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Biosorption performance of surface modified biomass obtained from *Pyracantha coccinea* for the decolorization of dye contaminated solutions

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ABSTRACT

The present research provides information on the dye biosorption potential of chemically modified non-conventional biomass obtained from *Pyracantha coccinea*. A cationic surfactant hegzadecylethyldimethylammonium bromide (HDEDMABr) was used as modification agent. Dye biosorption characteristics of modified biomass were explored by batch mode equilibrium studies, zeta potential measurements and FTIR studies. When compared with the dried natural biomass, modified biomass was found to have high biosorption yield for Acid Red 44 (AR44) dye. Kinetic measurements revealed that the biosorption equilibrium was established in about 40 min of contact time. The biosorption process could be explained by the pseudo-second-order kinetic model and also followed the intraparticle diffusion model up to 40 min, but diffusion is not the only rate controlling step. A comparison of the different isotherms indicated that the dye biosorption by using modified biomass was well described by the Langmuir isotherm model with maximum monolayer capacity of 105.0 mg dye g^{-1} biosorbent. Calculated thermodynamic parameters of biosorption indicated the exothermic and spontaneous process. Good biosorption yields ranged from 73.32 to 87.44% were obtained in the presence of the different concentrations of salt in the biosorption medium. Our results revealed that this developed biomass system may be useful for the decolorization of reactive dye contaminated solutions.

1. Introduction

Extensive use of synthetic dyes in many industrial processes such as textile, paint, solvent, pulp, paper, printing, food and cosmetic results in large quantities of colored effluents. Contamination of water bodies by these effluents is a worldwide environmental problem. Synthetic dyes have complex chemical structure. Although they are designated as resistant molecules to degradative conditions, cleavage of azo linkages in their structure can produce toxic aromatic amines. Therefore, adequate treatment of colored effluents prior to discharge into receiving bodies of water is of great importance for human health and environmental quality [1,2].

Recently, the removal of dyes by different kinds of biosorbent materials has been receiving more attention [3–7]. However, sometimes the tested sorbent materials do not have good sorption capacities or need long sorption equilibrium times. Hence there is a need to search for more effective adsorbents. The sorption potential of sorbent material can be improved by modification process. Recent studies by various research groups have shown that modified biosorbents exhibit good potential for the biosorption of heavy metals [8,9] and dyes [10,11] from contaminated media.

P. coccinea is a thorny perennial shrub native to SE Europe and Asia. It is one of the most common plants widely used in gardening and landscaping around the world [12]. Despite the use of this plant in traditional medicine due to diuretic, cardiac and tonic properties in its fruits [13,14] there is limited information in the literature about the biosorption potential of this biomass. Findings in our previous study demonstrated that the *P. coccinea* berries could be employed as biosorbent material for the removal of a cationic dye [15].

In this work, the biomass prepared from *P. coccinea* was modified with a cationic surfactant (HDEDMABr) through a simple method in order to prepare a novel, effective and alternative material for the biosorptive removal of an acid dye. The biosorption properties of the modified biomass were explored as a function of batch operating conditions including initial pH, contact time, biomass dosage and temperature. Kinetic and isotherm analysis of the biosorption process was performed in terms of the Lagergren first-order and the pseudo-second-order kinetic models and the Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models. The possible dye-biosorbent interactions were evaluated by FTIR analysis. The dye biosorption potential of modified biomass was also tested in the solutions having the different ionic strengths.

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2. Materials and methods

2.1. Biosorbent modification and dye solutions

The mature berries of *P. coccinea* were collected from a number of plants. It was washed with distilled water to remove both loosely adhering particles and water-soluble impurities. They were then dried in an oven at 70 °C and ground, passed through a 212 μm sieve. 1.5 g of powdered natural biomass sample was suspended in 150 mL of 1% (w/v) HDEDMABr solution. The mixture was stirred for 24 h at room temperature, filtered and the resulted modified biosorbent sample was washed with deionized water several times and then dried in an oven at 70 °C.

Acid Red 44 dye (chemical formula: $C_{20}H_{12}N_2O_7S_2Na_2$ MW: 502.4 g mol^{-1}, λ_{max} = 510 nm) obtained from Sigma–Aldrich Corporation, St. Louis, MO, USA, was used without further purification. A stock solution (1.0 g L^{-1}) of dye was prepared by dissolving appropriate amount of dye in deionized water and the other concentrations were obtained by diluting this stock dye solution.

2.2. Biosorption studies

Batch mode biosorption studies were performed in a series of 100 mL beakers with a sample volume of 25 mL. The working solutions containing 50–300 mg L^{-1} of dye were prepared by dilution of the stock solution with distilled water when necessary. The pH adjustment of the working solutions was made by adding 0.1 M HCl and/or 0.1 M NaOH solutions to obtain pH values ranging from 1.0 to 9.0. The amount of the modified biomass was varied from 0.4 to 1.6 g L^{-1}. Biosorbent and dye solution mixture were agitated on a magnetic stirrer at constant stirring rate of 200 rpm. Biosorbent was separated from the biosorption medium by centrifugation and the supernatant was analyzed using UV/Visible spectrophotometer (Shimadzu UV-2550) for its residual dye concentration. The influence of the ionic strength on the biosorption performance of the modified biosorbent was also tested using dye solutions including $NaNO_3$ at different concentrations.

