghavi, A. Bhatnagar, Box–Behnken design optimization of Acid Black 1 dye biosorption by different brown macroalgae, Chem. Eng. J. 179 (2012) 158–168.
- [19] R. Ahmad, R. Kumar, Adsorption studies of hazardous malachite green onto treated ginger waste, J. Environ. Manage. 91 (2010) 1032–1038.
- [20] S. Dawood, T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design, Water Res. 46 (2012) 1933–1946.
- [21] S. Noreen, H.N. Bhatti, S. Nausheen, S. Sadaf, M. Ashfaq, Batch and fixed bed adsorption study for the removal of Drimarine Black CL-B dye from aqueous solution using a lignocellulosic waste: A cost affective adsorbent, Ind. Crops Prod. 50 (2013) 568–579.
- [22] L.A. Sarabia, M.C. Ortiz, Response surface methodology, in: S.D. Brown, R. Tauler, B. Walczak (Eds.), Comprehensive Chemometrics: Chemical and Biochemical Data Analysis, vol. 1, Elsevier, Oxford, 2009, pp. 345–390.
- [23] M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, L.A. Escaleira, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, Talanta 76 (2008) 965–977.
- [24] A. Mittal, V. Gajbe, J. Mittal, Removal and recovery of hazardous triphenylmethane dye, Methyl Violet through adsorption over granulated waste materials, J. Hazard. Mater. 150 (2008) 364–375.

- [25] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Kinetic study and equilibrium isotherm analysis of Congo red adsorption by clay materials, Chem. Eng. J. 148 (2009) 354–364.
- [26] H.B. Senturk, D. Ozdes, C. Duran, Biosorption of Rhodamine 6G from aqueous solutions onto almond shell (*Prunus dulcis*) as a low cost biosorbent, Desalination 252 (2010) 81–87.
- [27] J. Tangaromsuk, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Cadmium biosorption by *Sphingomonas paucimobilis* biomass, Bioresour. Technol. 85 (2002) 103–105.
- [28] K. Vijayaraghavan, J. Mao, Y.S. Yun, Biosorption of Methylene Blue from aqueous solution using free and polysulfone-immobilized *Corynebacterium glutamicum*: Batch and column studies, Bioresour. Technol. 99 (2008) 2864–2871.
- [29] Y. Önal, C. Akmil-Basar, C.D. Eren, C. SarIcI-Özdemir, T. Depci, Adsorption kinetics of malachite green onto activated carbon prepared from Tunçbilek lignite, J. Hazard. Mater. 128 (2006) 150–157.
- [30] S. Sadaf, H.N. Bhatti, Batch and fixed bed column studies for the removal of Indosol Yellow BG dye by peanut husk, J. Taiwan Inst. Chem. Eng. 45 (2014) 541–553.

- [31] N.K. Amin, Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics, J. Hazard. Mater. 165 (2009) 52–62.
- [32] A. Khaled, A. Nemr, A. El-Sikaily, O. Abdelwahab, Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: Adsorption isotherm and kinetic studies, J. Hazard. Mater. 165 (2009) 100–110.
- [33] R. Patel, S. Suresh, Kinetic and equilibrium studies on the biosorption of Reactive Black 5 dye by Aspergillus foetidus, Bioresour. Technol. 99 (2008) 51–58.
- [34] T. Akar, B. Anilan, A. Gorgulu, S.T. Akar, Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: *Pyracantha coccinea* berries, J. Hazard. Mater. 168 (2009) 1302–1309.
- [35] A. Kausar, H.N. Bhatti, G. MacKinnon, Equilibrium, kinetic and thermodynamic studies on the removal of U(VI) by low cost agricultural waste, Colloids Surf., B 111 (2013) 124–133.
- [36] R.G. Candido. G.G. Godoy, A.R. Goncalves, Study of sugarcane bagasse pretreatment with sulfuric acid as a step of cellulose obtaining, World Acad. Sci. Eng. Technol. 61 (2012) 101–105.