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ORIGINAL PAPER

Optimization, equilibrium and kinetics studies on sorption of Acid Blue 9 using brown marine algae *Turbinaria conoides*

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Abstract In the present study, the parameters, temperature, adsorbent dose, contact time, adsorbent size and agitation speed were optimized for Acid Blue 9 removal from aqueous medium by using response surface methodology (RSM). The optimum conditions for maximum removal of Acid Blue 9 from an aqueous solution of 100 mg/l were found as follows: temperature (33°C), adsorbent dose (3 g/l), contact time (225 min), adsorbent size (85 mesh (0.177 mm)) and agitation speed (226 rpm). At these optimized conditions, batch adsorption experiments were conducted to study the effect of pH and initial dye concentration for the removal Acid Blue 9 dye. Kinetic and equilibrium studies were carried out for the experimental results. From the kinetic studies it was found that pseudo second order model suits the system well. From the equilibrium studies, the Freundlich and Redlich-Peterson isotherm fit the data well.

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Abbreviation

C_o	Initial concentration of the dye solution (mg/l)
C_i	Concentration of the dye solution at desired time t (mg/l)
V	Volume of the solution (l)
M	Mass of dry sorbent used (g)
C_e	Equilibrium concentration (mg/l)
q_e	Amount of dye adsorbed at equilibrium (mg/g)
q_m	Langmuir constants related to adsorption capacity(mg/g)
K_a	Langmuir constants related to energy of adsorption (l/mg)
K_F	Adsorption capacity
$1/n$	Measure of the adsorption intensity
k_1	Rate constant of pseudo-first-order adsorption (l/min)
k_2	Rate constant of pseudo-second-order adsorption (g/mg min)
a_R	Redlich-Petersen Isotherm Constant,$(dm^3\text{-}mmol^{-1})^{bR}$
b_R	Redlich-Petersen Isotherm exponent
k_R	Redlich-Petersen Isotherm Constant, (dm^3g^{-1})
k_a	Rate constant of adsorption
k_d	The rate constants for intraparticle diffusion
X_i	Uncoded value of the ith test variable
X_0	Uncoded value of the ith test variable at center point
β	Coefficients estimated from regression

Introduction

Contamination of water sources by many organic pollutants is a major factor of global environmental pollution for the number of years (Akhtar et al. 2006). Dyes and pigments represent one of the problematic groups. They are let into wastewaters from various industrial sources, mainly from the dye manufacturing and textile finishing and also from food coloring, cosmetics, paper and carpet industries (Malik 2003; Ramamoorthy Ramasamy et al. 2008). The presence of dyes in the aquatic environment has been of great concern because of their potential health hazards associated with the carcinogenic, mutagenic, allergenic and toxic natures as well as negative effects on the photosynthetic activity in aquatic life (Bakshi et al. 1999; Waranusantigul et al. 2003). Among the various kinds of dyes water-soluble and brightly colored anionic dyes are the most problematic as they tend to pass through conventional decolorization systems unaffected (Aksu 2005; Aksu and Tezer 2000). Acid dyes are extensively used for dyeing and printings in textile industries and dye effluents have resulted in serious environmental problems (Sumanjit Walia and Kaur 2007).

Currently, the major methods of textile wastewater treatment involve physical and chemical processes. Such methods are very costly and secondary pollution problem will arise because of excessive chemical use. Activated carbon adsorption is the most popular physicochemical treatment for the removal of dissolved dyes from wastewaters. However the applications of the above mentioned techniques in the large scale are usually restricted due to several disadvantages such as relatively high price, high operating cost, regeneration problem, formation of hazardous by-products and intensive energy requirements (Crini 2006; Padmesh et al. 2005; Gong et al. 2005). Therefore there is a growing interest to find cheap, renewable, locally available and effective alternative materials for the decolorisation of colored effluents. The dye sorption abilities of various agricultural origin materials or those of the by-products have been investigated so far. Sugarcane dust (Ho et al. 2005a), apple pomace and wheat straw (Robinson Chandran and Nigam 2002), tree fern (Ho et al. 2005b), coir pith (Namasivayam et al. 2001), neem sawdust (Khattri and Singh 2000), raw date pits (Banat et al. 2003), banana peel (Annadurai et al. 2002) and *Hydrilla verticillata* (Rajeshkannan et al. 2009) are a few examples.

Algae have been found to be potential suitable sorbents because of their cheap availability, both in fresh or saltwater, relatively high surface area and high binding affinity. Biosorption on algae has mainly been attributed to the cell wall properties where both electrostatic attraction and complexation can play a role (Ayla Ozer et al. 2006). Algae cell surfaces are naturally formed by various chemical groups such as hydroxyl, carboxylate, amino and phosphate which are believed to be responsible for the sequestration of unwanted materials from effluents. Moreover, most of the algal cells are often covered by mucilaginous layers characterized by a significant adsorption capacity due to the presence of alginate constituting 14–40% of the dry weight of the biomass. Many of the studies to date on metal biosorption by seaweeds have largely been restricted to various species of brown and green seaweeds (Kaewsarn 2002). On the other hand, the seaweeds species of marine algae *Turbinaria conoides,* have not been evaluated for the dye biosorption to any great extent. In this study, the parameters for the sorption of Acid Blue 9 onto *Turbinaria conoides* was optimized using response surface method and the equilibrium and kinetic parameters were determined.

Materials and methods

Seaweed collection and preparation

Seaweed species was collected from CSMCRI (Central Salt and Marine Chemicals Research Institute)-Marine Algal Research Station (Mandapam, Tamilnadu, India). Brown seaweed was washed with distilled water and sun-dried. Brown seaweeds were protonated using 0.1 M HCl for 3 h. The samples were then washed in distilled water and dried at 60°C overnight. All algal samples were ground and sieved to different particle sizes and subsequently used for sorption experiments.

Preparation of aqueous dye solution

The textile dye, Acid Blue (AB9) was obtained from Sigma Chemicals, New Delhi and used without further purification. Stock dye solution was prepared by dissolving 1 g of AB 9 in 1 l of deionized water. The other required concentrations were prepared by diluting the stock solution of AB9. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted using HCl or NaOH. The structure and properties of the dye are shown in Fig. 1 and Table 1.

Experimental design by response surface methodology (RSM)

RSM is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously. A full factorial design, which includes all possible factor combinations in each of the factors, is a powerful tool for understanding complex processes for describing factor interactions in multifactor systems. In order to describe the effects of temperature, adsorbent dosage, contact time, particle size and agitation speed on the percentage removal of Acid Blue 9 dye, batch experiments were conducted based on the central composite design. The coded values of the process parameters were determined by the following equation

$$x_i = \frac{X_i - X_o}{\Delta x} \quad (1)$$

where x_i–coded value of the ith variable, X_i–uncoded value of the ith test variable and X_0–uncoded value of the ith test variable at center point.

