



Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste

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ABSTRACT

In the present study a low-cost waste biomass derived from canned food plant, was tested for its ability to remove reactive textile dye from aqueous solutions. The batch biosorption experiments were carried out at various pH, biosorbent dosage, contact time and temperature. Optimum decolorization was observed at pH 2.0 and 1.6 g dm⁻³ of biomass dosage within 20 min. The first-order and the pseudo-second-order kinetics were investigated for the biosorption system. The applicability of the Langmuir and Freundlich isotherm models was examined. The thermodynamic parameters for the biosorption were also calculated. The experimental results in this study indicated that this low-cost biomaterial was an attractive candidate for the removal of textile dye Reactive Red 198 (RR198) from aqueous solutions.

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1. Introduction

The contamination of the industrial waters with the organic based chemicals has created a serious environmental problem. Synthetic dyes, one group of organic pollutants, are extensively used in several industries such as textile, paper, printing and dye houses. The effluents of these industries are highly colored [1,2] and discharge of dye containing effluents into the natural water bodies can pose hazardous effects on the living systems because of carcinogenic, mutagenic, allergenic and toxic nature of dyes. The presence of very small amounts of dyes in water (less than 1 mg dm⁻³ for some dyes) is highly visible and undesirable [3,4].

The conventional decolorization methods of dye bearing wastewaters involve the combination of physical and chemical processes such as precipitation, sedimentation, ultrafiltration, flotation, color irradiation, ozonation and coagulation. However the application of the above mentioned technologies is sometimes restricted due to technical and economical constraints [5,6]. Also synthetic dyes have a complex aromatic molecular structure, which makes them stable and resistant to biological degradation [7–9].

Adsorption is an effective alternative process for the treatment of contaminated wastewater [10]. Currently, activated carbon is the most popular and extensively used commercial biosorbent material due to its high adsorption capacity, surface area and degree of surface reactivity as well as microporous structures. But it shows some disadvantages such as high operating costs and regeneration problems [11–13]. Therefore, in the

recent years considerable amount of researches have been done on the development of effective, low cost and easily available alternative biosorbents. Different agricultural biomasses such as tree fern [9], peat and rice husk [14], peanut hull [15], sugarcane dust [16], apple pomace and wheat straw [17], bark [18], palm kernel fibre [19], banana peel and orange peel [20], coir pith [21], linseed cake [22] and sawdust [23] have been previously tried for the removal of different types of dyes, but high effective and more economical biosorbent materials are still needed to search.

The objective of this study was to investigate the potential usability of *Phaseolus vulgaris* L. (*P. vulgaris* L.), a waste biomass generated by a canned food factory for the decolorization of solutions containing a reactive textile dye. This non-conventional biosorbent is an abundant, low-cost and readily available biomass from the canned food industry and recently we have reported that the *P. vulgaris* L. waste biomass can remove an acid dye [6] from aqueous media as an excellent biosorbent. To the best of our knowledge, it has not been used yet for reactive textile dye removal from aqueous solutions. In our study RR198 dye biosorption properties of this waste biomass were investigated through the batch experiments as a function of pH, biosorbent dosage, contact time and temperature. Langmuir and Freundlich isotherm models were used to evaluate the experimental data. The biosorption rates of dye were analyzed by the first-order and the pseudo-second-order kinetic expressions. The thermodynamic parameters were also estimated from the biosorption experiments.

2. Materials and methods

2.1. Preparation of the biosorbent material

P. vulgaris L. waste biomass generated by the canned food production process was obtained from a local canned food plant in

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Turkey. The waste material was washed with distilled water three times in order to remove dust and then dried in an oven at 80 °C until constant weight. The dried biosorbent material was crushed and sieved to select particle fractions of less than 300 µm using ASTM Standard sieve. Powdered biosorbent was stored for further use and used without any further chemical or physical modification.

2.2. Preparation of dye solution

The reactive textile dye, Reactive Red 198 (RR198) (MW 984.2 g mol⁻¹) was obtained from a local company in Turkey and used without further purification. The dye showed a maximum absorbance at wavelength 515 nm. Stock dye solution (1000 mg dm⁻³) was prepared by dissolving an appropriate amount of RR198 in deionized water and other concentrations were prepared by dilution of the stock solution. The pH of the working solutions was adjusted to the required values by 0.1 M HCl or 0.1 M NaOH. All the chemicals used in this study were in analytical grade.

