

Optimization of pyrocatechol violet biosorption by *Robinia pseudoacacia* leaf powder using response surface methodology: kinetic, isotherm and thermodynamic studies

Neda Khorshidi and Ali Niazi

ABSTRACT

We have investigated the biosorption of pyrocatechol violet (PCV) from aqueous solutions by *Robinia pseudoacacia* tree leaves as a low-cost and eco-friendly biosorbent. A full factorial design was performed for screening the main variables and their interactions, which reduces the large total number of experiments. Results of the full factorial design (2^4) based on an analysis of variance (ANOVA) demonstrated that the initial PCV concentration, contact time, pH and temperature are statistically significant. Box-Behnken design, a response surface methodology, was used for further optimization of these selected factors. The ANOVA and some statistical tests such as lack-of-fit and coefficient of determination (R^2) showed good fit of the experimental data to the second-order polynomial model. The Langmuir and Freundlich isotherm models were used to describe the equilibrium isotherms. Equilibrium data fitted well with the Freundlich isotherm model ($R^2 > 0.97$). In addition, thermodynamic parameters (ΔG° , ΔH° and ΔS°) were calculated, these parameters show that the biosorption process was spontaneous ($\Delta G^\circ = -2.423$) and exothermic ($\Delta H^\circ = -9.67$). The biosorption kinetic data were fitted with the pseudo-second-order kinetic model ($R^2 > 0.999$). These results confirm that *R. pseudoacacia* leaves have good potential for removal of PCV from aqueous solution.

Key words | biosorption, kinetics, pyrocatechol violet dye removal, response surface methodology, *Robinia pseudoacacia*

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INTRODUCTION

Synthetic dyes are extensively used in industries such as textile, paper, plastic, printing, pharmaceuticals and dye manufacturing. Dyes have been the subject of much interest in recent years because of increasingly stringent restrictions on the organic content of industrial effluents (Abou Taleb *et al.* 2009). Dye-containing effluents are highly problematic wastewaters because they affect aesthetic merit and reduce light penetration and photosynthesis (Da Silva *et al.* 2011; De Menezes *et al.* 2012). Dyes can cause allergy, dermatitis, skin irritation and also provoke cancer and mutation in humans (Brookstein 2009; Carneiro *et al.* 2010). Therefore,

the removal of dyes from water and wastewater is very important for environmental safety.

Different physicochemical methods like adsorption (Dural *et al.* 2011; El Haddad *et al.* 2013), precipitation (Lee *et al.* 2011), electroflotation (Essadki *et al.* 2008), coagulation/flocculation (Verma *et al.* 2012), solvent extraction (Lee *et al.* 2000), membrane filtration techniques (Alventosa-deLara *et al.* 2012), irradiation (Paul *et al.* 2011), chemical oxidation (Türgay *et al.* 2011), amongst others, have been used for the treatment of dye-containing effluents. However, these techniques have high sludge production and

high cost. Therefore, the development of efficient, low-cost and environmentally friendly technologies to reduce dye content in wastewater is necessary. Among the numerous techniques for dye removal from wastewaters, biosorption is one of the most efficient for removal of different types of dyes (Wang 2010). It is considered an economical and eco-friendly practice in comparison with other available methods. The use of low-cost biosorbents for dye removal has been widely reviewed (Gupta & Suhas 2009). Some important biosorbents which have recently been studied for dye removal include pineapple leaf (Chowdhury *et al.* 2011), tamarind fruit shell (Saha *et al.* 2010), sugar beet (Malekbala *et al.* 2012), rice husk (Safa & Bhatti 2011), *Thuja orientalis* cone powder (Akar *et al.* 2013), *Luffa cylindrica* fiber (Demir *et al.* 2008), coffee bean (Baek *et al.* 2010), kenaf (Sajab *et al.* 2011), jackfruit leaf powder (Saha *et al.* 2012) and tree leaves (Deniz & Saygideger 2010). The main advantages of this process are simple operation, rapidity, potential cost effectiveness, selectivity and reusability of some biosorbents, and the low quantity of sewage sludge disposed of.

The biosorption process might be influenced by some variables such as pH, the biosorbent amount, sorbate concentration, contact time, and temperature. The aim of this study was to investigate the biosorption potential of *Robinia pseudoacacia* tree leaves to treat wastewaters contaminated with pyrocatechol violet dye. *R. pseudoacacia* tree leaves are in abundant supply, inexpensive and easily available in countries such as Iran. The experimental conditions were performed using multivariate optimization techniques. The multivariate chemometric approach is advantageous for the reduced number of laboratory experiments, the increased possibilities for evaluating interactions among the variables, and the relatively low cost compared to traditional univariate approaches.

Statistical methods of experimental design and system optimization, such as factorial design and response surface analysis, have been applied to different adsorption systems because of their capacity to extract relevant information from systems while requiring a minimum number of experiments. Response surface methodology is a collection of statistical tools for designing experiments, model development, evaluating the effects of factors and searching for optimum conditions of factors for desirable responses (Box *et al.* 1978). Box–Behnken statistical design is one type of

response surface methodology design, which is an independent, rotatable or nearly rotatable, quadratic design having the treatment combinations at the midpoints of the edges of the process space and at the center (Govender *et al.* 2005). The Box–Behnken design is a very efficient model, since it requires a small number of runs and, therefore, is an important alternative avoiding time-consuming experiments.

