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Chemical modification of a plant origin biomass using cationic surfactant ABDAC and the biosorptive decolorization of RR45 containing solutions

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ABSTRACT

This study focused on the improvement of the decolorization potential of biomass derived from *Pyracantha coccinea*. Alkyl benyzldimethyl ammonium chloride (ABDAC) was used as modification agent. Batch mode decolorization potential of modified biosorbent was explored at different operating conditions. ABDAC modification significantly increased the biosorption yield to 97.27%, which was 3.88 times higher than that of natural biomass. The prepared biosorbent was effectively used for the decolorization of Reactive Red 45 contaminated solutions after the optimization of biosorption conditions. The non-linear regression analysis was used to evaluate the isotherm and kinetic model parameters. Process followed the Langmuir isotherm model and the highest monolayer capacity of 152.49 mg g^{-1} was obtained with a small amount of modified biosorbent. Kinetic studies indicated fast decolorization rate of the process following the pseudo-first-order model. Biosorption performance of the prepared biosorbent was tested in RR45 containing real wastewater sample. The possible dye biosorbent interactions in the biosorption process were explored by zeta potential, scanning electron microscobe and FTIR analysis.

1. Introduction

Different kinds of synthetic organic dyes are extensively used in many industrial applications and important quantities of colored effluents are discharged into receiving water bodies. Because of their large – scale production and extensive application, synthetic dyes can cause considerable environmental pollution and have serious health risk factors. They are designated as highly stable in nature and dye contaminated wastewaters cannot effectively be decolorized by conventional treatment plants. Hence, elimination of color from contaminated waters is essential but it is very difficult. The researches for effective and practical treatments of the colored effluents have been attracted with increasing interest in recent years [1].

The biosorption process based on the biomaterial–pollutant interactions and represents an effective sequestration of organic and/or inorganic substances by certain types of non-living biomaterials. It is considered as a potential alternative over the traditional costly treatment technologies. Especially, if the used biomaterial is low-cost, readily available and has a good biosorption performance [2].

The yield of the biosorption process depends on several factors varying from the type of pollutant being studied to type of biosorbent used as well as other environmental parameters. This method has also some other advantages, such as greater profitability, ease of operation, greater efficiency, biosorbent regeneration and the possibility of pollutant recovery. These important advantages of the process attract researchers to exploit more bioresources as biosorbent in this field [3]. Literature survey reveals that different types of microbial and plant – derivative biomaterials have been used for the removal of synthetic dyes or heavy metals from contaminated aqueous media [4–12]. In recent years in order to improve the decolorization potential of biomaterials, surface modification procedures by different type of surfactants have been suggested [13–16].

In this direction, a cationic surfactant, alkylbenzyldimethylammonium chloride (ABDAC) was used as a modification agent and high decolorization efficiency was achieved by using a small amount of modified biosorbent for Reactive Red 45 (RR45) containing solutions. *Pyracantha coccinea* (*P. coccinea*) berries were chosen as target biomass source because of its known biosorption potential towards anionic and cationic dye molecules [17,18]. Firstly, required surfactant concentration was determined for modification procedure. Experimental parameters affecting the biosorption process such as initial pH, biosorbent dosage, contact time and temperature were examined. Then, batch biosorption behaviour of modified biosorbent was evaluated by means of modelling the

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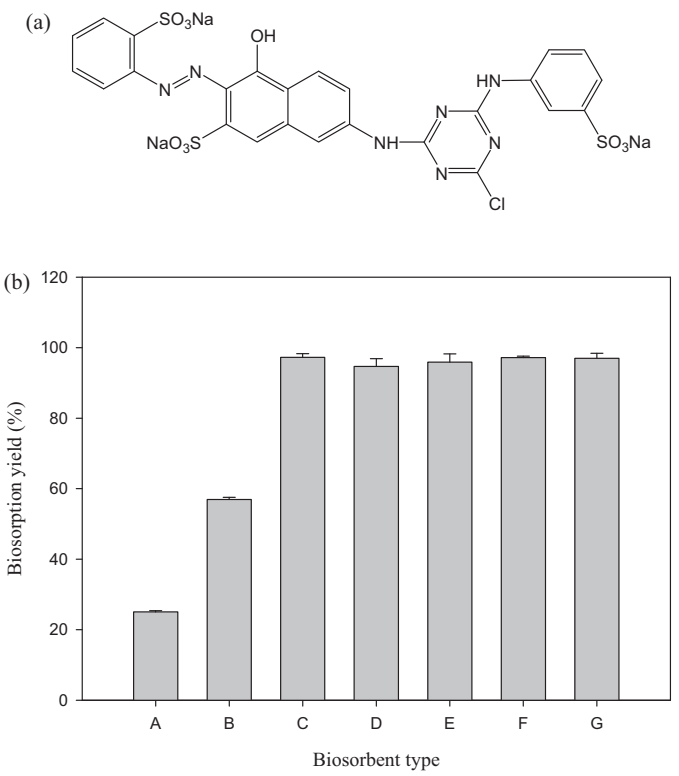

Fig. 1. (a) Chemical structure of RR45 dye, (b) effect of modified biosorbent type on the RR45 biosorption. A: unmodified dried biomass; B: modified biomass with 0.0625% ABDAC; C: modified biomass with 0.125% ABDAC; D: modified biomass with 0.25% ABDAC; E: modified biomass with 0.5% ABDAC; F: modified biomass with 1% ABDAC and G: modified biomass with 2% ABDAC (error bars indicate the standard error of the mean, $n = 3$).

isotherm and kinetic data. Finally, possible dye–biosorbent interactions were monitored by different instrumental analysis methods in addition to the investigation of biosorption performance of the suggested biosorbent in NaCl containing solutions and real wastewater conditions.

