RESEARCH ARTICLE

Multivariate optimization of the decolorization process by surface modified biomaterial: Box–Behnken design and mechanism analysis

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Abstract A natural biosorbent obtained from *Pyracantha coccinea* was modified with an anionic surfactant to facilitate its dye removal ability. Modified biosorbent was successfully employed for the decolorization of Methyl Violet (MV)-contaminated solutions. A three-variable Box–Behnken design for response surface methodology was used to examine the function of independent operating variables. Optimum pH and biosorbent amount were found to be 6.0 and 0.055 g, respectively. The effects of temperature and ionic strength on the dye removal performance of biosorbent were also investigated. A biosorption equilibrium was attained within 30 min and experimental data fitted well to the pseudo-second-order model. The Langmuir isotherm model fitted adequately to the equilibrium data. The maximum monolayer biosorption capacity of the modified biosorbent was found to be 254.88 mg g^{-1}. Good biosorption yields were also recorded in continuous biosorption system. Ion exchange and complexation could be suggested as possible mechanisms for the biosorption. The developed modified biosorbent was regenerated up to 80.30 % by 0.005 M HCl. At real wastewater conditions, it has 86.23±0.21 and 94.51±1.09 % dye removal yields in batch and column systems, respectively. Modified biomaterial can be used as an effective biosorbent for the removal of MV dye from aqueous solution with high biosorption performance.

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Introduction

Synthetic dyes are recalcitrant organic compounds and they often contaminate water resources as a result of their widespread use in textile and other industries. The treatments and disposal of colored effluents have been of great concern because of the toxic and carcinogenic effects of dye compounds. Colored effluents released into environment without adequate treatment not only produce visual pollution but also are hazardous to living sytems (Crini 2008; Wang et al. 2008).

Some technical and economic constraints in the application of the traditional decolorization methods have directed attention to the search for new alternative technologies in this field. Biosorption is a promising and attractive technology that utilizes the sorption potential of different biomasses to clean up the aquatic environment. This method bases on the interactions between pollutant and the biosorbent surface (Akar and Divriklioglu 2010). Generally, different types of biomaterials such as some polysaccharides (Barron-Zambrano et al. 2010), fungi (Akar et al. 2009b; Aksu et al. 2008; Fan et al. 2012; Yeddou-Mezenner 2010), bacteria (Mona et al. 2011; Walker and Weatherley 2000), algae (Aravindhan et al. 2007; Daneshvar et al. 2012a), yeast (Farah et al. 2007), and agricultural wastes (Ahmaruzzaman and Gupta 2011; Aksu and Isoglu 2007; Allen et al. 2005; Özcan et al. 2007; Tunali et al. 2007) showed good binding potential for various dyes and have been widely used in the field of environmental biotechnology.

In recent years, some attempts have been made to improve the dye biosorption characteristics of biomasses by applying different chemical modification procedures. Methanol-, formaldehyde-, and formic acid-treated *Aspergillus wentii*

(Khambhaty et al. 2012), acetonitrile- and acetic acid-treated *Citrus* waste (Asgher and Bhatti 2012), succinted *Corynebacterium glutamicum* (Vijayaraghavan et al. 2008b), potassium hydroxide-treated *Cupressus sempervirens* (Fernandez et al. 2012), and hydrochloric acid-treated *Saccharomyces cerevisiae* (Pratibha et al. 2010) are some examples of chemically modified biomaterials for decolorization purpose. In the literature, good metal removal performances were also reported for the surfactant-modified biomasses (Bingol et al. 2009; Loukidou et al. 2003). Hovewer, to our knowledge, there is a limited information on enhancing the decolorization potential of biomaterials by surfactant modification (Akar and Divriklioglu 2010; Kwon et al. 2008; Oei et al. 2009).

Response surface methodology (RSM) is a combination of mathematical and statistical techniques for empirical model building. The aim of this methodology is to optimize response (dependent) variable which is affected by various independent variables (factors). Furthermore, the usage of RSM has reduced the cost of expensive analysis methods. RSM was developed to model numerical experiments and experimental responses. Moreover, RSM is an empirical modeling technique which takes into account the relationships of a group of controlled experimental variables (factors) and observed results (response) (Kiran et al. 2007; Montgomery 2005; Nermeen and El-Sersy 2007; Sharma et al. 2009).

The goal of this study was to explore the potential use of sodium dodecyl sulfate (SDS)-modified *Pyracantha coccinea* biomass for decolorization of Methyl Violet (MV)-contaminated solutions. *P. coccinea* was chosen as biosorbent source because of its known cationic dye binding ability in its natural form (Akar et al. 2009a). On the other hand, increasing performance of the biosorbent by easily modification procedure can be considered as an imporant advantage for the application progress of *P. coccinea*. Decolorization conditions were investigated in both batch and continuous modes. pH, biosorbent dosage, and contact time were optimized to determine the single and interactive effects of the variables on response (dye removal yield, %). Isotherm and kinetic models were used to analyze the experimental data. Sorbent was characterized by some instrumental methods and biosorption mechanism was investigated. The proposed biomaterial was also applied to the real wastewater sample in addition to the evaluation of regeneration potential of biosorbent.

Materials and methods

Biosorbent modification and solutions

The mature berries of *P. coccinea* used as biomass were collected from a number of plants. The material was washed with distilled water several times and dried in an oven at 70 °C for 24 h. The dried biomass was grounded using a laboratory mill (IKA A11) and sieved to select the particle size of less than 212 μm. Four grams of powdered raw biomass sample was suspended in 100 mL of 0.1 mol L^{-1} SDS solution and stirred at 200 rpm overnight. The resulted biosorbent was separated from SDS solution by filtration and washed with deionized water thoroughly until free from sulfate ions. It was dried again as mentioned above.

MV (Merck, 100 % purity) (chemical formula, $C_{24}H_{28}ClN_3$; maximum wavelength, 580 nm) was chosen as model cationic dye in this study. The stock solutions of dye (1.0 g L^{-1}) were prepared by dissolving an appropriate amount of MV in deionized water. Other desired concentrations were obtained by diluting this stock solution. Fresh dilutions were used in each biosorption experiment. The initial pH adjustment of working solutions was made with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH and measurements were carried out by a pH meter (Hanna 221).

Biosorption experiments

Batch mode studies were performed by mixing an accurate weight of biosorbent sample with 25 mL of dye solution at desired concentration. These mixtures were agitated using a multipoint magnetic stirrer at 200 rpm. At the end of the each experiment, the biosorbent was separated from the mixture by centrifugation at 3,000 rpm for 3 min and the concentration of the residual dye in the supernatant liquid was analyzed by using Shimadzu UV−2550 spectrophotometer. Dynamic flow mode studies were performed in cylindrical glass columns with 11 mm internal diameter (i.d.). Biomass was packed between two glass wool filters in the column. Dye solutions were pumped out with the help of a peristaltic pump (Ismatec ecoline). Tygon tubing was used for the connection between pump and columns. Eluent was collected from the bottom of the column and analyzed for its MV concentration.