A four-factor Box–Behnken experimental design was used to investigate and validate the initial concentration of used dyes, pH, contact time and temperature of the aqueous solution influencing the removal of pyrocatechol violet (PCV) by *Robinia*. The data was analyzed by fitting to a second-order polynomial model, which was statistically validated by performing analysis of variance (ANOVA) and a lack-of-fit test to evaluate the significance of the model. The kinetic, isotherm and thermodynamic biosorption studies were conducted to evaluate the dye removal ability of *Robinia*.

MATERIALS AND METHODS

Preparation of the biosorbent

The *R. pseudoacacia* tree leaves were gathered from twigs into clean plastic bags, washed with ion-free distilled water and then dried at 80 °C for 24 h. The dried biomass was powdered with a mortar and pestle. The powdered biomass was sieved to pass through a 50 mesh sieve (0.29 mm) to obtain uniform particle size and then stored in plastic bags before being used as a biosorbent in batch studies. The mesh size sieve was examined in the range 30–70, and no significant effect was observed on adsorption. Modification of biomass with NaCl increased the amount of dye absorbed. This could be due to activation of the internal biosorbent surface and production of more binding sites for the dye. Modified biosorbent was treated with 0.1 mol L⁻¹ NaCl for 60 min and excess NaCl was removed by washing several times with distilled water. The final modified biosorbent was dried on a clean table and used as biosorbent for removal of dye.

Preparation of dye solutions

All chemicals used in this study were of analytical grade. PCV, also known as pyrocatechol sulphonphthalein, was

obtained from Merck. Its structure is shown in Figure 1. Dyes were used without further purification. The stock solution ($1,000 \text{ mg L}^{-1}$) was prepared by dissolving a precise amount of PCV in distilled water. Experimental solutions of various concentrations were obtained by successive dilution with distilled water. All solutions were prepared with double-distilled and deionized water.

Experimental procedure

In order to investigate the effect of various experimental parameters on dye biosorption by *R. pseudoacacia* biosorbent, batch biosorption experiments were carried out. These experiments were carried out to optimize the experimental parameters such as the effect of dye concentration, pH, temperature and contact time. In order to study the combined effect of these factors, experiments were performed for different combinations of the physical parameters using statistically designed experiments. In each run, 10 mL aliquots of dye solution at different pH values, initial dye concentration, temperature and contact time were shaken on an incubator shaker (LsI-3016A shaking incubator, Labtech, Korea) at a constant speed (150 rpm). Samples obtained from the shaken dye solution were filtered with Whatman filter paper 41, and then the dye concentration was analyzed by UV/Vis spectrophotometer (Hewlett-Packard 8,453 diode array) at the maximum absorption wavelength of 435 nm. The pH of the solutions was adjusted with 0.1 mol L^{-1} HCl and NaOH, and the pH values were measured with a pH

meter (780 Metrohm pH-meter). A universal buffer was prepared using acetic acid, boric acid, and phosphoric acid (0.04 mol L^{-1}) solution. According to statistical analysis, the optimum experimental conditions were obtained. Experimental designs were obtained by using Minitab Version 16. Finally, the dye removal efficiency (R), the amount of absorbed dye per unit mass of biosorbent at equilibrium (q_e , mg g^{-1}) was calculated by applying Equation (1) and Equation (2), respectively:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e (mg L^{-1}) is the initial and equilibrium concentrations of dye solution, respectively, V is the volume of dye solution (L) and m is the mass of the biosorbent (g).

Full factorial design

Biosorption capacity may be significantly influenced by several factors, such as pH, initial concentration of dye, temperature, contact time, and speed of shaking. In this study, initial dye concentration, pH, temperature and contact time are taken as independent variables, while the other variables like the mass of biosorbent and shaking speed were kept constant. Screening techniques such as factorial design allow the analyst to select which factors are significant and allow subsequent optimization. With a factorial design, it is possible to determine the main effects as well as the interactive effects of the selected factors. The full factorial design was performed for screening the main variables and their interactions, which reduced the large total number of experiments. Two-level full factorial design was applied with a number of runs equal to $2^k + n$, where k is the number of factors and n is the number of center points. The range and levels used in the experiments, determined from the preliminary experiments, are listed in Table 1. The experiments were run at random to minimize errors due to possible systematic trends in the variables. Thus, 19 experiments including three at the center point were performed.

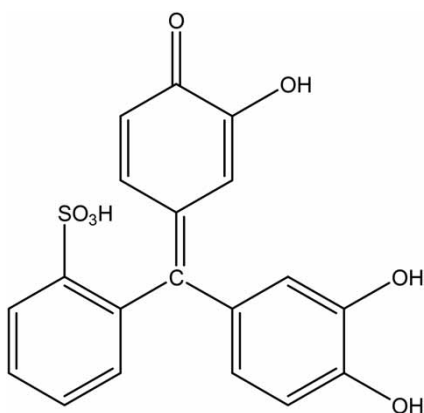


Figure 1 | The structure of PCV.