2. Materials and methods

2.1. Preparation of biosorbent material and solutions

P. coccinea berries were collected from a number of plants in nature. They were washed several times with distilled water, dried in an oven at 60 °C for 24 h and grounded using a laboratory mill (IKA A11). Powdered biomass was sieved to select particle size of less than 212 μm. The raw biomass sample (2.5 g) was treated with 250 mL of ABDAC solutions with different concentrations (0.0625%, 0125%, 0.25%, 0.5%, 1.0%, and 2.0% (w/v)). The suspensions were stirred at 200 rpm for 24 h. Finally, modified biomass was separated from solution by filteration, washed with deionized water several times and then dried again at the conditions as mentioned above.

The textile dye, RR45, was selected as model sorbate. The chemical structure of this dye is shown in Fig. 1a. The stock dye solutions ($1.0\,g\,L^{-1}$) were prepared by dissolving an appropriate amount of RR45 in deionized water. Other concentrations were obtained by diluting this stock solution. Fresh dilutions were used in each biosorption trials. The pH of working solutions was adjusted to desired values by adding either 0.1 M HCl or 0.1 M NaOH solutions and measured by using a pH meter (Hanna 221). Biosorbent–free blank samples were analyzed to ensure that no biosorption was taking place on the vessel walls and it was found that the biosorption of RR45 onto flasks was negligible.

2.2. Experimental design of biosorption and characterization studies

The optimum biosorption conditions were investigated by contacting an accurate weight of biosorbent sample with 25 mL of dye solutions. Biosorption mixture in 100 mL of beakers was agitated on a multipoint magnetic stirrer at 200 rpm. Batch mode parameters screened are: initial pH (1.0–9.0), biosorbent amount ($0.4–1.2\,g\,L^{-1}$), temperature (25, 35 and 45 °C) and salt concentration ($0.02–0.5\,mol\,L^{-1}$). For kinetic modelling, contact time was varied from 5 to 90 min. Isotherm studies were conducted with the dye solutions at different concentrations. Biosorption performance of the modified biosorbent was also investigated in the real wastewater sample as indicated in our previous study [19]. Wastewater sample (25 mL) was spiked with $100\,mg\,L^{-1}$ of RR45 dye prior to biosorptive treatment. After the biosorption experiments mixtures were centrifuged at 4500 rpm for 5 min in order to separate solid and liquid phases. Dye concentration in the liquid phase was analyzed using Shimadzu UV-2550 spectrophotometer at a maximum wavelength of 520 nm. The amount of RR45 biosorbed onto biomaterial (q_e) and biosorption yield (%) were determined using the following relationships:

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

$$\text{Biosorption yield } (\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

where, C_i and C_e are the initial and the equilibrium RR45 concentrations ($mg\,L^{-1}$), respectively, V is the volume of aqueous phase (L) and m is the weight of the biosorbent (g). The BET surface area, total pore volume, average pore size and micro pore volume of the biosorbents were determined from the N_2 adsorption isotherm with a surface area and pore size analyzer (Quantachrome Instruments, Autosorb 1). The surface charges of the natural and modified biosorbent material at the above mentioned pH values were examined by zeta potential analyzer (Malvern zeta sizer). The effect of modification on the surface structure and the functional groups of biosorbent were analyzed by FTIR spectroscopy. FTIR spectra were recorded in the range of $4000–400\,cm^{-1}$. SEM micrographs of the modified biosorbent were obtained with JEOL 560 LV scanning electron microscope at 20 kV acceleration voltage and 1500× image magnification. Before analysis, biosorbent samples were sputter coated in a Polaron SC-7620 Sputter Coater using a gold–palladium target to improve electron conductivity and image quality. Thermal analysis of the samples was carried out using a Perkin–Elmer Diamond TG/DTA Thermal Analyzer in a static air atmosphere at a heating rate of $10\,°C\,min^{-1}$ in the temperature range 30–600 °C using platinum crucibles.

Data presented are the mean values from three independent experiments. The statistical treatment of the results was done using SPSS 15.0 for Windows. The isotherm and kinetic data were fitted with different models by non-linear regression using the method of least squares. The statistical analyses and curve fitting were performed using Sigma Plot 10.0. The determination coefficient (R^2) and standard error of estimate (SE) obtained from non-linear regression were used to select the best model.