Characterization studies

The BET surface area, total pore volume, average pore size, and micro pore volume of the biosorbents were determined from N_2 adsorption isotherm with a surface area and pore size analyzer (Quantachrome Instruments, Autosorb 1).

The surface charges of the biosorbent material at the different pH values were examined by zeta potential analyzer (Malvern zeta sizer).

IR spectra were recorded using Bruker Tensor 27 spectro-photometer in the wavenumber range of 400–4,000 cm^{-1} via KBr pressed-disc technique.

The surface microstructure of the biomaterial was characterized by a scanning electron microscope (SEM) using JEOL 560 LV SEM at 20 kV acceleration voltage and ×1,500 image magnification. Prior to analysis, biomaterial was sputter coated in a Polaron SC-7620 Sputter Coater using a gold–palladium target to improve electron conductivity and image quality.

RSM and statistical analysis

RSM is an empirical modeling technique which takes into account the relationship of a set of controlled experimental variables (factors) and observed results (response). To optimize a system with response variable Y which depends on the factor variables (X_1, X_2,…X_n), the relationship between the response and factor variables is defined as follows:

$$Y = f(X_1, X_2, …X_n) + \varepsilon \qquad (1)$$

where f is a response function and ε is errors. The analysis of these relationships between response and factor variables can be identified as a surface of the X_1, X_2,…X_n coordinates graphical approach (Nermeen and El-Sersy 2007; Sharma et al. 2009).

In this study, the experiments were fulfilled according to the Box–Behnken design which is a type of RSM. The number of experiments required for Box–Behnken experiment design can be obtained as follows (Pouralinazar et al. 2012):

$$N = 2k \times (k-1) + \mathrm{cp}, \qquad (2)$$

where k is the factor number (independent numerical variables) and cp is the replicate number of the central point. Experimental design was carried out using Design-Expert Software version 8.0. A system with three independent variables (factors) (X_1, X_2, X_3) and the response variable (Y) can be represented by a quadratic equation;

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 \qquad (3)$$
$$+ \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2$$

where Y is the response variable (biosorption of MV).

X_1, X_2, and X_3 are the levels of factor variables (mainly pH (3.0, 6.0, and 9.0), biosorbent amount (0.01, 0.055, and 0.10 g), and contact time (5, 32.5, and 60 min) and identified in Table 1; β_0 is the regression coefficient at the center point; β_1, β_2 and β_3 are linear coefficients; and β_{12}, β_{13} and β_{23} are quadratic coefficients. The fitting of the quadratic model was determined by the coefficient of determination, R^2.

Results and discussion

Effect of modification

Preliminary experiments showed that the modification of *P. coccinea* by SDS significantly enhanced the dye removal potential of the biosorbent. In order to systematically compare the biosorption yields of natural and modified biosorbents, the biosorption studies were carried out at different biosorbent dosages. The biosorption yield of the natural biosorbent increased from 33.34±2.95 to 91.30±0.06 % when the biosorbent dosage was changed from 0.4 to 5.0 g L^{-1} ($p < 0.05$). On the other hand, the biosorption yield of the SDS-modified biosorbent reached to 97.22±0.16 % with the biosorbent dosage of 2.40 g L^{-1}. These results clearly indicated that the SDS-modified *P. coccinea* exhibited higher biosorption yield than the natural one with a smaller amount of biosorbent.

Modeling of MV biosorption

The Model F value of 8.45 (Prob. <0.05) implies that the model is statistically significant at the 0.05 level. Furthermore, the coefficients of X_1, X_3, $X_1 X_3$, and X_1^2 are statistically significant model terms at the 0.05 level also. Probability values greater than 0.10 indicate that the model coefficients are not statistically significant. The quadratic regression model estimated is presented as follows:

$$MV\,Removal(\%) = 92.65 + 12.51X_1 + 3.91X_2 + 17.07X_3 \qquad (4)$$
$$- 0.81X_1 X_2 - 10.73X_1 X_3 - 0.36X_2 X_3$$
$$- 13.94X_1^2 + 2.08X_2^2 - 9.71X_3^2$$

The design matrix and the responses are given in Table 2 and an empirical relationship between the factor variables and the response variable in coded units was expressed by model in Eq. (4). This quadratic model was also used to obtain predicted values of removal efficiency of MV given in Table 2. The results of analysis of variance (ANOVA) for removal efficiency of MV are displayed in Table 3.

Interactive effects of operating parameters on the removal of MV

The contour plot of Fig. 1a indicates the interaction effects of pH and contact time on the response. Time–dependent experiments were carried out at a constant temperature of 25 °C. The biosorption yield of the biosorbent increased with an

Table 1 Levels of variables in Box–Behnken experimental design

		Variable levels			
Variables	Symbol	Low (−1)	Center (0)	High(+1)	∇x_i
pH	x_1	3	6	9	3
Time (min)	x_2	5	32.5	60	27.5
Biosorbent amount (g)	x_3	0.01	0.055	0.1	0.045

increase in the pH and contact time. Figure 1a indicated a fast rate of MV biosorption in the initial stage of the contact and this may be attributed to an increase in the number of vacant binding sites on the biosorbent surface (Saha et al. 2012). This was followed by a longer period of much slower dye uptake due to decreasing available sites. Finally, an equilibrium was attained within 30 min and the biosorption capacity of the modified biosorbent did not further change with the contact time.

The initial pH of the biosorption medium is one of the important parameters which affect the biosorption performance of the modified biosorbent. At acidic conditions, the number of negatively charged biosorbent sites decreased due to the protonation of the biosorbent surface. Hence, the electrostatic repulsion forces between positively charged dye cations and biosorbent surface predominate and a competition for the binding to the active sites of the biosorbent between hydronium ions and dye cations takes place (Senturk et al. 2010). On the other hand as the pH increased, the surface of the biosorbent was more negatively charged probably due to the deprotonation of the functional groups on the biosorbent

(Tian et al. 2010). Thus, MV biosorption yield of the modified biosorbent increased up to pH 6.0 and then nearly remained constant. Zeta potentials at different pH values given in Fig. 2 showed the similar trend for the surface charge of the modified biosorbent. SDS-modified *P. coccinea* negatively charged at the pH range of 3.0 to 9.0. At pH 3.0, the modified biosorbent has the lowest negative charge (−13.00±0.46 mV). As pH increases, negative charge on the biosorbent surface continues to increase. This finding indicated that the electrostatic interaction is not the only mechanism but also the chemisorption might be involved in MV biosorption (Tian et al. 2010).