The biosorption capacity of the biosorbent material was calculated by the following mass-balance equation.

$$q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

where q_e (mg g^{-1}) is the equilibrium biosorption capacity of biomass, C_i and C_e (mg L^{-1}) are the initial and equilibrium dye concentrations in liquid phase, respectively, V (L) is the volume of the dye solution, and m (g) is the dry weight of the modified biomass.

The zeta potential values of the modified biomass were measured by zeta potential analyzer (Malvern zeta sizer) in the solutions with the pH range of 1.0–9.0.

Data presented are the mean values from three independent experiments. Experimental errors were estimated and are depicted with error bars and the standard deviations are indicated wherever necessary. The statistical analysis of the experimental data was done using SPSS 10.0 for Windows where it is possible to evaluate whether the effect and the interaction among the investigated factors are significant with respect to the experimental error.

3. Results and discussion

3.1. Effect of modification on the biosorption capacity of biomass

In order to investigate the effect of modification on the dye biosorption capacity of biomass, the dried and chemically modified biomass of *P. coccinea* were assessed for their biosorption abilities at pH 2.0 and 100 mg L^{-1} of initial dye concentration. The biosorption capacities were found to be 15.31 mg g^{-1} (15.43%) and 91.58 mg g^{-1} (91.51%) for dried and modified biomass, respectively. The modification of the biomass with cationic surfactant increased the biosorption capacity of biosorbent by about 6 folds ($p < 0.05$). This may be attributed to the increased positive charge density on the biomass surface after the modification process. Further biosorption studies were carried out using HDEDMABr modified biomass.

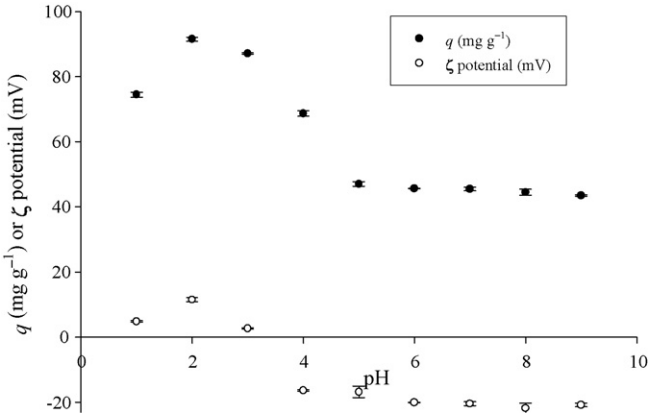

Fig. 1. Biosorption capacities and ζ potential values of modified biosorbent at different pH values (the bars represent the standard error of the mean).

3.2. Effect of initial pH

The initial pH of the biosorption medium is an important factor affecting the dye biosorption capacity of biosorbents. Fig. 1 shows the biosorption capacity and the surface charge of the biomass at the various pH values. The ζ potential values for the modified biosorbent were recorded as 4.91, 11.55 and 2.68 at the pH values of 1.0, 2.0 and 3.0, respectively. The point of zero charge (PZC) was observed at about pH 3.0. The modified biosorbent was negatively charged above this pH value and the ζ potentials changed from −16.30 to −20.80 mV when the pH was increased from 4.0 to 9.0. The high positive charge on the biosorbent surface at pH 2.0 resulted in higher biosorption capacity because of the larger attraction forces between the anionic dye molecules and the biosorbent surface. As the pH of the aqueous medium increased from 2.0 to 9.0, the biosorption capacity of biomass decreased about 53% ($p < 0.05$). A decrease observed in the biosorption capacity can be explained by the increased negative charge density on the biosorbent surface. Our previous findings indicated that unmodified form of *P. coccinea* biomass has the point of zero charge at about pH 2.5 [15]. In this study modified sorbent showed positive surface charge even at pH 3.0.

3.3. Effect of biosorbent amount

The biosorption of dye onto modified sorbent as a function of biomass dosage is shown in Fig. 2. It can be seen that, the dye removal percentage of biomass increased with increasing biomass amount and almost 91.16% of removal was achieved by 1.0 g L^{-1} biomass dosage. The reason for such behavior may be attributed to greater surface area and the large number of vacant biosorption sites thus favoring more dye biosorption. Further increase in the biosorbent concentration from 1.0 g L^{-1} did not significantly change dye removal percentage of biomass ($p > 0.05$) because of the establishment of equilibrium between biomass and dye molecules. The similar trend was also reported in the literature for Basic Blue 9 and Basic Red 5 biosorption by modified rice straw [16], for Methylene Blue biosorption by *Spirodela polyrrhiza* [17] and for Acid Yellow 17 biosorption by non-living aerobic granular sludge [18].

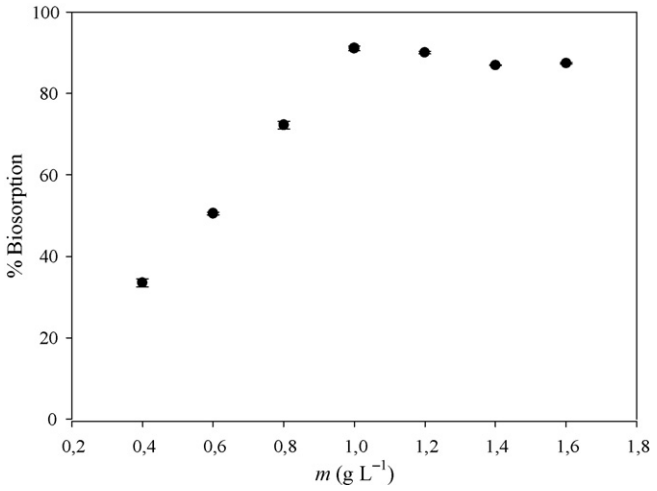

Fig. 2. Effect of biosorbent concentration on the biosorption of AR44 by modified biosorbent (the bars represent the standard error of the mean).