3. Results and discussion

3.1. Effect of surfactant concentration

The influence of surfactant concentration on the decolorization yield of biomaterial is shown in Fig. 1b. The results indicated that the biosorptive decolorization yield of natural biomaterial was only 25.05%. It was increased by about 3.88 times after the

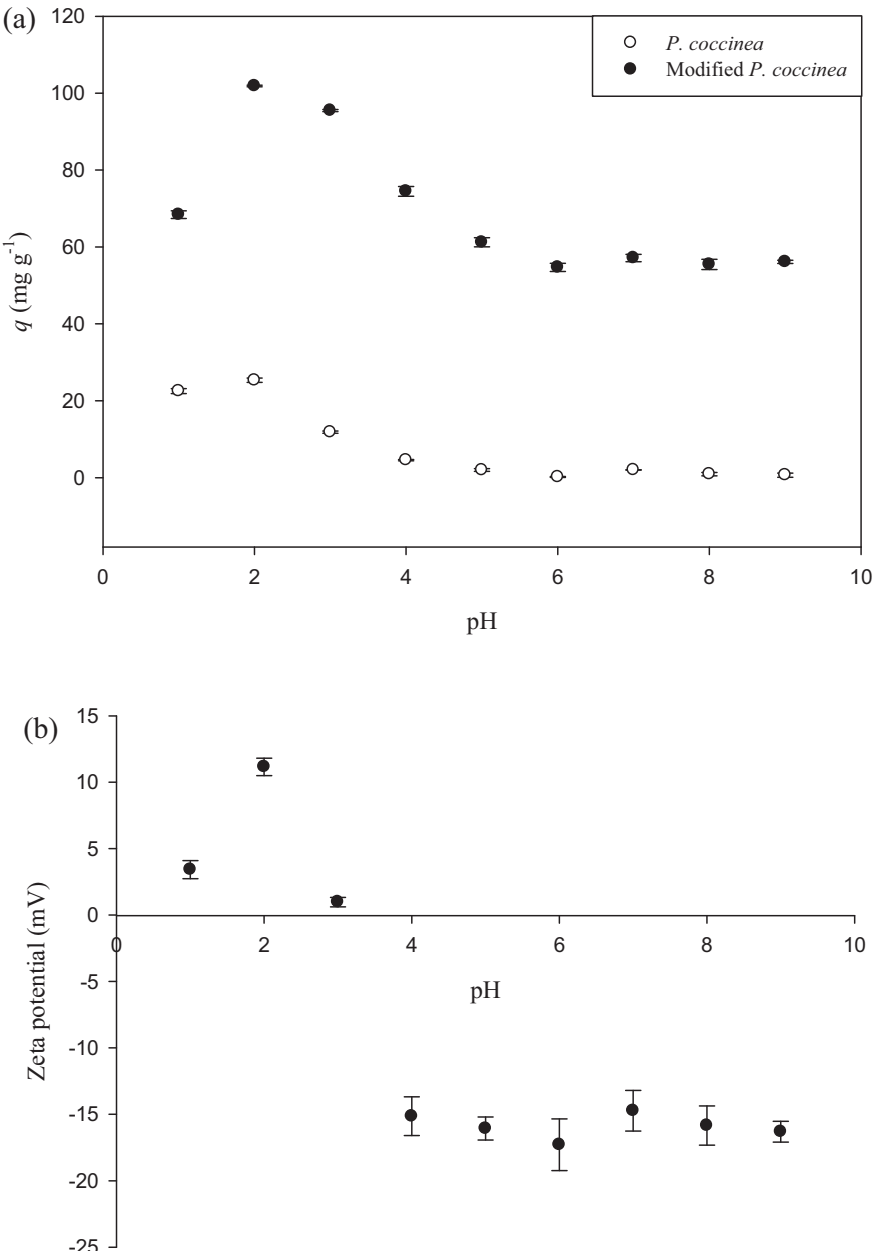

Fig. 2. (a) Effect of solution pH on the RR45 biosorption capacity of the natural and modified biomass. (b) Zeta potential values of the modified biosorbent at different pH values (error bars indicate the standard error of the mean, $n = 3$).

modification process ($p < 0.05$) and reached to 97.27% with 0.125% ABDAC modification (Biomass type C). Further increase in the surfactant concentration up to 2.0% did not significantly change the decolorization yield of the biomass ($p > 0.05$). Hence, the modification process of the biosorbent was carried out using ABDAC solution at a minimum concentration (0.125%).

3.2. pH effect on the biosorption process

The pH dependence of dye biosorption is related to a combine result of charges on dye molecules in the biosorption medium and the surface functional groups of the biomaterial [20]. Reactive dyes are known to ionize to a high degree in aqueous solutions to form coloured anions due to the sulfonate groups present in their structure [21]. RR45 dye has three sulfonate groups in its structure (Fig. 1a.). Fig. 2a represents the effect of initial pH on the RR45 biosorption process. The greatest capacities of natural and modified biomaterial were obtained at pH 2.0. As can be seen in this figure the biosorption capacities of both biosorbent decreased with increasing pH and reached to lowest values at pH 6.0. At lower pH values dye binding sites on the biomaterial surface would be closely associated with the hydronium ions. This means that negatively charged dye molecules attract positively charged binding sites and biosorption capacity of biomaterial enhances. Negative charge density on the biomaterial surface increases with an increase in the medium pH as a result of deprotonization of the active sites. Hence, repulsive forces restrict the access of dye molecules to the binding sites of the biosorbent. Previous researchers have reported similar findings for the biosorption of Reactive Brillant Red K-2BP [22], Reactive Red 4 [23], Yellow 2G and Reactive Brillant Red K-2G [24] by different types of biosorbents. The modified biomaterial exhibited higher biosorption capacity than natural biomaterial at the all studied pH values. This enhanced biosorption potential can be attributed to the coverage of the biomaterial surface by cationic surfactant