The combined effect of pH and biosorbent dosage on the biosorption of MV onto SDS-modified *P. coccinea* is presented in contour plot of Fig. 1b. According to this figure, pH and biomass amount significantly affect the biosorption performance of the modified biosorbent. The biosorption yield of SDS-modified *P. coccinea* increased by simultaneous increase in the initial pH and biosorbent dosage. An increase in the biosorption yield with biosorbent dosage may be attributed to the increased surface area of the biosorbent and availability of possible biosorption sites (Aksu and Çağatay 2006). The

Table 2 Box–Behnken design matrix of three factors along with experimental and predicted % biosorption yield of MV

Runs	Coded level of variables			Actual level of variables			MV biosorption yield (%)		
	X_1	X_2	X_3	X_1	X_2	X_3	Observed	Predicted	Residual
1	1	−1	0	9.00	5.00	0.06	88.01	90.2	−2.19
2	0	0	0	6.00	32.50	0.06	92.63	92.65	−0.02
3	0	0	0	6.00	32.50	0.06	92.53	92.65	−0.12
4	0	−1	−1	6.00	5.00	0.01	71.98	63.68	8.3
5	1	0	−1	9.00	32.50	0.01	69.07	75.18	−6.11
6	−1	−1	0	3.00	5.00	0.06	64.63	63.57	1.06
7	0	−1	1	6.00	5.00	0.10	91.38	98.54	−7.16
8	1	0	1	9.00	32.50	0.10	97.21	87.86	9.35
9	0	0	0	6.00	32.50	0.06	92.7	92.65	0.05
10	−1	0	−1	3.00	32.50	0.01	19.34	28.69	−9.35
11	1	1	0	9.00	60.00	0.06	95.36	96.42	−1.06
12	−1	1	0	3.00	60.00	0.06	75.2	73.01	2.19
13	0	0	0	6.00	32.50	0.06	92.75	92.65	0.1
14	0	1	1	6.00	60.00	0.10	97.36	105.66	−8.3
15	0	0	0	6.00	32.50	0.06	92.65	92.65	0
16	0	1	−1	6.00	60.00	0.01	79.39	72.23	7.16
17	−1	0	1	3.00	32.50	0.10	90.41	84.3	6.11

Table 3 Analysis of variance (ANOVA) for the biosorption of MV onto SDS modified-*P. coccinea*

Variation source	Coefficients	Sum of squares	df	Mean square	F value	p value Prob>F
Intercept	92.65					
x_1	12.51	1,251.75	1	1,251.75	17.46	0.0041
x_2	3.91	122.54	1	122.54	1.71	0.2323
x_3	17.07	2,331.76	1	2,331.76	32.53	0.0007
$x_1 x_2$	−0.81	2.59	1	2.59	0.036	0.8546
$x_1 x_3$	−10.73	460.75	1	460.75	6.43	0.0389
$x_2 x_3$	−0.36	0.51	1	0.51	0.007133	0.9351
x_1^2	−13.94	817.74	1	817.74	11.41	0.0118
x_2^2	2.08	18.29	1	18.29	0.26	0.6290
x_3^2	−9.71	396.86	1	396.86	5.54	0.0509
Model		5,450.52	9	605.61	8.45	0.0051
Residual		501.71	7	71.67		

$R^2 = 0.9157$
Adj. $R^2 = 0.8073$

constant performance of the biosorbent at higher biomass concentrations could be explained by the binding of almost all dye molecules to the biosorbent surface and the establishment of an equilibrium between the dye molecules on the biosorbent and in the solution (Tunali Akar et al. 2011).

Figure 1c shows the contour plot of interactive effects of contact time and biosorbent dosage. According to this figure, the removal efficiency significantly increased with increasing biosorbent amount and slightly increased with contact time.

Optimization of operating parameters by RSM

Optimum operating parameters were found to maximize the biosorption of MV from quadratic model equations. Two variables (X_2 and X_3) were selected at the lowest level based on practicality and economic viability for the maximum dye biosorption. Thus, the optimum values for initial pH (X_1), biosorbent amount (X_2), and contact time (X_3) in this study were found to be 6.0, 0.055 g, and 30 min, respectively. The maximum MV removal yield was found as 94.09 % at these optimized conditions. The obtained desirability value of 0.958 indicated that the estimated function may represent the experimental model and desired conditions.

Goodness of fit of the model in Eq. (4) was also presented by comparing predicted values with observed values, and the relationship was plotted in Fig. 3. This figure shows that the quadratical regression model is best-fit model for removal efficiency of MV, since the predicted values are quite close to observed values. Determination coefficient (R^2) of a model identifies the amount of variation in the observed response variable arising from factor variables in model. In this case, the value of determination coefficient ($R^2 = 0.9157$) of Eq.(4)

presents that the quadratic regression model is fitting model for predicting removal efficiency of MV biosorption. In addition, the value of adjusted ($R^2 = 0.8073$) which takes into consider the number of independent variables incorporated in the model points out that 80.73 % of total variations are explained by the model presented in Eq. (4).

Effect of ionic strength

The effect of ionic strength on the biosorption yield of SDS-modified biosorbent was investigated in the presence of increasing concentrations of KCl in the biosorption medium (Fig. 4). The biosorption yield of MV decreased from 94.64±0.28 to 89.86±0.27 % ($p<0.05$) when the ionic strength of the medium was adjusted to 0.08 mol L^{-1}. The biosorption yield did not change with the further increase in the ionic strength of the dye solution ($p>0.05$). This decreasing trend (~4.8 %) in the biosorption performance of the modified biosorbent may be explained by the competition between potassium ions and positively charged dye molecules for the same binding sites of the biosorbent material. The adverse effect of ionic strength on the dye biosorption process indicated that the biosorption of MV onto SDS-modified biosorbent was ionic strength-dependent. This behavior may also be attributed to a cation-exchange mechanism for MV biosorption as reported by Nanseu-Nanseu-Njiki et al. (2010), Kaushik and Malik (2009).

