

# Biosorption of textile dye reactive blue 221 by capia pepper (*Capsicum annum L.*) seeds

Levent Gürel

## ABSTRACT

Peppers are very important foodstuffs in the world for direct and indirect consumption, so they are extensively used. The seeds of these peppers are waste materials that are disposed of from houses and factories. To evaluate the performance of this biomass in the treatment of wastewaters, a study was conducted to remove a textile dye, reactive blue 221, which is commercially used in textile mills. Raw seed materials were used without any pre-treatment. The effects of contact time, initial concentration of dye, pH and dose of biosorbent were studied to determine the optimum conditions for this biomass on color removal from wastewaters. The optimum pH value for dye biosorption was found to be 2.0. At an initial dye concentration of 217 mg L<sup>-1</sup>, treatment efficiency and biosorption capacity were 96.7% and 95.35 mg g<sup>-1</sup>, respectively. A maximum biosorption capacity of 142.86 mg g<sup>-1</sup> was also obtained. Equilibrium biosorption of dye by capia seeds was well described by the Langmuir isotherm with a correlation coefficient above 99%. The biosorption process was also successfully explained with the pseudo-second order kinetic model. This biomass was found to be effective in terms of textile dye removal from aqueous solutions.

**Key words** | biosorption, capia peppers, dye treatment, reactive blue 221

## Levent Gürel

Environmental Engineering Department, Faculty of Engineering,  
Pamukkale University,  
Denizli,  
Turkey  
E-mail: [lgurel@pau.edu.tr](mailto:lgurel@pau.edu.tr)

## INTRODUCTION

Industrialization grows very quickly, and the use of dyes in industries all over the world increases with the need of people for colors (Geetha *et al.* 2015). Contamination of the aqueous environment by several dyes resulting from various industries such as textile, leather, paper, printing, iron-steel, petroleum, solvent, pharmaceuticals and cosmetics has become a crucial environmental problem at the present time (Daneshvar *et al.* 2012a, 2012b; El Haddad *et al.* 2014; Oguntimein 2015; Deniz & Kepekci 2016). Approximately 60% of the total dyes produced for coloring various fabrics are consumed by textile mills. A percentage (10–15%) of these dyes originating from the textile industry are dispersed to wastewaters (Oguntimein 2015). The effluents of this industry are intensely polluting to the aquatic environment. The color resulting from dyes reduces the sunlight and oxygen penetrating to the aqueous environment and creates a negative impact on photosynthetic aquatic life. Furthermore, some dyes may contain toxic or carcinogenic groups (Argun 2012; El Haddad *et al.* 2013; Guerrero-Coronilla *et al.* 2015; Yavari *et al.* 2015).

Reactive dyes, among the synthetic dyes used in industries, are very crucial in the contamination of aqueous media. Cotton is the most commonly-used textile fiber to be colored by this kind of dye, therefore the production of these dyes continues incrementally. Reactive dyes are highly soluble in water, thus 20–50% of unfixed and hydrolyzed dye can be discarded from textile mills as an effluent (Wangpradit & Chitprasert 2014). These dyes have low biodegradability and a high salt content, and contribute extensively to the organic load of waters. They contain triarylmethane, azo and anthraquinone chromophoric groups. The concentrations of reactive dyes in textile mill wastewaters are in the range of 60 to 250 mg/L (Argun 2013).

There are numerous dye removal techniques in the literature. Oxidative processes, adsorption, ion exchange, membrane filtration, electro coagulation, biological treatment with living organisms and biosorption can be used to decolorize wastewaters (Robinson *et al.* 2001; Aksu & Karabayir 2008). Biosorption is a challenging technology that uses several biosorbents such as bacteria, algae, yeast, fungi, and agricultural

and industrial by-products to remove various ionic contaminants and dyes from wastewaters (Kim *et al.* 2015). This technology is a cheap and effective way to remove color from aqueous solutions (Ozcan *et al.* 2005; Srinivasan & Viraraghavan 2010). Cheap and alternative types of biomass have been studied by researchers worldwide, and new biosorbent materials are also being investigated today (Deniz 2013).

Some of the types of biomass used in various researches include malt bagasse (Fontana *et al.* 2016), *S. platensis* (Dotto *et al.* 2012), *Cladosporium* sp. (Fan *et al.* 2012), *Spirogyra* sp. (Kha-tae *et al.* 2013), olive stone biomass (Albadarin & Mangwandi 2015), *Aspergillus versicolor* (Huang *et al.* 2016), marine brown macroalgae (Daneshvar *et al.* 2012a, 2012b), *Cucumis sativus* peel (Lee *et al.* 2015), *Cupressus sempervirens* cone chips (Fernandez *et al.* 2012), and rice husk (Safa & Bhatti 2011).

In this study, capia pepper seeds were used as a biosorbent material to remove a textile dye, reactive blue 221, from aqueous solutions. There are have only been a few studies conducted using this biomass to remove ionic substances and dye from aqueous solutions. In one of these studies, Ozcan *et al.* (2005) investigated the biosorption performance of *Capsicum annuum* seeds on copper removal from aqueous solutions. Seeds were used without any pre-treatment in this study, and the copper adsorption equilibrium was obtained in 60 minutes with this biomass (Ozcan *et al.* 2005). Also, another study on the pepper seeds was reported by Akar *et al.* (2011). In this work, the seeds were pre-treated with acetone and successfully removed reactive blue 49 from dye solutions (Akar *et al.* 2011).

So, there are no more studies known in the literature conducted with various pepper seeds. Also, a few adsorption studies treating reactive blue 221 dye with sepiolite (Alkan *et al.* 2005, 2007) and kaolinite (Karaoglu *et al.* 2010) are found in the literature.

A detailed study was conducted to observe the dye removal performance of capia pepper seeds, without any pre-treatment, as a natural biosorbent. Some optimization tests were also carried out. The effects of solution pH, adsorbent dosage, contact time and initial dye concentration were studied. Also, kinetic and isotherm studies were made to define the biosorption process.