Table 1 | Experimental ranges and levels of the factors used in the factorial design

Factors	Symbol	Low Level (−1)	High Level (+1)
Initial dye concentration (mg L ^{−1})	X1	10	50
pH	X2	1	3
Contact time (min)	X3	10	70
Temperature (°C)	X4	15	30

RESULTS AND DISCUSSION

Full factorial design

In this study, a full factorial design included 2⁴ experiments used to identify effective factors and their interactions. Table 2 represents the design matrix for experimental factors and response. The ANOVA was carried out to find the significance of the main and interaction effects of the factors on the biosorption process (Bingol *et al.* 2010; Alam *et al.* 2012). The

Table 2 | Design matrix and responses for the full factorial design

Run no.	Actual level of factors				Removal efficiency (R%)
	X ₁	X ₂	X ₃	X ₄	
1	X ₁	X ₂	X ₃	X ₄	
2	50	1	10	15.0	80.9 ± 0.1
3	50	1	70	30.0	82.3 ± 0.3
4	10	3	70	30.0	64.0 ± 0.2
5	50	1	10	30.0	76.6 ± 0.2
6	50	1	70	15.0	80.4 ± 0.5
7	10	1	70	15.0	72.4 ± 0.1
8	10	1	10	15.0	66.2 ± 0.2
9	10	3	70	15.0	65.1 ± 0.5
10	10	1	70	30.0	62.3 ± 0.6
11	10	1	10	30.0	63.3 ± 0.3
12	50	3	10	30.0	66.6 ± 0.5
13	30	2	40	22.5	91.2 ± 0.2
14	30	2	40	22.5	92.2 ± 0.3
15	10	3	10	30.0	66.3 ± 0.5
16	30	2	40	22.5	92.5 ± 0.1
17	50	3	10	15.0	65.9 ± 0.4
18	10	3	10	15.0	57.3 ± 0.3
19	50	3	70	15.0	72.9 ± 0.2
20	50	3	70	30.0	65.5 ± 0.5

results of ANOVA for the biosorption study of PCV are reported in Table 3. The results from ANOVA showed that all the main factors, initial dye concentration (X₁), pH (X₂), contact time (X₃), temperature (X₄) and interaction factors (X₁X₂, X₂X₄ and X₃X₄) have a *p*-value <0.05, indicating they are significant. In order to better evaluate each factor and its interactions, the normal probability plot of standardized effects for *R. pseudoacacia* is presented in Figure 2(a). Each point on the plot represents an effect. The effects that are not statistically significant are located close to the reference line and are left unlabeled. The effects represented by points far from the reference line are considered statistically significant. According to Figure 2(a), all the main factors (A, B, C, and D) and their interactions (AB, CD, BD, ABD, BCD and ACD) are considered to be significant. The Pareto chart is used to assess the relative importance of the main effects and their interactions for response (Figure 2(b)). The values that exceed a reference line, i.e., those corresponding to the 95% confidence level, are significant values (Mathialagan & Viraraghavan 2005). According to Figure 2(b), the main factors (A, B, C, and D) and their interactions (AB, CD, BD, ABD, BCD, and ACD) that extend beyond the reference line were significant at the level of 0.05. The initial dye concentration (A) represented

Table 3 | ANOVA for the full factorial design

Variables	DF	SS	MS	F-values	p-value
X ₁	1	344.10	344.10	742.67	0.001
X ₂	1	231.04	231.04	498.65	0.002
X ₃	1	29.70	29.70	64.11	0.015
X ₄	1	12.60	12.60	27.20	0.035
X ₁ X ₂	1	89.30	89.30	192.74	0.005
X ₁ X ₃	1	0.01	0.01	0.02	0.897
X ₁ X ₄	1	1.00	1.00	2.16	0.280
X ₂ X ₃	1	0.06	0.06	0.13	0.749
X ₂ X ₄	1	17.22	17.22	37.17	0.026
X ₃ X ₄	1	23.04	23.04	49.73	0.020
X ₁ X ₂ X ₃	1	0.01	0.01	0.02	0.897
X ₁ X ₂ X ₄	1	39.69	39.69	85.66	0.011
X ₁ X ₃ X ₄	1	14.82	14.82	31.99	0.030
X ₂ X ₃ X ₄	1	18.49	18.49	39.91	0.024
X ₁ X ₂ X ₃ X ₄	1	8.12	8.12	17.53	0.053

DF, degree of freedom; SS, sum of squares; MS, mean square.

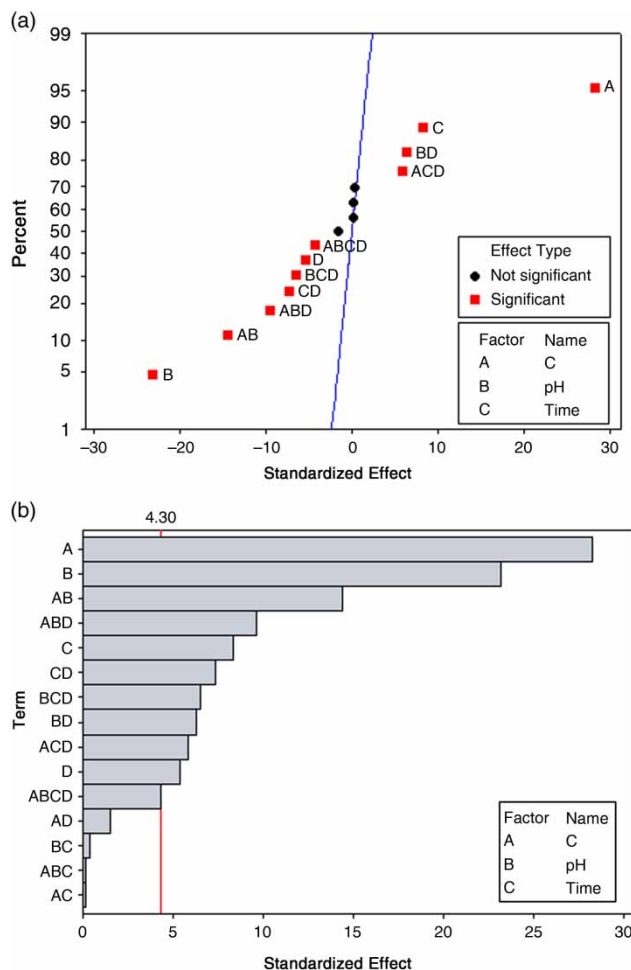


Figure 2 | (a) Normal probability plot of standardized effects at $p = 0.05$ and (b) Pareto chart of the standardized effects at $p = 0.05$.