2.3. Dye biosorption experiments

Batch biosorption experiments were performed on a magnetic stirrer at 200 rpm using 100 cm³ beakers containing 50 cm³ of dye solutions. In order to determine the effective biosorption conditions, experiments were conducted with different pH values, biosorbent and initial dye concentrations. The effect of initial pH on the biosorption was determined by adjusting the pH values of the dye solutions between 1.0 and 11.0. The effect of the biosorbent amount was studied in the concentration range of 0.4 to 4.0 g dm⁻³. Kinetic studies at various temperatures of 20, 30, 40 and 50 °C under optimum conditions were conducted to verify the fitting of the experimental data to the first-order and the pseudo-second order kinetic models. Varying concentrations (100–300 mg dm⁻³) of relevant dye were prepared and used for the investigation of the appropriateness of Langmuir and Freundlich isotherm models in the same temperature range. The end of the each equilibrium experiment, the biosorbent was removed from suspension by centrifugation at 4500 rpm for 5 min and the residual dye concentrations in the solutions were measured using UV spectrophotometer (UV/Vis, Unicam UV2-100). The dye biosorption capacity of the biosorbent was calculated using the following general equation:

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

where C_i and C_e are the initial and the equilibrium dye concentrations (mg dm⁻³), V is the volume of the solution (dm³) and m is the amount of biosorbent used (g).

3. Results and discussion

3.1. Effect of pH

Previous studies in the literature have provided that solution pH is an important parameter affecting the biosorption process [15,24]. Fig. 1 shows the variation of the equilibrium dye uptake with different pH values. It was observed that the pH significantly affected the RR198 decolorization potential of biomass. The negligible dye biosorption was observed in the pH range of 6.0–11.0. As the pH of the aqueous medium decreased, the biosorption capacity of the biomass increased. The maximum dye uptake capacity of the biosorbent was found to be 49.51 mg g⁻¹ at an initial pH value of 2.0. The biosorbent surface has many different functional groups and the net charge on the biosorbent surface is pH-dependent. Therefore, the pH of the medium is an important environmental parameter for dye removal from the

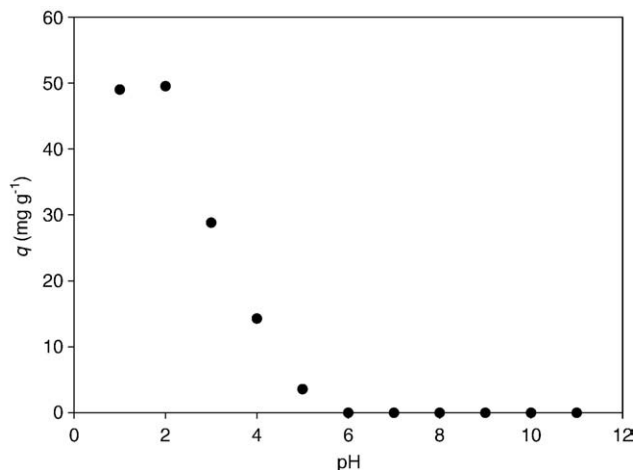


Fig. 1. Effect of pH for the biosorption of RR198 onto *P. vulgaris* L. at 20 °C.

aqueous medium [25]. Previous researches revealed that the necessity of lower pH values for maximum reactive dye biosorption [26–28]. At strongly acidic conditions the surface of the biosorbent gets positively charged thus provides attractive forces for negatively charged dye molecules. When the pH of the solution increased the number of negatively charged sites increased. Lower biosorption capacity of biomass observed at alkaline pH is because of the competition between the excess hydroxyl ions and the negatively charged dye ions for the binding sites. These results suggest that the one type of mechanism for the biosorption of RR198 should be the electrostatic attraction between the positively charged biosorbent surface and the negatively charged dye anions.