## MATERIALS AND METHODS

### Biosorbent material preparation

Capia peppers were bought from a traditional market place in Dikili, Izmir, Turkey. The seeds in the peppers were separated

from the body and washed thoroughly with tap, distilled and deionized water, respectively. The biomass was dried in an oven at 70 °C for 2 days. After the drying process, the seeds were ground and sieved to a particle size of 250–500 µm. The sieved biosorbents were kept in an oven at 55 °C for 2 days and then stored in a container without contact with air for further tests.

### Chemicals

Commercial grade CI reactive blue 221 (Molecular weight: 1082.83 g/mol, chemical formula: C<sub>33</sub>H<sub>24</sub>ClCuN<sub>9</sub>Na<sub>3</sub>O<sub>15</sub>S<sub>4</sub>, CAS number: 93051-41-3) (Argun 2012) textile dye was chosen as the model dye in this work and supplied by Alfa Kimya. This dye was dissolved in deionized water to prepare the desired dye solutions. 0.1–4.0 N HNO<sub>3</sub> or NaOH solutions were used to adjust the pH of the wastewater to be treated. HNO<sub>3</sub> and NaOH were obtained from Merck Co. All reagents were of analytical grade and used without any further purification.

### Procedure

All experimental studies were conducted at batch scale. 100 mL of dye solutions containing particular amounts of biomass in 250 mL Erlenmeyer flasks were mixed in an incubator shaker at 180 rpm and 25 °C for various periods (0.25–48 h). At the end of the mixing period, the dye solutions were centrifuged at 5,000 rpm for 8 minutes to separate the pepper seeds from the solutions. Time, pH, biosorbent dosage and initial dye concentration were studied to evaluate the performance of the biomass. The dye concentration was determined by using a calibration graph prepared with known amounts of dye solutions at an optimum wavelength of 610 nm using a Hach-Lange DR500 Spectrophotometer. Biosorption yield, biosorption uptake capacity at time t and capacity at equilibrium were calculated according to the following equations, respectively.

$$E\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (2)$$

$$q_e = \frac{(C_0 - C_e) V}{m} \quad (3)$$

where E% is the efficiency of the biosorption process, C<sub>0</sub>, C<sub>t</sub> and C<sub>e</sub> are the dye concentrations at the beginning, time t

and equilibrium, respectively.  $V$  is the volume of dye treated and  $m$  is the mass of dry biomass used for volume  $V$ . The Langmuir and Freundlich isotherms were used to assess the biosorption process.  $q_e$  and  $q_t$  are the adsorbed amounts of dye ( $\text{mg g}^{-1}$ ) at equilibrium and time  $t$ , respectively. The Langmuir (Langmuir 1916) and Freundlich (Freundlich 1906) isotherms in linear forms can be written as the following equations, respectively.

$$\frac{C}{X/m} = \frac{1}{q_m b} + \frac{C}{q_m} \quad (4)$$

where  $X$  (mg) is the amount of dye adsorbed in  $V$  volume,  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum biosorption uptake capacity and  $b$  ( $\text{L mg}^{-1}$ ) is a constant related to the biosorption rate.

$$\log X/m = \log k_f + \frac{1}{n} \log C \quad (5)$$

where  $k_f$  and  $1/n$  are the biosorption capacity of the biomass and the biosorption intensity, respectively.

A dimensionless constant separation factor can be used to define the biosorption type of the removal process according to the Langmuir isotherm constant ( $b$ ). The separation factor is defined as follows:

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (6)$$

In the above equation, the highest initial dye concentration used in the study is shown as  $C_0$ . The change in suitability of the adsorbent to the adsorbate with the  $R_L$  value is given in Table 1 (Deniz & Karaman 2011).

In kinetic studies, pseudo-first order (Lagergren 1898) and pseudo-second order (Ho & McKay 1999) models were used to evaluate the kinetic data and these models are also given in Equations (7) and (8), respectively.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

**Table 1** | Values of separation factor for adsorption behavior

Separation factor, $R_L$	Langmuir isotherm type
0	Irreversible
$0 < R_L < 1$	Favorable
1	Linear
$> 1$	Unfavorable

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where  $k_1$  is the rate constant of the pseudo-first order model ( $\text{h}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{h}^{-1}$ ) is the rate constant of the pseudo-second order model at equilibrium.

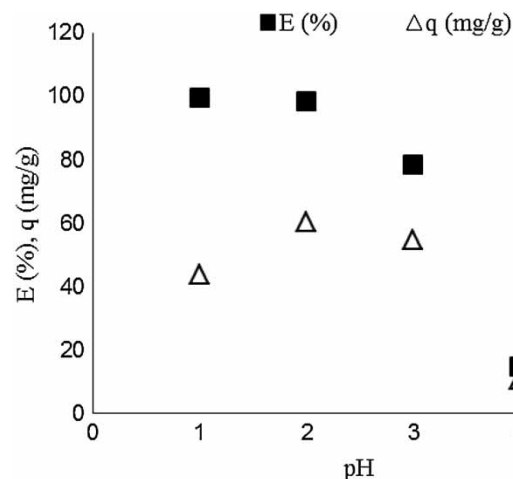
Linear regression analyses were conducted by plotting  $\log (q_e - q_t)$  and  $t/q_t$  against  $t$ .

## RESULTS AND DISCUSSION

### The effect of pH on dye biosorption

A study was conducted to determine the optimum pH value for biosorption of RB 221. In the tests conducted, a pH range of 1.0–5.0 was investigated. Removal efficiencies and the biosorption capacities of the biosorbent at several pH values are shown in Figure 1. A biosorbent dosage of 1.6 g/L was used for an average dye concentration of  $100 \text{ mg L}^{-1}$  (dye concentrations varied in the range of  $70\text{--}117 \text{ mg L}^{-1}$  due to pH adjustment tests).