Effect of temperature

MV biosorption process onto SDS-modified biosorbent was studied while the reaction temperature was fixed at different temperatures. The biosorption capacities of the modified
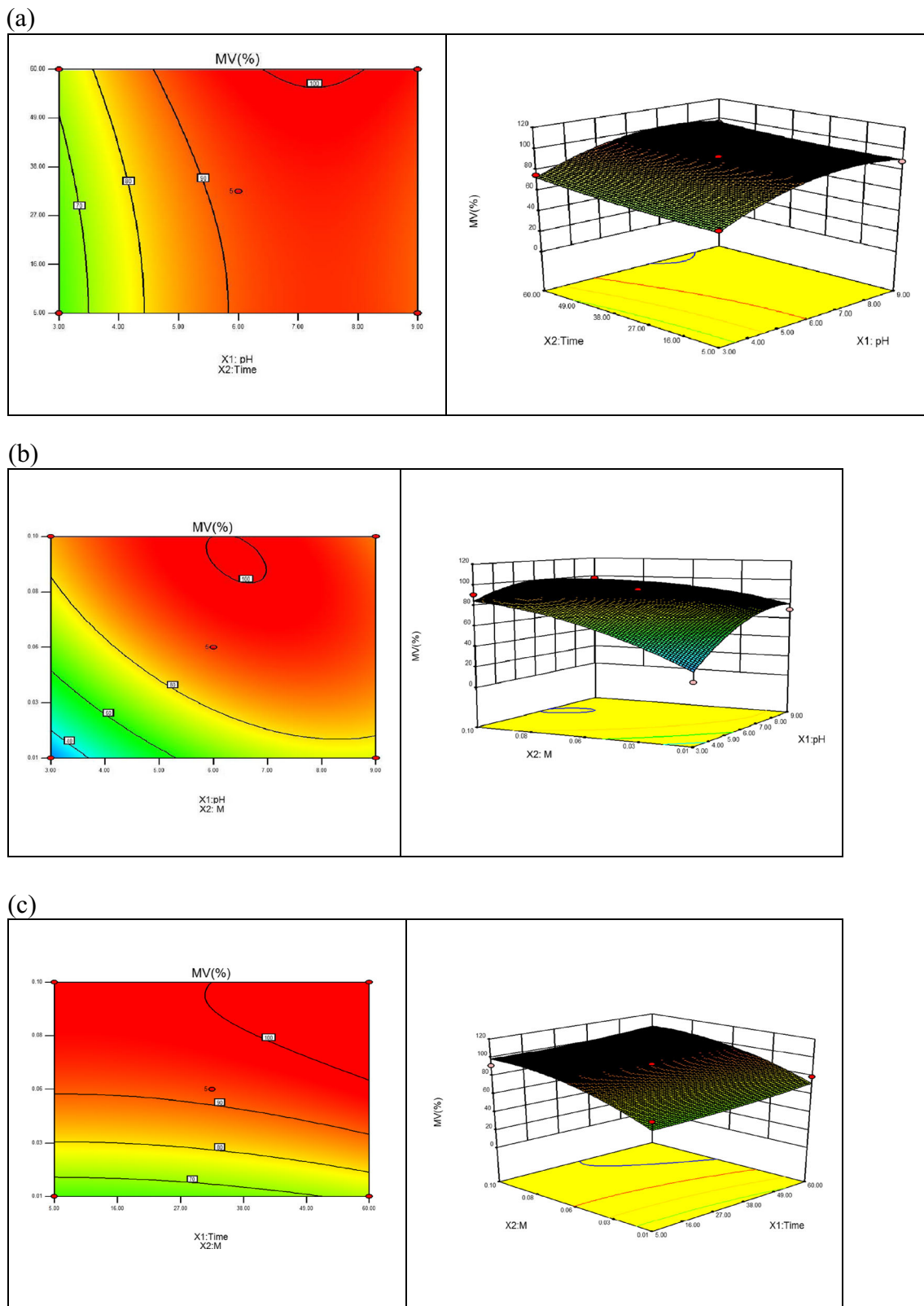
(a)

(b)

(c)

Fig. 1 Contour and 3-D surface plots for the interactive effects of pH and contact time (**a**), pH and biosorbent dosage (**b**), and biosorbent dosage and contact time (**c**) on MV biosorption yield of SDS modified-*P. coccinea*

biosorbent were obtained as 36.31, 36.96, and 37.02 mg g^{-1} at 15, 30, and 45 °C, respectively. As shown from these results, temperature did not significantly affect the biosorption performance of the modified biosorbent ($p > 0.05$). Temperature-
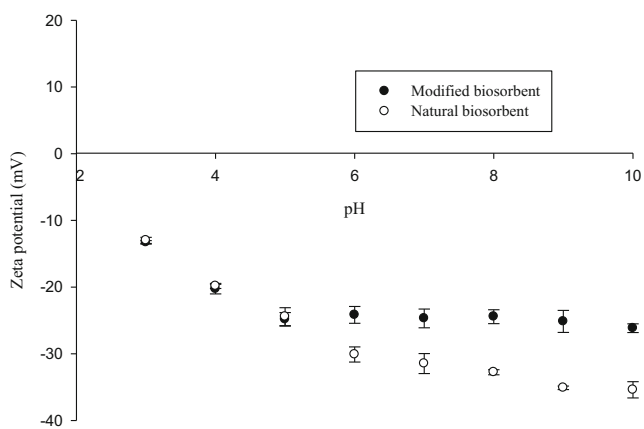
Fig. 2 Zeta potential values of the natural and SDS modified-*P. coccinea* at different pH values

Fig. 4 Effect of ionic strength on the biosorption of MV onto SDS modified-*P. coccinea*

independent biosorption of MV may be explained by the biosorbent structure, diffusion of the dye molecules, and dye–biosorbent interactions. The pore sizes of the biosorbent could not be enlarged with an increase in the temperature from 15 to 45 °C and diffusion and penetration rate of dye molecules into these pores could not changed (Saleem et al. 2005).

Biosorption kinetics

The pseudo-first-order (Lagergren 1989) and the pseudo-second-order (Ho 2006) kinetic models and the intraparticle diffusion model (Weber and Morriss 1963) were tested to investigate the biosorption kinetics for the biosorption of MV onto SDS-modified *P. coccinea*. The linear equations of these models are given in the Appendix. Fitting curves were not shown for the kinetic models. Equilibrium biosorption capacities and rate constants for these models along with their respective R^2 values are listed in Table 4. These parameters
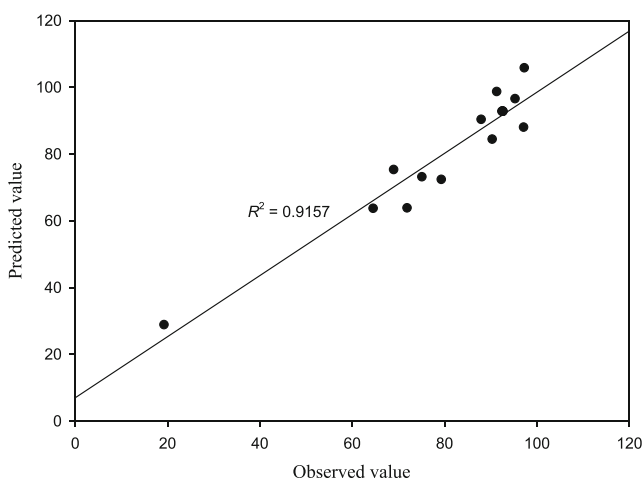