3.2. Effect of biomass dosage

Fig. 2 shows the plot of the percentage of dye biosorption against different biosorbent concentrations. As it can be seen from this figure, an increase in the biosorbent concentration from 0.4 to 1.6 g dm⁻³ the biosorption yield increased from 41.00% to 99.30% which is the maximum value, whereas the biosorption capacity of the biosorbent decreased from 102.50 mg g⁻¹ to 62.06 mg g⁻¹. A decrease in the biosorption capacity at higher biosorbent concentration may be attributed to overlapping or partial aggregation of biosorption sites on the biosorbent surface. This fact results in a decrease in effective surface area of the biosorbent available to the dye [29–31]. Further

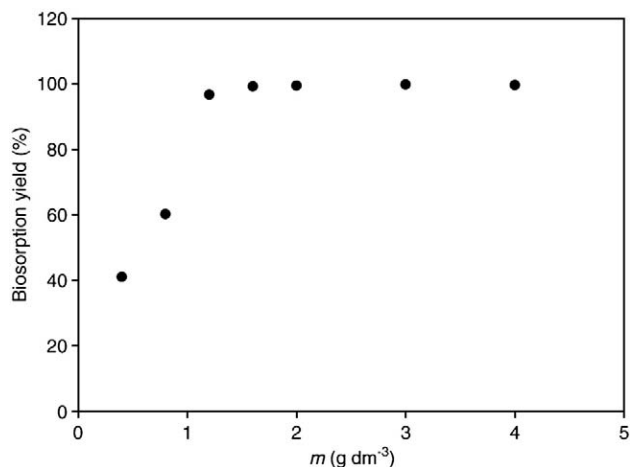


Fig. 2. Effect of biosorbent dosage for the biosorption yield of RR198 onto *P. vulgaris* L. at 20 °C.

increase in the biosorbent concentration up to 4.0 g dm^{-3} did not significantly change the biosorption yield. This is due to the binding of almost all dye ions to biosorbent surface and the establishment of an equilibrium between the dye molecules on the biosorbent and in the solution [32,33].

3.3. Kinetics of RR198 biosorption

The influence of the contact time and temperature on the biosorption capacity of *P. vulgaris* L. for RR198 is presented in Fig. 3. It can be seen that the biosorbed RR198 increased with contact time up to 20 min, after that a maximum removal is attained. Therefore, 20 min was selected as the optimum contact time for all further experiments. The biosorption capacity of the biomass decreased with an increase in the temperature from 20 to 50 °C. It was suggested that the biosorption of RR198 onto *P. vulgaris* L. surface was favored at lower temperatures and it is controlled by an exothermic process.

The determination of the biosorption kinetics is an important stage for designing batch biosorption systems. Also in order to select the optimum operating conditions for full scale batch systems, information on the kinetics of solute uptake is required [34]. In this study in order to determine the kinetic behavior of RR198 biosorption, the dynamical experimental data were analyzed by the first-order and the pseudo-second-order kinetic models. The first-order rate equation [35] can be expressed as follows:

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t} \quad (2)$$

where q_e and q_t are the amounts of RR198 dye biosorbed at equilibrium and at time t (mg g^{-1}), and k_1 is the first-order rate constant (min^{-1}) for the biosorption. The values of k_1 were calculated from the plot of $1/q_t$ versus $1/t$ (Figure is not shown).

The pseudo-second-order kinetic model expression [36] can be written as follows:

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

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). Values of k_2 and q_e can be calculated from the plot of t/q_t against t . Fig. 4 shows the plots of linear form of the pseudo-second-order kinetic model at 20, 30, 40 and 50 °C. The kinetic parameters for the RR198 biosorption are given in Table 1. Considering the correlation coefficients in Table 1, biosorption of RR198 followed by the pseudo-