It can be clearly seen from Figure 1 that the maximum removal efficiency and uptake capacity using a natural biosorbent were obtained at a pH of 2. The dye removal efficiencies at pH 1 and 2 were nearly the same, while the uptake capacities were found to be higher at pH 2. The removal efficiency of the pH 1 test was high because of the dilution effect resulting from the pH adjustment. Therefore, in the other tests conducted to examine the biomass performance, the pH of dye solutions was adjusted to 2. At pH values above 3, the removal efficiency and uptake



**Figure 1** | The variation of removal efficiency and uptake capacity of biomass with pH.

capacity decreased. Therefore, the studies were not conducted at higher pH values. The same pH trend for several dyes was observed in the studies conducted in the literature by several researchers (Çolak *et al.* 2009; Kiran *et al.* 2009; Asgher & Bhatti 2010; Akar *et al.* 2011). Despite the high removal efficiency of the biosorption process and the low cost of the biomass, it has some disadvantages. In the textile sector, the pH of wastewater may be so variable that it needs to be neutralized before discharge to the environment. Before treatment by biosorbent, the pH value should be adjusted to 2 for effective removal of dye. After treatment process neutralization is unavoidable.

The pH value of the treated media affects the biosorption capacity of the biomass, the solubility properties of the dyes and also the hue of the aforementioned media. Reactive dyes such as Reactive Blue 221 represent anionic characteristics. At lower pH values, the biosorbent surface is positively charged, thus attracting the negatively-charged dye ions. So, the anionic groups of the dye solution may be bound by the protonated surface of the biosorbent material, and the color of the dye has been successfully removed from the contaminated aqueous media probably by this electrostatic attraction (Akkaya & Özer 2005). At higher pH values, the binding areas deprotonate and a negative charge occurs. Dye removal efficiency decreases due to the repulsive forces between the biosorbent surface and the dye (Akar *et al.* 2011). These cases prove the results obtained in this study.

### Biosorbent dosage effect on biosorption

Biosorbent dosage is a very important factor in biosorption processes. With this test, it is possible to determine the optimum biomass amount for a given initial dye concentration. To investigate the effect of the biosorbent amount on dye removal, six different biosorbent doses were applied to the dye solution at 25 °C. The initial dye concentration in the solution was 184 mg L<sup>-1</sup>. The removal efficiencies and uptake capacities of the biomass after biosorption are given in Figure 2.

The performance of the biomass regarding removal efficiency increased with increasing biosorbent dosage, and reached a maximum 97% with 2.8 g capia pepper seeds per liter. It can be concluded that a higher biomass dosage affects the treatment efficiency and hue removal performance in a positive way. However, the increment of the biomass amount in the solution reduced the biosorption capacity. Doses of 1.6 g L<sup>-1</sup> and 2.2 g L<sup>-1</sup> were found to be optimum in terms of both removal efficiency and uptake amounts.

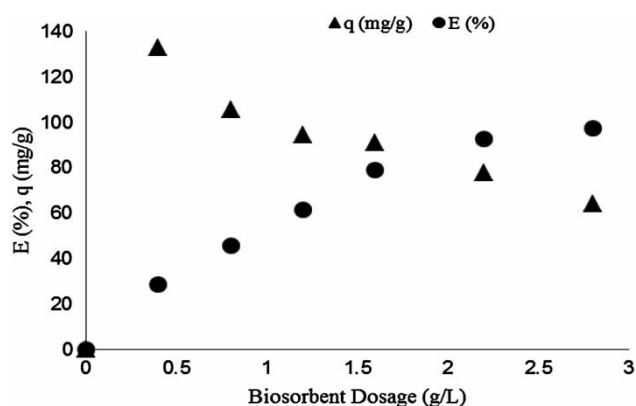


Figure 2 | Biosorbent dosage effect on efficiency and uptake capacity.

The increment of dye removal efficiency with higher dosages of biosorbents and the contrast between efficiency and biosorption capacity was also observed in several dye removal studies in the literature (Akar *et al.* 2009a, 2009b). It can be told that increasing the biosorbent dosage raises the biosorbent surface area and also the quantity of prospective binding sites. The decrease in the uptake capacity of the biomass occurs because of probable biosorbent aggregation. Hence, the effective surface area of the biomass diminishes (Barka *et al.* 2011).

### The effects of initial dye concentration on biosorption of dye

Initial dye concentration is a very important factor in biosorption studies. In this work, the effect of the initial dye solution concentration (217–482 mg L<sup>-1</sup>) on the removal efficiency and biosorption capacity is shown in Figure 3. For this test, the biosorbent dosage of 2.2 g L<sup>-1</sup> was selected for the process.

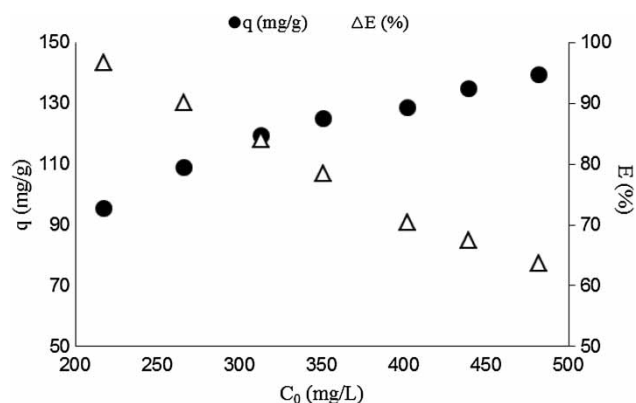


Figure 3 | The effect of initial dye concentration on removal efficiency and biosorption capacity.

Dye removal efficiency decreased with increasing concentrations of dye solution. On the other hand, the biosorption capacity of the biomass increased directly proportionally to the initial dye solution concentration. A maximum removal efficiency above 96% was obtained with an initial dye concentration of  $217 \text{ mg L}^{-1}$ . Biosorption uptake capacity for this concentration was determined as  $95.35 \text{ mg g}^{-1}$ .

Removal efficiency was also reported to decrease at higher dye concentrations in various studies. With the increase in the dye concentration, the available active adsorption sites on the biomass surface diminish, so there are no more places for the adsorption of dye onto pepper seeds (Khataee *et al.* 2013; Geetha *et al.* 2015).

