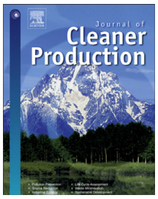
Journal of Cleaner Production 112 (2016) 4844–4853

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro



Treatment design and characteristics of a biosorptive decolourization process by a green type sorbent

Tamer Akar [a], [*], Serpil Turkyilmaz [b], Sema Celik [c], Sibel Tunali Akar [a]

[a] Department of Chemistry, Faculty of Arts and Science, Eskişehir Osmangazi University, 26480, Eskişehir, Turkey
[b] Department of Mathematics, Faculty of Arts and Science, Bilecik Şeyh Edebali University, 11210, Bilecik, Turkey
[c] Department of Chemistry, Graduate School of Natural and Applied Sciences, Eskişehir Osmangazi University, 26480, Eskişehir, Turkey

ARTICLE INFO

Article history:
Received 30 December 2014
Received in revised form
22 May 2015
Accepted 10 June 2015
Available online 19 June 2015

Keywords:
Biosorption
Box-Behnken design
Isotherms
Pisum sativum
Reactive Violet 1 (RV1)

ABSTRACT

Contamination of water sources by synthetic dyes is a problem of global concern given their potential toxicities and environmental impacts. A significant increase has been noted in the studies related to developing alternative and efficient systems for the treatment of coloured effluents. This study focused on the development of an environmentally friendly process for the treatment of dye contaminated aqueous media. A natural biosorbent prepared from spent biomass of *Pisum sativum* was characterized and employed for the removal of a reactive dye for the first time in the literature. Experimental design, modelling and optimization techniques were applied to the batch biosorption process. Process variables were screened using response surface methodology coupled with a Box-Behnken design matrix. Solution pH, biosorbent dosage, reaction time and temperature were considered as key factors. The interactive effects of factor variables on the biosorption, characteristics of the biosorbent and possible dye–biosorbent interactions were discussed. The maximum decolourization yield of biomaterial was 83.2% at an initial concentration of 100 mg L^{-1}. The best operating conditions were as follows: pH: 2.0, biosorbent amount: 0.6 g (in 25 mL dye solution), reaction time: 56.9 min and temperature 27.3 °C. The Langmuir isotherm model satisfactorily described the equilibrium biosorption data. IR spectra of unloaded and dye-loaded biosorbent indicated the functional groups on the biosorbent, such as a carbonyl that interacted with Reactive Violet 1 dye molecules. SEM micrographs indicated that microprecipitation can also play a role in the decolourization process. This study demonstrates that developed waste biosorbent could be successfully employed as an effective and eco-friendly alternative cleaner to remove reactive dyes from wastewaters.

1. Introduction

The colouration of natural freshwater sources as a result of improper discharge of industrial waste streams, including dyestuff, textile and related industries, an environmental problems experienced by many industrialized countries. In addition to visual pollution, dyes reduced the photosynthetic activity and dissolved oxygen concentration in contaminated water. These dyes exert acute or chronic effects on living systems depending on their concentrations and length of exposure. In addition, toxic aromatic amine compounds can be produced from dyes under degradative conditions (Pereira and Alves, 2012; Rangabhashiyam et al., 2013; Solís et al., 2012). Therefore, the decolourization of contaminated aqueous effluents by effective technologies is an issue of great environmental concern (Allen et al., 2004). In this context, cleaner production is an effective and integrated solution to pollution control that reduces or eliminates organic or inorganic pollutants at the source during production processes (Murali et al., 2013).

Biosorption based on pollutant-biomass functional group interactions has attracted great interest in recent years as a promising technology in terms of cleaner production (Rathod et al., 2014). This technology is related to the "use of renewable resources" principle of green chemistry (Pritee and Shalini, 2010). The main principles of green chemistry provide a structured framework for researchers to design new materials, products and processes that are important for environment and human health (Sanjay et al., 2010). The biosorption potentials of the green type of biomasses or their derivatives play an

---

[*] Corresponding author. Tel.: +90 222 2393750x2871; fax: +90 222 2393578.
E-mail address: takar@ogu.edu.tr (T. Akar).

http://dx.doi.org/10.1016/j.jclepro.2015.06.049
0959-6526/

important role in the applications aimed to clean the environment (Al-Asheh et al., 2003; Martín-Lara et al., 2014; Moawed, 2013). The pollution removal potential of different types of biomasses produced from fungi, bacteria, algae, yeast, plants, etc. is related to possible interactions between pollutants and functional groups of the macromolecules localized on the cell surface of these biomass, such as hydroxyl, carboxyl, sulfhydryl, amine and amino moieties (Nitayaphat and Jintakosol, 2015; Pritee and Shalini, 2010; Volesky, 2007). Moreover, the efficiency of biosorption applications is affected by several experimental variables, such as solution pH, pollutant concentration, temperature etc (Fomina and Gadd, 2014; Özcan et al., 2009; Yargıç et al., 2015).

The lab-scale optimization studies for biosorption processes have generally been performed by ignoring the simultaneous interaction between other experimental variables. Response surface methodology (RSM) is a combination of mathematical and statistical techniques that aid in the investigation of the interactive effects among operation variations during the process design and data analysis (Myers and Montgomery, 2002). This technique has been successfully to optimize various biochemical and chemical researches using different types of experimental design, such as the Box-Behnken Design (BBD), central composite design and face-centred central composite design. The Box-Behnken quadratic design (Box and Behnken, 1960) is an efficient and economical approach because it requires a limited number of experiments and minimum time (Kaiser et al., 2013; Montgomery, 2005; Witek-Krowiak et al., 2014).

The goal of this study involves as the evaluation of the biosorption potential of the spent biomass of *Pisum sativum* peels (PSP) for the treatment of textile dye-contaminated waters. The statistical design of the process was also performed. To our knowledge, the natural form of this biomass is only used in the removal of the cationic dye methylene blue from aqueous solutions (Dod et al., 2012). In addition, the sorption abilities of activated carbons prepared from *P. sativum* peels were reported for the same dye (Dod et al., 2012; Geçgel et al., 2013). In our study, the natural form of PSP was first suggested as a reactive dye remover. In addition, RSM involving three levels of BBD was employed for multivariate optimization of the decolourization process when considering the different factors affecting the treatment system on an industrial scale. The biosorption process was analysed by isotherm and mechanism studies. Subsequently, IR, SEM and BET analyses, as well as zeta potential measurements were used to characterize the biosorbent.

2. Materials and method

To obtain information regarding the applicability of suggested biomaterial in the field of water treatment, process variables should be optimized in addition to sorbent characterization.

2.1. Preparation of biosorbent and dye solutions

An agricultural waste PSP was employed as low-cost biosorbent for the removal of Reactive Violet (RV1) from aqueous solutions. *P. sativum* was provided from local markets in Eskişehir, Turkey, and peels were separated from their edible peas. The peels were cut into small pieces, washed with tap water and deionized water until neutral pH to remove adhered dust and impurities soluble in water. The washed material was oven-dried at 60 °C overnight, ground and sieved to particle size range of 212 to 149 μm.