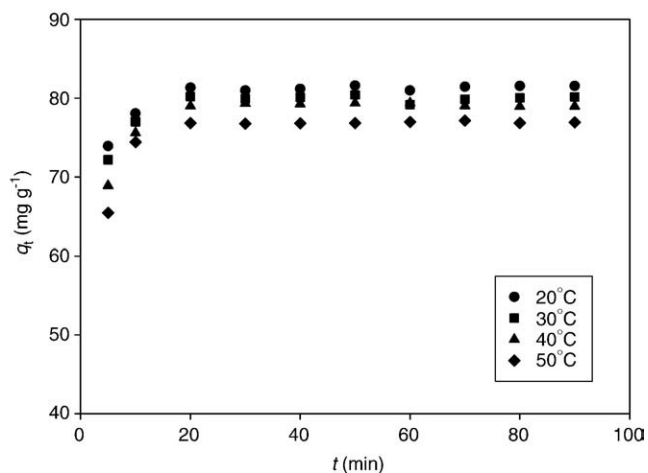


Fig. 3. Effect of contact time for the biosorption of RR198 onto *P. vulgaris* L. at different temperatures.

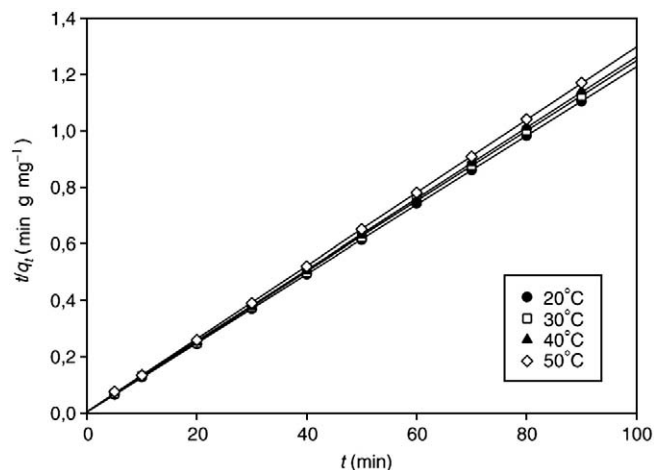


Fig. 4. The pseudo-second-order kinetic plots for the biosorption of RR198 onto *P. vulgaris* L. at different temperatures.

second-order kinetic model. Therefore the theoretical biosorption capacities are very close to experimental biosorption capacities for the pseudo-second-order kinetic model at all studied temperatures.

3.4. Isotherms of RR198 biosorption

The data obtained from biosorption experiments are generally represented with equilibrium isotherms. These provided more important parameters for designing and optimizing of the biosorption systems. Different isotherm models can be used to determine the biosorption characteristics of a biosorbent. In the present study the RR198 biosorption was analyzed by Langmuir and Freundlich isotherm models.

The fundamental assumption of the Langmuir isotherm model is that biosorption takes place at specific sites within the biosorbent. Once a biosorbate occupies a binding site, no further biosorption occurs at this site. In the other words Langmuir model assumes that biosorbed layer is one molecule thickness (monolayer biosorption). The linearized form of the Langmuir equation is given below [37]:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max} K_L} \right) \frac{1}{C_e} \quad (4)$$

where q_e and C_e are the amounts of dye biosorbed at equilibrium (mg g^{-1}) and unbiosorbed dye concentration in aqueous solution (mg dm^{-3}), respectively, q_{\max} is the monolayer biosorption capacity of the biosorbent (mg g^{-1}), and K_L is the Langmuir biosorption constant ($\text{dm}^3 \text{mg}^{-1}$) and related to the free energy of biosorption.

The Langmuir isotherm plots for the biosorption of RR198 by *P. vulgaris* L. at different temperatures were presented in Fig. 5. The effect of isotherm shape has been discussed [38] with a view to predict whether a biosorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of ' R_L ', a dimensionless constant referred to as separation factor

Table 1

Kinetic parameters for the biosorption of RR198 onto *P. vulgaris* L. at different temperatures.