Uptake by the biomass increased with an increase in initial dye concentrations in the other studies in the literature (Safa & Bhatti 2011; Oguntimein 2015). This may be due to the increasing driving force (Aksu & Tezer 2005). The mass transfer resistance between the aqueous and solid phases was overcome by this driving force. Also with higher initial dye concentrations, interaction between the dye molecules and biosorbent can increase by affecting the biosorption in a positive way (Aksu & Tezer 2005).

#### Variation of dye removal with contact time

Removal of textile model dye RB221 by the pepper seed biosorbent with time is exhibited in Figure 4. The biomass dosage and the temperature of the treatment media for this study were  $1.6 \text{ g L}^{-1}$  and  $25 \text{ }^\circ\text{C}$ . The dye concentration for this test was  $195 \text{ mg L}^{-1}$ .

The dye biosorption performance with raw biomass enhanced with time. Tests were conducted for 48 hours.

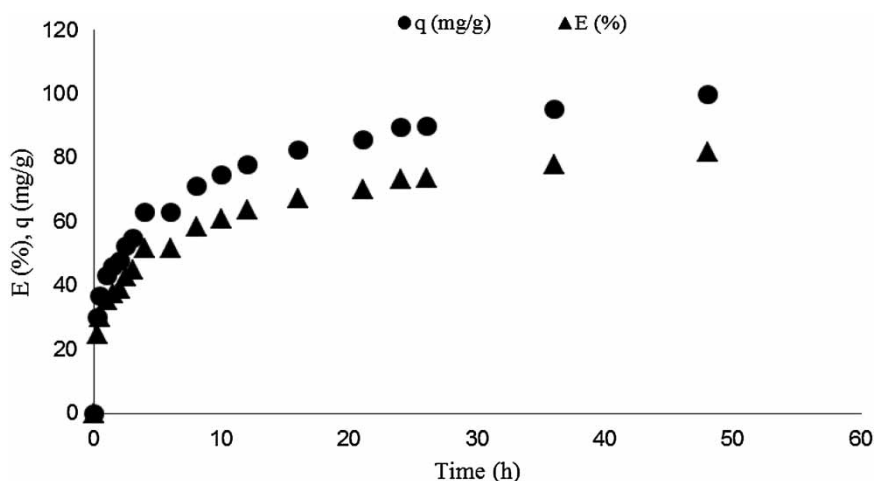


Figure 4 | The effect of contact time on the removal of RB221.

In 21 hours, dye removal started to decelerate and approximately reached equilibrium. In the first 2.5 hours of the treatment a biosorption capacity of  $52.44 \text{ mg g}^{-1}$  was obtained, which is nearly half of the 48 hour uptake amount ( $99.83 \text{ mg g}^{-1}$ ). The biosorption process was very rapid at the beginning of the process, but the removal rate decreased with advancing contact time. This case can be explained as follows: at the beginning of the study, there are too many available adsorption sites for rapid dye adsorption onto the biomass. In advancing periods of biosorption, the dye molecules fill all the free sites of the biomass, so the removal slows down (Oguntimein 2015).

This biomass retained remarkable amounts of dye. This process can be accelerated by pretreating this biomass with several chemicals. It should be kept in mind that the cost of this biosorption process will increase with this pretreatment.

#### Biosorption kinetics

To design an adsorption system, the rate of the process is a very important factor. Also, the kinetic parameters are important for the modeling of biosorption systems (Srivastava *et al.* 2015). In order to investigate the kinetics of RB221 dye biosorption onto pepper seeds, two kinetic models, pseudo-first order and pseudo-second order models, were used in this study.

These kinetic studies are important, because they provide knowledge regarding the probable biosorption mechanism and also make it possible to improve suitable mathematical models for describing the interactions. The parameters and rates obtained from kinetic studies can be used to improve biosorbents for industrial applications, and also the

complicated dynamics of the biosorption can be understood by these data (Sen Gupta & Bhattacharyya 2011).

Equation (7) was used to obtain kinetic parameters according to the pseudo-first order model and Figure 5 was generated by plotting  $\log(q_e - q_t)$  versus time,  $t$ .

The  $R^2$  value for this model was found to be 0.98. The other parameters,  $q_e$  and  $k_1$ , were  $57.80 \text{ mg g}^{-1}$  and  $0.071 \text{ h}^{-1}$ , respectively. The calculated and experimental equilibrium values are  $57.80$  and  $99.83 \text{ mg g}^{-1}$ , respectively. The calculated and experimental uptake capacities do not match each other. So, this model cannot describe the sorption kinetics.

To determine the kinetics of this process, another model known as the pseudo-second order model, described in

Equation (8), was used. It is known to be the most suitable kinetic model for most of the dye and metal removal studies in the literature. This model was evaluated using a graph, which was constituted by plotting  $t/q_t$  versus  $t$ . The results are shown in Figure 6.

According to the model,  $q_e$  and  $k_2$  were found to be  $97.09 \text{ mg g}^{-1}$  and  $0.005 \text{ g mg}^{-1} \text{ h}^{-1}$  with a correlation coefficient of 0.99. This  $R^2$  value is higher than that of the pseudo-first order model. Also, the calculated and experimental values for  $q_e$  were  $97.09 \text{ mg g}^{-1}$  and  $99.83 \text{ mg g}^{-1}$ , respectively. These values are closer to each other, showing that the more appropriate model for RB221 biosorption is the pseudo-second order kinetic model. The kinetic results are also summarized in Table 2.

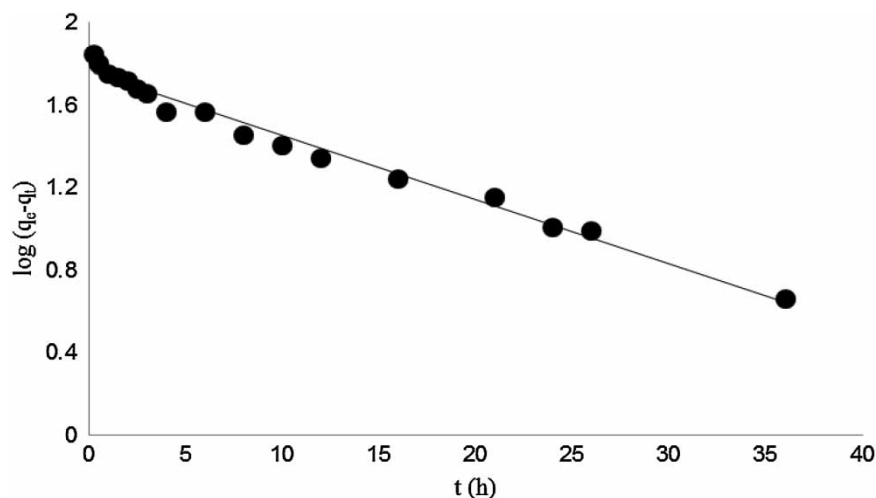


Figure 5 | Pseudo-first order model for RB221 biosorption by pepper seeds.