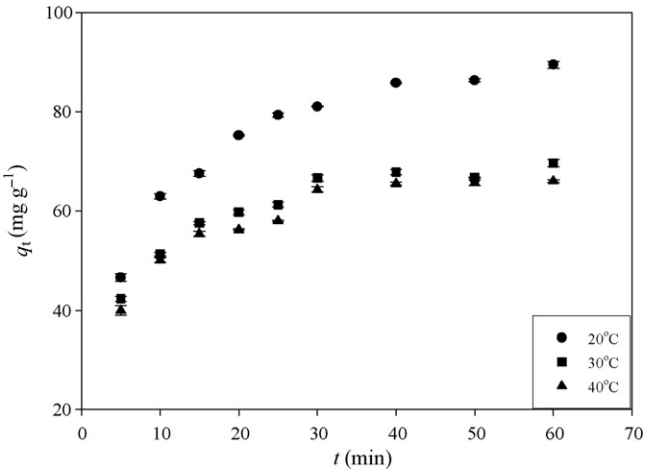

Fig. 3. Time profiles for the biosorption of AR44 by modified biosorbent at different temperatures (the bars represent the standard error of the mean).

3.4. Kinetics of the biosorption and temperature effect

Fig. 3 presents the biosorption of AR44 dye at different temperatures (20, 30 and 40 °C) as a function of contact time. In order to investigate the controlling mechanism and dynamics of the dye biosorption process, the Lagergren pseudo-first-order and the pseudo-second-order kinetic models were applied to experimental data.

The pseudo-first-order rate expression of Lagergren is given by the following equation [19]:

$$\ln(q_e - q_t) = \ln q_e - K_L t \quad (2)$$

where q_e and q_t are the amounts of biosorbed AR44 dye (mg g^{-1}) on the biomass at equilibrium and time t, respectively. K_L is the rate constant of the pseudo-first-order biosorption (min^{-1}). A straight line of $\ln(q_e - q_t)$ versus t (figure not shown) suggests the applicability of this kinetic model and K_L and q_e were determined from the slope and intercept of the plot. From the kinetic data in Table 1, it can be clearly seen that the pseudo-first-order mechanism does not describe the AR44 dye removal process adequately.

The pseudo-second-order rate expression [20] is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (3)$$

where q_2 is the maximum biosorption capacity (mg g^{-1}) and k_2 is the equilibrium rate constant of the pseudo-second-order biosorption (g mg^{-1} min^{-1}). Values of k_2 and q_2 were calculated from the plot of t/q_t versus t (figure not shown). The corresponding parameters and r^2 values are depicted in Table 1. The r^2 values of the kinetic models indicated that the biosorption process of AR44 onto modified sorbent obeys pseudo-second-order model rather than the pseudo-first-order kinetic model at all studied temperatures. The appropriateness of the pseudo-second-order kinetic model for the biosorption of different kinds of dyes was previously reported by several research groups [4,21,22].

This finding suggests that the rate-limiting step of the biosorption system may be chemisorption. Also the theoretical q_2 values estimated from the pseudo-second-order model are close to experimental q values in this study. The values of rate constants were found to increase from 1.75×10^{-3} to 3.22×10^{-3} g mg^{-1} min^{-1} with an increase in the solution temperatures from 20 to 40 °C, indicating that the biosorption of AR44 dye onto modified biomass is rate-controlled (Table 1). The dye biosorption capacity of the biosorbent from this model was found to decrease from 97.58 to 71.27 mg g^{-1} with an increase in the solution temperatures from 20 to 40 °C. Therefore, the biosorption of AR44 by modified biomass, in the favors of lower temperature and exothermically occurred. In the literature, Wang et al. [23] and Tunali et al. [24] reported the similar trends for Rhodamine B biosorption by anaerobic sludge and Acid Red 57 biosorption by *Phaseolus vulgaris* L., respectively.

The intraparticle diffusion equation [25] is:

$$q_t = k_p t^{1/2} + C, \quad (4)$$

where C is the intercept and k_p is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$). According to this model, a plot of uptake, q_t, versus the square root of time, $t^{1/2}$ (figure not shown), should be linear if intraparticle diffusion is involved in the biosorption system and when these lines pass through the origin, and then intraparticle diffusion is the rate controlling step [26–29]. If these plots do not pass through the origin, this is an evidence for some degree of boundary layer control. Furthermore, this indicates that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of biosorption, simultaneously. Therefore, the slope of the linear portion of the figure is defined as rate parameter, k_p, for the intraparticle diffusion, and biosorption rate characteristic in this region where intraparticle diffusion is the rate-limiting factor [30]. Although r_p^2 values obtained for the intraparticle diffusion model at different temperatures are lower than that of the pseudo-second-order model (Table 1), this model indicated that the AR44 biosorption process may be followed by an intraparticle diffusion model up to 40 min.