T (°C)	k_1 (min^{-1})	q_e (mg g^{-1})	r_1^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	r_2^2
20	2.44	82.00	0.949	3.59×10^{-2}	81.97	0.999
30	1.43	81.13	0.937	2.96×10^{-2}	80.65	0.999
40	0.92	80.74	0.959	2.95×10^{-2}	79.37	0.999
50	0.90	78.60	0.913	2.99×10^{-2}	77.52	0.999

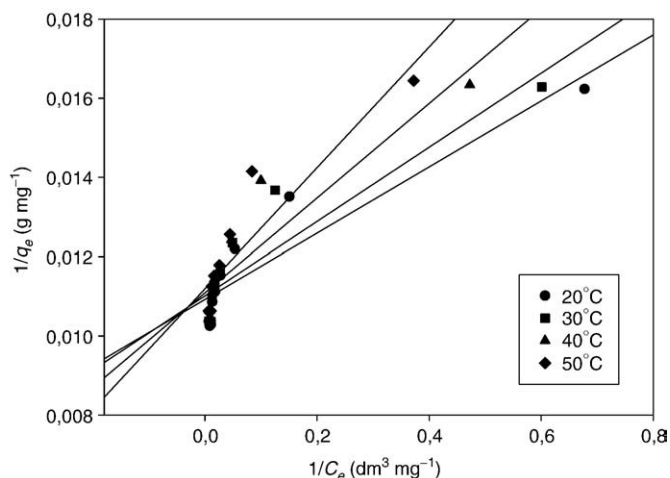


Fig. 5. Langmuir isotherm plots for the biosorption of RR198 onto *P. vulgaris* L. at different temperatures.

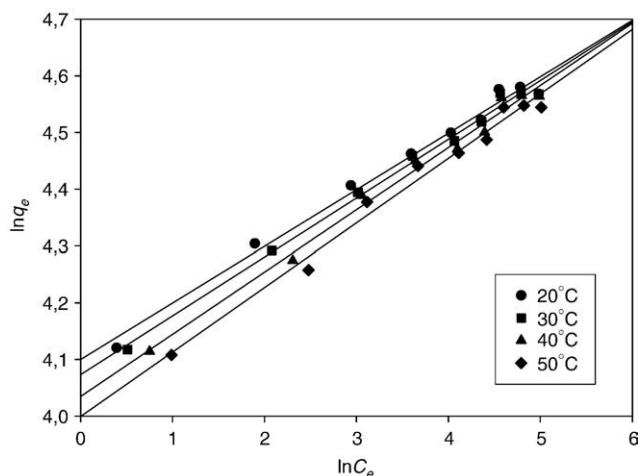


Fig. 6. Freundlich isotherm plots for the biosorption of RR198 onto *P. vulgaris* L. at different temperatures.

or equilibrium parameter. R_L is calculated using the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 is the initial RR198 concentration (mg dm^{-3}). The values of R_L indicate the shape of isotherms to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) [38,39]. The R_L values obtained at different temperatures in this study are given in Table 2. The R_L values indicated that RR198 biosorption process was favorable at all the studied temperatures. Table 2 also indicated that R_L values increased with increasing temperature and this implies that the RR198 biosorption process was more favorable at 20 °C.

The Freundlich isotherm is an empirical equation based on biosorption on heterogeneous surface and also possibly in multi-layer biosorption. Linear form of the Freundlich equation [40] is commonly presented as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where K_F ($\text{dm}^3 \text{g}^{-1}$) and n (dimensionless) are Freundlich constants, being indicative of the extent of the biosorption and the degree of nonlinearity between solution concentration and biosorption, respectively.

The plots of $\ln q_e$ versus $\ln C_e$ for the biosorption of RR198 onto *P. vulgaris* L. (Fig. 6) were drawn. The Langmuir and Freundlich constants and regression coefficients for the RR198 biosorption are presented in Table 2. According to these results RR198 biosorption process was well described by the Freundlich isotherm model with the r^2 values of higher than 0.982.

Table 2

Biosorption isotherm constants for the biosorption of RR198 onto *P. vulgaris* L. at different temperatures.