The range and levels of individual variables are given in Table 2. The experimental design is given in Table 3, along with experimental data and predicted responses. The regression analysis was performed to estimate the response function as a second order polynomial

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_{ii}^2 + \sum_{i=1,i<j}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \quad (2)$$

Where Y is the predicted response, β_i, β_j, β_{ij} are coefficients estimated from regression. They represent the linear, quadratic and cross products of x_1, x_2, x_3 on response (Umesh Garg et al. 2008).

A statistical program package Design Expert 7.1.5, was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical tests called the ANOVA analysis. The significance of each term in the equation is to

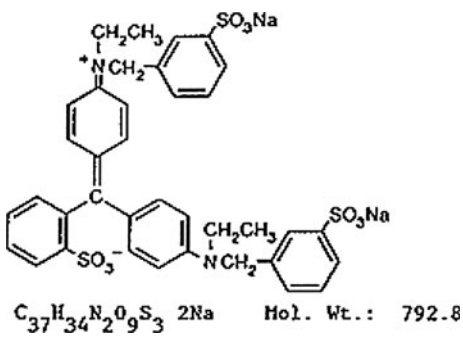

Fig. 1 Chemical structure of Acid Blue 9

Table 1 Information of the dye used

Name of dye	Acid Blue 9
Color index number	42000
Empirical formula	$C_{37}H_{34}N_2Na_2O_9S_3$
Molecular weight	792.84
Dye content	90%
λ_{max}	625 nm

Table 2 Levels of different process variables in coded and uncoded form for adsorption of Acid Blue 9

Variable	Code	Levels				
		−2.38	−1	0	+1	+2.38
Temperature, °C	A	20	30	40	50	60
Sorbent dosage, g	B	0.1	0.2	0.3	0.4	0.5
Contact time, min	C	100	150	200	250	300
Particle size, mesh	D	44	60	85	120	200
Stirring Speed, rpm	E	100	150	200	250	300

Table 3 Experimental conditions and observed response values of 2^5 central composite design

Run. No	A-temperature	B-sorbent dosage	C-contact time	D-particle size	E-stirring speed	Percentage colour removal	
						Experimental	Theoretical
1	−1	−1	1	−1	1	54.1	55.59
2	−1	1	1	1	−1	63.5	61.62
3	−1	1	−1	1	1	43.2	47.11
4	0	0	0	0	0	61.5	63.42
5	1	−1	−1	1	1	50.2	50.96
6	1	1	1	1	1	52.1	53.76
7	0	0	0	−2.37841	0	42.1	43.65
8	1	1	1	−1	1	59.1	57.39
9	1	1	−1	−1	1	50.9	48.41
10	0	0	0	0	0	61.5	63.41
11	0	0	0	0	0	61.5	63.41
12	1	1	−1	1	1	43.1	41.41
13	−1	1	−1	1	−1	43.8	48.17
14	0	0	0	0	0	61.5	63.41
15	1	1	−1	−1	−1	32.8	36.24
16	2.37841	0	0	0	0	32	63.41
17	0	0	0	0	0	61.5	32.82
18	1	1	−1	1	−1	31	52.26
19	1	−1	1	−1	1	57	44.70
20	0	2.37841	0	0	0	48	39.72
21	1	1	1	−1	−1	37.9	54.21
22	−1	−1	−1	−1	1	57	50.49
23	1	−1	1	1	1	50	45.92
24	1	−1	−1	−1	−1	49	56.90
25	−1	1	1	−1	−1	58	64.66
26	−1	1	1	1	1	63	56.91
27	−1	−1	−1	1	−1	56	53.70
28	−1	−1	−1	−1	−1	51	57.54
29	−1	−1	1	1	−1	56	41.17
30	1	−1	1	1	−1	38	50.97
31	−1	−1	1	−1	−1	50.1	41.93
32	0	0	0	0	−2.37841	40.9	37.98
33	1	−1	1	−1	−1	42.2	63.41
34	0	0	0	0	0	61.5	63.41
35	0	0	0	0	0	61.5	46.82
36	−1	1	−1	−1	−1	48.7	63.41
37	0	0	0	0	0	61.5	48.99
38	0	−2.37841	0	0	0	47	45.75
39	1	−1	−1	1	−1	51	58.45
40	−2.37841	0	0	0	0	61	57.65
41	0	0	0	0	2.37841	60	57.20
42	−1	−1	1	1	1	59	64.91
43	−1	1	1	−1	1	60	63.41

Table 3 continued

Run. No	A-temperature	B-sorbent dosage	C-contact time	D-particle size	E-stirring speed	Percentage colour removal	
						Experimental	Theoretical
44	0	0	0	0	0	61.5	49.78
45	0	0	−2.37841	0	0	52	52.46
46	−1	−1	−1	1	1	51	50.72
47	−1	1	−1	−1	1	50	43.14
48	0	0	0	2.37841	0	46	56.10
49	1	−1	−1	−1	1	50.3	41.05
50	0	0	0	0	0	61.5	63.41

estimate the goodness of fit in each case. Response surfaces were drawn to determine the individual and interactive effects of the test variable on the percentage removal of Acid Blue 9. The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units.

Experimental procedure

The adsorption of Acid Blue 9 from aqueous solution onto *Turbinaria conoides* was performed under shaking conditions in an orbital shaker (REMI-12, India). The experiments were performed according to the central composite design. To each 100 ml solution of Acid Blue 9, a desired quantity of the *Turbinaria conoides* biomass was added in 250 ml Erlenmeyer flasks. The mixture was agitated in an incubated orbital shaker at the desired temperature and desired speed for predetermined time intervals. The supernatant was clarified by centrifugation at 4000 rpm for 10 min. The residual concentration in the supernatant was determined. The dye concentration in raw and treated sample was determined by UV–Vis (Elico, SL V 164) spectrophotometry. The analyses were carried out at a wavelength of 625 nm. From the noted absorbance value the initial concentration, the concentration of the treated dye sample was determined. The response, i.e., removal efficiency of Acid Blue 9 was calculated as

$$R(\%) = \frac{(C_o - C_i)}{C_o} \times 100. \quad (3)$$

All experiments were carried out in triplicate and the mean values were reported. The maximum deviation was found to be ±3%

The process variables, temperature, adsorbent dosage, contact time, particle size and agitation speed were optimized and at these optimized conditions, the effect of pH and initial dye concentration were studied. The amount of equilibrium adsorption, q_e (mg/g), was calculated by:

$$q_e = \frac{V(C_o - C_e)}{M} \quad (4)$$

where C_o and C_e (mg/l) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (l) is the volume of the solution and M (g) is the mass of dry sorbent used.