Table 1
The kinetic parameters for the biosorption of AR44 by modified biosorbent.

t (°C)	The pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion kinetic model		
	K_L (min^{-1})	q_e (mg g^{-1})	r_1^2	k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})	r_2^2	k_p (mg g^{-1} min$^{-1/2}$)	C (mg g^{-1})	r_p^2
20	6.37×10^{-2}	54.24	0.983	1.75×10^{-3}	97.58	0.999	7.49	39.99	0.970
30	5.76×10^{-2}	29.75	0.902	3.16×10^{-3}	74.10	0.998	5.23	39.09	0.950
40	7.78×10^{-2}	32.75	0.816	3.22×10^{-3}	71.27	0.998	4.92	35.06	0.933

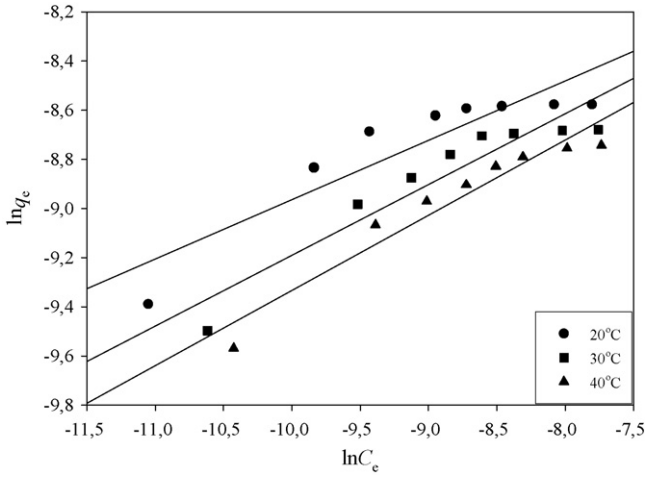

Fig. 4. Freundlich isotherm plots for the biosorption of AR44 by modified biosorbent.

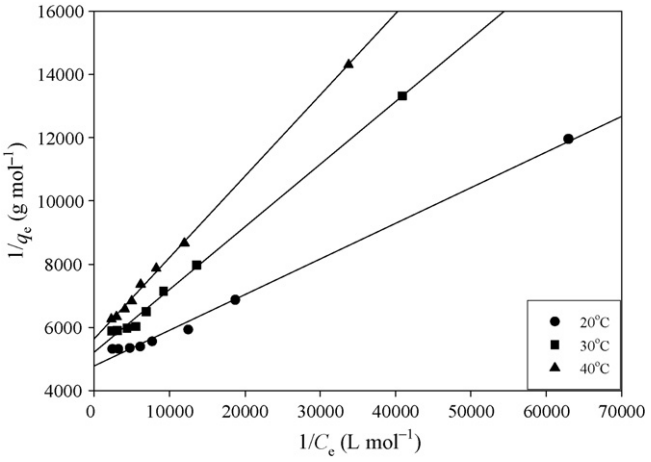

Fig. 5. Langmuir isotherm plots for the biosorption of AR44 by modified biosorbent.

3.5. Biosorption isotherms

The concentration of sorbate in the solid phase as a function of the concentration in liquid-phase of sorbate at equilibrium is called as "isotherm". The equilibrium sorption isotherm is fundamental in describing the interactive behavior between sorbates and sorbent and is important in the design and analysis of sorption systems [31,32]. Biosorption equilibrium data are widely evaluated by different isotherm models. In the present investigation the isotherm study of AR44 dye was conducted at different temperatures by changing the initial AR44 concentration in the range of 50–300 mg L^{-1}. The Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models were used to describe the equilibrium biosorption data.

The Freundlich isotherm model involves heterogeneous biosorption over the surface of the biosorbent and it can be presented by the following linearized equation [33]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where K_F (L g^{-1}) and n (dimensionless) are the Freundlich sorption isotherm constants. High values of these constants indicate that the binding capacity has reached its highest value and the affinity between the biomass and dye molecules was also higher. The value of n greater than unity implies favorable sorption and the repulsive forces between sorbed molecules [34,35]. Values of K_F and n are obtained from the intercept and slope of the linear plots in Fig. 4 and are represented in Table 2.

The Langmuir isotherm model assumes that the biosorption takes place in the monolayer form at specific homogeneous sites within the biosorbent, meaning that once a sorbate occupies a site, no further biosorption can occur at this site. The linear form of the Langmuir equation [36] is expressed as follows:

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

where q_e and q_{max} are the equilibrium and monolayer biosorption capacities of the biosorbent material (mol g^{-1}), respectively, C_e is the equilibrium dye concentration in the liquid-phase (mol L^{-1}) and K_L is the biosorption equilibrium constant (L mol^{-1}) related with the free energy of biosorption. The Langmuir plot for the biosorption of AR44 dye onto modified biosorbent (Fig. 5) shows a straight line of slope $1/q_{max} K_L$, and intercept, $1/q_{max}$.

In order to predict whether the biosorption system favorable or unfavorable, the shape of the Langmuir isotherm has been discussed [37].

The essential feature of the Langmuir isotherm can be expressed by means of 'R_L'. This dimensionless constant called as separation factor or equilibrium parameter and is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where C_0 is the highest initial AR44 concentration (mol L^{-1}). The type of the isotherm can be classified as follows according to value of the separation factor [37,38]:

$R_L > 1$: unfavorable isotherm;
$R_L = 0$: linear isotherm;
$0 < R_L < 1$: favorable isotherm;
$R_L < 0$: irreversible isotherm.