the most significant effect on response. These results confirm the previous normal probability plot and the values of Table 3.

Box–Behnken designs

After performing a screening of factors using a full 2^4 factorial design, a Box–Behnken response surface design was carried out according to experiments described in Table 4. A significant advantage of Box–Behnken statistical design is that it is a more cost-effective technique compared with other techniques such as central composite design, three-level factorial design and D-optimal design, which require fewer experimental runs and less time for optimization of a process.

A four-factor, three-level factorial Box–Behnken design was employed to investigate the effects of selected variables.

Table 4 | Factors and their levels in the Box–Behnken experimental design

Run no.	Actual level of factors				Removal efficiency (R%)
	X_1	X_2	X_3	X_4	
1	50	2	70	22.5	90.0 ± 0.3
2	10	2	10	22.5	81.3 ± 0.2
3	50	2	40	30.0	87.6 ± 0.2
4	30	2	40	22.5	91.2 ± 0.1
5	30	1	70	22.5	81.7 ± 0.4
6	50	3	40	22.5	72.3 ± 0.5
7	30	2	40	22.5	92.3 ± 0.1
8	30	3	40	15.0	73.1 ± 0.3
9	30	3	70	22.5	71.5 ± 0.2
10	50	2	40	15.0	87.7 ± 0.5
11	30	2	10	15.0	84.4 ± 0.3
12	30	1	40	30.0	78.6 ± 0.4
13	30	2	10	30.0	80.4 ± 0.5
14	10	2	40	30.0	80.0 ± 0.3
15	10	1	40	22.5	75.0 ± 0.3
16	50	1	40	22.5	82.8 ± 0.1
17	10	2	70	22.5	83.0 ± 0.4
18	10	2	40	15.0	85.7 ± 0.2
19	30	2	40	22.5	93.7 ± 0.2
20	10	3	40	22.5	70.0 ± 0.5
21	30	2	70	30.0	84.9 ± 0.1
22	30	1	40	15.0	78.1 ± 0.3
23	30	3	40	30.0	66.5 ± 0.1
24	50	2	10	22.5	84.0 ± 0.2
25	30	2	70	15.0	89.7 ± 0.2
26	30	3	10	22.5	67.1 ± 0.5
27	30	1	10	22.5	78.1 ± 0.3

The number of experiments (N) required for the development of a Box–Behnken design is defined as $N = 2k(k - 1) + C_0$, (where k is number of factors and C_0 is the number of central points). The Box–Behnken design and the responses are illustrated in Table 4. The second-order polynomial analysis and quadratic model were employed to find out the relationship between variables and responses. To predict the optimal point, the full quadratic equation model was expressed according to following equation:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where Y is the predicted response and X_i represents the effect of the independent variables. Thus, X_i^2 and X_iX_j represent the quadratic and interaction terms, respectively; β_0 , β_{ii} and β_{ij} ($i \neq j$) are the coefficient of linear, quadratic and interaction, respectively. β_0 and ε represent the constant and the random error, respectively (Zhang & Zheng 2009). The second-order quadratic model expressed by the following equation represents removal efficiency (Y) as a function of initial dye concentration (X_1), pH (X_2), contact time (X_3), temperature (X_4).

$$Y = 92.4 + 2.45X_1 - 4.4833X_2 + 2.125X_3 - 1.7250X_4 - 1.3750X_1X_2 + 1.075X_1X_3 + 1.4X_1X_4 + 0.2X_2X_3 - 1.775X_2X_4 - 0.2X_3X_4 - 3.5042X_1^2 - 14.0792X_2^2 - 3.9167X_3^2 - 3.8417X_4^2 \quad (4)$$

The ANOVA was carried out to determine the significance of the model equation and the model terms (Table 5).

Table 5 | ANOVA for Box–Behnken design for the biosorption of PCV by *Robinia pseudoacacia* powder

Variables	DF	SS	MS	F-values	p-value
Model	14	1,504.62	107.47	112.46	0.000 ^a
X_1	1	72.03	72.03	75.37	0.000
X_2	1	241.20	241.20	252.40	0.000 ^a
X_3	1	54.19	54.19	56.70	0.000 ^a
X_4	1	35.71	35.71	37.37	0.000 ^a
X_1^2	1	4.97	65.49	68.53	0.000 ^a
X_2^2	1	943.16	1,057.19	1,106.28	0.000 ^a
X_3^2	1	41.69	81.81	85.61	0.000 ^a
X_4^2	1	78.71	78.71	82.37	0.000 ^a
X_1X_2	1	7.56	7.56	7.91	0.016 ^b
X_1X_3	1	4.62	4.62	4.84	0.048 ^b
X_1X_4	1	7.84	7.84	8.20	0.014 ^b
X_2X_3	1	0.16	0.16	0.17	0.690 ^c
X_2X_4	1	12.60	12.60	13.19	0.003 ^b
X_3X_4	1	0.16	0.16	0.17	0.690 ^c
Residual	12	11.47	0.96		
Lack-of-fit	10	8.33	0.83	0.53	0.798
Pure error	2	3.14	1.57		
Total	26	1,516.08			

$R^2 = 99.24$; Predicted $R^2 = 96.37$; Adjusted $R^2 = 98.36$.