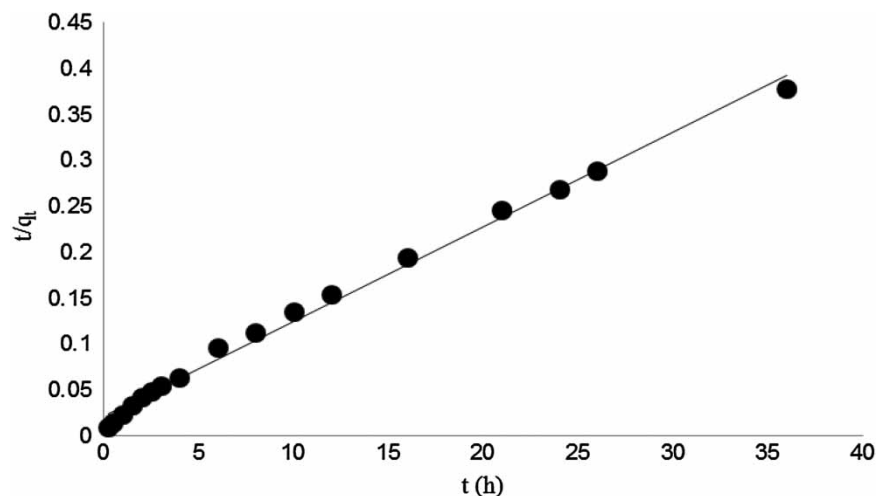


Figure 6 | Pseudo-second order model for RB221 biosorption by pepper seeds.

**Table 2** | A summary of the kinetic results

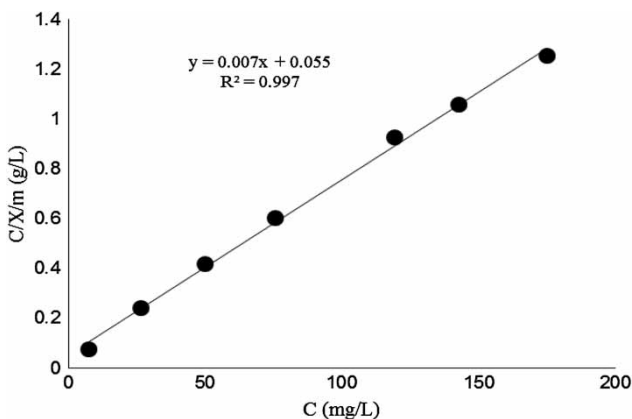
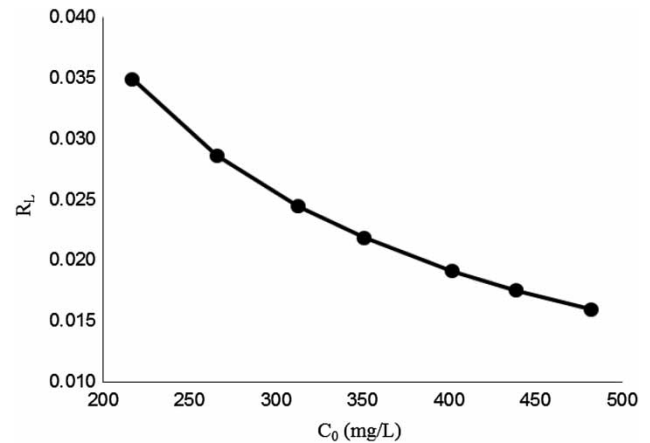
Adsorbent	Experimental value $q_e$ (mg g <sup>-1</sup> ),	Pseudo-first order			Pseudo-second order		
		$k_1$ (h <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	R <sup>2</sup>	$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	R <sup>2</sup>
Pepper seeds	99.83	0.071	57.80	0.98	0.005	97.09	0.99

It is clearly seen from Table 2 that the data obtained from the kinetic tests fitted the pseudo-second order model better than the first-order model. This means that the rate limiting step in the biosorption of RB221 dye by this biomass may be chemisorption. This conformity has been interpreted as surface sorption in the literature (Saha *et al.* 2012). As a result of chemical interactions, the electrons are probably exchanged or shared between the dye adsorbent and adsorbate (Ho & McKay 2000; Yeddou-Mezenner 2010).

There are many studies in the literature showing that the pseudo-second order model dominates many dye biosorption processes. Some of them are: dye removal by marine brown macroalgae (Daneshvar *et al.* 2012a, 2012b), *Cladosporium* sp. (Fan *et al.* 2012), *Cucumis sativus* peel (Lee *et al.* 2015), sepiolite (Alkan *et al.* 2007).

### Isotherm studies

To determine the equilibrium of dye biosorption by the biomass, isotherm studies should be carried out using different isotherm models. In this study, the Langmuir and Freundlich isotherm models were used to evaluate the equilibrium conditions. As mentioned in Equation (4), C/X/M was plotted versus C to obtain the Langmuir parameters. Also from Equation (5), log X/M was plotted against log C to determine the Freundlich parameters. The plots of the Langmuir and Freundlich isotherms are shown

**Figure 7** | Langmuir isotherm model for dye biosorption by pepper seeds.**Figure 8** | The variation of separation factor value with initial dye concentration.

in Figures 7 and 9, respectively. Also the separation factor,  $R_L$ , is shown in Figure 8. The results of the isotherm studies are summarized in Table 3.