Fig. 3 The predicted values versus observed experimental values for MV biosorption onto SDS modified-*P. coccinea*
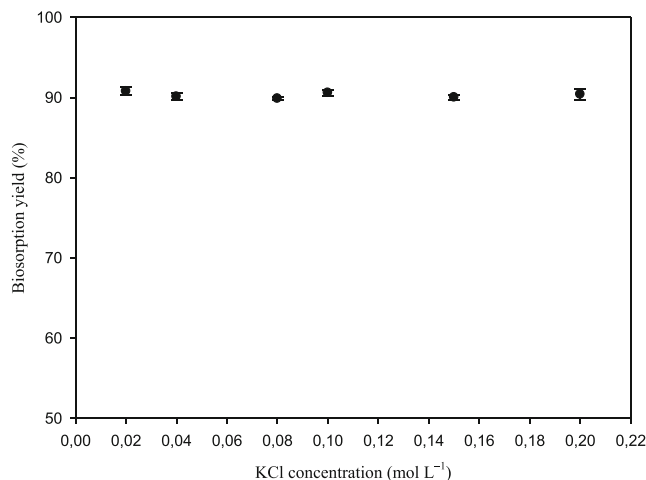
were estimated by linear fitting of time-dependent data obtained at room temperature. R^2 values of the pseudo-first-order model are reasonably low and the calculated q_e values obtained from this kinetic model do not give reasonable values. Therefore, it can be suggested that MV biosorption process was not a first-order reaction. On the other hand, the determination coefficient for the pseudo-second-order kinetic model was 0.999 and the theoretical values of q_e also agreed well with the experimental data. Therefore, the pseudo-second-order rate equation suitably interpreted the overall process for MV biosorption onto modified biosorbent. This indicated that the chemisorption was the rate-limiting step (Bhatnagar et al. 2010) for the biosorption of MV onto SDS-modified *P. coccinea*.

Since these two models above cannot identify the diffusion mechanism during the biosorption process, the data are also evaluated by the intraparticle diffusion model. The slightly lower R^2 value for this model indicated that the biosorption of MV onto SDS-modified *P. coccinea* may be followed by the intraparticle diffusion model. A boundary layer resistance between biosorbent and sorbate may occur since the linear plot of this model did not pass through the origin (Liu et al. 2012).

Biosorption isotherms

In order to estimate the maximum biosorption capacity and affinity of the SDS-modified biosorbent towards MV molecules, three isotherm models, specifically the Langmuir (Langmuir 1918), Freundlich (Freundlich 1906), and Dubinin–Radushkevich (Dubinin and Radushkevich 1947) were applied to equilibrium data. The linear isotherm equations for these models are presented in the Appendix. Langmuir, Freundlich, and D−R isotherm plots for the biosorption of MV onto modified biosorbent are included in

Table 4 Kinetic parameters for the biosorption of MV onto modified *P. coccinea*

Pseudo-first-order			Pseudo-second-order				Intraparticle diffusion		
k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	h (mg g^{-1} min^{-1})	R^2	k_p (mg g^{-1} min$^{-1/2}$)	C (mg g^{-1})	R^2
9.26×10^{-3}	1.83	0.468	3.68×10^{-2}	37.40	51.47	0.999	0.94	31.54	0.885

Fig. 5 Calculated isotherm constants and the corresponding coefficient of determination (R^2) values for these models are also listed in Table 5. By considering the R^2 values and biosorption models applied in this study, it can be concluded that the equilibrium biosorption data were well represented by Langmuir isotherm model. This further evidenced the mono-layer coverage of MV molecules onto the homogeneous surface of SDS-modified *P. coccinea* with maximum monolayer biosorption capacity of 6.47×10^{-4} mol g^{-1} (254.88 mg g^{-1}). According to Langmuir theory, an interaction between two dye molecules is also negligible (Ofomaja and Ho 2008) and biosorbed layer on the biosorbent surface is unimolecular (Anjaneya et al. 2009). The essential characteristics of the Langmuir isotherm were expressed in terms of a dimension-less constant, R_L (Eq. 11). The value of R_L indicates whether the type of isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Hall et al. 1966). Since R_L value in this study is 3.81×10^{-2}, the biosorption of MV onto modified biosorbent is favorable. The Freundlich isotherm is purely empirical based on the biosorption on a heterogeneous surface with a nonuniform distribution of biosorption heat over the surface (Belala et al. 2011). R^2 value (0.908) of Freundlich model was lower than that of Langmuir model. Since n value which is measure of the deviation from linearity of the biosorption was found to be higher than 1, the biosorption system is favorable (Farah et al. 2007). The equilibrium data in this study were also fitted by (D–R) isotherm model. The mean free energy of biosorption (E) was calculated as 15.28 kJ mol^{-1}. This value indicated that MV was likely to be removed via chemical ion-exchange mechanism (Daneshvar et al. 2012b). Table 6 compares the maximum monolayer sorp-tion capacities of some sorbent materials for MV. This table shows that the SDS-modified *P. coccinea* studied in this work exhibited biosorption capacity generally higher than most of the reported sorbents (Table 6).

Column studies

Effect of flow rate

Flow rate is an important parameter for evaluating biosorbents for the treatment of dye containing effluents in column sys-tems. The flow rate in this study was varied from 0.4 to

6.0 mL min^{-1} while the biosorbent amount and initial dye concentration were maintained at 0.06 g and 100 mg L^{-1}, respectively. The results in Fig. 6a showed that the biosorption of MV onto modified biosorbent increased from 95.11 ± 0.28 to 99.95 ± 0.09 % when the flow rate was decreased from 6.0 to 1.3 mL min^{-1} ($p < 0.05$). This trend may be attributed to reducing contact time between solution and biosorbent with an increase in the flow rate (Aksu et al. 2007). At lower flow rate of influent, dye solution had more time to contact with modified biosorbent and this resulted in higher removal of MV in the column. After this point, the biosorption performance of the modified biosorbent did not change with a decrease in the flow rate ($p > 0.05$). Therefore, 1.3 mL min^{-1} was selected as optimum flow rate in this study in order to complete the biosorption process in a short time.

Effect of column i.d.

In order to optimize the column size, column i.d. was changed from 9 to 19 mm when the MV concentration, column height, biosorbent amount, and flow rate were kept constant at 100 mg L^{-1}, 100 mm, 0.06 g, and 1.3 mL min^{-1}, respectively. The results are plotted in Fig. 6b. The biosorption yield of the modified biosorbent slightly decreased when the i.d. of the column was changed from 9 to 13 mm ($p < 0.05$). The biosorption performance of the modified biosorbent did not change with further increase in the column i.d. ($p > 0.05$). When the column i.d. was decreased, the bed height increased due to the constant amount of loading biomass into the col-umn. This resulted in more contact time for the interaction of dye and biosorbent in the column. Hence, higher removal efficiency for MV in column was observed in 9 and 11 mm i.d. of column. Further biosorption experiments were carried out using column with 11 mm i.d. from the practical point of view.