DF, degree of freedom; SS, sum of squares; MS, mean square.

^aHighly significant.

^bSignificant.

^cNon-significant.

Significance of model terms is checked by their respective p -values: a p -value less than 0.05 suggests model terms are significant and less than 0.0001 are highly significant. It was concluded that all the linear and quadratic terms were highly significant, while interaction terms, except for the interaction of X_2X_3 and X_3X_4 , were also found to be significant at the 95% confidence level. The interaction of X_2X_3 and X_3X_4 demonstrated the lowest effect on the PCV removal efficiency ($p = 0.69$).

To further validate the model, the quality of the fitted model was evaluated by the coefficients of determination (R^2). Normally, a regression model with $R^2 > 0.90$ is considered to have a very high correlation (Haaland 1989). The high R^2 value (0.9924) suggested an excellent correlation between experimental and predicted values; 99.24% variability of the response could be explained by the model, and only about 0.76% of the total variation cannot be explained by this model. Also, an acceptable agreement with the adjusted determination coefficient is necessary. The adjusted R^2 value (0.9836) was found to be very close to R^2 . The lack of fit test measures the failure of the model to represent experimental data in the experimental domain at points which are not included in regression analysis (Sharma *et al.* 2009). Lack of fit was found to be non-significant ($p = 0.798$) and it indicated that the model equation was valid for the biosorption PCV onto *Robinia* powder.

The significance of each coefficient was determined by p -values, which are listed in Table 6. As can be seen, the constant term and the linear and square coefficients were statistically significant at a confidence interval of 95%. In contrast, the interaction of X_2X_3 and X_3X_4 were statistically insignificant. Therefore, by elimination of insignificant terms, the model can be rewritten with significant terms (Equation (5)):

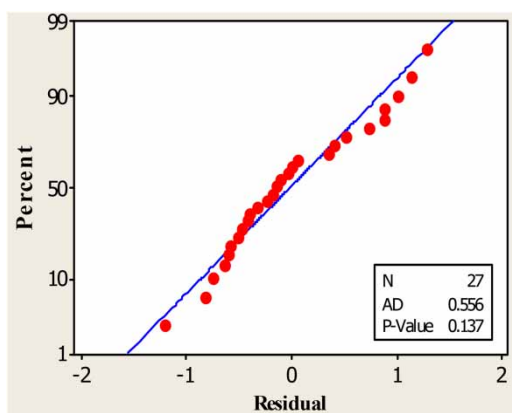
$$Y = 92.4 + 2.45X_1 - 4.4833X_2 + 2.125X_3 - 1.7250X_4 - 1.3750X_1X_2 + 1.075X_1X_3 + 1.4X_1X_4 - 1.775X_2X_4 - 3.5042X_1^2 - 14.0792X_2^2 - 3.9167X_3^2 - 3.8417X_4^2 \quad (5)$$

$\frac{\partial Y}{\partial X_1}$, $\frac{\partial Y}{\partial X_2}$, $\frac{\partial Y}{\partial X_3}$ and $\frac{\partial Y}{\partial X_4}$ were each equated to zero and the resulting three equations were solved simultaneously to obtain the values of X_1 , X_2 , X_3 and X_4 corresponding to the maximum of Y . The optimum values of the tested parameters were obtained as follows: $X_1 = 38.28$, $X_2 = 1.82$, $X_3 = 50.0$ and $X_4 = 21.66$.

Table 6 | Regression coefficients for Box–Behnken and their statistical parameters

Source	Coefficients	T-values	p-value
β_0	92.4000	163.715	0.000
β_1	2.4500	8.682	0.000
β_2	-4.4833	-15.887	0.000
β_3	2.1250	7.530	0.000
β_4	-1.7250	-6.113	0.000
β_{12}	-1.3750	-2.813	0.016
β_{13}	1.0750	2.199	0.048
β_{14}	1.4000	2.864	0.014
β_{23}	0.2000	0.409	0.690
β_{24}	-1.7750	-3.631	0.003
β_{34}	-0.2000	-0.409	0.690
β_1^2	-3.5042	-8.278	0.000
β_2^2	-14.0792	-33.261	0.000
β_3^2	-3.9167	-9.253	0.000
β_4^2	-3.8417	-9.076	0.000

For the statistical analysis of the experimental data, it is necessary to assume that the data come from a normal distribution (Antony 2003). The normality of the data can be checked by plotting a normal probability plot of the residuals (Figure 3). A residuals distribution was evaluated for normality according to the Anderson–Darling test. The figure clearly shows that residuals lie approximately along a straight line, suggesting normal distribution. The p -value for this test (0.137) confirmed this conclusion.

**Figure 3** | The normal probability plot of residuals.

Biosorption kinetics

Biosorption kinetics is one of the most important parameters that significantly depict the features of a biosorbent. Adsorption kinetics shows a strong dependence on the physical and/or chemical characteristics of the sorbent material, which also influences the sorption mechanism (Ofomaja 2010). In the present study, the commonly used models, pseudo-first and pseudo-second order models were chosen to describe the kinetic biosorption data.