It can be clearly seen from Figure 7 that the data fit very well to the Langmuir model with a correlation coefficient value of 0.997. Maximum biosorption uptake capacity was found to be 142.86 mg/g. The constant  $b$  was calculated as 0.127 L/mg for biosorption of RB221 dye by pepper seed biomass. Also, the separation factor was calculated using initial dye concentrations and constant 'b' obtained from the Langmuir model.

It can be seen from Figure 8 that the dimensionless separation factor is reduced with an increase in the initial RB221 dye concentration. This means that the biosorption of RB221 onto pepper seed biomass improves with higher concentrations of dye solution. Also, the  $R_L$  value is in the

**Table 3** | A summary for isotherm results in equilibrium studies

Models	Parameters	Values
Langmuir	$q_m$ (mg g <sup>-1</sup> )	142.86
	$b$ (L mg <sup>-1</sup> )	0.127
	R <sup>2</sup>	0.997
Freundlich	$k_f$ (mg g <sup>-1</sup> )(L mg <sup>-1</sup> ) <sup>1/n</sup>	75.28
	$n$	8.576
	R <sup>2</sup>	0.991

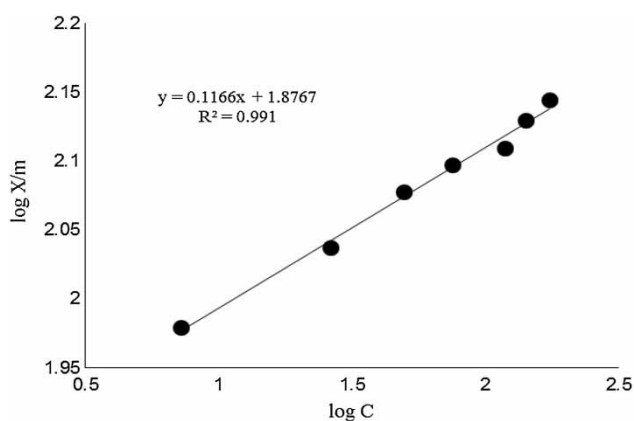


Figure 9 | Freundlich isotherm model for dye biosorption by pepper seeds.

range of 0.016 to 0.035, and shows that the biosorption process is favorable at all concentrations studied in this work. The biosorbent pepper seed is appropriate for RB221 dye solution in the light of these data. This case was observed in the other studies in the literature (Flores-Garnica *et al.* 2013; Guerrero-Coronilla *et al.* 2015).

In Figure 9, the correlation coefficient was estimated to be 0.991 according to the Freundlich isotherm. The  $k_f$  and  $n$  parameters of the Freundlich isotherm were  $75.28 \text{ (mg g}^{-1}\text{)}$   $(\text{L mg}^{-1})^{1/n}$  and 8.576, respectively.

The results of the two isotherm studies are summarized in Table 3. The correlation coefficients are very high for both Langmuir and Freundlich isotherms. But with a 0.997  $R^2$  value, the Langmuir model seems more appropriate for the experimental data.

So, these results show that the monolayer coverage of the biosorbent surface is the main situation in the biosorption of RB221 dye by pepper seed biosorbent. In some studies of dye removal conducted in the literature, the same trend was observed using bivalve shell and treated

*Zea mays* L. (maize) husk leaf (Jalil *et al.* 2012), sea shell powder (Chowdhury & Saha 2010), treated *Capsicum annuum* seeds (Akar *et al.* 2011), malt bagasse (Fontana *et al.* 2016). For the comparison of some biosorbents used for the removal of dye from wastewaters, some uptake capacities from various works are given in Table 4.

## CONCLUSIONS

Capia pepper seeds, as a natural waste material, were used to remove RB221 from contaminated solutions. The effects of pH, initial dye concentration, biosorbent dosage and contact time have been evaluated to optimize the dye biosorption process. Also, kinetic analyses and isotherm studies were conducted to define the biosorption of RB221 dye onto Capia pepper seeds. Langmuir and Freundlich isotherm models were used to assess the experimental data. Experimental results were very well suited to the Langmuir isotherm model, with a correlation coefficient of 0.997. Maximum biosorption uptake capacity of the capia pepper seeds was found to be  $142.86 \text{ mg g}^{-1}$  for RB221 dye removal. This uptake capacity seems very high compared with the other biosorbents used for dye removal in the literature. In the kinetic studies, pseudo-first order and pseudo-second order kinetic models were used, and it was found that the pseudo-second order kinetic model was appropriate for the experimental data with a correlation coefficient of 0.99. This work shows that a natural waste material, capia pepper seeds, has a large potential for removal of color originating from dyes used mostly in textile industries. As a result, it is possible to evaluate this waste material as a source for treatment. The optimum pH region for this biosorbent in dye removal studies was found to be 2. To decrease the amount of pH adjustment reagents, a pH

Table 4 | The comparison of the results obtained from dye removal studies

Dye	Adsorbent	$q_m \text{ (mg g}^{-1}\text{)}$	Ref.
Orange solimax TGL	Malt bagasse	23.20	Fontana <i>et al.</i> (2016)
Reactive blue 221	Kaolinite	12.02	Karaoglu <i>et al.</i> (2010)
Acid red 27	Water hyacinth leaves	70.00	Guerrero-Coronilla <i>et al.</i> (2015)
Methyl Orange	Almond shell residues	40.65	Deniz (2013)
Reactive red 238	Pistachio	109.54	Deniz & Kepekci (2016)
Reactive blue 49	<i>Capsicum annuum</i> (acetone treated)	96.35	Akar <i>et al.</i> (2011)
Reactive blue 221	Sepiolite	60.53	Alkan <i>et al.</i> (2005)
Acid blue 113	<i>Cucumis sativus</i> peel	59.81	Lee <i>et al.</i> (2015)
Reactive blue 221	Capia pepper seeds	142.86	This study



value up to 3 can be used in future biosorption studies. After the treatment process, further studies may be carried out to determine the regeneration potential of the spent biomass. If regeneration is not possible, it should be disposed of as a hazardous material.