The target biosorbate, in this study (RV1) was provided from a local textile company in ~100% pure form. To prepare a stock solution (1000 mg L^{-1}) of dye, 1 g RV1 was sensitively weighed and dissolved in 1 L deionized water. More dilute solutions for biosorption experiments were obtained by suitable dilution procedures. The initial pH values of the solutions were adjusted by the addition of NaOH and/or HCl solutions.

2.2. Dye biosorption studies

Twenty-nine experiments designed by RSM were performed in a batch system to investigate the influences of initial pH, biosorbent amount, contact time and temperature. For these experiments, 25 mL of RV1 solutions at specific pH values was placed into 100-mL beakers, and weighed amounts of PSP were added to each flask. The mixtures were stirred at 200 rpm, and the biosorbent was then separated from the biosorption medium by centrifugation. The supernatant was analysed for its residual RV1 concentration.

Biosorption experiments were triplicated at same conditions. Biosorption yield and biosorption capacity (q_e) of PSP were calculated by the following equations:

$$\text{Biosorption yield } (\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$q_e = \frac{V(C_i - C_e)}{m}, \tag{2}$$

where C_i and C_e are the dye concentrations in the solutions initially and at equilibrium (mg L^{-1}), respectively; V is the solution volume (L) and m is the weight of biosorbent (g).

2.3. Statistical (Box-Behnken) design

In this study, optimum conditions for the biosorption of RV1 onto PSP were determined by means of BBD, which is the most common design used in RSM. RSM is a statistical and mathematical approach used for analysing, modelling and optimization problems in various fields. Moreover, the methodology consists of empirical techniques to analyse the relationships between controlled experimental factors and measured responses according to one or more selected criteria. In RSM, all variables are assumed to be measurable and the response surface can be implied as follows (Aslan and Cebeci, 2007; Şanal et al., 2005):

$$y = f(x_1, x_2, \ldots x_k), \tag{3}$$

where, y is the answer of the system (dependent variable), and x_i are variables of factors (independent variables).

The aim of RSM is to optimize the response variable y. Furthermore, it is presumed that factor variables are continuous and controlled by the experiments with negligible errors. In the first step of RSM, a suitable method is introduced to obtain the true relationship between the dependent (response) variable and the group of independent (factor) variables. If knowledge about the shape of the true response surface is insufficient, the preliminary first order model is improved by adding high-order terms to the model. In the next step, the behaviour of the system is clarified by the following quadratic model (Amini et al., 2009; Aslan, 2007; Ferreira et al., 2007a):

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon, \tag{4}$$

where y is the process response (dependent variable), k is the number of factors, i and j are the index number of factor variables, β_0 is the constant, β_i is the first order main effect, β_{ii} is the quadratic effect, β_{ij} is the interaction effect, and ε is the random error between predicted and measured variables. The factor variables (x_1, x_2, …x_k) are coded as the following transformation:

$$X_i = (x_i - x_0)/\Delta x_i, \tag{5}$$

where X_i is dimensionless coded value of the ith independent variable, x_i is the uncoded value of the ith independent variable, x_0 is the uncoded ith independent variable of the centre point, and Δx_i is the step change value (Amini et al., 2009; Yetilmezsoy et al., 2009).

The Box-Behnken experimental design developed by Box and Behnken in 1980 is a very useful method for developing second-order response surface models. This design has been applied for the optimization of several chemical processes and the determination of the number of experiments in processes. It also permits designs with desirable statistical properties (Myers and Montgomery, 2002). This experimental design requires at least three levels for each factor (independent) variable and less total runs compared with central composite design. Thus, the quadratic model is appropriate. It is an important feature in some experimental situations. Box-Behnken designs enable less costly experimentation if actual samples are being used in the experimentation. In Box-Behnken experimental designs, the level of one factor (independent) variable is fixed as the centre level for all levels of the other factor (independent) variables (Ferreira et al., 2007a, 2007b; Myers and Montgomery, 2002).

The required experimental number for Box-Behnken experimental design can be calculated as follows:

$$N = 2k^{*}(k-1) + cp, \tag{6}$$

where k is the factor number and cp is the replicate number of the central point (Aslan and Cebeci, 2007; Pouralinazar et al., 2012; Yetilmezsoy et al., 2009).

2.4. Instrumentation

RV1 concentrations in the solutions were measured using a UV/Vis spectrophotometer (Shimadzu UV-2550). IR spectra of dye powder, unloaded and dye loaded biosorbents were recorded on a Bruker Tensor 27 FTIR spectrophotometer. SEM images for these biosorbents were obtained with a scanning electron microscope (JEOL 560 LV SEM) at 20 kV. A pH meter (WTW Inlolab 720) was used to measure pH values of the solutions. Zeta potentials of PSP at various pH values were measured using a Zetasizer Nano ZS (Malvern Instruments,UK). The BET surface area of PSP was determined from an N_2 adsorption isotherm with a surface area analyzer (Quantachrome Instruments, Autosorb 1).

3. Results and discussion

The statistical design results and optimization conditions are discussed in the first part of this section. The biosorption process was identified by means of the isotherm models. Biosorption mechanism was characterized using IR, SEM and EDX analyses.

3.1. Modelling of the RV1 biosorption process

In this study, a Box-Behnken design with four-factors is performed to investigate the effects of significant factors on the response variable(s) of the process and to achieve the optimum conditions of experimental design. Design-Expert Software trial version 8.0 was used to design the number of experiments to be applied, evaluate the results of experiment design and optimize the process. The total number of experiments with four variables and three -levels in the Box-Behnken design was 29 experimental runs, including five replications at the centre points. Table 1 displays the levels and ranges of the four factors of the Box-Behnken statistical design. The low, centre and high levels for each factor variable are coded as −1, 0 and +1, respectively. The central values for the experimental design are pH = 5, biosorbent amount = 0.51 g, time = 47.50 min and temperature = 30 °C in uncoded form. To examine the effects of factor variables (pH, biosorbent amount, time and temperature) on RV1 removal efficiency (%), 29 runs of experimental data and observed results are included in Table 2.

The coded and actual values of factor variables as well as observed and predicted RV1 removal efficiency values are presented in Table 2 and used for the optimization of the chemical process.

3.2. Fitting model

The statistical significance of the quadratic model was evaluated via analysis of variance (ANOVA). The analysis results for RV1 removal efficiency are presented in Table 3. According to results of multiple regression analysis in Table 3, an empirical relationship between the factor variables and the response variable in coded units can be expressed by the following model:

$$\begin{aligned}\text{RV1 biosorption yield (\%)} = {} & 62.18 - 8.91x_1 + 28.13x_2 \\ & + 3.72x_3 + 7.40x_4 + 9.02x_1x_2 \\ & + 0.09x_1x_3 + 6.72x_1x_4 \\ & + 5.96x_2x_3 + 7.57x_2x_4 \\ & + 0.54x_3x_4 + 8.76{x_1}^2 - 27.95{x_2}^2 \\ & - 3.96{x_3}^2 - 4.00{x_4}^2\end{aligned} \tag{7}$$

This model was also used to obtain predicted values of RV1 removal efficiency in Table 2. The predicted values were quite close to observed values, thereby suggesting that the quadratic regression model was the best-fit model for RV1 biosorption on PSP. The determination coefficient (R^2) of a model identifies the amount of variation in the observed response variable arising from factor variables the in model. In this study, the value of the determination coefficient ($R^2 = 0.9746$) of Eq. (7) revealed that the regression model was the best model for predicting the performance of RV1 biosorption. In addition, adjusted R^2 value (adj. $R^2 = 0.9493$) indicated that 94.93% of total variations were explained by the model provided in Eq. (7). The F-value (38.42) with a very low p-value (<0.0001) of the model indicated that the quadratic model was statistically significant for RV1 biosorption on PSP. As noted in Table 3, all of the p-values for x_1, x_2, x_3, x_4, x_1x_2, x_1x_4, x_2x_4, x_1^2 and x_2^2 were less than significant level at $\alpha = 0.05$ (5%). These findings indicate that the variables were statistically significant and have important effects on the RV1 biosorption capacity of PSP.