Effect of biosorbent amount

The effect of biosorbent amount on the biosorption of MV onto SDS-modified *P. coccinea* was also investigated in con-tinuous mode and the results are illustrated in Fig. 6c. The amount of the modified biosorbent was changed from 0.01 to 0.06 g. The biosorption yield of the modified biosorbent

Fig. 5 Langmuir (**a**), Freundlich (**b**), and D-R (**c**) isotherm plots for the biosorption of MV onto SDS modified-*P. coccinea*
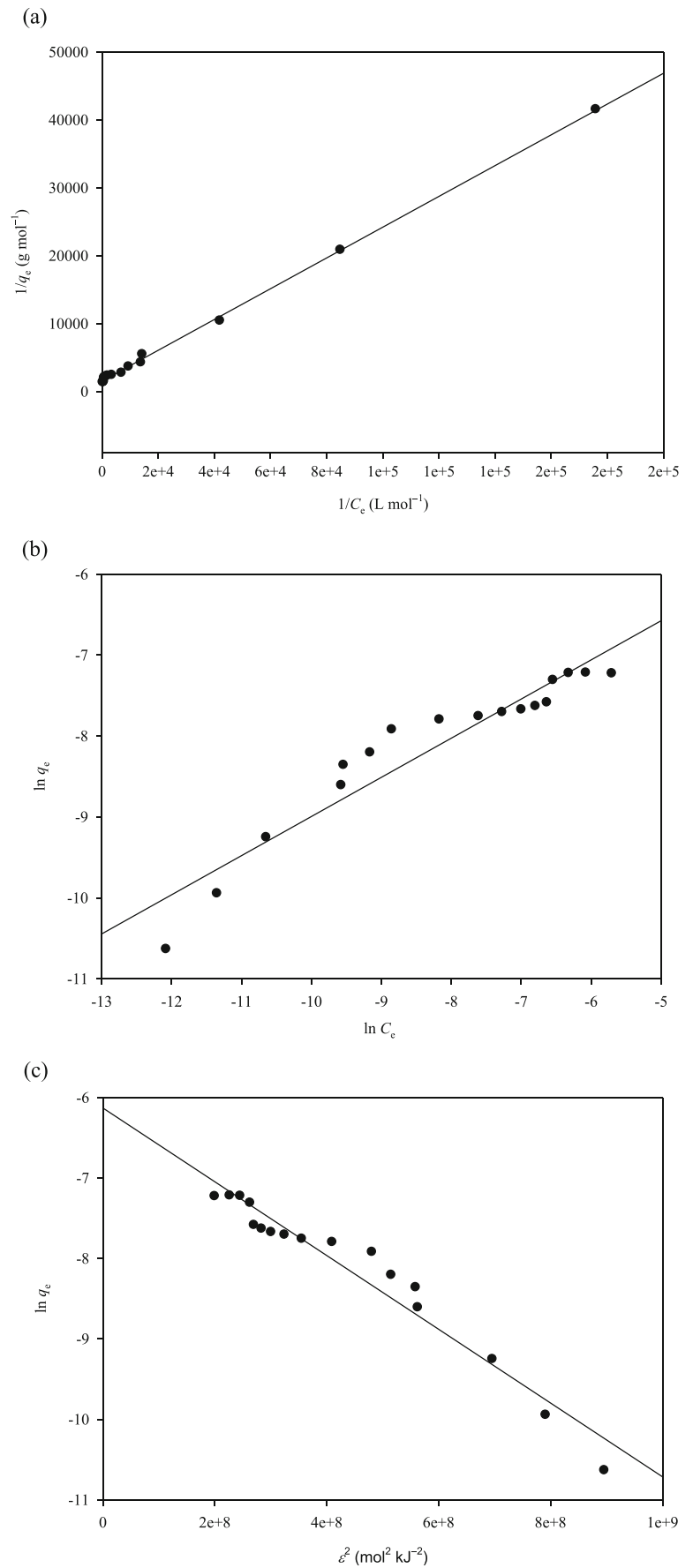
(a)

(b)

(c)

Table 5 Isotherm model parameters for the biosorption of MV onto modified *P. coccinea*

Langmuir				Freundlich			Dubinin–Radushkevich (D–R)			
q_{max} (mol g^{-1})	K_L (L mol^{-1})	r_L^2	R^2	n	K_F (L g^{-1})	R^2	q_m (mol g^{-1})	β (mol^2 kJ^{-2})	R^2	E (kJ mol^{-1})
6.47×10^{-4}	6.82×10^4	3.81×10^{-2}	0.999	2.07	1.56×10^{-2}	0.908	2.18×10^{-3}	2.14×10^{-3}	0.950	15.28

increased from 63.74±1.74 to 99.98±0.02 % with an increase in the amount of biomass from 0.01 to 0.04 g ($p<0.05$). This may be due to an increase in the surface area of the biosorbent as a result of higher bed heights with increasing amount of the biosorbent (Han et al. 2007). After definite biosorbent amount (0.04 g), the biosorption performance of the modified biosorbent did not change ($p>0.05$) due to the saturation of the biosorbent surface with MV molecules. Therefore, 0.04 g was selected as the most efficient amount of the modified biosorbent for further column studies.

Desorption studies

Desorption studies are important to make the biosorption process attractive and to evaluate the recycling property of the spent biosorbent (Kumar and Ahmad 2011). Selection of an appropriate reagent for desorption is an important subject and depends on the biosorbent structure and biosorption mechanism (Vijayaraghavan et al. 2008a). Acidic pH conditions will be necessary to remove binding MV from the biosorbent due to occurring maximum biosorption at basic pH values. Therefore, acetic acid, hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and sulfuric acid (H_2SO_4) were tested for the regeneration of MV from SDS-modified biosorbent. Desorption yields of various reagents for MV are represented in Fig. 6d. As seen from this figure, H_2SO_4 and 5.0×10^{-2} mol L^{-1} HCl did not show any desorption due to the decomposition of dye structure at

strongly acidic conditions (pH <2.0). AcOH (5.0×10^{-2} mol L^{-1}) removed MV only by 27.60 % from modified biosorbent while it was desorbed by H_3PO_4 (5.0×10^{-2} and 5.0×10^{-3} mol L^{-1}) with 58.75 and 67.40 % yield, respectively. HCl was tested at varying concentrations from 2.5×10^{-3} mol L^{-1} to 5.0×10^{-2} mol L^{-1}. The maximum desorption performance was obtained as 80.30 % with 5.0×10^{-3} mol L^{-1} of HCl. Inefficient desorption in AcOH, H_3PO_4, and 2.5×10^{-3} mol L^{-1} HCl may be attributed to the chemisorption mechanism for the binding of MV onto SDS-modified *P. coccinea* (Vijayaraghavan et al. 2008a).