Dubinin–Raduskevich (D–R) isotherm model describes the biosorption nature of the sorbate on the biosorbent and it is used to calculate the mean free energy of biosorption. Characteristic biosorption curve is related to the porous structure of the biosorbent according to this model. The linearized form of (D–R) equation [39] can be written as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

where q_m is the biosorption capacity of the biosorbent (mol g^{-1}), β is a constant related to the biosorption energy, ε is Polanyi potential

Table 2
The isotherm constants for the biosorption of AR44 by modified biosorbent.

Langmuir					Freundlich			Dubinin–Radushkevich (D–R)			
t (°C)	q_{max} (mol g^{-1})	K_L (L mol^{-1})	r_L^2	R_L	n	K_F (L g^{-1})	r_F^2	q_m (mol g^{-1})	β (mol^2 kJ^{-2})	r_{D-R}^2	E (kJ mol^{-1})
20	2.09×10^{-4}	4.24×10^4	0.995	3.79×10^{-2}	4.15	1.43×10^{-3}	0.824	4.77×10^{-4}	1.49×10^{-3}	0.865	18.34
30	1.92×10^{-4}	2.62×10^4	0.997	5.99×10^{-2}	3.47	1.82×10^{-3}	0.887	5.00×10^{-4}	1.58×10^{-3}	0.917	17.77
40	1.77×10^{-4}	2.19×10^4	0.999	7.10×10^{-2}	3.27	1.89×10^{-3}	0.929	4.84×10^{-4}	1.59×10^{-3}	0.951	17.75

Table 3
Sorption capacities of various sorbent materials from the literature for some acid dyes.

Sorbent material	Dye	Biosorption capacity (mg g^{-1})	pH	References
Thuja orientalis	Acid blue 40	97.06	1.0	[5]
Non-living aerobic granular sludge	Acid Yellow 17	133.3	2.0	[18]
Azolla filiculoides	Acid Red 88	109.0	7.0	[45]
Azolla filiculoides	Acid Green 3	133.5	3.0	[45]
Azolla filiculoides	Acid Orange 7	109.6	3.0	[45]
Paenibacillus macerans	Acid Blue 225	94.98	1.0	[46]
Paenibacillus macerans	Acid Blue 062	95.08	1.0	[46]
Agaricus bisporus	Acid Red 44	59.80	2.0	[47]
Sawdust carbon	Acid Yellow 36	183.8	3.0	[48]
Rice husk carbon	Acid Yellow 36	86.90	3.0	[48]
Monoamine modified magnetic silica	Acid Orange 10	61.33	3.0	[49]
Mesoporous granular pine-cone derived activated carbon	Acid Black 1	452.9	7.0	[50]
Mesoporous granular pine-cone derived activated carbon	Acid Blue113	298.4	7.4	[50]
(HDEDMABr) modified *P. coccinea*	Acid Red 44	105.0	2.0	This study

which can be presented as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (9)$$

where R is the universal gas constant (J mol^{-1} K^{-1}) and T is the temperature (K). The values of D–R isotherm constants, β and q_m can be obtained with the help of slope and intercept of the linear plot presented in Fig. 6.

The constant β gives an idea about the mean free energy of biosorption and E value can be computed using the following relationship [40–42].

$$E = \frac{1}{(2\beta)^{1/2}} \quad (10)$$

The magnitude of E value may characterize the type of the biosorption as chemical ion exchange (E = 8–16 kJ mol^{-1}) [43], or physical sorption (E < 8 kJ mol^{-1}) [44]. The mean free energy of biosorption (E) is found between 17.75 and 18.34 kJ mol^{-1} at different temperatures, which implies that, the biosorption of AR44 on modified biomass may be considered as chemical biosorption.

The Langmuir, Freundlich and D–R isotherm model parameters are summarized in Table 2. K_F and n at the different temperatures were between 1.43×10^{-3} to 1.89×10^{-3} L g^{-1} and 4.15–3.27, respectively.

According to r^2 values in Table 2 the Langmuir isotherm model fits the AR44 biosorption data better than the other isotherm models at all studied temperatures. The suitability of the Langmuir isotherm model suggests monolayer coverage of dye molecules on the biosorbent surface. Langmuir model indicated that the maximum monolayer biosorption capacity of the modified biosorbent is 105.0, 96.47 and 88.93 mg g^{-1} at 20, 30 and 40 °C. In this study, the values of R_L found between 3.79×10^{-2} and 7.10×10^{-2} indicate that the AR44 biosorption behavior of modified biomass can be considered as favorable ($0 < R_L < 1$).

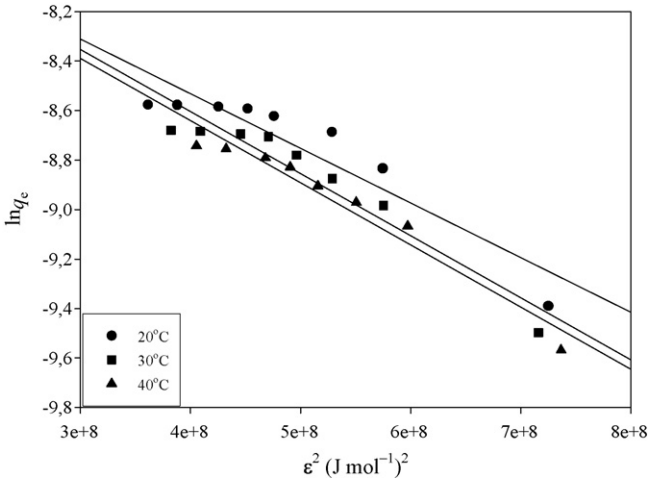

Fig. 6. D–R isotherm plots for the biosorption of AR44 by modified biosorbent.