Table 1
Variable levels in Box-Behnken experimental design.

Variables	Variable levels				
	Symbol	Low (−1)	Center (0)	High (+1)	∇x_i
pH	x_1	2	5	8	3
Biosorbent amount (g)	x_2	0.02	0.51	1	0.49
Time (min)	x_3	5	47.50	90	42.50
Temperature (°C)	x_4	10	30	50	20

Table 2
Box-Behnken design matrix with four factors in coded and actual units.

Runs	Coded level of variables				Actual level of variables				RV1 removal (%)		
	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Observed	Predicted	Residual
1	0	1	0	−1	5	1	47.5	10	47.490	43.390	4.10
2	0	−1	−1	0	5	0.02	5	30	0.203	4.383	−4.18
3	1	0	0	−1	8	0.51	47.5	10	44.159	43.907	0.25
4	1	0	−1	0	8	0.51	5	30	63.969	54.265	9.70
5	1	1	0	0	8	1	47.5	30	63.969	71.238	−7.27
6	−1	−1	0	0	2	0.02	47.5	30	37.087	32.796	4.29
7	0	0	−1	−1	5	0.51	5	10	36.342	43.634	−7.29
8	−1	0	1	0	2	0.51	90	30	72.209	79.522	−7.31
9	0	0	0	0	5	0.51	47.5	30	62.189	62.185	0.00
10	0	0	0	0	5	0.51	47.5	30	62.469	62.185	0.28
11	0	0	0	0	5	0.51	47.5	30	62.168	62.185	−0.02
12	0	0	1	1	5	0.51	90	50	70.203	65.889	4.31
13	−1	0	0	1	2	0.51	47.5	50	76.863	76.528	0.34
14	1	−1	0	0	8	0.02	47.5	30	0.000	−3.051	3.05
15	0	1	0	1	5	1	47.5	50	77.260	73.333	3.93
16	1	0	1	0	8	0.51	90	30	60.831	61.890	−1.06
17	0	0	−1	1	5	0.51	5	50	55.173	57.358	−2.19
18	0	0	0	0	5	0.51	47.5	30	61.747	62.185	−0.44
19	1	0	0	−1	2	0.51	47.5	10	80.434	75.166	5.27
20	0	−1	0	−1	5	0.02	47.5	10	0.733	2.270	−1.54
21	−1	0	−1	0	2	0.51	5	30	75.704	72.256	3.45
22	0	0	1	−1	5	0.51	90	10	49.202	49.994	−0.79
23	−1	1	0	0	2	1	47.5	30	64.985	71.014	−6.03
24	1	0	0	1	8	0.51	47.5	50	67.484	72.164	−4.68
25	0	1	−1	0	5	1	5	30	49.229	48.725	0.50
26	0	−1	1	0	5	0.02	90	30	0.000	−0.084	0.08
27	0	1	1	0	5	1	90	30	72.850	68.082	4.77
28	0	−1	0	1	5	0.02	47.5	50	0.235	1.945	−1.71
29	0	0	0	0	5	0.51	47.5	30	62.351	62.185	0.17

Table 3
Analysis of Variance (ANOVA) for the quadratic model.

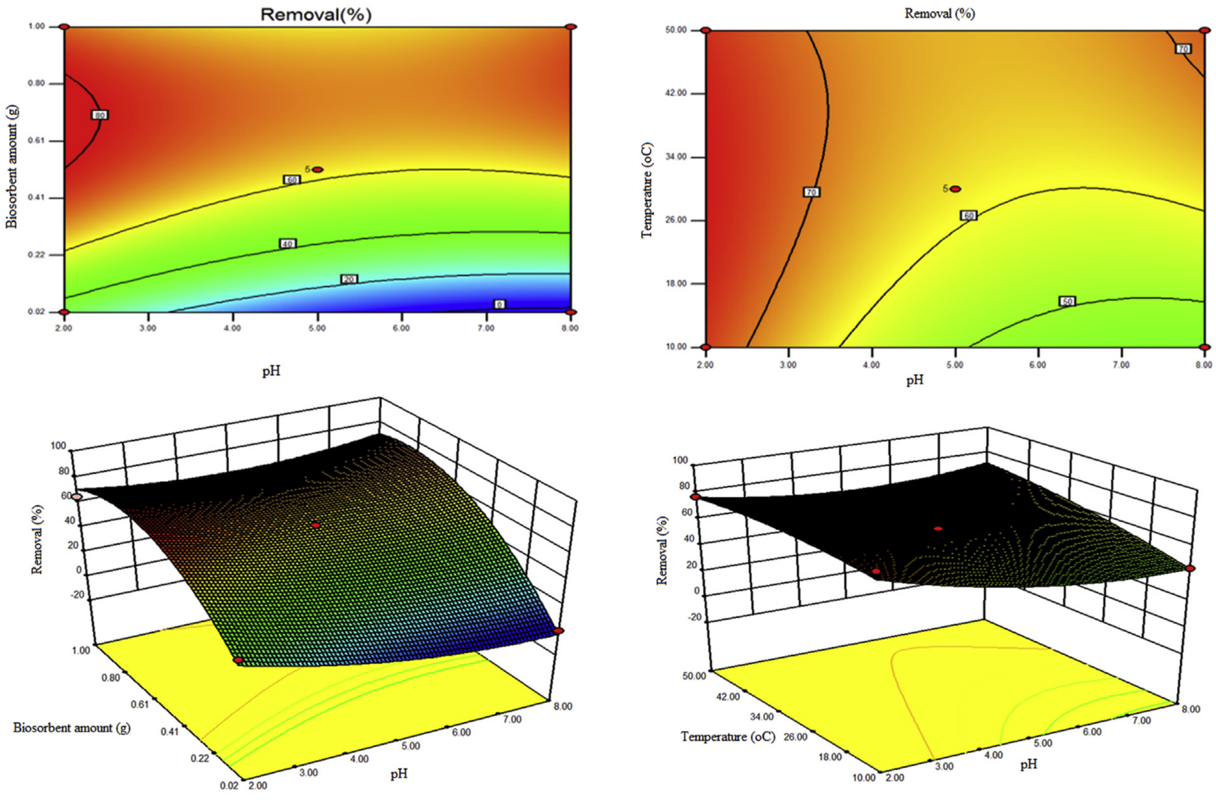
Variation source	Coefficients	Sum of squares	df	Mean square	*F*-value	*p*-value Prob > *F*
Intercept	62.18					
x_1	−8.91	951.76	1	951.76	27.60	0.0001
x_2	28.13	9493.51	1	9493.51	275.26	<0.0001
x_3	3.72	166.31	1	166.31	4.82	0.0454
x_4	7.40	657.98	1	657.98	19.08	0.0006
x_1x_2	9.02	325.27	1	325.27	9.43	0.0083
x_1x_3	0.09	0.03	1	0.03	0.00	0.9761
x_1x_4	6.72	180.84	1	180.84	5.24	0.0381
x_2x_3	5.96	141.90	1	141.90	4.11	0.0620
x_2x_4	7.57	229.04	1	229.04	6.64	0.0219
x_3x_4	0.54	1.18	1	1.18	0.03	0.8561
x_1^2	8.76	497.82	1	497.82	14.43	0.0020
x_2^2	−27.95	5065.90	1	5065.90	146.88	<0.0001
x_3^2	−3.96	101.82	1	101.82	2.95	0.1078
x_4^2	−4.00	103.99	1	103.99	3.02	0.1044
Model		18551.78	14	1325.13	38.42	<0.0001
Residual		482.85	14.00	34.49		
$R^2 = 0.9746$						
Adj. $R^2 = 0.9493$						