The pseudo-first order kinetic model can be expressed by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_e and q_t (mg g^{-1}) refer to the amounts of dye adsorbed at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order sorption. The k_1 and q_e were determined from the slope and intercept of plots of $\ln(q_e - q_t)$ versus t , respectively, as shown in Figure 4(a).

The pseudo-second-order kinetic model can be expressed by Equation (7) (Ho & McKay 1999):

$$\frac{t}{q_t} = \frac{k_1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant for the pseudo-second-order kinetic model. The plot of t/q_t versus t gives a straight line with a slope of $1/q_e$ and an intercept of $1/k_2 q_e^2$ (Figure 4(b)). Kinetic parameters and regression coefficients (R^2) for the two kinetic models were obtained and are presented in Table 7.

The sorption system will follow a specific kinetic model if the R^2 value exceeds 0.98 and the calculated q_e value is comparable to that of the experimental value (Farooq *et al.* 2010). The correlation coefficients (R^2) for the pseudo-first and pseudo-second order kinetic model were higher than 0.99 (Table 7 and Figure 4). Moreover, the experimental q_e value (4.288 mg g^{-1}) were very close to the theoretical q_e value (4.308 mg g^{-1}) calculated from the pseudo-second-order kinetic model. These results indicated that the biosorption of PCV on *R. pseudoacacia* can be well described by the pseudo-second-order

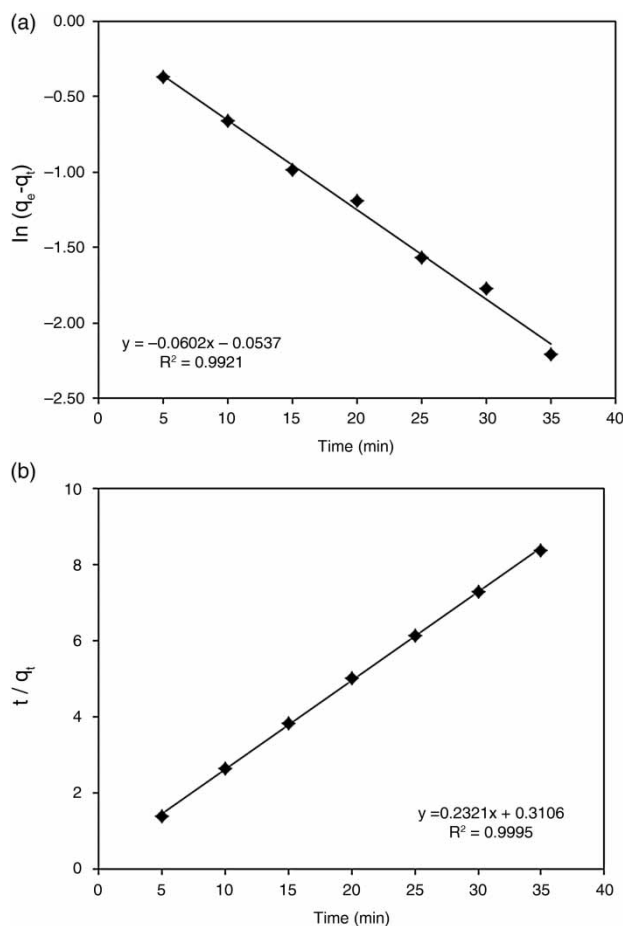


Figure 4 | Plots of (a) pseudo-first order, (b) pseudo-second order kinetics of PCV biosorption onto *R. pseudoacacia*.

Table 7 | Parameters of pseudo-first-order and pseudo-second-order kinetics model

$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_{e,cal}$ (mg g^{-1})	R^2
4.288	0.0602	0.948	0.992	0.173	4.308	0.999

kinetics. The pseudo-second-order model is based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between biosorbent and sorbate (Bayramoglu *et al.* 2009). This model implies a chemisorption mechanism for PCV biosorption.

Biosorption isotherms

Equilibrium isotherm studies are important for the understanding of the biosorption mechanism (Akar & Divriklioglu 2010). Biosorption equilibrium data were analyzed using the most commonly used isotherms, the Langmuir and Freundlich isotherm expressions. The Langmuir adsorption is based on the assumption of monolayer adsorption on a structurally homogeneous adsorbent, where all the sorption sites are identical and energetically equivalent. The linear form of the Langmuir equation can be expressed as follows (Langmuir 1918):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (8)$$

where C_e is the concentration of PCV at equilibrium (mg L^{-1}), q_e is the amount of dye biosorbed per unit mass of biosorbent at equilibrium (mg g^{-1}), q_m is the maximum monolayer biosorption capacity of the biosorbent (mg g^{-1}); and K_L is the Langmuir constant and related to the free biosorption energy (L mg^{-1}). The values of q_m and K_L are obtained from the slope and intercept of the linear plot of C_e/q_e versus C_e .

The suitability of the biosorbent for the biosorbate and feasibility of biosorption process can be determined by the separation factor R_L in the analysis of data by Langmuir isotherm, which is defined by the following equation (Hall *et al.* 1966; Yang *et al.* 2011):

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

where K_L is the Langmuir constant (L mg^{-1}) and C_0 is the initial concentration (mg L^{-1}). It is considered to be a favorable process when R_L is between 0 and 1 and unfavorable when R_L is greater than 1 (Ong *et al.* 2009). R_L values in this study under different C_0 were between 0.298 and 0.955 and indicated the favorable biosorption process for PCV removal onto *Robinia*.