## REFERENCES

- Akar, S. T., Özcan, A. S., Akar, T., Özcan, A. & Kaynak, Z. 2009a Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste. *Desalination* **249** (2), 757–761.
- Akar, T., Tosun, I., Kaynak, Z., Ozkara, E., Yeni, O., Sahin, E. N. & Akar, S. T. 2009b An attractive agro-industrial by-product in environmental cleanup: dye biosorption potential of untreated olive pomace. *Journal of Hazardous Materials* **166** (2–3), 1217–1225.
- Akar, S. T., Gorgulu, A., Akar, T. & Celik, S. 2011 Decolorization of Reactive Blue 49 contaminated solutions by *Capsicum annum* seeds: batch and continuous mode biosorption applications. *Chemical Engineering Journal* **168** (1), 125–133.
- Akkaya, G. & Özer, A. 2005 Biosorption of Acid Red 274 (AR 274) on *Dicranella varia*: determination of equilibrium and kinetic model parameters. *Process Biochemistry* **40** (11), 3559–3568.
- Aksu, Z. & Karabayir, G. 2008 Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal-complex dye. *Bioresource Technology* **99** (16), 7730–7741.
- Aksu, Z. & Tezer, S. 2005 Biosorption of reactive dyes on the green alga *Chlorella vulgaris*. *Process Biochemistry* **40** (3–4), 1347–1361.
- Albadarin, A. B. & Mangwandi, C. 2015 Mechanisms of Alizarin Red S and Methylene blue biosorption onto olive stone by-product: isotherm study in single and binary systems. *Journal of Environmental Management* **164**, 86–93.
- Alkan, M., Çelikçapa, S., Demirbaş, Ö. & Doğan, M. 2005 Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite. *Dyes and Pigments* **65** (3), 251–259.
- Alkan, M., Demirbaş, Ö. & Doğan, M. 2007 Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite. *Microporous and Mesoporous Materials* **101** (3), 388–396.
- Argun, H. 2012 Advanced oxidation of reactive blue 221 by Fenton's process. *Journal of Advanced Oxidation Technologies* **5**, 340–347.
- Argun, H. 2013 Electrochemical oxidation of reactive blue 221 based on Fenton's process. *Fresenius Environmental Bulletin* **22** (2), 310–317.
- Asgher, M. & Bhatti, H. N. 2010 Mechanistic and kinetic evaluation of biosorption of reactive azo dyes by free, immobilized and chemically treated *Citrus sinensis* waste biomass. *Ecological Engineering* **36** (12), 1660–1665.
- Barka, N., Abdennouri, M. & Makhfouk, M. E. L. 2011 Removal of Methylene Blue and Eriochrome Black T from aqueous solutions by biosorption on *Scolymus hispanicus* L.: kinetics, equilibrium and thermodynamics. *Journal of the Taiwan Institute of Chemical Engineers* **42** (2), 320–326.
- Chowdhury, S. & Saha, P. 2010 Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal* **164** (1), 168–177.
- Çolak, F., Atar, N. & Olgun, A. 2009 Biosorption of acidic dyes from aqueous solution by *Paenibacillus macerans*: kinetic, thermodynamic and equilibrium studies. *Chemical Engineering Journal* **150** (1), 122–130.
- Daneshvar, E., Kousha, M., Jokar, M., Koutahzadeh, N. & Guibal, E. 2012a Acidic dye biosorption onto marine brown macroalgae: isotherms, kinetic and thermodynamic studies. *Chemical Engineering Journal* **204–205**, 225–234.
- Daneshvar, E., Kousha, M., Sohrabi, M. S., Khataee, A. & Converti, A. 2012b Biosorption of three acid dyes by the brown macroalga *Stoechospermum marginatum*: isotherm, kinetic and thermodynamic studies. *Chemical Engineering Journal* **195–196**, 297–306.
- Deniz, F. 2013 Dye removal by almond shell residues: studies on biosorption performance and process design. *Materials Science and Engineering C* **33** (5), 2821–2826.
- Deniz, F. & Karaman, S. 2011 Removal of Basic Red 46 dye from aqueous solution by pine tree leaves. *Chemical Engineering Journal* **170** (1), 67–74.
- Deniz, F. & Kepekci, R. A. 2016 Dye biosorption onto pistachio by-product: a green environmental engineering approach. *Journal of Molecular Liquids* **219**, 194–200.
- Dotto, G. L., Cadaval, T. R. S. & Pinto, L. A. A. 2012 Use of *Spirulina platensis* micro and nanoparticles for the removal synthetic dyes from aqueous solutions by biosorption. *Process Biochemistry* **47** (9), 1335–1345.
- El Haddad, M., Slimani, R., Mamouni, R., Laamari, M. R., Rafqah, S. & Lazar, S. 2013 Evaluation of potential capability of calcined bones on the biosorption removal efficiency of safranin as cationic dye from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers* **44** (1), 13–18.
- El Haddad, M., Regti, A., Slimani, R. & Lazar, S. 2014 Assessment of the biosorption kinetic and thermodynamic for the removal of safranin dye from aqueous solutions using calcined mussel shells. *Journal of Industrial and Engineering Chemistry* **20** (2), 717–724.
- Fan, H., Yang, J., Gao, T. & Yuan, H. 2012 Removal of a low-molecular basic dye (Azure Blue) from aqueous solutions by a native biomass of a newly isolated *Cladosporium* sp.: kinetics, equilibrium and biosorption simulation. *Journal of the Taiwan Institute of Chemical Engineers* **43** (3), 386–392.
- Fernandez, M. E., Nunell, G. V., Bonelli, P. R. & Cukierman, A. L. 2012 Batch and dynamic biosorption of basic dyes from binary solutions by alkaline-treated cypress cone chips. *Bioresource Technology* **106**, 55–62.
- Flores-Garnica, J. G., Morales-Barrera, L., Pineda-Camacho, G. & Cristiani-Urbina, E. 2013 Biosorption of Ni(II) from aqueous solutions by *Litchi chinensis* seeds. *Bioresource Technology* **136**, 635–643.
- Fontana, K. B., Chaves, E. S., Sanchez, J. D. S., Watanabe, E. R. L. R., Pietrobelli, J. M. T. A. & Lenzi, G. G. 2016 Textile dye