Real sample application

In order to test the performance of SDS-modified *P. coccinea* at real conditions, a wastewater sample taken from entrance of a wastewater purification plant in Eskişehir. This sample (25 mL) was spiked with 100 mg L^{-1} of MV dye prior to biosorptive treatment in both batch and column systems. MV biosorption yields of SDS-modified biomaterial in real wastewater conditions were recorded as 86.23±0.21 % in batch and 94.51±1.09 % in column modes at optimum conditions. The good biosorption performances of the modified biomaterial at real wastewater conditions in both systems may be considered as an important advantage for the usability of large-scale applications of the developed biosorbent.

Biosorbent characterization

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}, 2.21×10^{-3} cm^3 g^{-1}, 2.24×10^2 Å, and 3.98×10^{-2} cm^3 g^{-1}, respectively. After the modification, these values changed to 381.55 m^2 g^{-1}, 1.70×10^{-3} cm^3 g^{-1}, 5.45×10^1 Å, and 4.19×10^{-1} cm^3 g^{-1}, respectively.

The surface morphologies of natural, modified, and dye-loaded modified *P. coccinea* biosorbent were characterized by scanning electron microscopy and the micrographs are presented in Fig. 7. The undulate and porous surface of biomass in natural form (Fig. 7a), turned looser and more irregular (Fig. 7b) which is considered helpful for the biosorption of dye molecules onto different parts of

Table 6 Comparison for the MV biosorption capacities of different biosorbents from the literature

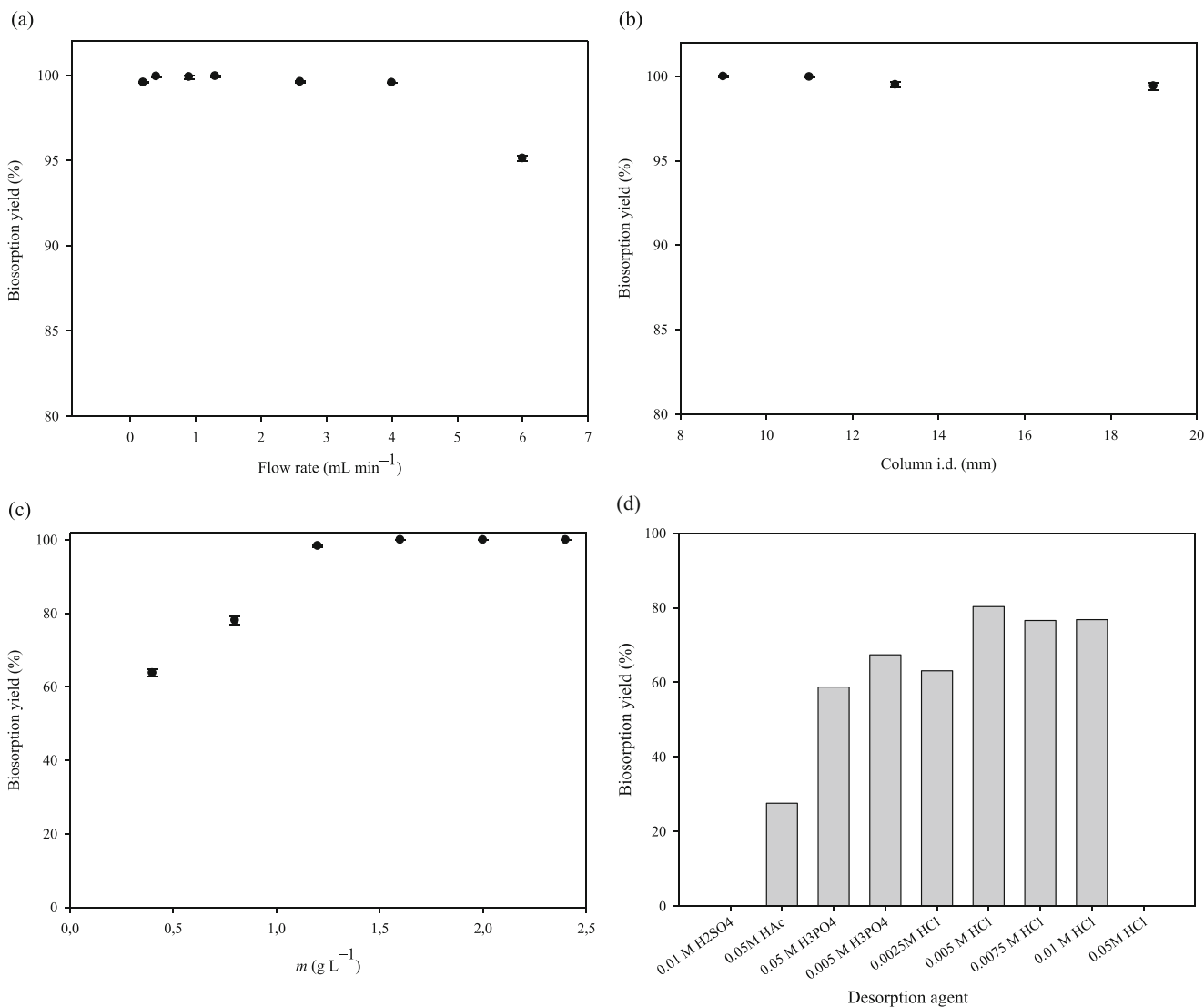| Biosorbent	q_e (mg g^{-1})
Modified baker's yeast (Tian et al. 2010)	60.84
Pu-erh tea powder (Li et al. 2010)	294.12
Palm kernel fiber (Ofomaja et al. 2011)	115.01
Agricultural waste (Hameed 2008)	92.59
Bagasse fly ash (Mall et al. 2006)	26.25
Mansonia wood sawdust (Ofomaja and Ho 2008)	24.60
Mansonia sawdust (Ofomaja 2008)	16.11
Modified *Pyracantha coccinea*	254.88

Fig. 6 Effect flow rate (**a**), column i.d. (**b**), and biosorbent amount (**c**) on the biosorption of MV onto modified *P. coccinea* in continuous system and desorption potential of the modified *P. coccinea* by various eluents (**d**)

SDS-treated biosorbent. After the dye removal process, the surface structure of the modified biosorbent slightly changed (Fig. 7c). Decolorization induced the blocking of the some pores and the surface of modified biosorbent became more smooth.