3.3. Effects of model components and their effects on RV1 removal efficiency

As mentioned in the previous section, one of the purposes of the Box-Behnken design method was to obtain the significant effects of the process variables (pH, biosorbent amount, contact time and temperature) on the RV1 removal efficiency of PSP. Contour and 3D response surface plots were used to examine the effects of all factor variables on the response variable.

Fig. 1 illustrates the interactive effects of the combination of factor variables on RV1 removal efficiency (%) via contour and 3-D surface plots. These plots are presented as a function of two independent variables by holding other variables at a fixed level.

Fig. 1(A) demonstrates that the interactive effect of pH (2, 5 and 8) and biosorbent amount (0.02, 0.51 and 1.0 g) on RV1 biosorption yield is significant. The dye removal efficiency of the biosorbent increases by increasing the amount of PSP and decreasing the pH value. The poor dye biosorption in the high pH range could be ascribed to competition of anionic dye molecules with OH^- ions for biosorptive sites on the biosorbent surface. At lower pH values, the surface of the biosorbent is positively charged; thus, acidic pH values favour RV1 biosorption on PSP. Increasing biosorption yield



(A)

(B)

Fig. 1. Contour and 3-D surface plots for the interactive effects of pH and biosorbent amount on RV1 removal efficiency (%) onto PSP (A), Contour and 3-D surface plots for the interactive effects of pH and temperature on RV1 removal efficiency (%) onto PSP (B), Contour and 3-D surface plots for the interactive effects of biosorbent amount and contact time on RV1 removal efficiency (%) onto PSP (C), Contour and 3-D surface plots for the interactive effects of biosorbent amount and temperature on RV1 removal efficiency (%) onto PSP (D), Contour and 3-D surface plots for the interactive effects of contact time and temperature on RV1 removal efficiency (%) onto PSP (E) and Contour and 3-D surface plots for the interactive effects of pH and contact time on RV1 removal efficiency (%) onto PSP (F) (Initial dye concentration: 100 mg L^{-1}; stirring rate: 250 rpm).

by increasing the biosorbent amount is attributed to the increased surface area and the availability of more active sites on the biosorbent (Akar et al., 2013b; Ghaedi et al., 2014; Sathishkumar et al., 2012).

The effects of pH (2, 5 and 8) and temperature (10, 30 and 50 °C) on the RV1 biosorption potential of PSP were also examined. The biosorption yields of PSP were 80.23, 76.90 and 76.96% at 10, 30 and 50 °C, respectively. According to these results, temperature did not significantly affect RV1 biosorption efficiency of the biosorbent (Fig. 1(B)). This feature may be an important advantage for the practical applications of the suggested biosorption system to real wastewaters.

According to Fig. 1(C), the effect of contact time (5, 47.5 and 90 min) can be ignored. This finding may be explained by the establishment of a biosorption equilibrium in a short time.

Fig. 1(D) and (E) present the interactive effects of temperature-biosorbent amount and temperature-contact time on the dye removal efficiency of PSP, respectively. The RV1 biosorption potential of PSP is increased by an increase in the biosorbent amount, whereas no significant temperature effect was observed.

3.4. Optimization

The optimum predicted point of maximum RV1 biosorption (%) onto PSP obtained by means of the Box-Behnken method was approximately 83.22%. The independent variables of the biosorption process were as following: pH = 2.0, biosorbent amount = 0.62 g, contact time = 56.94 min and temperature = 27.33 °C.

3.5. Evaluation of the optimized biosorbent

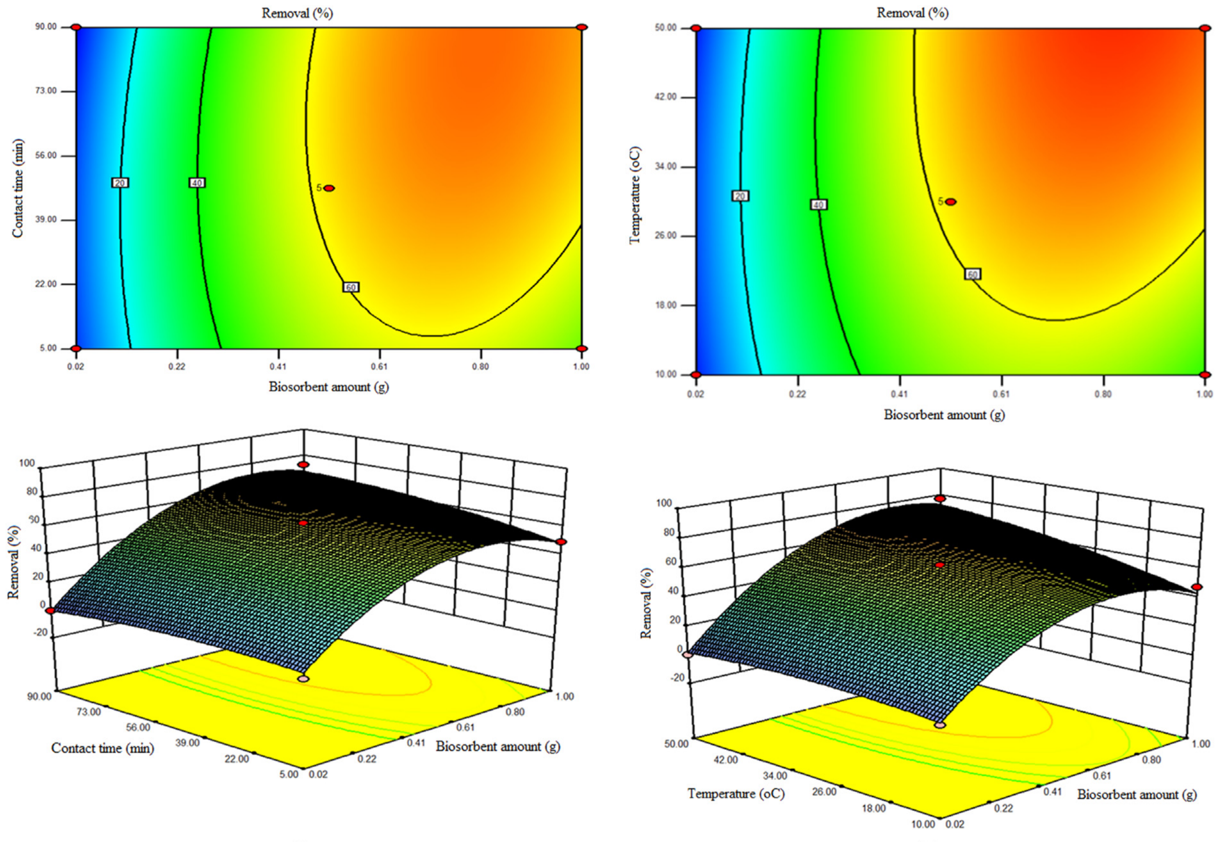
To test the validity of RSM, biosorption experiments under the optimum conditions were performed. The biosorption yield of PSP was determined as 91.60% with the optimum variables. Equilibrium biosorption data were evaluated by isotherm models, whereas the biosorbent structure was characterized using IR and SEM analyses.