Acid dye sorption capacities of different kinds of sorbent materials [5,45–51] reported in the literature are summarized in Table 3. The biosorption capacity of modified biosorbent in our study was found to be comparable to and moderately higher than those of many corresponding sorbent materials.

3.6. Thermodynamic analysis of dye removal process

In order to determine the temperature dependence of the dye removal process by modified biosorbent, the changes in the thermodynamic parameters (free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°)) were analyzed. K_L is used as the equilibrium constant due to its dependence on temperature. The following equations were used to calculate the thermodynamic parameters.

$$\Delta G^\circ = -RT \ln K_L \quad (11)$$

$$\ln K_L = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (12)$$

The plot of ln K_L as function of $1/T$ yields a straight line from which ΔH° and ΔS° were calculated from the slope and intercept, respectively. The results are presented in Table 4. The negative values of ΔG° indicate that the biosorption process was spontaneous in nature and confirm the affinity of the biosorbent towards the dye molecules. The negative value of ΔH° (−25.33) suggests the exothermic nature of the biosorption process. The positive entropy value (+1.81) indicates increased randomness at the solid/liquid interface during the biosorption process.

3.7. Effect of salt concentration

The effect of salt concentration on the dye biosorption potential of the modified biosorbent material was studied in the presence of increasing concentrations of $NaNO_3$ in the biosorption medium

Table 4
Thermodynamic parameters for the biosorption of AR44 by modified biomass.

t (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
20	−25.86	−25.33	1.81
30	−25.88		
40	−25.89		

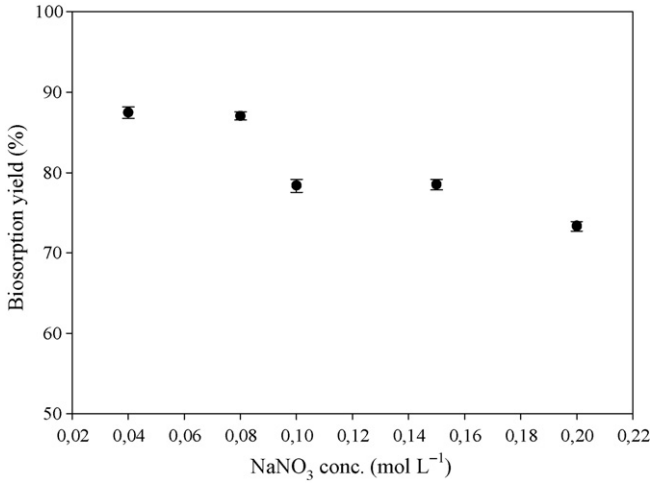

Fig. 7. Effect of ionic strength on the biosorption of AR44 by modified biosorbent (the bars represent the standard error of the mean).

(Fig. 7). The biosorption of AR44 decreased by about 15% as the salt concentration varied from 0.04 to 0.2 mol L^{-1}. This observed trend may be explained by the competition between nitrate anions and negatively charged dye molecules (sulfonate groups of dye molecules) for same binding sites of the biosorbent material. The adverse effect of ionic strength on dye biosorption process may be ascribed to possibility of ion exchange mechanism. Several research groups have reported the similar trends for the biosorption of dyes [32] and chromium (VI) [51,52].

3.8. FTIR analysis

The significant band positions of the complex nature of dried *P. coccinea* biomass are noted as 3415 cm^{-1}, 2926 and 2856 cm^{-1}, 1739 cm^{-1}, 1621 cm^{-1}, 1516 cm^{-1} and between 1421 and 587 cm^{-1} [15]. The FTIR spectra of HDEDMABr modified and dye-loaded biomass are given in Fig. 8. The intensities of the peaks at 2923 and 2852 cm^{-1} on the FTIR spectrum of modified biomass, ascribed to $-CH_2$ stretching vibrations were stronger than that of the natural biomass. The spectrum of modified biomass also displays the absorption peaks at about 1461 and 1371 cm^{-1}, corresponding to $-CH_3$ and $-CH_2$ bending vibrations, respectively. These observations may be explained by introduction of the $-CH_2$ and $-CH_3$ groups to the biomass surface following modification with HDEDMABr. The FTIR spectrum of the modified biomass exposed to dye indicated no significant change in any of the characteristic absorption peaks present in the modified biomass with the exception of very small increase in the intensity of the peak at about 620 cm^{-1} which may be indicative of aromatic $-CH_2$ vibrations. As mentioned previously an increase in the ζ potential values of the modified biomass at studied pH value confirmed the increase of the positive charge intensity on the biomass surface. This observation supports the electrostatic attraction between negatively charged dye molecules and positively charged modified sorbent. Namavisyam and Sureshkumar [31] have been reported similar increases in the intensity of the peak about 2921 cm^{-1} in the FTIR spectrum and in the ζ potential values for coconut coir pith after from hexadecyltrimethylammonium (HDTMA) bromide modification.