IR analysis was used to obtain information on the modification effect on the biomass and nature of possible biosorbent–dye interactions. The major functional groups present on the natural form of *P. coccinea* are noted as: –OH and –NH groups (3,415 cm^{-1}), (CH$_n$) groups (2,926 and 2,856 cm^{-1}), C=O groups (1,739 cm^{-1}), amid-I (1,621 cm^{-1}), amid II (1,516 cm^{-1}), COO^{-} groups (1,421 cm^{-1}), and phosphate groups (1,078 cm^{-1}) (Akar et al. 2009a). IR spectra (figure not shown) of modified biosorbent before and after dye loading were also evaluated. The new peaks at 1,375, 1,159, and 1,107 cm^{-1} in the spectrum of modified biosorbent can be ascribed to –CH$_3$, –CH$_2$ bending vibrations, C−N strecthing vibrations, and C−O strecthing vibrations, respectively. SDS-modified biosorbent indicated the shifted bands at 1,442 and 1,055 cm^{-1} when compared with that of natural biomass which showed the same absorption bands at 1,421 and 1,078 cm^{-1}. An increase was noted in the intensities of C=O and amid-II peaks after SDS modification. The intensities of the peaks at 1,375 and 1,159 cm^{-1} in the spectrum of SDS-modified biosorbent increased after the biosorption process. These peaks appeared at 1,369 and 1,167 cm^{-1} in the spectra of dye-loaded modified biosorbent. Also the band observed at 1,587 cm^{-1} in the spectrum of modified biosorbent after MV biosorption may be attributed to aromatic C=C stretching vibrations. These findings confirmed the modification of *P. coccinea* with SDS and possible dye−biosorbent interactions in the decolorization process.

Fig. 7 SEM micrographs of
P. coccinea (**a**) SDS-modified
P. coccinea (**b**), and MV loaded
SDS-modified *P. coccinea* (**c**)

(a)

(b)

(c)
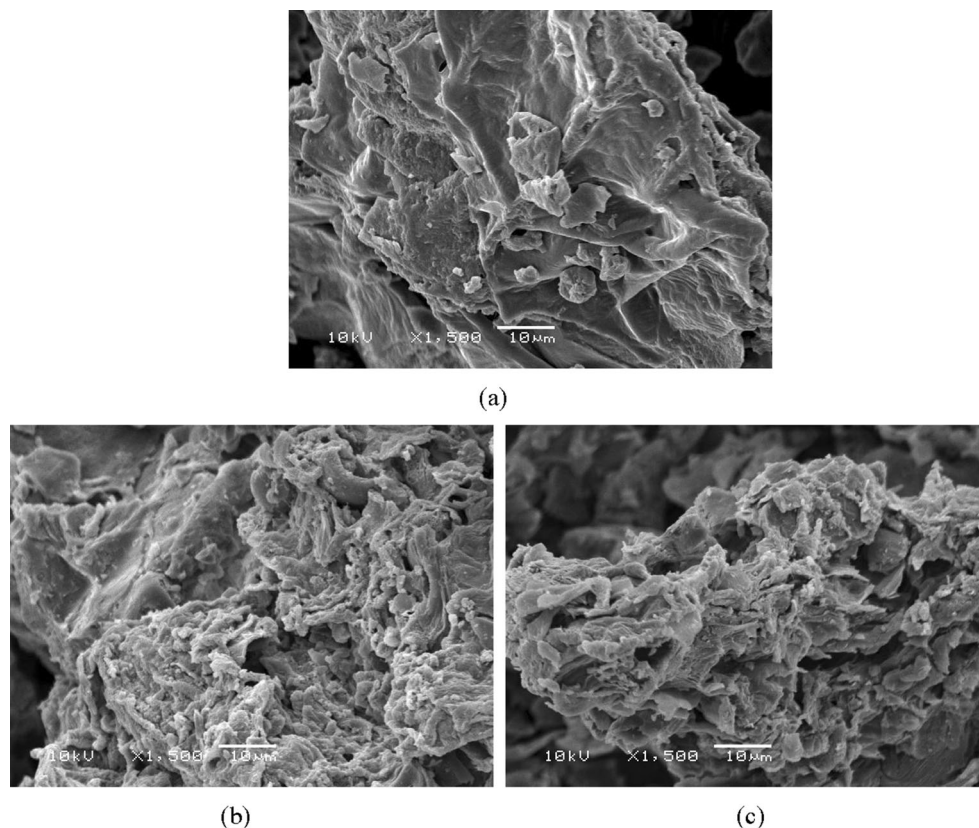
Conclusions

1. *P. coccinea*, an abundant and cost effective natural plant, could be effectively used for the removal of MV dye from aqueous solutions after the modification with an anionic surfactant.
2. Developed biosorbent exhibited the good performance for the removal of MV from real wastewater.
3. The optimum values of pH, biosorbent amount, and contact time were found to be 6.0, 0.055 g, and 30 min, respectively, by using Box–Behnken design of RSM.
4. ANOVA results showed the fitness of the suggested quadratic model during the MV biosorption process.
5. There is no need for pH adjustment of dye solution.
6. No temperature effect was observed and the biosorption equilibrium was rapidly established (within 30 min).
7. Biosorption kinetics of MV was found to conform to the pseudo-second-order kinetics.
8. The Langmuir isotherm equation gave the best correlation for the biosorption of MV onto SDS-modified *P. coccinea*.
9. The modified biosorbent was successfully used in the continuous system at a flow rate of 1.3 mL min^{-1} and a column size of 11 mm.

10. Consequently, SDS-modified *P. coccinea* berries could be employed as effective and low-cost alternative biosorbent material for the removal of MV from synthetic and real aqueous media.

Appendix

Kinetic and isotherm model equations

The pseudo-first-order equation;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

The pseudo-second-order rate equation;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

$$h = k_2 q_e^2 \tag{7}$$

The intraparticle diffusion equation;

$$q_t = k_p t^{1/2} + C \tag{8}$$

which k_1 is rate constant of pseudo-first-order biosorption (min^{-1}), k_2 is the equilibrium rate constant of pseudo-second-order biosorption (g mg^{-1} min^{-1}), q_e and q_t are biosorption capacity at equilibrium and at time t (mg g^{-1}), respectively, h is the initial biosorption rate (mg g min^{-1}), C is the intercept (mg g^{-1}), and k_p is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$).

Freundlich isotherm equation;

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (9)$$

Langmuir isotherm model;

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max}K_L}\right)\frac{1}{C_e} \qquad (10)$$

$$R_L = \frac{1}{1 + K_L C_o} \qquad (11)$$

D−R isotherm model;

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (12)$$

$$E = 1/(2\beta)^{1/2} \qquad (13)$$

where q_e (mol g^{-1}) and C_e (mol L^{-1}) are the amount of biosorbed dye per unit weight of biosorbent and unbiosorbed dye concentration in solution at equilibrium, respectively, K_F (L g^{-1}) and n (dimensionless) are Freundlich constants, q_{max} is the maximum monolayer biosorption capacity (mol g^{-1}), K_L is Langmuir constant related to the energy of biosorption (L mol^{-1}), R_L is separation factor, C_o is the initial solute concentration (mol L^{-1}), q_m is the biosorption capacity (mol g^{-1}), β is the activity coefficient related to the biosorption energy, and E (kJ mol^{-1}) is the mean free energy.

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