3.6. Characterization

The moisture, volatile compounds and ash in the biosorbent were 9.5, 82.0 and 93.7%, respectively. The specific surface area of PSP was 6.51×10^{-1} m^2 g^{-1}.

The IR spectrum of RV1 dye (Fig. 2(a)) indicated specific absorption bands, 3433 cm^{-1} (OH stretching), 3030 cm^{-1} (aromatic C–H stretching), 2380 cm^{-1} (NH_2 stretching), 1618 cm^{-1} (NH bending), 1419 cm^{-1} (asymmetric CH bending), 1128 cm^{-1} (CO stretching) and 1045 cm^{-1} (Ar–Cl).

IR spectra of PSP before and after the decolourization procedure are also presented in Fig. 2. A broad characteristic band at 3362 cm^{-1}corresponds to the stretching vibrations of –OH and/or –NH groups. The peaks at 2924 cm^{-1} and 1738 cm^{-1} indicated the stretching vibrations of aliphatic C–H and carboxylate C=O, respectively. The peak located at 1628 cm^{-1} was attributed to



(C)

(D)

Fig. 1. (*continued*).

carbonyl stretching vibrations of amide groups. The peak at 1420 cm^{-1} can be assigned as bending vibrations of C—H groups. C—O stretching vibrations at 1256 and 1055 cm^{-1}were other significant bands observed in the fingerprint region. Similar surface functional groups were reported for the natural biomass prepared from sugar beet pulp (Akar et al., 2013a). The spectra of PSP biomass after contacting with RV1 dye indicated significant peak shifts from 1628, 1420 and 1256 cm^{-1} to 1639, 1425 and 1232 cm^{-1}, respectively (Fig. 2). In addition, the intensity of the peak at 1628 cm^{-1} significantly increased after the decolourization process. These findings implied that the mentioned functional groups are likely to participate in the decolourization process. The new peaks appeared at approximately 1516 cm^{-1} and 1373 cm^{-1} in the spectra of dye-loaded biomass are attributed to —N=N— and C—H bending vibrations of biosorbent dye molecules.

The scanning electron micrographs (SEM) at different magnifications of PSP biomass before and after the decolourization process are presented in Fig. 3. SEM images of PSP before contact with dye exhibited a heterogeneous and rough structure. In addition, a number of gaps with different sizes are observed in the surface structure of the natural biomass. After the decolourization process, some agglomerations are noted in these gaps and are probably due to microprecipitation of dye molecules that play a role in the decolourization process via another mechanism.

Zeta potential values at different pH values were measured to determine pHzc of the biosorbent. Fig. 4 presents the changes of the surface charge of PSP with acidic and basic pH values. At pH 1 and 2, the surface of PSP was positively charged whereas negative zeta potential values were observed at higher pH values. The pHzc of PSP was 3.2. These results can explain the preferential biosorption of anionic dye onto positively charged biosorbent surfaces and indicate that the electrostatic interaction plays an important role in dye biosorption onto PSP.

3.7. Equilibrium modelling

The biosorption of RV1 on PSP was performed using different initial dye concentrations. Obtained data were fitted to Freundlich (Freundlich, 1906) and Langmuir (Langmuir, 1918) isotherm models. The least squares method for non-linear regression was used to fit the equilibrium data for the biosorption of RV1 on PSP.

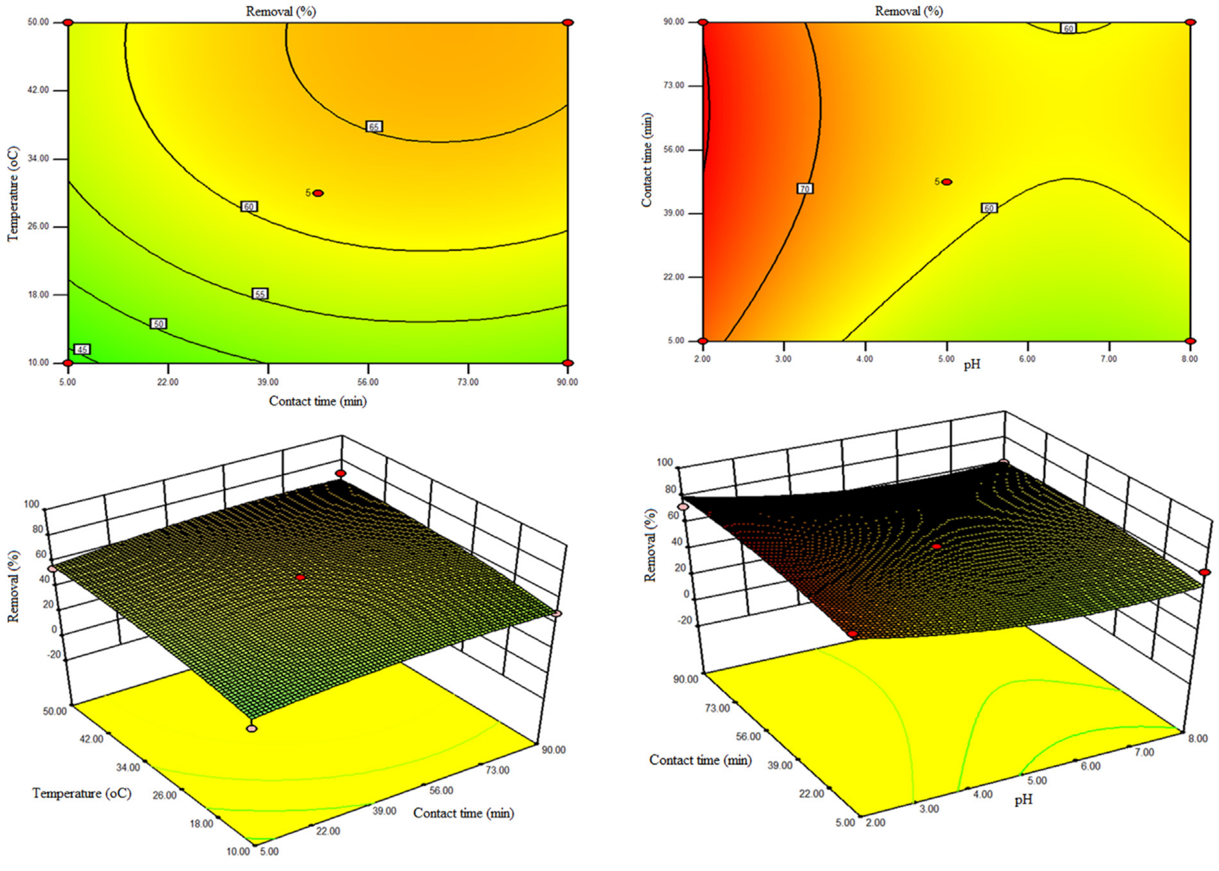
The Langmuir biosorption isotherm assumes that biosorption at one binding site does not affect another site and that biosorption occurs on homogeneous surfaces (Shin et al., 2011). The non-linear Langmuir equation is shown:

$$q_e = \frac{q_{\max} K_L C_e}{1 + q_{\max} K_L}, \tag{8}$$

where $q_{\max}$ is the maximum uptake capacity of RV1 in mmol g^{-1}, C_e is the unbiosorbed RV1 concentration in the solution in mol L^{-1}, and K_L is Langmuir constant related to the binding energy of biosorption in L mg^{-1} and used for the calculation of a dimensionless separation factor, R_L. R_L is calculated as follows:

$$R_L = \frac{1}{1 + K_L C_o}, \tag{9}$$

where C_0 is the initial RV1 concentration (mol L^{-1}). The R_L value indicates the biosorption nature as unfavourable if $R_L > 1$, linear if



(E)

(F)

Fig. 1. (*continued*).

$R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$ (Hall et al., 1966; Rangabhashiyam et al., 2014).

In contrast to Langmuir model, the Freundlich isotherm is applicable to the biosorption on heterogeneous surfaces. The Freundlich equation is represented as follows:

$$q_e = K_F C_e^{1/n}, \tag{10}$$

where K_F is the Freundlich constant (L mg^{-1}) and $1/n$ is the heterogeneity factor.

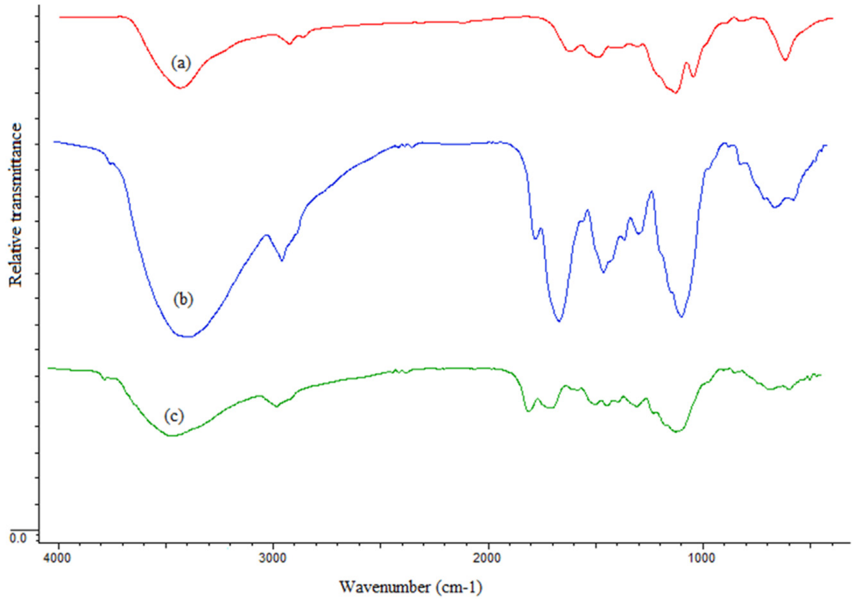
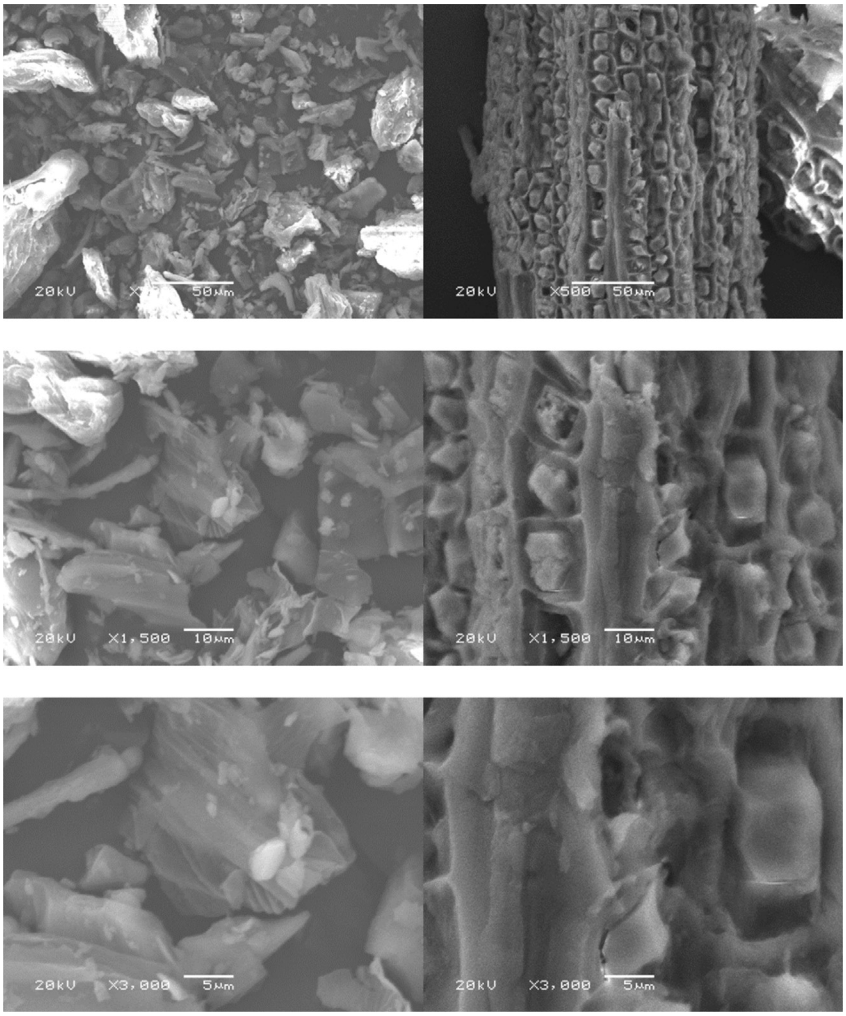


Fig. 2. IR spectrum of unloaded PSP (a), IR spectrum of RV1-loaded PSP (b) and IR spectrum of RV1 dye (c).



Unloaded biosorbent (a) Dye loaded biosorbent (b)

Fig. 3. SEM micrographs of unloaded and RV1-loaded PSP.

Fig. 5 indicates the experimental data and the predicted isotherm curves for the biosorption of RV1 on PSP at pH 2.0 and 25 °C. The calculated model parameters and constants for the biosorption process as well as the R^2 values are included in Table 4.