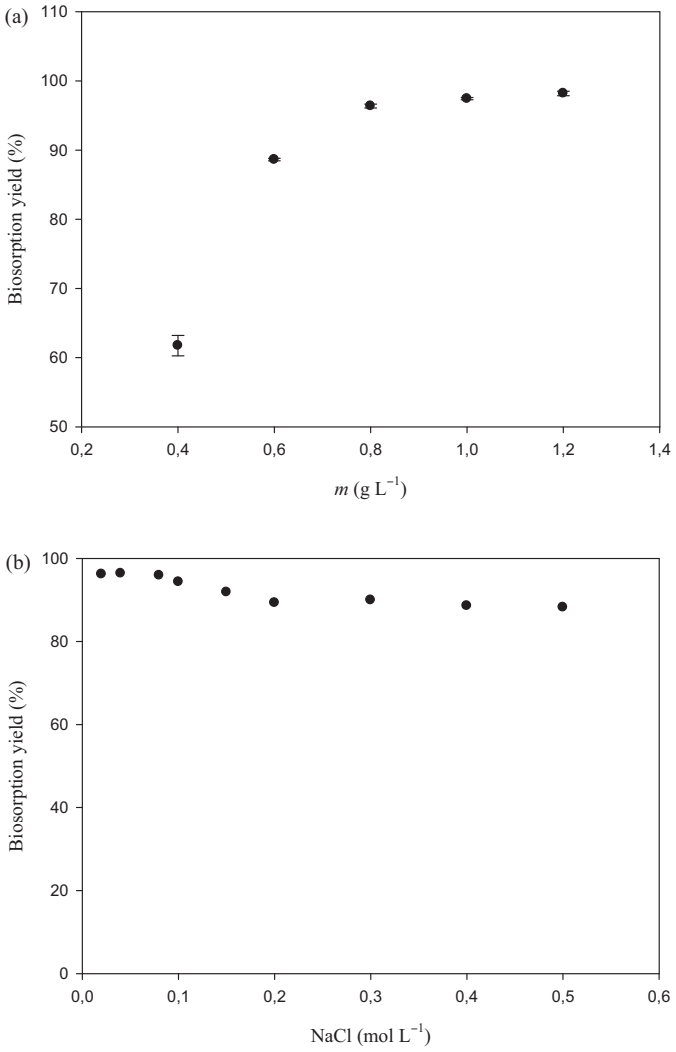

Fig. 3. (a) Effect of modified biosorbent amount on the biosorption of RR45. (b) Effect of salt concentration on the biosorption of RR45 by modified biosorbent (error bars indicate the standard error of the mean, $n = 3$).

[25]. It is apparent from Fig. 2b zeta potential values of the modified biomaterial varied from +3.42 to −16.31 mV when the medium pH was changed from 1.0 to 9.0. Point of zero charge (pzc) of the modified biosorbent was observed at about pH 3.0 and it has more positive zeta potential (+11.15 mV) at pH 2.0. This observation was also supported by the optimum pH value of 2.0 for RR45 removal process.

3.3. Biosorbent dosage effect on the biosorption process

The effect of modified biosorbent amount on the biosorption of RR45 dye was investigated in the range of 0.4–1.2 g L^{-1} and the results were presented in Fig. 3a. The biosorption of RR45 dye increased proportionally with increasing biomaterial dosage and reached a plateau at 0.8 g L^{-1}. Then it remained almost constant up to 1.2 g L^{-1}. Hence, 0.8 g L^{-1} was chosen as the optimum biomaterial dosage. Increasing biosorption yield with biomaterial dosage can be attributed to the availability for more binding sites of the biosorbent. Similar trends were noticed by Chowdhury et al. [26] for the biosorption of Basic green onto *Ananas comosus* and Aravindhan et al. [7] for the biosorption of Sandocryl golden yellow onto green alga *Caulerpa scalpelliformis*.

3.4. Temperature effect on the biosorption process

The variation in the biosorption capacity of modified biomaterial as a function of temperature was investigated with 200 mg L^{-1} RR45 solutions using optimum pH value and biomaterial dosage. The equilibrium biosorption capacities were recorded as 148.86, 149.74 and 150.01 mg g^{-1} at 25, 35 and 45 °C, respectively. These values indicated that the temperature has no significant effect on the biosorption process ($p > 0.05$). This may be an indicative of the energy independent physicochemical mechanism [27,28] for the biosorption of RR45 onto modified biosorbent. It may also be noted as an advantage for the real sample applications of the suggested material. Therefore, further decolorization studies were conducted at a temperature of 25 °C.

3.5. Salt effect on the biosorption process and real wastewater application

The effect of ionic strength on the RR45 biosorption was investigated at the salt (NaCl) concentration range from 0.02 to 0.5 mol L^{-1} and the results are plotted in Fig. 3b. When NaCl concentration in the biosorption medium was increased from 0.02 to 0.4 mol L^{-1}, decolorization yield of the modified biosorbent decreased slightly from 96.20 to 88.57%. Even at 0.5 mol L^{-1} of salt concentration, modified biosorbent still exhibited good biosorption yield of higher than 88.00%. This slight decrease in the biosorption capacity can be attributed to the competition between chloride and dye anions for the biomaterial binding sites. On the other hand, RR45 biosorption yield of the modified biomaterial in real wastewater conditions was recorded as 96.23%. The good biosorption performances of biomaterial in the salt containing medium and at real conditions can be considered as another important advantage for the usability of large-scale application of the suggested biomaterial.