Results and discussion

Experimental design and fitting of quadratic model

To examine the combined effect of five different process parameters viz. temperature, adsorbent dosage, contact time, particle size and agitation speed, on percentage color removal of Acid Blue 9, 50 experiments were performed. Eq. 5 represents the mathematical model relating the percentage color removal with the independent process variables and the second order polynomial coefficient for each term of the equation determined through multiple regression analysis using the Design Expert 7.1.5. The

experimental and predicted values of percentage adsorption of Acid Blue 9 are given in Table 3.

$$\begin{aligned}\text{Percentage color removal} = {} & 63.4145 - 4.67A - 0.90322B + 2.40203C - 0.106761D \\ & + 3.3044E - 1.0468AB - 1.3031AC - 0.84687AD + 2.4156AE + 3.20312BC \\ & - 0.4656BD + 0.84689BE + 0.84063CD + 1.02813CE - 1.24063DE - 2.83996A^2 \\ & - 2.9284B^2 - 1.399C^2 - 3.53823D^2 - 2.4069E^2 \end{aligned} \quad (5)$$

The results were analyzed by using ANOVA i.e. and shown in Table 4. The ANOVA of the quadratic regression model indicates the model to be significant. The Model *F*-value of 17.6 implies that the model is significant. The smaller the magnitude of the *P*, the more significant is the corresponding coefficient. Values of *P* less than 0.05 indicate the model term is significant. From the P values it was found that, among the test variables used in the study, A, C, E, AC, AE, BC, DE, CE, A^2, B^2, C^2, D^2, and E^2 are significant model terms.

The predicted R^2 of 0.716 is in reasonable agreement with the adjusted R^2 of 0.876. The fit of the model was also expressed by the coefficient of

Table 4 Analysis of variance (ANOVA) for response surface quadratic model

Source	Coefficient factor	Sum of square	DF	Mean square	*F*	*P* value *P* > *F*
Model	63.4145	3557.64	20	177.88	17.59	<0.0001
A	−4.677	878.25	1	878.25	86.87	<0.0001
B	0.90312	40.64	1	40.64	4.02	0.0544
C	2.402	186.49	1	186.49	18.45	0.0002
D	−0.106761	1.54	1	1.54	0.15	0.6988
E	3.30444	477.32	1	477.32	47.21	<0.0001
A*A	−2.83996	40.92	1	40.92	4.05	0.0536
B*B	−2.9283	60.93	1	60.93	6.03	0.0203
C*C	−1.3992	28.06	1	28.06	2.78	0.1065
D*D	−3.53826	193.85	1	193.85	19.17	0.0001
E*E	−2.40685	288.05	1	288.05	28.49	<0.0001
A*B	−1.04688	10.25	1	10.25	1.01	0.3224
A*C	−1.30313	28.06	1	28.06	2.78	0.1065
A*D	−0.84687	15.85	1	15.85	1.57	0.2205
A*E	2.41562	39.61	1	39.61	3.92	0.0573
B*C	3.20312	38.21	1	38.21	3.78	0.0617
B*D	−0.4656	429.26	1	429.26	42.46	<0.0001
B*E	0.846785	375.46	1	375.46	37.14	<0.0001
C*D	0.840625	21.48	1	21.48	2.12	0.1557
C*E	1.02813	576.27	1	576.27	57.00	<0.0001
D*E	−1.24063	237.74	1	237.74	23.51	<0.0001
Residual		293.20	29	10.11		
Lack of fit		293.20	20	14.66		
Pure error		0.000	9	0.000		
Cor total		3850.84	49			

$S = 3.29000$; $R^2 = 92.5\%$; $R^2(\text{pred}) = 71.6\%$; $R^2(\text{adj}) = 87.64\%$

regression R^2, which was found to be 0.925, indicating that 92.5% of the variability in the response could be explained by the model. This implies that the prediction of experimental data is quite satisfactory.

Response surface estimation for maximum removal of Acid Blue 9

As discussed in previous section, response surface methodology was used with five process variables to evaluate their effect on the adsorption process. To investigate the interactive effect of two factors on the percentage of the dye, the response surface methodology was used and three-dimensional plot was drawn. The inferences so obtained are discussed below.

Response surface plots as a function of two factors at a time, maintaining all other factors at fixed levels are more helpful in understanding both the main and the interaction effects of these two factors. These plots can be easily obtained by calculating from the model, the values taken by one factor where the second varies with constraint of a given Y value. The response surface curves were plotted to understand the interaction of the variables and to determine the optimum level of each variable for maximum response. The response surface curves for percentage dye removal were shown in Figs. (2, 3, 4, 5, 6, 7, 8, 9,

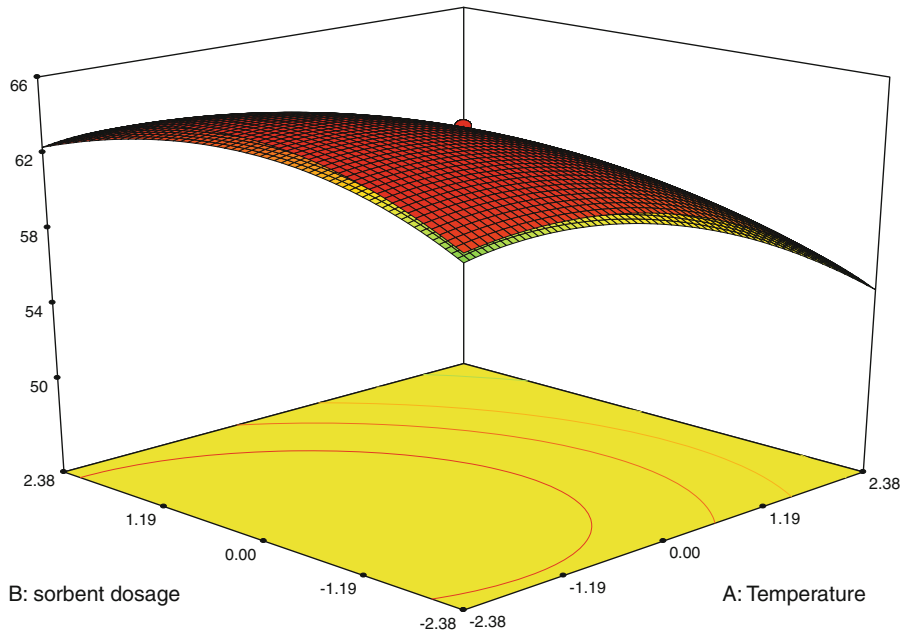

Fig. 2 Response surface plot of the combined effects of temperature and sorbent dosage on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

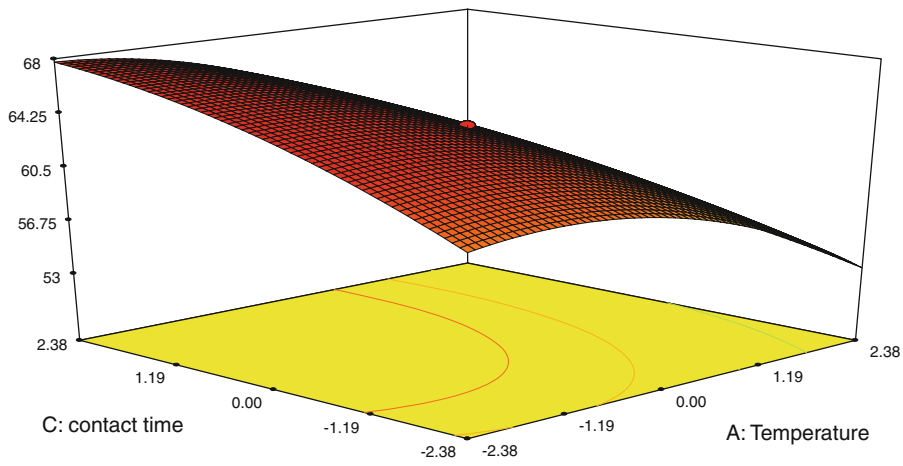

Fig. 3 Response surface plot of the combined effects of temperature and contact time on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