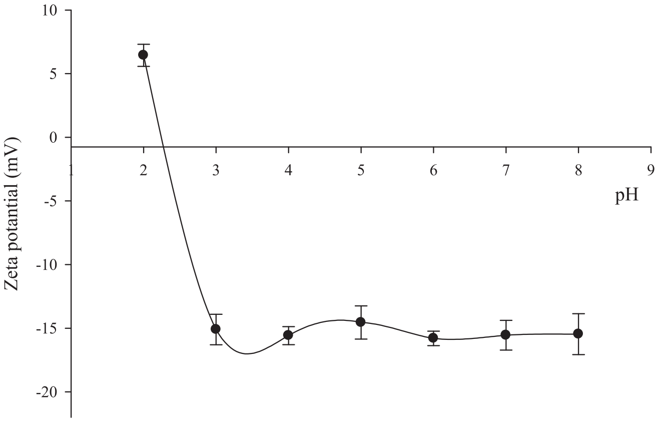


Fig. 4. Zeta potentials of PSP at different pH values.

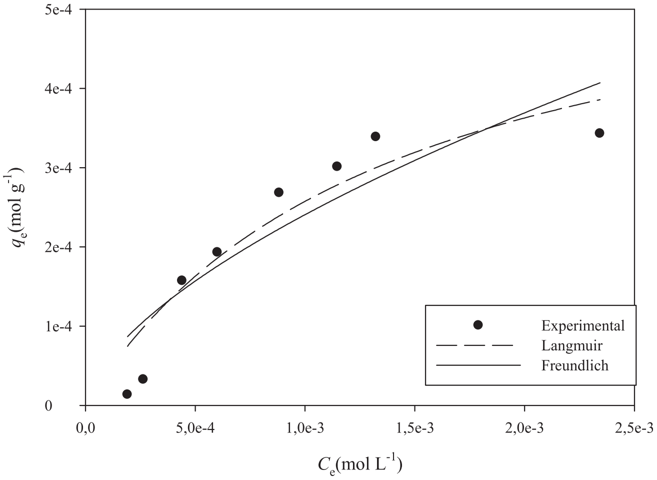


Fig. 5. Experimental equilibrium data and the predicted isotherm curves for the biosorption of RV1 onto PSP.

Table 4
Langmuir and Freundlich isotherm model parameters for the biosorption of RV1 onto PSP.

Parameter		t	p
Langmuir isotherm			
$q_{\max}$ (mol g^{-1})	6.13×10^{-4}	3.853	0.0084
K_L (L mol^{-1})	7.23×10^{2}	1.913	0.1042
R^2: 0.892; *S.E.*: 0.0005; *F*: 49.355			
Freundlich isotherm			
n	1.620	4.176	0.0058
K_F (L g^{-1})	0.0171	1.012	0.3508
R^2: 0.818; *S.E.*: 0.0006; *F*: 27.005			

Based on the R^2 values in this table, the RV1 biosorption was best described by the Langmuir isotherm model. t values of model coefficients were statistically significant, and the value of standard error is 0.0005. This result would depict the monolayer biosorption of RV1 onto PSP. In this study, the Freundlich isotherm model presented a poor description for RV1 biosorption onto PSP. A n value greater than 1 in Table 4 indicated a good biosorption intensity and favourable biosorption process at the studied concentration range (Ma et al., 2012).

3.8. *Kinetic study*

Fig. 6 indicated the changes in the biosorption capacity of PSP with contact time. The biosorption rate increased rapidly in the first 5 min, and equilibrium was achieved in 10 min. This fast biosorption of RV1 onto PSP could be an important advantage for real application of the suggested biosorption system. On the other hand, extremely fast biosorption did not enable a correct fitting of the results according to the usual kinetic models namely pseudo-first-order (Lagergren, 1989) and pseudo-second-order (Ho and McKay, 1999).

4. Conclusions

In this work, highly efficient and economic biosorbent was prepared from *P. sativum* through a simple procedure and successfully used for the removal of a reactive dye from contaminated aquatic media. BBD was used for the first time to simultaneously optimize the different parameters for reactive dye biosorption onto PSP. This design allowed evaluation of these interactive parameters by reducing the number of experiments. The most significant effects on RV1 biosorption included pH and biosorbent amount, whereas the temperature did not cause any important change in the dye removal efficiency of PSP. The appropriate isotherm model for fitting the equilibrium data was the Langmuir model. The findings indicated that PSP can be used as costless and environmental friendly biosorbent for the efficient removal of reactive dyes from contaminated waters with greener and cleaner treatment process. This study can also be a model for predictions regarding the use of PSP as biosorbent material for the removal of other reactive dyes under various conditions. This study serves an example of an alternative utilization for a waste biosorbent in an environmental remediation. When required conditions are provided, the suggested biosorbent can be successfully applied for the treatment of real wastewaters.

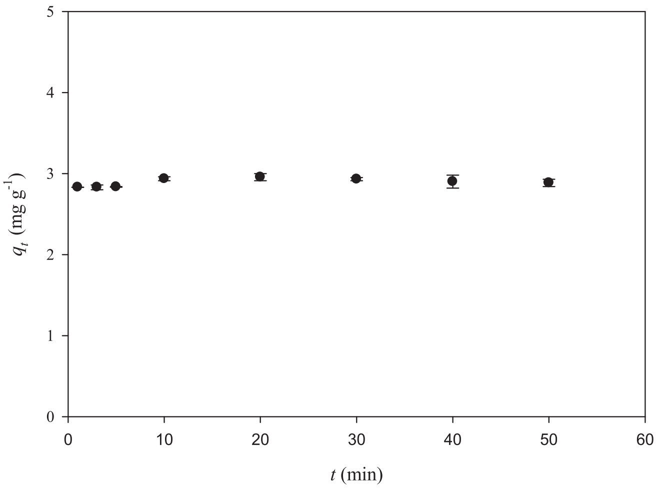


Fig. 6. The effect of the contact time on the biosorption of RV1 onto PSP.

References

Akar, S.T., Yilmazer, D., Celik, S., Balk, Y.Y., Akar, T., 2013a. On the utilization of a lignocellulosic waste as an excellent dye remover: modification, characterization and mechanism analysis. Chem. Eng. J. 229, 257–266.

Akar, T., Kulcu, A., Akar, S.T., 2013b. Effective decolorization potential of *Thamnidium elegans*: biosorption optimization, modelling, characterization and application studies. Chem. Eng. J. 221, 461–468.

Al-Asheh, S., Banat, F., Al-Rousan, D., 2003. Beneficial reuse of chicken feathers in removal of heavy metals from wastewater. J. Clean. Prod. 11, 321–326.

Allen, S.J., McKay, G., Porter, J.F., 2004. Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. J. Colloid Interf. Sci. 280, 322–333.

Amini, M., Younesi, H., Bahramifar, N., 2009. Statistical modeling and optimization of the cadmium biosorption process in an aqueous solution using *Aspergillus niger*. Colloid Surf. A 337, 67–73.

Aslan, N., 2007. Modeling and optimization of multi-gravity separator to produce celestite concentrate. Powder Technol. 174, 127–133.

Aslan, N., Cebeci, Y., 2007. Application of Box-Behnken design and response surface methodology for modeling of some Turkish coals. Fuel 86, 90–97.

Box, G.E.P., Behnken, D.W., 1960. Some new three level designs for the study of quantitative variables. Technometrics 2, 455–475.