3.6. Kinetic modelling of the biosorption process

The variation of the RR45 biosorption capacity of the modified biomaterial as a function of contact time is given in Fig. 4a. Obviously, the biosorption process was very fast in the first 5 min. 15 min of contact was sufficient to achieve the biosorption equilibrium. Therefore, it was selected as equilibrium time for further studies. The good biosorption performance observed in a short time is an important feature for the practical application of the suggested biomaterial in treatment technology.

Kinetics of the RR45 biosorption process were investigated with Lagergren's pseudo-first-order [29] (Eq. (3)) and the pseudo-second-order [30] (Eq. (4)) kinetic models.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where q_e and q_t are the biosorption capacities (mg g^{-1}) of the biomaterial at equilibrium, and time t, respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants for the pseudo-first-order and pseudo-second-order biosorption The least squares method for non-linear regression was used to fit the time-dependent data and to obtain the parameters of two kinetic models. The experimental data and the predicted kinetic curves are presented in Fig. 4a and the corresponding model parameters are given Table 1. The highest R^2 value was obtained to be 0.992 with the pseudo-first-order kinetic model. All coefficients of this model are statistically significant and the standard error value is 0.058. This result indicates that the pseudo-first-order model is the best kinetic model for explaining the biosorption of RR45 onto modified biosorbent. The calculated q_e value from this model (120.77 mg g^{-1}) is in agreement

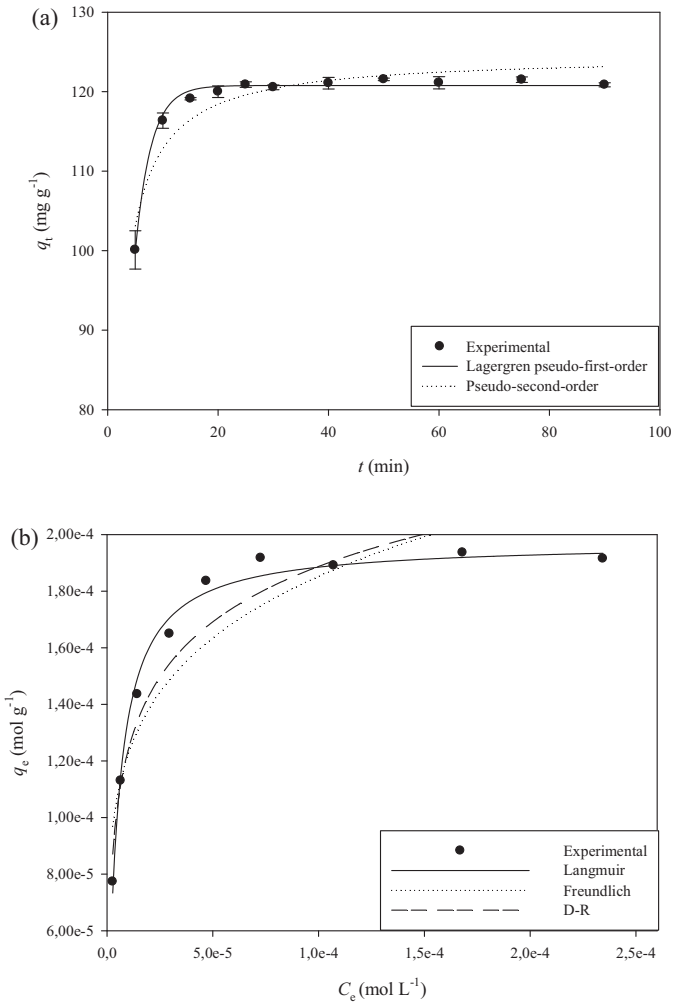

Fig. 4. (a) Experimental data and the predicted kinetic curves for the biosorption of RR45 by modified biosorbent. (b) Experimental equilibrium data and the predicted isotherm curves for the biosorption of RR45 by modified biosorbent (error bars indicate the standard error of the mean, $n = 3$).

with the experimental q_e (119.11 mg g^{-1}). Thus, the biosorption of RR45 onto modified biomass is better described by a first–order reaction.

3.7. Isotherm modelling of the biosorption process

The experimental equilibrium data for the biosorption of RR45 onto modified biosorbent were evaluated by three isotherm models which are namely Freundlich [31], Langmuir [32] and D–R [33]. For this purpose, several non-linear regression models are estimated

Table 1
Kinetic parameters for the biosorption of RR45 onto modified biosorbent ($n = 3$).

Parameter		t	p
Pseudo-first-order			
q_e (mg g^{-1})	120.77	574.74	<0.0001
k_1 (min^{-1})	0.35	61.63	<0.0001
R^2: 0.992; SE: 0.058; F: 1128.92			
Pseudo-second-order			
q_e (mg g^{-1})	124.56	8.26	<0.0001
k_2 (g mg^{-1} min^{-1})	7.71×10^{-3}	7.88	<0.0001
R^2: 0.904; SE: 0.202; F: 84.89			

SE, standard error of the estimate.