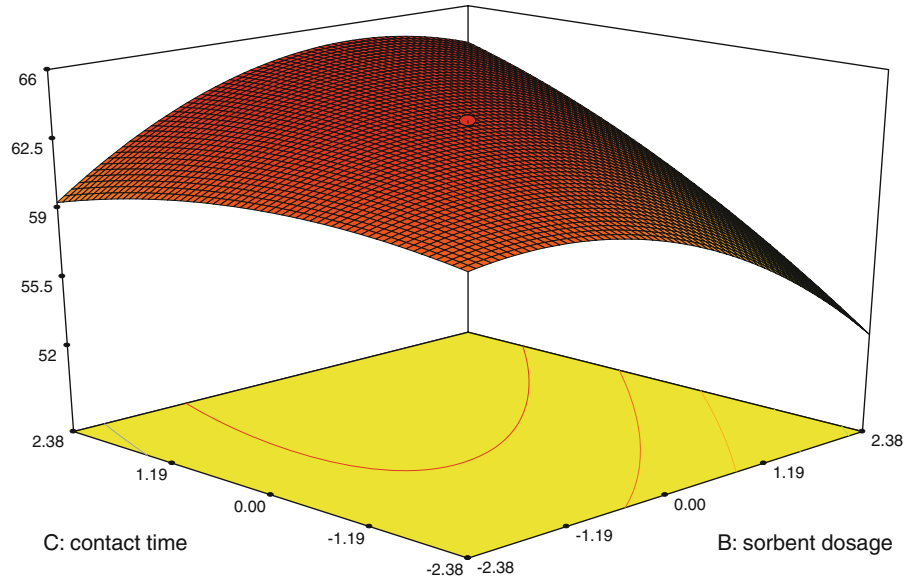

Fig. 4 Response surface plot of the combined effects of sorbent dosage and contact time on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

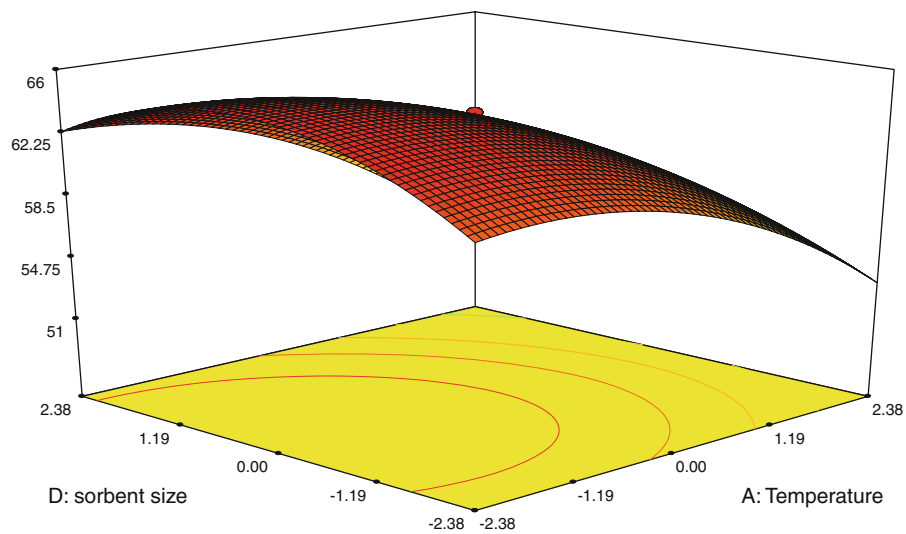

Fig. 5 Response surface plot of the combined effects of temperature and sorbent size on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

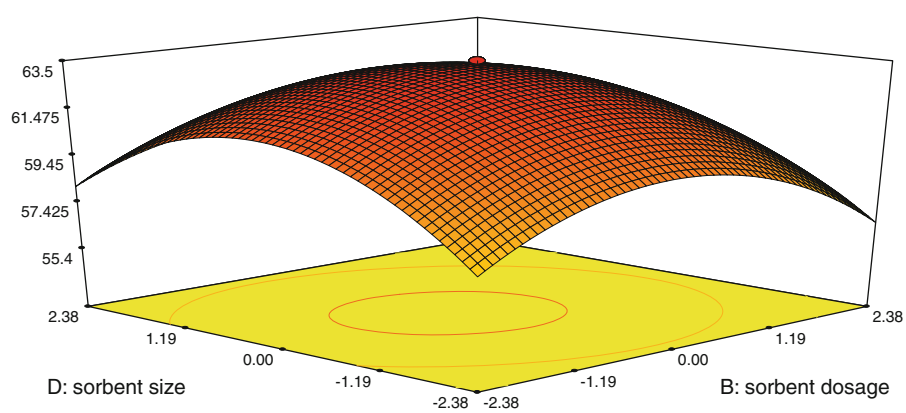

Fig. 6 Response surface plot of the combined effects of sorbent dosage and sorbent size on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

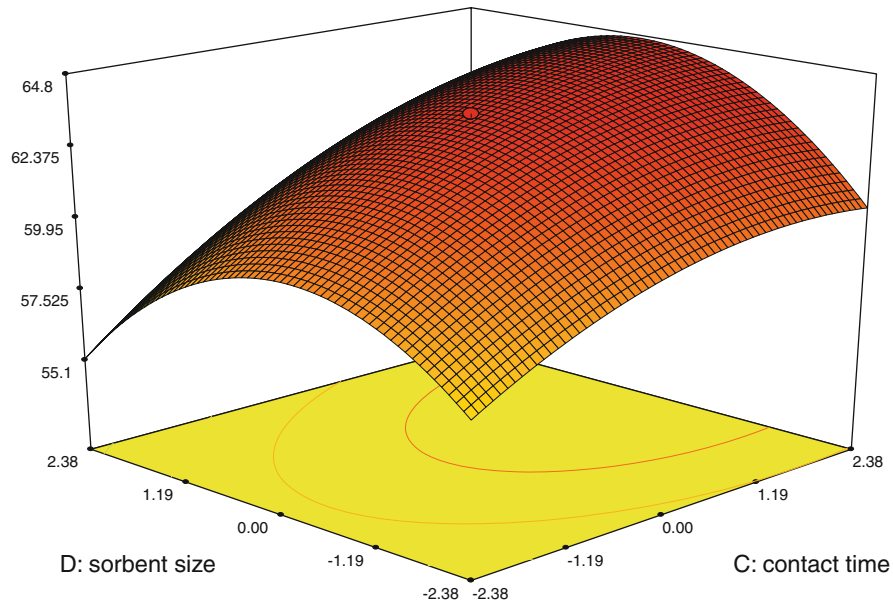

Fig. 7 Response surface plot of the combined effects of contact time and sorbent size on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