T (°C)	Langmuir				Freundlich		
	q_{\max} (mg g^{-1})	K_L ($\text{dm}^3 \text{mg}^{-1}$)	r_L^2	R_L	n	K_F ($\text{dm}^3 \text{g}^{-1}$)	r_F^2
20	91.533	1.309	0.864	1.91×10^{-3}	10.037	60.348	0.988
30	90.795	1.176	0.843	2.12×10^{-3}	9.645	58.753	0.993
40	90.152	0.929	0.831	2.68×10^{-3}	9.122	56.535	0.988
50	89.351	0.734	0.838	3.40×10^{-3}	8.796	54.573	0.983

3.5. Estimation of the thermodynamic parameters for RR198 biosorption

K_C is the equilibrium constant obtained from pseudo-second-order kinetic model, and it can be used to estimate the thermodynamic parameters. The changes of free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated with the biosorption process due to its dependence with temperature were determined by using the following equations:

$$K_C = \frac{C_A}{C_S} \quad (7)$$

$$\Delta G^\circ = -RT \ln K_C \quad (8)$$

where K_C is the equilibrium constant (Table 3), C_A is the amount of RR198 biosorbed on the biosorbent at equilibrium (mg dm^{-3}), C_S is the equilibrium concentration of RR198 in the solution (mg dm^{-3}). ΔG° is the Gibbs free energy change (kJ mol^{-1}), R is a gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is temperature (K). This equation can be rearranged related to enthalpy (ΔH°) and entropy changes (ΔS°) as follows:

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

ΔH° and ΔS° were calculated from the slope and intercept of van't Hoff plot of $\ln K_C$ against $1/T$ (Fig. 7). The values of the thermodynamic parameters are given in Table 3. The negative values of ΔG° indicate that the RR198 biosorption onto *P. vulgaris* L. is spontaneous and feasible at all the studied temperatures (20, 30, 40 and 50 °C). Similarly the negative value of ΔH° ($-9.74 \text{ kJ mol}^{-1}$) shows the exothermic in nature of biosorption. The similar findings were reported in the literature [41,42]. The negative value of ΔS° also

Table 3

Thermodynamic parameters calculated from the pseudo-second-order kinetic model for the biosorption of RR 198 by *P. vulgaris* L. at different temperatures.

T (°C)	K_C	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° ($\text{J K}^{-1} \text{ mol}^{-1}$)
20	6.957	-4.744	-9.74	-17.04
30	6.154	-4.573		
40	5.517	-4.403		
50	4.777	-4.232		

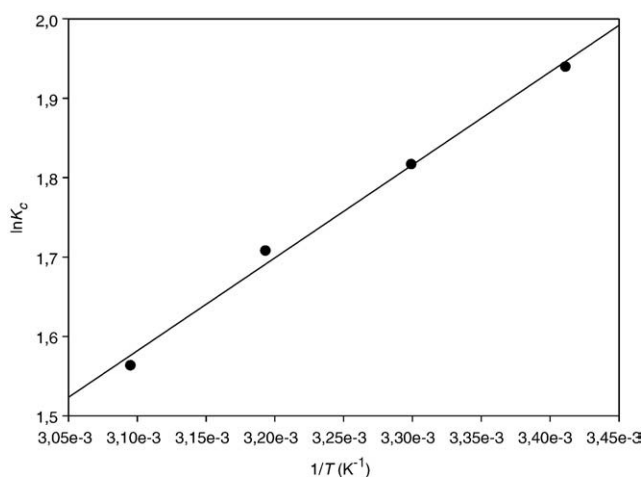


Fig. 7. The plot of $\ln K_c$ versus $1/T$ for estimation of thermodynamic parameters for the biosorption of RR198 onto *P. vulgaris* L.

suggests decreased randomness at the solid/solution interface during the RR198 biosorption onto *P. vulgaris* L.

4. Conclusions

The present study investigates the RR198 biosorption potential of an agricultural waste biomass, *P. vulgaris* L. as an alternative biosorbent material. This agricultural residue is cheap and easily available material from canned food production process. Optimum pH and biosorbent dosage were determined as 2.0 and 1.6 gdm^{-3} , respectively, for color removal process. Biosorption equilibrium data were analyzed by the isothermal data and the equilibrium data fitted well to Freundlich isotherm model at 20, 30, 40 and 50 °C. The biosorption process was followed by the pseudo-second-order kinetic model and the thermodynamic parameters showed that RR198 dye biosorption was favorable, spontaneous and exothermic in nature. The results indicate that *P. vulgaris* L. may be used as an effective and inexpensive biosorbent for the removal of RR198 dye from aqueous solutions.

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