Table 2
Isotherm parameters for the biosorption of RR45 onto modified biosorbent ($n = 3$).

Parameter		t	p
Langmuir isotherm			
q_{max} (mol g^{-1})	1.97×10^{-4}	18.2165	<0.0001
K_L (L mol^{-1})	2.16×10^{5}	15.9920	<0.0001
R^2: 0.991; SE: 0.0004; F: 874.862			
Freundlich isotherm			
n	5.552	6.3482	0.0004
K_F (L g^{-1})	0.0010	3.5315	0.0096
R^2: 0.875; SE: 0.002; F: 49.009			
D–R isotherm			
q_{max} (mol g^{-1})	4.00×10^{-4}	15.1620	<0.0001
β (mol^2 kJ^{-2})	5.32×10^{-3}	10.2970	<0.0001
E (kJ mol^{-1})	9.69		
R^2: 0.938; SE: 0.0010; F: 106.027			

SE, standard error of the estimate.

to fitting the isotherm data. The experimental data and the predicted curves were included in Fig. 4b and the calculated model parameters are presented in Table 2.

Freundlich isotherm model assumes that the biosorption takes place on heterogenous surface of the biosorbent. According to Langmuir model, biosorption takes place at specific sites at the outer surface of the biosorbent and once a sorbate occupies a binding site, no further biosorption occurs at this site. The Freundlich (Eq. (5)), Langmuir (Eq. (6)) and D–R (Eq. (7)) equations are expressed as follows:

$$\text{Freundlich} \quad q_e = K_F C_e^{1/n} \tag{5}$$

$$\text{Langmuir} \quad q_e = \frac{q_{max} K_L Ce}{1 + q_{max} K_L} \tag{6}$$

$$\text{D} - \text{R} \quad \text{In} \quad q_e = \text{In} \quad q_m - \beta\varepsilon^2 \tag{7}$$

where K_F (L g^{-1}) and n (dimensionless) are Freundlich constants, being indicative of the extent of the biosorption and the degree of non-linearity between solution concentration and biosorbent, respectively. q_e and C_e are the amount of dye biosorbed at equilibrium (mol g^{-1}) and residual dye concentration in solution (mol L^{-1}), respectively, q_{max} is the maximum monolayer biosorption capacity of the biosorbent (mol g^{-1}) and K_L is the Langmuir constant (L mol^{-1}) and related to the free energy of biosorption. q_m is D–R biosorption capacity (mol g^{-1}), β is the constant related to the biosorption energy (mol^2 kJ^{-2}) and ε (kJ mol^{-1}) is the Polanyi potential shown in Eq. (8):

$$\varepsilon = RT \quad \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

where, R is the universal gas constant and T is the absolute temperature (K).

The biosorption free energy (E), can be calculated from the following equation:

$$E = \frac{1}{(2\beta)^{1/2}} \tag{9}$$

The magnitude of this value gives information about the biosorption type, chemical ion exchange ($E = 8$–16 kJ mol^{-1}) or physical sorption ($E < 8$ kJ mol^{-1}) [34,35]. The corresponding modelling results from these isotherms are listed in Table 2. According to this table, all models have high values of R^2. In addition, t values of coefficients are statistically significant for all models. Furthermore, it is known that the model giving lower values of standard error is a better one between different models. With respect to the R^2 and standard error of the model, the Langmuir model can be accept

Table 3
Reactive dye biosorption capacities of some different biosorbents from the literature.

Biosorbent material	Dye	Biosorption capacity ($mg\,g^{-1}$)	Reference
Na-CMC immobilized *Aspergillus fumigatus*	Reactive Brilliant Red K-2BP	78	[36]
Na-CMC immobilized *Aspergillus fumigatus*	Reactive Brilliant Blue KN-R	86.7	[36]
Agaricus bisporus/*Thuja orientalis* mixture	Reactive Red 45	108.90	[37]
Citrus sinensis	Reactive Red 45	18.28	[10]
Citrus sinensis (Acetonitrile treated)	Reactive Red 45	31.45	[10]
Capsicum annuum seeds (Acetone treated)	Reactive Blue 49	96.35	[38]
Aqai stalk	Reactive Black 5	52.3	[39]
Aqai stalk (acid treated)	Reactive Black 5	72.3	[39]
Aqai stalk	Reactive Orange 16	61.3	[39]
Aqai stalk (acid treated)	Reactive Orange 16	156	[39]
Peanut hull	Reactive Black 5	55.55	[40]
Bacillus subtilis EPS	Reactive Blue 4	42.93	[41]
Laminaria sp. (acid treated)	Reactive Black 5	101.5	[42]
ABDAC modified *P. coccinea* biomass	Reactive Red 45	152.49[a]	This study

[a] $n = 3$.

the best model for describing the equilibrium biosorption data. This finding would indicate the monolayer coverage of the biosorbent surface by RR45 molecules. The q_{max} value predicted from the Langmuir model ($152.49\,mg\,g^{-1}$) was also in agreement with the experimental q_e value ($148.41\,mg\,g^{-1}$). By comparing the maximum reactive dye biosorption capacities of various biomaterials (Table 3), ABDAC modified *P. coccinea* can be considered as an efficient and alternative biosorbent. On the other hand, the mean free energy value of biosorption ($9.69\,kJ\,mol^{-1}$) implies that chemical ion-exchange biosorption may also play a role in the decolorization process.