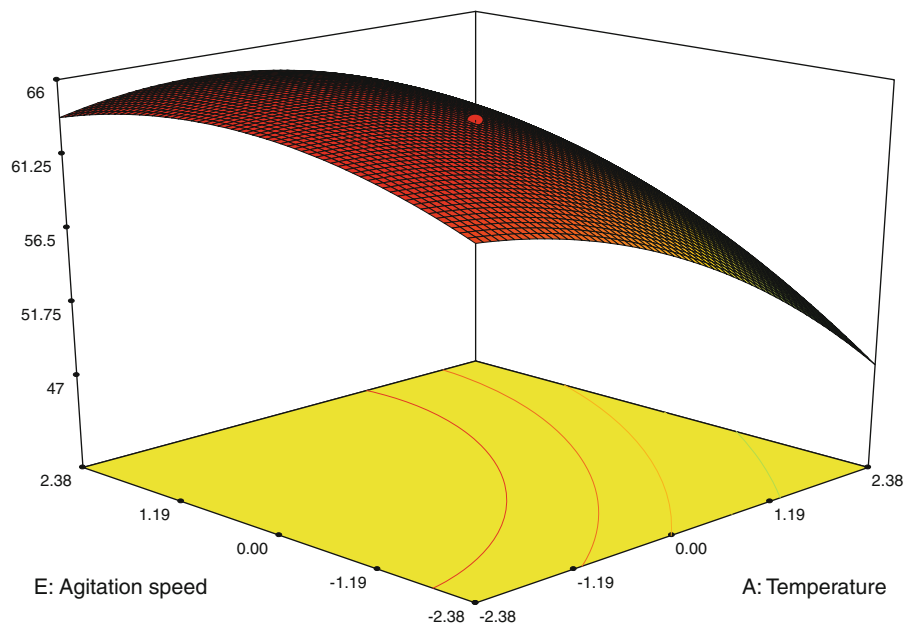

Fig. 8 Response surface plot of the combined effects of temperature and agitation speed on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

10, 11). The nature of the response surface curves shows the interaction between the variables. The elliptical shape of the curve indicates good interaction of the two variables and circular shape indicates no interaction between the variables. From figures it was observed that the elliptical nature of the contour in graphs depicted the mutual interactions of all the variables. There was a relative significant interaction between every two variables, and there was a maximum predicted yield as indicated by the surface confined in the smallest ellipse in the contour diagrams.

The magnitude of P and F values in Table 4 gives the maximum negative contribution of temperature, adsorbent dosage and adsorbent size and positive effect of contact time and agitation speed on the percentage dye removal. The quadratic terms of temperature, adsorbent dose, contact time, adsorbent size and agitation speed have negative effect on

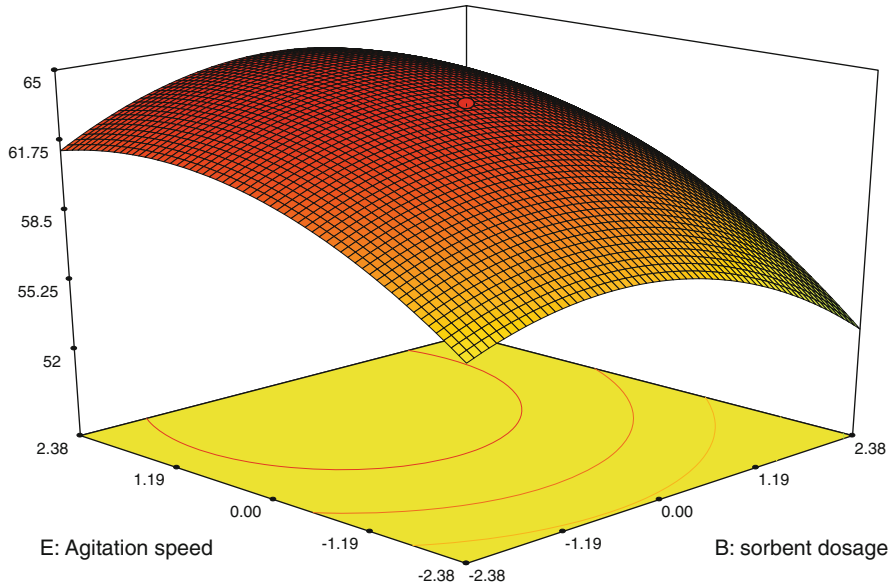

Fig. 9 Response surface plot of the combined effects of sorbent dosage and agitation speed on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

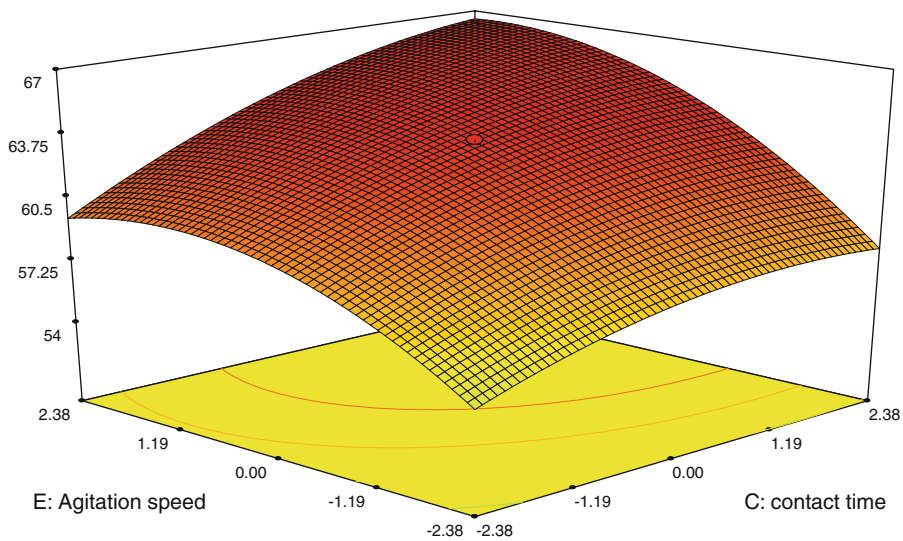

Fig. 10 Response surface plot of the combined effects of contact time and agitation speed on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

percentage color removal. Further, the interactions of 'temperature and agitation speed', 'adsorbent dosage and agitation speed', 'contact time and adsorbent size', 'contact time and agitation speed' have positive effect, whereas the interactions of 'temperature and adsorbent dosage', 'temperature and contact time' and 'temperature and adsorbent size', 'adsorbent dosage and adsorbent size', 'adsorbent dosage and contact time', 'adsorbent size and agitation speed' have negative effect on percentage color removal (Figs. 2, 3, 4, 5, 6, 7, 8, 9, 10, 11).