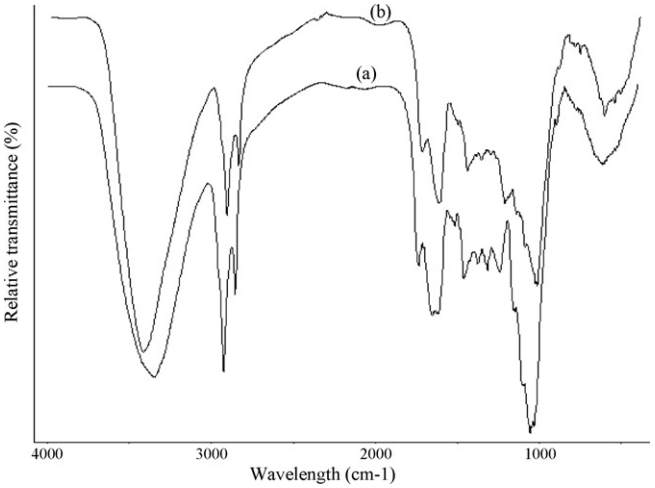

Fig. 8. FTIR spectra of modified (a) and dye-loaded modified (b) biosorbent.

4. Conclusion

P. coccinea was modified with cationic surfactant by a simple procedure and the reactive dye biosorption properties of this modified biosorbent were characterized. The results showed that the developed biosorbent exhibited a good potential for decolorization process. The biosorption efficiency of the biosorbent was affected from various parameters i.e. pH, contact time, biosorbent concentration, temperature and initial dye concentration. The relatively rapid biosorption was observed in the first 40 min. ζ potential measurements and FTIR analysis confirmed the modification process. The kinetic and equilibrium data explained adequately by the pseudo-second-order kinetic model and the Langmuir isotherm model, respectively. The presence of the different concentrations of competing ions (Na^+ and NO_3^-) was not strongly inhibited the biosorption yield of biomass. As a conclusion, the suggested biosorbent material may be an alternative to existing costly sorbent materials for the decolorization of acid dye contaminated solutions.

References

[1] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, Process Biochem. 40 (2005) 997–1026.
[2] O.J. Hao, H. Kim, P.C. Chiang, Decolorization of wastewater, Crit. Rev. Environ. Sci. Technol. 30 (2000) 449–505.
[3] O. Anjaneya, M. Santoshkumar, S.N. Anand, T.B. Karegoudar, Biosorption of acid violet dye from aqueous solutions using native biomass of a new isolate of *Penicillium* sp, Int. Biodeter. Biodegrad. 63 (2009) 782–787.
[4] R. Aravindhan, J.R. Rao, B.U. Nair, Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*, J. Hazard. Mater. 142 (2007) 68–76.
[5] T. Akar, A.S. Ozcan, S. Tunali, A. 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 (2008) 3057–3065.
[6] Z. Zhang, S. Xia, X. Wang, A. Yang, B. Xu, L. Chen, Z. Zhu, J. Zhao, N. Jaffrezic-Renault, D. Leonard, A novel biosorbent for dye removal: extracellular polymeric substance (EPS) of *Proteus mirabilis* TJ-1, J. Hazard. Mater. 163 (2009) 279–284.
[7] A. Bhatnagar, M. Sillanpää, Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review, Chem. Eng. J. 157 (2010) 277–296.
[8] R. Nadeem, M.A. Hanif, F. Shaheen, S. Perveen, M.N. Zafar, T. Iqbal, Physical and chemical modification of distillery sludge for Pb(II) biosorption, J. Hazard. Mater. 150 (2008) 335–342.
[9] C. Namavisyam, M.V. Sureshkumar, Removal of chromium (VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent, Bioresour. Technol. 99 (2008) 2218–2225.
[10] B.C. Oei, S. Ibrahim, S. Wang, H.M. Ang, Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution, Bioresour. Technol. 100 (2009) 4292–4295.
[11] G. Bayramoglu, G. Celik, M.Y. Arica, Biosorption of Reactive Blue 4 dye by native and treated fungus *Phanerocheate chrysosporium*: batch and continuous flow system studies, J. Hazard. Mater. 137 (2006) 1689–1697.
[12] A.E. de Villalobos, D.P. Vazquez, J.-L. Martin, Soil disturbance, vegetation cover and the establishment of the exotic shrub *Pyracantha coccinea* in southern France, Biol. Invasions. doi:10.1007/s10530-009-9519-z.
[13] Z. Kowaleuki, M. Mrugasiewicz, Neue flavanonheteroside in *Crataegus phenophyrum*, Planta Med. 19 (1971) 311–313.