3.8. Possible dye–biosorbent interactions and mechanism analysis

The surface area, micro pore volume, average pore diameter and total pore volume of the unmodified *P. coccinea* were found to be $7.10\,m^2\,g^{-1}$, $2.21 \times 10^{-3}\,cm^3\,g^{-1}$, 2.24×10^2 Å and $3.98 \times 10^{-2}\,cm^3\,g^{-1}$, respectively. After the modification, these values decreased to $2.14\,m^2\,g^{-1}$, $6.90 \times 10^{-4}\,cm^3\,g^{-1}$, 1.03×10^2 Å and $5.74 \times 10^{-3}\,cm^3\,g^{-1}$, respectively.

The thermal behavior of the biosorbents was investigated by TG analysis and the thermograms were presented in Fig. 5a. The first mass loss until ~120 °C (6.0% for unmodified and 7.1% for modified biomass) could be attributed to the removing moisture from the biosorbent. In the temperature range between 250 and 360 °C second mass loss and third mass loss is observed between 360 and 550 °C which corresponds to organic matter. Finally, no further mass loss was detected with increasing temperature up to 600 °C. Similar trends were also shown in DTA and DTG curves of the unmodified and modified biosorbents. Increasing peak area of the second peak (related to organics) in DTA curve for the modified biosorbent also indicates the modification of *P. coccinea* biomass with ABDAC.

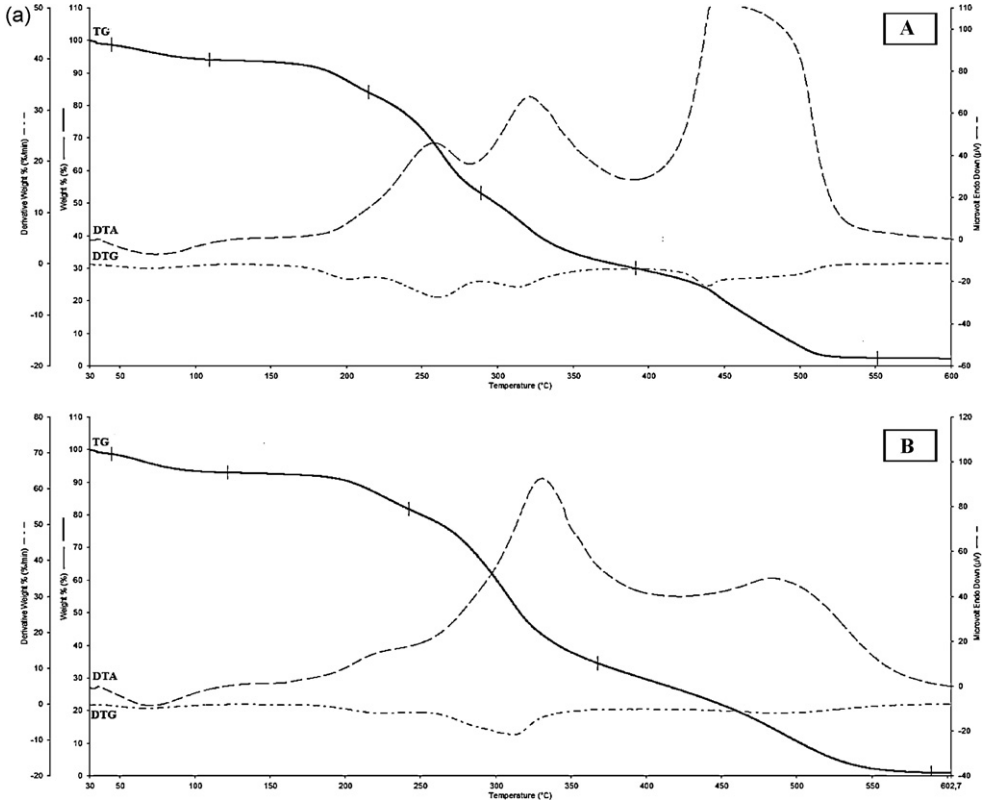

Fig. 5. (a) TG curves of modified biosorbent (A) and dye loaded modified biosorbent (B). (b) SEM micrograph of modified biosorbent (A) and dye loaded modified biosorbent (B). (c) FTIR spectra of modified biosorbent (A) and dye loaded modified biosorbent (B).