Optimum conditions for percentage colour removal of Acid Blue 9 dye using *Turbinaria conoides* were obtained by using RSM. Second order polynomial models obtained in this study were utilized for each response in order to determine the specified optimum conditions. The optimum values obtained by substituting the respective coded values of variables are: temperature (33°C), adsorbent dose (3 g/l), contact time (225 min), adsorbent size (85 mesh (0.177 mm)) and agitation speed (226 rpm). At this condition the maximum percentage color removal was calculated.

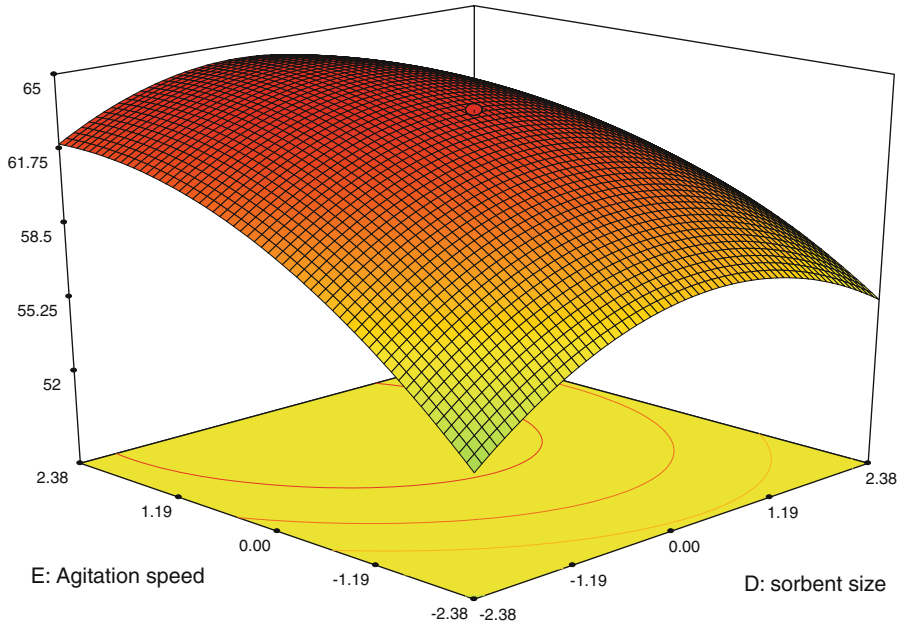

Fig. 11 Response surface plot of the combined effects of sorbent size and agitation speed on the percentage colour removal of Acid Blue 9 by *Turbinaria conoides*

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 color removal is indicated by the surface confined in the smallest curve of the contour diagram (Gopal et al. 2002). The optimum values drawn from these figures are in close agreement with those obtained by optimizing the regression model Eq. 5.

The sequential quadratic programming in MATLAB 7 is used to solve the second-degree polynomial regression Eq. 5. The optimum values of the test variables were: temperature (33°C), adsorbent dose (3 g/l), contact time (225 min), adsorbent size (85 mesh (0.177 mm)) and agitation speed (226 rpm). The optimal values for the variables as predicted by MATLAB were found to be within the design region. This showed that the model correctly explains the influence of the chosen variables on the percentage color removal of Acid Blue 9.

Effect of pH

In this work, the effect of pH on the Acid Blue 9 adsorption onto *Turbinaria conoides* was studied in the range of 1–9. While the initial dye concentration, temperature, adsorbent dosage, contact time, particle size and agitation speed were fixed at 100 mg/l, 33°C, 0.3 g, 225 min, 85 mesh and 226 rpm, respectively. Solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbent. The effect of pH on the adsorption of Acid Blue 9 by the *Turbinaria conoides* was shown in Fig. 12. The equilibrium sorption capacity was maximum at pH 1 (20.69 mg/g) and decreases monotonically up to pH 7, further increase in pH leads to drastic decrease in percentage adsorption. The absence of sorption at high pH can be explained by the fact that at this basic pH, H^+ may compete with dye ions for the adsorption sites of adsorbent, thereby inhibiting the adsorption

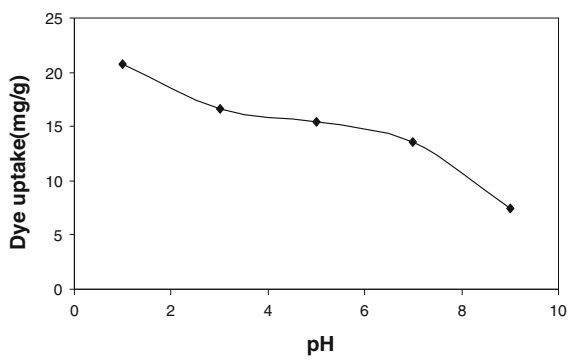

Fig. 12 Effect of pH on equilibrium uptake of Acid Blue 9($W = 0.3$ g: $V = 0.1$ l; $C_o = 100$ mg/l)

of dye. Similar result was reported in removal of Acid Blue 40 using cone Biomass (Tamer et al. 2007).

Effect of initial dye concentration

The effect of initial dye concentration on the Acid Blue 9 adsorption onto *Turbinaria conoides* biomass was studied in the range of 10–100 mg/l. The pH, temperature, adsorbent dosage, contact time, particle size and agitation speed were fixed at 1, 33°C, 0.3 g, 225 min, 85 mesh and 226 rpm, respectively. The color removal profiles were obtained using the absorbance measurements. It was found that dye uptake increases with increasing dye concentration; it is shown in the Fig. 13.

Equilibrium isotherms

Two commonly used isotherms, Langmuir (Langmuir 1916) and Freundlich (Freundlich 1906), were employed in the present study. The nonlinear Langmuir and Freundlich isotherms are represented by Eqs. 6 and 7:

$$q_e = \frac{q_{max} K_a C_e}{1 + K_a C_e} \quad (6)$$

The values of q_e and K_a can be determined from the linear plot of C_e/q_e versus C_e. The Langmuir equation is used for homogeneous surfaces.

$$q_e = K_F C e^{1/n} \quad (7)$$

where C_e (mg/l) is the equilibrium concentration, q_e (mg/g) is the amount of dye adsorbed at equilibrium, and q_m (mg/g) and K_a (l/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. K_F (mg/g) is the adsorption capacity and $1/n$ (mg/g) is a measure of the adsorption intensity.

The fitting of the experimental isotherm results to Eqs. 6 and 7 was done by linear regression. The values of the estimated parameters are presented in Table 6. Figure 14 shows the fitted equilibrium data in Freundlich and Langmuir isotherms. The fitting results, i.e. isotherm parameters and the coefficients of determination, R^2, are shown in Table 5. It can be seen in Fig. 14 that, Freundlich isotherm fits the data better than Langmuir isotherm. This is also confirmed by the high value of R^2 in case of Freundlich (0.997) compared to Langmuir (0.942). The *Turbinaria conoides* biomass adsorbent used in this work had a relatively large adsorption capacity (38.46 mg/g) compared to some other adsorbents reported in the literatures (Table 5). This indicates that *Turbinaria conoides* biomass is effective for the removal of Acid Blue 9 from aqueous solutions.