Dod, R., Banerjee, G., Saini, S., 2012. Adsorption of methylene blue using green pea peels (*Pisum sativum*): a cost-effective option for dye-based wastewater treatment. Biotechnol. Bioprocess Eng. 17, 862–874.

Ferreira, S.L.C., Bruns, R.E., da Silva, E.G.P., dos Santos, W.N.L., Quintella, C.M., David, J.M., de Andrade, J.B., Breitkreitz, M.C., Jardim, I.C.S.F., Neto, B.B., 2007a. Statistical designs and response surface techniques for the optimization of chromatographic systems. J. Chromatogr. A 1158, 2–14.

Ferreira, S.L.C., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandão, G.C., da Silva, E.G.P., Portugal, L.A., dos Reis, P.S., Souza, A.S., dos Santos, W.N.L., 2007b. Box-Behnken design: an alternative for the optimization of analytical methods. Anal. Chim. Acta 597, 179–186.

Fomina, M., Gadd, G.M., 2014. Biosorption: current perspectives on concept, definition and application. Bioresour. Technol. 160, 3–14.

Freundlich, H., 1906. Über die absorption in lösungen. Universität Leipzig, 98p.

Geçgel, Ü., Özcan, G., Gürpınar, G.Ç., 2013. Removal of methylene blue from aqueous solution by activated carbon prepared from pea shells (*Pisum sativum*). J. Chem. 2013, 1–9.

Ghaedi, M., Zeinali, N., Ghaedi, A.M., Teimuori, M., Tashkhourian, J., 2014. Artificial neural network-genetic algorithm based optimization for the adsorption of methylene blue and brilliant green from aqueous solution by graphite oxide nanoparticle. Spectrochim. Acta A 125, 264–277.

Hall, K.R., Eagleton, L.C., Acrivos, A., V, T., 1966. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant pattern conditions. Ind. Eng. Chem. Fundam. 5, 212–223.

Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. Process Biochem. 34, 451–465.

Kaiser, S., Verza, S.G., Moraes, R.C., Pittol, V., Peñaloza, E.M.C., Pavei, C., Ortega, G.G., 2013. Extraction optimization of polyphenols, oxindole alkaloids and quinovic acid glycosides from cat's claw bark by Box-Behnken design. Ind. Crop Prod. 48, 153–161.

Lagergren, S., 1989. Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens, Handlingar, vol. 24, pp. 1–39.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40, 1361–1403.

Ma, X., Li, L., Yang, L., Su, C., Wang, K., Yuan, S., Zhou, J., 2012. Adsorption of heavy metal ions using hierarchical $CaCO_3$–maltose meso/macroporous hybrid materials: adsorption isotherms and kinetic studies. J. Hazard. Mater. 209–210, 467–477.

Martín-Lara, M.A., Blázquez, G., Trujillo, M.C., Pérez, A., Calero, M., 2014. New treatment of real electroplating wastewater containing heavy metal ions by adsorption onto olive stone. J. Clean. Prod. 81, 120–129.

Moawed, E.A., 2013. Effect of heating processes on Salvadora persica (Miswak) and its application for removal and determination of aniline blue from wastewater. J. Taibah Univ. Sci. 7, 26–34.

Montgomery, D.C., 2005. Design and Analysis of Experiments, sixth ed. John Wiley&Sons, New Jersey.

Murali, K., Karuppiah, P.L., Nithish, M., Kumar, S.S., Raja, V.S., 2013. COD reduction using low cost biosorbent as part of cleaner production. Int. J. Sci. Res. Publ. 3, 48–50.

Myers, R.H., Montgomery, D.C., 2002. Response Surface Methodology Process and Product Optimization Using Designed Experiments, second ed. John Wiley.

Nitayaphat, W., Jintakosol, T., 2015. Removal of silver(I) from aqueous solutions by chitosan/bamboo charcoal composite beads. J. Clean. Prod. 87, 850–855.

Özcan, A.S., Tunali, S., Akar, T., Özcan, A., 2009. Biosorption of lead(II) ions onto waste biomass of Phaseolus vulgaris L.: estimation of the equilibrium, kinetic and thermodynamic parameters. Desalination 244 (1–3), 188–198.

Pereira, L., Alves, M., 2012. Dyes—Environmental impact and remediation. In: Malik, A., Grohmann, E. (Eds.), Environmental Protection Strategies for Sustainable Development. Springer, Netherlands, pp. 111–162.

Pouralinazar, F., Yunus, M.A.C., Zahedi, G., 2012. Pressurized liquid extraction of *Orthosiphon stamineus* oil: experimental and modeling studies. J. Supercrit. Fluid 62, 88–95.

Pritee, G., Shalini, S., 2010. Smart biomaterials. In: Green Chemistry for Environmental Sustainability. CRC Press, pp. 79–92.

Rangabhashiyam, S., Anu, N., Selvaraju, N., 2013. Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents. J. Environ. Chem. Eng. 1, 629–641.

Rangabhashiyam, S., Anu, N., Giri Nandagopal, M.S., Selvaraju, N., 2014. Relevance of isotherm models in biosorption of pollutants by agricultural byproducts. J. Environ. Chem. Eng. 2, 398–414.

Rathod, M., Mody, K., Basha, S., 2014. Efficient removal of phosphate from aqueous solutions by red seaweed, *Kappaphycus alverezii*. J. Clean. Prod. 84, 484–493.

Şanal, İ.S., Bayraktar, E., Mehmetoğlu, Ü., Çalımlı, A., 2005. Determination of optimum conditions for SC-(CO_2+ethanol) extraction of β-carotene from apricot pomace using response surface methodology. J. Supercrit. Fluids 34, 331–338.

Sanjay, K.S., Ackmez, M., Wei, Z., 2010. Green chemistry and engineering. In: Green Chem. Environ. Sustain. CRC Press, pp. 1–52.

Sathishkumar, P., Arulkumar, M., Palvannan, T., 2012. Utilization of agro-industrial waste *Jatropha curcas* pods as an activated carbon for the adsorption of reactive dye Remazol Brilliant Blue R (RBBR). J. Clean. Prod. 22, 67–75.

Shin, K.-Y., Hong, J.-Y., Jang, J., 2011. Heavy metal ion adsorption behavior in nitrogen-doped magnetic carbon nanoparticles: isotherms and kinetic study. J. Hazard. Mater. 190, 36–44.

Solís, M., Solís, A., Pérez, H.I., Manjarrez, N., Flores, M., 2012. Microbial decolouration of azo dyes: a review. Process Biochem. 47, 1723–1748.

Volesky, B., 2007. Biosorption and me. Water Res. 41, 4017–4029.

Witek-Krowiak, A., Chojnacka, K., Podstawczyk, D., Dawiec, A., Pokomeda, K., 2014. Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. Bioresour. Technol. 160, 150–160.

Yargıç, A.Ş., Yarbay Şahin, R.Z., Özbay, N., Önal, E., 2015. Assessment of toxic copper(II) biosorption from aqueous solution by chemically-treated tomato waste (*Solanum lycopersicum*). J. Clean. Prod. 88, 152–159.

Yetilmezsoy, K., Demirel, S., Vanderbei, R.J., 2009. Response surface modeling of Pb(II) removal from aqueous solution by *Pistacia vera* L.: Box-Behnken experimental design. J. Hazard. Mater. 171, 551–562.