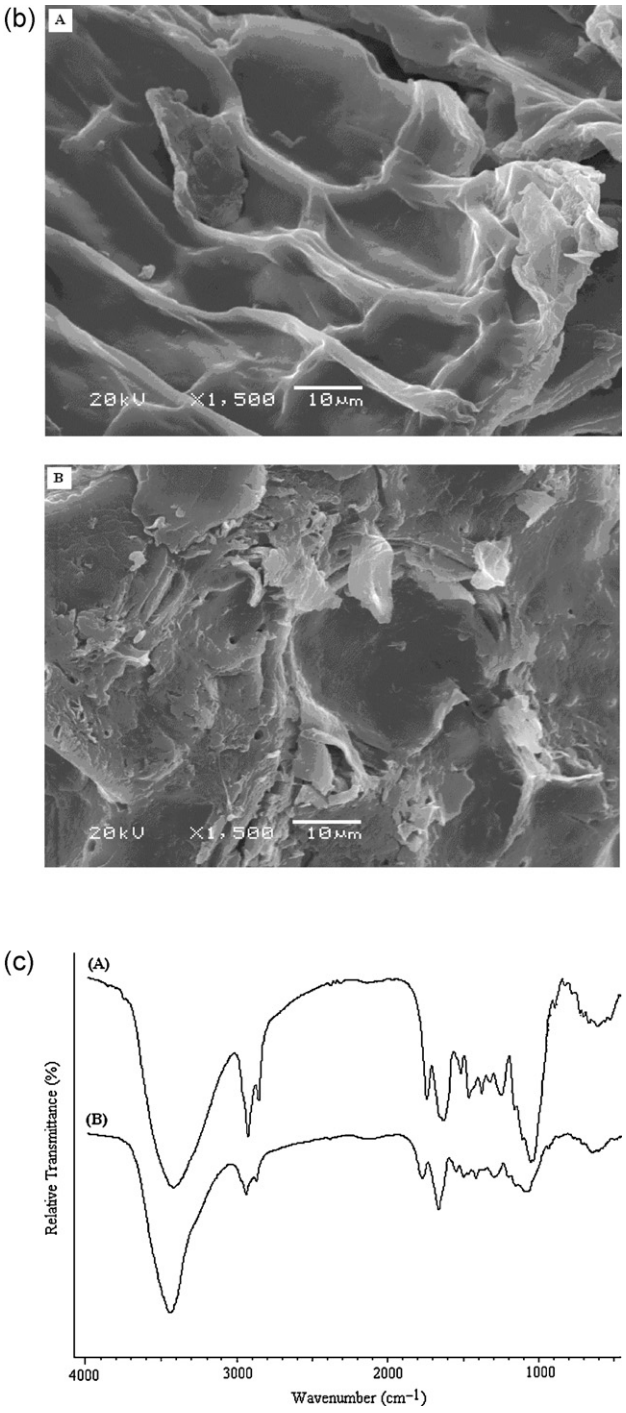

Fig. 5. (*Continued*).

The comparison of the SEM micrographs of ABDAC modified *P. coccinea* before and after decolorization process (Fig. 5b) shows that rough and porous biomass surface (A) was clearly altered and it looked more smooth (B) as a result of dye localization.

The FTIR spectra of modified and dye loaded modified biomass are presented in Fig. 5c. The significant band positions for the natural *P. coccinea* biomass are noted as 3415, 2926, 2856, 1739, 1621, 1516 cm^{-1} and between 1421 and 587 cm^{-1} [17]. The intensities of the peaks at 2925 and 2854 cm^{-1} on the FTIR spectrum of modified biomass, ascribed to CH stretching vibrations of $-CH_2$ and $-CH_3$ groups were stronger than that of the natural biomass. The spectrum of modified biomass (A) also displayed new peaks at about 1160 cm^{-1} may be ascribed to C—N stretching vibrations [43] and at 1377 cm^{-1} ascribed to $-CH_3$, $-CH_2$ bending vibrations. These observations may be explained by the introduction of C—N, CH_3 and CH_2 groups to the biomass surface following modification process. Besides the bands at 3415 cm^{-1} (indicative of —OH, —NH groups), 1621 cm^{-1} (indicative of chelate stretching of amide I), and 1078 cm^{-1} (indicative of organic phosphate groups) shifted to 3421, 1633 and 1054 cm^{-1}, respectively after surfactant modification. The intensity of the last peak also decreased. The new peak at 1107 cm^{-1} on the spectrum of modified biomass can be assigned to C—O stretching vibration of carboxylic acid and alcohols [44].

The FTIR spectroscopic analysis of modified biomass exposed to dye (B), indicated an intensity decrease of the bands at 1741 cm^{-1} (indicative of C=O groups) and 1516 cm^{-1} (indicative of amid II group). The intensity of the band at 1245 cm^{-1} in the spectrum of modified biomass significantly reduced and shifted to 1261 cm^{-1} (indicative of $-SO_3$ group) after the dye biosorption process. Finally, it is also noted that phosphate band at 1053 cm^{-1} in the FTIR spectrum of the modified biomass disappeared after biosorption. These observations show possibly involvement of these functional groups on the modified sorbent surface in dye removal process.

4. Conclusion

The surfactant-modified biomass of *P. coccinea* was used as biosorbent for decolorization of RR45 containing solutions. Modification of the biomass surface by ABDAC greatly improved the dye-loading yield of the biosorbent. The decolorization process follows Langmuir isotherm model with the high monolayer biosorption capacity. Kinetic study showed that the pseudo-first-order model well described the process. The good biosorption yields were recorded by the suggested biosorbent in the salt containing medium and at real wastewater conditions. The rapid biosorption was observed within the 15 min and temperature did not produce any significant effect in the process. Mechanism studies revealed that a combined action of the different functional groups of the biosorbent played a role in the dye removal process. In conclusion, the suggested biosorbent may be a good alternative to existing costly dye sorbents with the advantages of high biosorption capacity, fast biosorption property and large availability of the used biomass.

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