[14] G. Fico, A.R. Bilia, I. Morelli, F. Tome, Flavanoid distribution in *Pyracantha coccinea* plants at different growth phases, Biochem. Syst. Ecol. 28 (2000) 673–678.
[15] T. Akar, B. Anilan, A. Gorgulu, S. Tunali Akar, Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: *Pyracantha coccinea* berries, J. Hazard. Mater. 168 (2009) 1302–1309.
[16] R. Gong, Y. Jin, J. Chen, Y. Hu, J. Sun, Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw, Dyes Pigments 73 (2007) 332–337.
[17] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*), Environ. Pollut. 125 (2003) 385–392.
[18] J. Gao, Q. Zhang, K. Su, R. Chen, Y. Peng, Biosorption of Acid Yellow 17 from aqueous solution by non-living aerobic granular sludge, J. Hazard. Mater. 174 (2010) 215–225.
[19] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (1898) 1–39.
[20] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, Process Saf. Environ. Prot. 76 (B2) (1998) 183–191.
[21] M.Y. Arica, G. Bayramoglu, Biosorption of Reactive Red-120 dye from aqueous solution by native and modified fungus biomass preparations of *Lentinus sajor-caju*, J. Hazard. Mater. 149 (2007) 499–507.
[22] X.F. Sun, S.G. Wang, X.W. Liu, W.X. Gong, N. Bao, B.Y. Gao, H.Y. Zhang, Biosorption of Malachite Green from aqueous solutions onto aerobic granules: kinetic and equilibrium studies, Bioresour. Technol. 99 (2008) 3475–3483.
[23] Y. Wang, Y. Mu, Q.B. Zhao, H.Q. Yu, Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge, Sep. Purif. Technol. 50 (2006) 1–7.
[24] S. Tunali, A. Özcan, Z. Kaynak, A.S. Özcan, T. Akar, Utilization of the *Phaseolus vulgaris* L. waste biomass for decolorization of a textile dye Acid Red 57: determination of equilibrium, kinetic and thermodynamic parameters, J. Environ. Sci. Health A 42 (2007) 591–600.
[25] W.J. Weber Jr., J.C. Morriss, Kinetics of adsorption on carbon from solution, J. Sanitary Eng. Div. Am. Soc. Civil Eng. 89 (1963) 31–39.
[26] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, Dyes Pigments 51 (2001) 25–40.
[27] T.D. Khokhlova, Y.S. Nikitin, A.L. Detistova, Modification of silicas and their investigation by dye adsorption, Adsorp. Sci. Technol. 15 (1997) 333–340.
[28] W.T. Tsai, K.J. Hsien, J.M. Yang, Silica adsorbent prepared from spent diatomaceous earth and its application to removal of dye from aqueous solution, J. Colloid Interface Sci. 275 (2004) 428–433.
[29] K.R. Ramakrishna, T. Viraraghavan, Use of slag for dye removal, Waste Manage. 17 (1998) 483–488.
[30] S.V. Mohan, N.C. Rao, J. Karthikeyan, Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study, J. Hazard. Mater. 90 (2002) 189–204.
[31] C. Namasivayam, M.V. Sureshkumar, Removal of chromium(VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent, Bioresour. Technol. 99 (2008) 2218–2225.
[32] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH, Bioresour. Technol. 97 (2006) 512–521.
[33] H.M.F. Freundlich, Über die adsorption in lösungen, Z. Phys. Chem. 57 (1906) 385–470.
[34] R.S. Bai, T.E. Abraham, Studies on chromium (VI) adorption-desorption using immobilized fungal biomass, Bioresour. Technol. 87 (2003) 17–26.
[35] K. Vijayaraghavan, Y.S. Yun, Biosorption of C.I. Reactive Black 5 from aqueous solution using acid-treated biomass of brown seaweed *Laminaria* sp, Dyes Pigments 76 (2008) 726–732.
[36] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[37] T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed-bed adsorbers, J. Am. Inst. Chem. Eng. 20 (2) (1974) 228–238.
[38] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (2) (1966) 212–223.
[39] M.M. Dubinin, L.V. Radushkevich, Proc. Acad. Sci. USSR Phys. Chem. Sect. 55 (1947) 331–333.
[40] J.P. Hobson, Physical adsorption isotherms extending from ultrahigh vacuum pressure, J. Phys. Chem. 73 (8) (1969) 2720–2727.
[41] S.M. Hasany, M.H. Chaudhary, Sorption potential of Hare River sand for the removal of antimony from acidic aqueous solution, Appl. Radiat. Isot. 47 (4) (1996) 467–471.
[42] S.S. Dubey, R.K. Gupta, Removal behavior of Babool bark (*Acacia nilotica*) for submicro concentrations of Hg^{2+} from aqueous solutions: a radiotracer study, Sep. Purif. Technol. 41 (1) (2005) 21–28.
[43] F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962.
[44] M.S. Onyango, Y. Kojima, O. Aoyi, E.C. Bernardo, H. Matsuda, Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, J. Colloids Interface Sci. 279 (2004) 341–350.
[45] T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran, M. Velan, Batch and column studies on biosorption of acid dyes on fresh water macro alga *Azolla filiculoides*, J. Hazard. Mater. 125 (2005) 121–129.
[46] F. Colak, N. Atar, A. Olgun, Biosorption of acidic dyes from aqueous solution by *Paenibacillus macerans*: kinetic, thermodynamic and equilibrium studies, Chem. Eng. J. 150 (2009) 122–130.
[47] T. Akar, I. Tosun, Z. Kaynak, E. Kavas, G. Incirkus, S. Tunali Akar, Assessment of the biosorption characteristics of a macro-fungus for the decolorization of Acid Red 44 (AR44) dye, J. Hazard. Mater. 171 (2009) 865–871.
[48] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, Dyes Pigments 56 (2003) 239–249.
[49] A.A. Atia, A.M. Donia, W.A. Al-Amrani, Adsorption/desorption behavior of Acid Orange 10 on magnetic silica modified with amine groups, Chem. Eng. J. 150 (2009) 55–62.
[50] M. Hadi, M.R. Samarghandi, G. McKay, Equilibrium two-parameter isotherms of acid dyes sorption by activated carbons: study of residual errors, Chem. Eng. J. 160 (2010) 408–416.
[51] G. Donmez, Z. Aksu, Removal of chromium(VI) from saline wastewaters by *Dunaliella* species, Process Biochem. 38 (2002) 751–762.
[52] Z. Aksu, E. Balibek, Chromium(VI) biosorption by dried *Rhizopus arrhizus*: effect of salt (NaCl) concentration on equilibrium and kinetic parameters, J. Hazard. Mater. 145 (2007) 210–220.