The Freundlich isotherm (Freundlich 1906) is an empirical equation which is applicable to adsorption on heterogeneous surfaces and is not restricted to the formation of a monolayer. The linear form of Freundlich equation can

be expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (10)$$

where q_e represents the amount of dye adsorbed at equilibrium (mg g^{-1}), K_F is the Freundlich constant related to the sorption capacity of the biosorbent (L g^{-1}), and n (dimensionless) is a Freundlich constant related to sorption intensity. The values of K_F and $1/n$ are calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$. It was reported that n values in the range of 1–10 suggest favorable biosorption (Basha & Murthy 2007). The value of n (1.2) indicated that the biosorption process was favorable under the conditions studied.

The Langmuir and Freundlich isotherm plots are shown, respectively, in Figures 5(a) and (b), and the parameters related to each isotherm with R^2 values are shown in Table 8. The correlation coefficients (R^2) of the Langmuir and Freundlich models were 0.749 and 0.995, respectively. By comparing the correlation coefficient values obtained from the Langmuir and Freundlich isotherm models, it can be concluded that the Freundlich isotherm model is more suitable for describing PCV biosorption onto *Robinia* powder. From the Langmuir adsorption isotherm, the maximum biosorption capacity (q_m) of *R. pseudoacacia* is estimated to be 82.640 mg g^{-1} . This is much greater than the value (14.200 mg g^{-1}) reported in the only previous study of removal of color from textile wastewater by *R. pseudoacacia* (Aktas *et al.* 2014).

Biosorption thermodynamics

The thermodynamic parameters reflect the feasibility and spontaneous nature of the biosorption process. The thermodynamic parameters such as standard Gibbs free energy changes (ΔG°), standard enthalpy changes (ΔH°) and standard entropy changes (ΔS°) were also studied to understand better the effect of temperature on the adsorption (Lian *et al.* 2009). The values of enthalpy (ΔH°) and entropy (ΔS°) changes may be determined from the Van't Hoff equation given below (Smith & Van Ness 1987):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

$$\Delta G^\circ = -RT \ln K_C \quad (12)$$

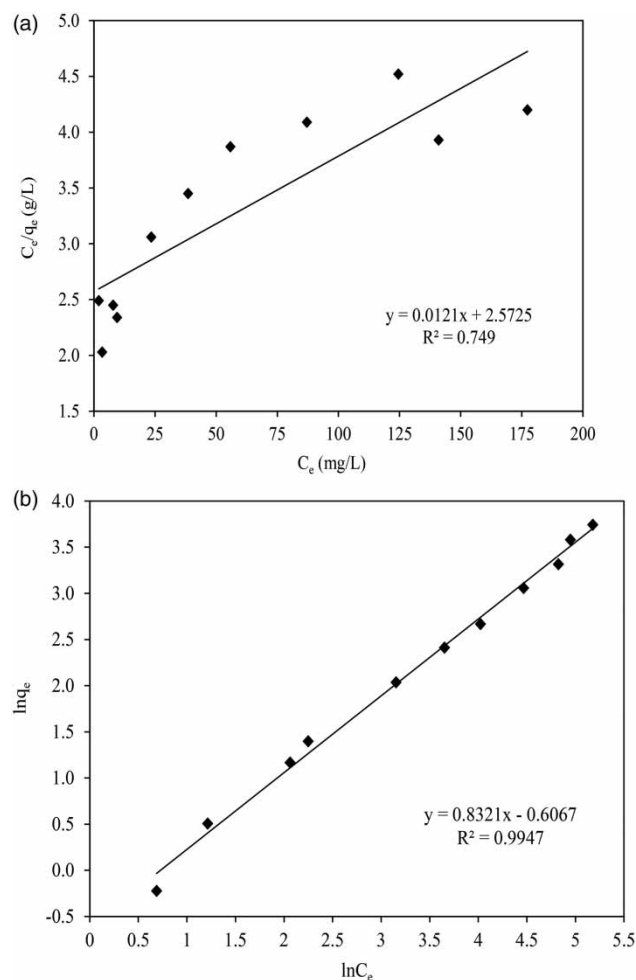


Figure 5 | The (a) Langmuir and (b) Freundlich isotherm plots for the biosorption of PCV onto *R. pseudoacacia*.

Table 8 | Equilibrium parameters for Langmuir and Freundlich models

Langmuir			Freundlich		
$K_L (\text{L mg}^{-1})$	$q_{\max} (\text{mg g}^{-1})$	R^2	n	$K_F (\text{L g}^{-1})$	R^2
0.005	82.640	0.749	1.2	1.834	0.995

$$K_C = \frac{C_s}{C_e} \quad (13)$$

The combination of Equations (11) and (12) gives:

$$\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (14)$$

where ΔG° (kJ mol^{-1}), ΔH° (kJ mol^{-1}) and ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$) are changes of Gibbs free energy, enthalpy and entropy, respectively; R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$) and T is the absolute temperature in Kelvin; K_c is the ratio of concentration of C_s on biosorbent at equilibrium (q_e) to the remaining concentration of the dye in solution at equilibrium (C_e). By plotting a graph of $\ln K_c$ versus $1/T$, the enthalpy (ΔH°) and entropy (ΔS°) of biosorption were estimated from the slope and intercept, respectively (Figure 6). Table 9 shows the thermodynamic parameters obtained. The negative values of ΔG° obtained in the temperature range of 296–313 K were due to the fact that the biosorption process was spontaneous and feasible thermodynamically. The observed decrease in negative values of ΔG° with increasing temperature implied that the adsorption became less favorable at higher temperatures. The negative value of enthalpy change ($\Delta H^\circ = -9.67 \text{ kJ mol}^{-1}$) confirms the exothermic nature of the biosorption process. Furthermore, the positive value of ΔS° reveals the increased randomness at the solid–solution interface during the biosorption of PCV onto *Robinia* powder.