Redlich-Peterson isotherm

Jossens and co-workers modified the three-parameter isotherm first proposed by Redlich and Peterson to incorporate features of both the Langmuir and Freundlich equations (Jossens et al. 1978). It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} \quad (8)$$

At low concentrations the Redlich-Peterson isotherm approximates to Henry's law and at high concentrations its behavior approaches that of the Freundlich isotherm.

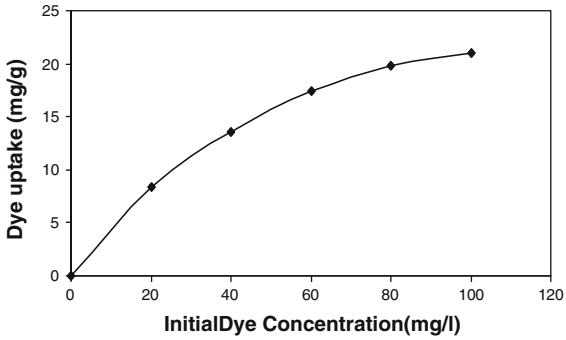

Fig. 13 Effect of initial dye concentration on equilibrium uptake of Acid Blue 9 ($W = 0.3$ g: $V = 0.1$ l; $C_o = 100$ mg/l)

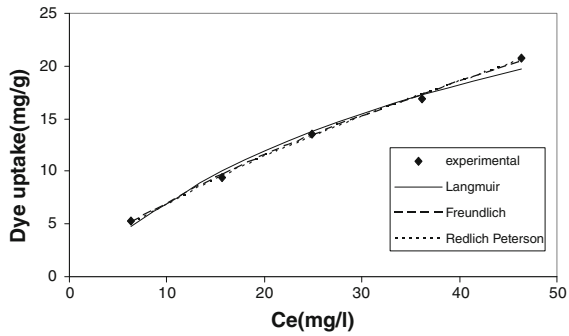

Fig. 14 Isotherm plot for Acid Blue 9 adsorption onto *Turbinaria conoides* biomass

Table 5 Comparison of adsorption capacities of various adsorbents for textile dyes

Adsorbent	q_m (mg/g)	T (°C)	References
Turbinaria conoides biomass	38.46	33	This work
Aspergillus niger	17.58	30	(Fu and Viraraghavan 2002)
Arundo donax root carbon	8.70	30	(Zhang et al. 2008)
Bentonite clay	7.72	35	(Tahir and Rau 2006)
Activated carbons commercial grade (ACC)	8.27	30	(Mall et al. 2005)
Acid activated low cost carbon	9.74	30	(Hema and Arivoli 2008)

Table 6 Isotherm constants and kinetic models parameters for AB 9 adsorption on *Turbinaria conoides*

Langmuir isotherm	
q_{max} (mg/g)	38.46
K_a (l/mg)	0.023
R^2	0.942
Freundlich isotherm	
K_f	1.468
n	1.456
R^2	0.997
Redlich-Petersen isotherm	
k_R	5478
a_R	3987
b_R	0.2949
R^2	0.997
Pseudo first order model	
q_{exp} (mg/g)	20.49
q_e (mg/g)	21.92
R^2	0.861
Pseudo-second-order model	
q_e (mg/g)	30.39
$k_2 \times 10^4$	2.83
R^2	0.968

Figure 14 shows the comparison of experimental data with Redlich-Peterson isotherm. The constants K_R, a_R and b_R and the coefficients of correlation are given in Table 6. The higher R^2 value shows the validity of the Redlich-Peterson isotherm. The solubility of a dye is an essential property to enable the dye to penetrate into the porous structure of the *Turbinaria conoides* biomass. Clearly it could be expected that small, highly soluble molecules would be ideal molecules for adsorption process. However dyes will associate in aqueous solution to form dimmers and possibly larger micelles. Such larger groups of molecules will not have an easy progression through the porous structure of the *Turbinaria conoides* biomass. The process will be assisted if the dye is ionic and the adsorbent carries an opposite charge. This is the case for the *Turbinaria conoides* biomass anionic dye sorption process currently under study. The different dye ions will experience different physical and electrical attraction forces according to their structure molecular size and functional groups.

Kinetic modeling

In order to investigate the mechanism of biosorption and potential rate controlling steps, such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data of Acid Blue 9 aqueous solutions. When the biomass is employed as a free and small-sized *Turbinaria conoides* biomass suspension in a well-agitated batch system, all the sorbent binding sites are readily available for the dye uptake.

Lagergren's pseudo-first-order model (Eq. 9) (Lagergren 1898), and Ho's pseudo-second-order model (Eq. 10) (Ho 1995) are

$$q = q_e\left(1 - e^{-k_1 t}\right) \tag{9}$$

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{10}$$

Where q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium, q (mg/g) is the amount of adsorbate adsorbed at time t, k_1 (l/min) is the rate constant of pseudo-first-order adsorption, k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption.

The fitting of the experimental kinetic results to Eqs. 9 and 10 was done by linear regression. The values of the estimated parameters are presented in Table 6. R^2 value of the pseudo-second-order model

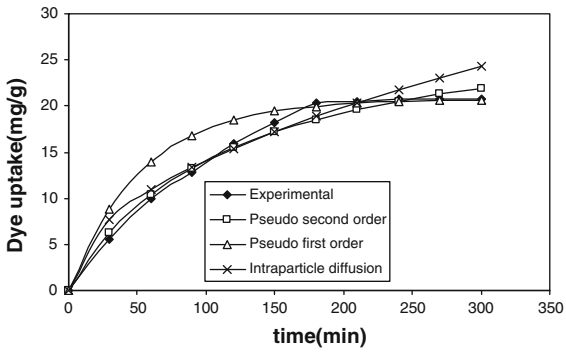

Fig. 15 Kinetic study plot for Acid Blue 9 adsorption onto *Turbinaria conoides* biomass

are higher than those of the first-order model. The goodness of fit (Fig. 15) and the accurate prediction of q_e both indicate that the pseudo-second-order model better describes the adsorption of Acid Blue 9 on *Turbinaria conoides* biomass.

Intra particle diffusion

In order to establish the possibility of the dye being transported with in the pores of the *Turbinaria conoides*. The amount of Acid Blue 9 sorbed at optimum initial dye concentration 100 mg/l on *Turbinaria conoides* biomass against the time of uptake ($t^{1/2}$) was investigated.

$$q_e = k_d t^{0.5} \quad (11)$$

All the plots had the same general features, an initial curve portion followed by linear portion. The rate constants for intraparticle diffusion (k_d) are obtained from the slopes of the linear portion of the plots q versus $t^{1/2}$ for Acid Blue 9. The k_d and r^2 values are listed in Table 7. The high R^2 value indicates the applicability of this model to the experimental data. It shows that intra particle diffusion process took place.