- removal from aqueous solutions by malt bagasse: isotherm, kinetic and thermodynamic studies. *Ecotoxicology and Environmental Safety* **124**, 329–336.
- Freundlich, H. 1906 Over the adsorption in solution. *Journal of Physical Chemistry* **57**, 385–470.
- Geetha, P., Latha, M. S. & Koshy, M. 2015 Biosorption of malachite green dye from aqueous solution by calcium alginate nanoparticles: equilibrium study. *Journal of Molecular Liquids* **212**, 723–730.
- Guerrero-Coronilla, I., Morales-Barrera, L. & Cristiani-Urbina, E. 2015 Kinetic, isotherm and thermodynamic studies of amaranth dye biosorption from aqueous solution onto water hyacinth leaves. *Journal of Environmental Management* **152**, 99–108.
- Ho, Y. S. & McKay, G. 1999 Pseudo-second order model for sorption processes. *Process Biochemistry* **34** (5), 451–465.
- Ho, Y. S. & McKay, G. 2000 The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Research* **34** (3), 735–742.
- Huang, J., Liu, D., Lu, J., Wang, H., Wei, X. & Liu, J. 2016 Biosorption of reactive black 5 by modified *Aspergillus versicolor* biomass: kinetics, capacity and mechanism studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **492**, 242–248.
- Jalil, A. A., Triwahyono, S., Yaakob, M. R., Azmi, Z. Z. A., Sapawe, N., Kamarudin, N. H. N., Setiabudi, H. D., Jaafar, N. F., Sidik, S. M., Adam, S. H. & Hameed, B. H. 2012 Utilization of bivalve shell-treated *Zea mays* L. (maize) husk leaf as a low-cost biosorbent for enhanced adsorption of malachite green. *Bioresource Technology* **120**, 218–224.
- Karaoğlu, M. H., Doğan, M. & Alkan, M. 2010 Kinetic analysis of reactive blue 221 adsorption on kaolinite. *Desalination* **256** (1–3), 154–165.
- Khataee, A. R., Vafaei, F. & Jannatkah, M. 2013 Biosorption of three textile dyes from contaminated water by filamentous green algal *Spirogyra* sp.: kinetic, isotherm and thermodynamic studies. *International Biodeterioration and Biodegradation* **83**, 33–40.
- Kim, S. Y., Jin, M. R., Chung, C. H., Yun, Y. S., Jahng, K. Y. & Yu, K. Y. 2015 Biosorption of cationic basic dye and cadmium by the novel biosorbent *Bacillus catenulatus* JB-022 strain. *Journal of Bioscience and Bioengineering* **119** (4), 433–439.
- Kiran, I., Ilhan, S., Caner, N., Iscen, C. F. & Yildiz, Z. 2009 Biosorption properties of dried *Neurospora crassa* for the removal of Burazol Blue ED dye. *Desalination* **249** (1), 273–278.
- Lagergren, S. 1898 About the theory of so-called adsorption of soluble substances. *K. Sven. Vetenskapsakad. Handl.* **24**, 1–39.
- Langmuir, I. 1916 The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American Chemical Society* **38** (11), 2221–2295.
- Lee, L. Y., Gan, S., Yin Tan, M. S., Lim, S. S., Lee, X. J. & Lam, Y. F. 2015 Effective removal of Acid Blue 113 dye using overripe *Cucumis sativus* peel as an eco-friendly biosorbent from agricultural residue. *Journal of Cleaner Production* **113**, 194–203.
- Oguntimein, G. B. 2015 Biosorption of dye from textile wastewater effluent onto alkali treated dried sunflower seed hull and design of a batch adsorber. *Journal of Environmental Chemical Engineering* **3** (4), 2647–2661.
- Ozcan, A., Ozcan, A. S., Tunali, S., Akar, T. & Kiran, I. 2005 Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of *Capsicum annum*. *Journal of Hazardous Materials* **124** (1–3), 200–208.
- Robinson, T., McMullan, G., Marchant, R. & Nigam, P. 2001 Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology* **77** (3), 247–255.
- Safa, Y. & Bhatti, H. N. 2011 Biosorption of Direct Red-31 and Direct Orange-26 dyes by rice husk: application of factorial design analysis. *Chemical Engineering Research and Design* **89** (12), 2566–2574.
- Saha, P. D., Chakraborty, S. & Chowdhury, S. 2012 Batch and continuous (fixed-bed column) biosorption of crystal violet by *Artocarpus heterophyllus* (jackfruit) leaf powder. *Colloids and Surfaces B: Biointerfaces* **92**, 262–270.
- Sen Gupta, S. & Bhattacharyya, K. G. 2011 Kinetics of adsorption of metal ions on inorganic materials: a review. *Advances in Colloid and Interface Science* **162** (1), 39–58.
- Srinivasan, A. & Viraraghavan, T. 2010 Decolorization of dye wastewaters by biosorbents: a review. *Journal of Environmental Management* **91** (10), 1915–1929.
- Srivastava, S., Agrawal, S. B. & Mondal, M. K. 2015 Biosorption isotherms and kinetics on removal of Cr(VI) using native and chemically modified *Lagerstroemia speciosa* bark. *Ecological Engineering* **85**, 56–66.
- Wangpradit, R. & Chitprasert, P. 2014 Chitosan-coated *Lentinus polychrous* Lév.: integrated biosorption and biodegradation systems for decolorization of anionic reactive dyes. *International Biodeterioration and Biodegradation* **93**, 168–176.
- Yavari, S., Mahmodi, N. M., Teymouri, P., Shahmoradi, B. & Maleki, A. 2015 Cobalt ferrite nanoparticles: preparation, characterization and anionic dye removal capability. *Journal of the Taiwan Institute of Chemical Engineers* **59**, 320–329.
- Yeddou-Mezenner, N. 2010 Kinetics and mechanism of dye biosorption onto an untreated antibiotic waste. *Desalination* **262** (1–3), 251–259.

First received 29 August 2016; accepted in revised form 23 January 2017. Available online 7 February 2017