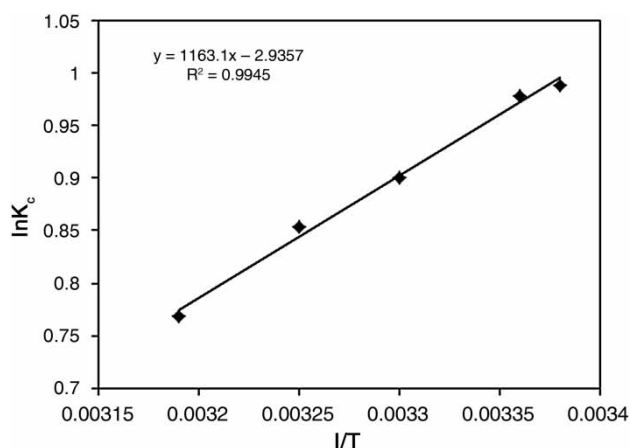


Figure 6 | Plot of $\ln K_c$ versus $1/T$ for PCV biosorption onto *R. pseudoacacia*.

Desorption and regeneration studies

To evaluate the possibility of regeneration of *R. pseudoacacia* biosorbent, we performed desorption experiments. The reusability of biosorbents is of great importance as a cost-effective process in water treatment and is crucial in assessing their potential for commercial application. The regeneration of biosorbent was studied via several biosorption–desorption cycles. We carried out desorption and regeneration studies by using 0.1 mol L^{-1} NaOH solution. The desorbed *R. pseudoacacia* powder was washed several times with deionized water and was used in the next biosorption–desorption cycle. The results are presented in Figure 7. It can be seen that after four biosorption–desorption cycles, the biosorption efficiency of *R. pseudoacacia* powder decreased by 10% after the fourth cycle. This behavior indicates that the *R. pseudoacacia* powder can be used successfully four times after regeneration for the PCV biosorption from aqueous solution.

CONCLUSION

In this study, the potential of *R. pseudoacacia* tree leaves as a natural biosorbent was investigated for removal of PCV from aqueous solution. The full factorial design was used to screen variables affecting the biosorption process, to estimate the main effects and interaction effects of different variables. Based on the results of the ANOVA test, main factors such as dye concentration, contact time, pH and temperature were determined as effective factors and should be optimized. According to the normal probability plot and Pareto chart, the initial dye concentration and pH are the most significant factors in the response. As a specific amount of biosorbent must be used for removal of PCV from aqueous solution, and by considering the biosorption capacity, the amount of dye was essentially an

Table 9 | Thermodynamic parameters calculated for the biosorption of PCV by *R. pseudoacacia* powder at different temperatures

ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$)	ΔG° (kJ mol^{-1})				
		296 k	298 k	303 k	308 k	313 k
−9.670	24.407	−2.433	−2.423	−2.270	−2.184	−2.001

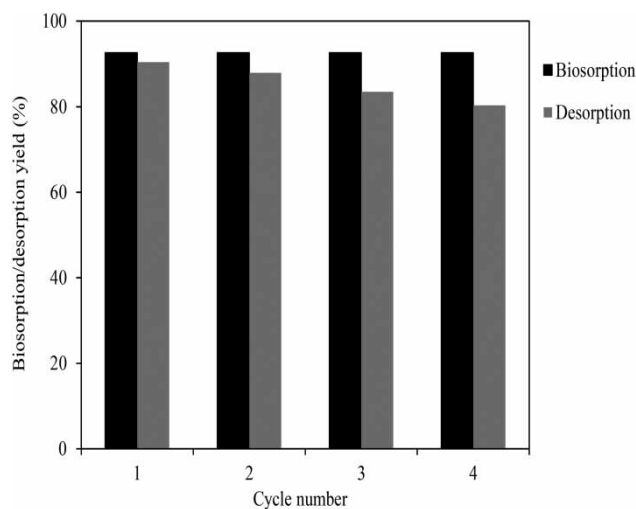


Figure 7 | Reusability of *R. pseudoacacia* powder.

important factor. pH may be of great importance as the dye structure is changed by changing the pH, which affects the acidic and basic groups present in the structure of the dye.

Box–Behnken experimental design, as a powerful response surface methodology, was utilized for optimization. A second-order polynomial model successfully described the effects of variables on the PCV dye removal. The experimental data indicated that biosorption of PCV dye onto *R. pseudoacacia* powder was spontaneous and exothermic in nature and the kinetic data were best described by the pseudo-second order model. The equilibrium data could be well fitted by the Freundlich isotherm models. The results of the present study suggest that *R. pseudoacacia* tree leaves could be used as an effective, low cost and eco-friendly biosorbent for the removal PCV from aqueous solutions.

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