Table 7 Rate constants for intraparticle diffusion of Acid Blue 9 onto *Turbinaria conoides*

C_o mg/l	Acid Blue 9 k_d/min	R^2
100	1.404	0.976

Conclusions

In this study, *Turbinaria conoides*, cheap and widely available brown marine algae is used for the removal of Acid Blue 9 from dilute aqueous solutions. The results obtained from the present investigation revealed the ability of *Turbinaria conoides* in removing Acid Blue 9 from aqueous solution. The optimum condition for the removal of Acid Blue 9 using *Turbinaria conoides* was found to be: temperature (33°C), adsorbent dose (3 g/l), contact time (225 min), adsorbent size (85 mesh (0.177 mm)) and agitation speed (226 rpm). The maximum adsorption capacity was obtained (38.46 mg/g). From the kinetic and equilibrium studies it was found that pseudo II order kinetics and Freundlich and Redlich-Petersen isotherm fit the data well, respectively. Although, further studies are needed in understanding the interaction behavior between the activated biomass and other dyes, the results indicate that *Turbinaria conoides* can be employed as low-cost alternative to commercial materials in wastewater treatment for the removal of dyes.

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References

Akhtar M, Bhanger MI, Iqbal S, Hasany SM (2006) Sorption potential of rice husk for the removal of 2, 4-dichlorophenol from aqueous solutions: Kinetic and thermodynamic investigations. J Hazard Mater 128:44–52

Aksu Z (2005) Application of biosorption for the removal of organic pollutants: a review. Process Biochem 40:997–1026

Aksu Z, Tezer S (2000) Equilibrium and kinetic modelling of biosorption of Remazol Black B by *Rhizopus arrhizus* in a batch system: effect of temperature. Process Biochem 36:431–439

Annadurai G, Juang RS, Lee DJ (2002) Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. J Hazard Mater 92:263–274

Ayla Ozer A, Akaka G, Turabik M (2006) Biosorption of acid blue 290 (AB 290) and acid blue 324(AB 324) dyes on *Spirogyra rhizopus*. J Hazard Mater B135:355–364

Bakshi DK, Gupta KG, Sharma P (1999) Enhanced biodecolorization of synthetic textile dye effluent by Phanerochaete chrysosporiumunder improved culture conditions. World J Microbiol Biotechnol 15:507–509

Banat F, Al-Asheh M, Al-Makhadmeh L (2003) Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. Process Biochem 39:193–202

Crini G (2006) Non-conventional low-cost adsorbents for dye removal: a review. Bioresour Technol 97:1061–1085

Freundlich HMF (1906) Over the adsorption in solution. J Phys Chem 57:385–470

Fu Y, Viraraghavan T (2002) Dye biosorption sites in *Aspergillus niger*. Bioresour Technol 82:39–145

Gong R, Ding LM, Yang LH, sun Y (2005) Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. Dyes Pigm 64:187–192

Gopal M, Pakshirajan K, Swaminathan T (2002) Heavy metal removal by biosorption using *Phanerochaete Chrysosporium*. Appl Biochem Biotechnol 102:227–237

Hema M, Arivoli S (2008) Adsorption kinetics and thermodynamics of malachite green dye unto acid activated low cost carbon. J Appl Sci Environ Manage 12(1):43–51

Ho YS (1995) Adsorption of heavy metals from waste streams by peat. Ph.D.Thesis. Unive rsity of Birmingham, Birmingham, UK

Ho YS, Chiu WT, Wang CC (2005a) Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. Bioresour Technol 96:285–1291

Ho YS, Chiang TH, Hsueh YM (2005b) Removal of basic dye from aqueous solution by tree fern as a biosorbent. Process Biochem 40:119–124

Jossens L, Prausnitz JM, Fritz WE, Schlunder U, Myers AL (1978) Thermodynamics of multi-solute adsorption from dilute aqueous solutions. Chem Eng Sci 33:1097–1106

Kaewsarn Pairat (2002) Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae Padina sp. Chemosphere 47:1081–1085

Khattri SD, Singh MK (2000) Colour removal from synthetic dye wastewater using a bioadsorbent. Water Air Soil Poll 120:283–294

Lagergren S (1898) About the theory of so-called adsorption of soluble substances. K.Sven Vetenskapsakad Handl 24(4):1–39

Langmuir I (1916) The constitution and fundamental properties of solids and liquids. J Am Chem Soc 38(11):2221–2295

Malik PK (2003) Use of activated carbons prepared from sawdust and rice husk for adsorption of acid dyes: a case study of acid yellow 36. Dyes Pigm 56:239–249

Mall ID, Srivastava VC, Agarwal NK, Mishra IM (2005) Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses. Colloids Surf A Physicochem Eng Aspects 264:17–28

Namasivayam C, Kumar MD, Selvi K, Begum RA, Vanathi T, Yamuna RT (2001) Waste coir pith–a potential biomass for the treatment of dyeing wastewaters. Biomass Bioenerg 21:477–483

Padmesh TVN, Vijayaraghavan K, Sekaran G, Velan M (2005) Batch and column studies on biosorption of acid dyes on fresh water macro alga Azolla. liculoides. J Hazard Mater 125:121–129

Rajeshkannan R, Rajamohan N, Rajasimman M (2009) Removal of malachite green from aqueous solution by sorption on *Hydrilla verticillata* biomass using response surface methodology. Front Chem Eng China 3(2):146–154

Ramamoorthy R, Renganathan S, Velan M, Dharmendira Kumar M, Raajenthiren M (2008) Biosorption of Acid Blue 5 by Biomass Derived from Eichhornia crassipes: batch and column studies. Int J Chem Reactor Eng 6: article A67

Robinson Chandran B, Nigam P (2002) Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. Water Res 36:2824–2830

Sumanjit Walia TPS, Ravneet K (2007) Removal of health hazards causing acidic dyes from aqueous solutions by the process of adsorption. online J Health Allied Sci 6(3)

Tahir SS, Rau N (2006) Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. Chemosphere 63:1842–1848

Tamer A, Akar A, Ozcan Safa, Tunali Sibel (2007) Adnan ozcan, biosorption of a textile dye (acid blue 40) by cone biomass of *Thuja orientalis*: estimation of equilibrium, thermodynamic and kinetic parameters. Bioresour Technol 99(8):3057–3065

Umesh Garg K, Kaur MP, Garg VK, Sud D (2008) Removal of Nickel (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. Bioresour Technol 99:1325–1331

Waranusantigul P, Pokethitiyook P, Kruatrachue M, Upatham ES (2003) Kinetics of basic dye (methylene blue) biosorption by giantduckweed (*Spirodela polyrrhiza*). Environ Pollut 125:385–392

Zhang J, Li Y, Zhang C, Jing Y (2008) Adsorption of malachite green from aqueous Solution onto carbon prepared from Arundo donax root. J Hazard Mater 150:774–782