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Equilibrium and kinetic studies of azo dye molecules biosorption on phycocyanin-extracted residual biomass of microalga *Spirulina platensis*

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ABSTRACT

The capability and mechanism of a model azo dye, C.I. Basic Red 46 removal by phycocyanin extraction residue of *Spirulina platensis* were investigated in this study. The biosorption data were analyzed using Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) isotherm models. Langmuir model was more adequate to represent the data of biosorption equilibrium. The dye biosorption capacity was obtained as 23.06 mg g^{-1} for the biosorbent. The dye removal potential of phycocyanin-extracted biomass was very close to that of the virgin alga (25.46 mg g^{-1}). D–R model displayed that the dye was probably to be removed mainly via physical biosorption. The pseudo-first-order, pseudo-second-order, logistic, and intraparticle diffusion models were used for the evaluation of biosorption kinetics. The logistic model presented the best fit to the experimental kinetic data. The intraparticle diffusion model showed that this biosorption process was a complex process involving more than one mechanism. Thus, this waste microalga biomass can be used as a low-cost biosorbent for dye removal.

Keywords: Azo dye; Biosorption; Phycocyanin extraction; *Spirulina platensis*

1. Introduction

Synthetic dyes have complex chemical structures that make them persistence to light, oxidation, and biodegradable process. The presence of residual dyes in water sources cause reduction of sunlight penetration, photosynthetic activity, and gas solubility in addition to visual pollution [1–3]. Moreover, some dyes are toxic and mutagenic and have potential to release carcinogenic amines [2,4]. Although, several methods such as ozonation, ion exchange, and coagulation are used for dye removal from industrial effluents, they tend to be expensive due to operational cost, not eco-friendly and ineffective [2].

In recent years, biosorption has emerged as a cost-effective and efficient alternative for the removal of synthetic dyes from aqueous solutions. Biosorption is a physicochemical process that employs cheap live or dead biomass to remove contaminants and deals with the sorption of a chemical substance in/on a biological matrix/surface [5]. Many types of biomass including

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plant, bacteria, fungi, and algae have been examined for their capability to remove synthetic dyes and other organic pollutants [5–9]. In recent studies, it has been revealed that algal biosorbents are highly effective, reliable, and economic in the removal of dyes from contaminated waters [3,10–12].

Spirulina platensis, a member of blue-green algae, is available in large quantities, largely cultivated throughout worldwide and relatively cheap [11,13]. This blue-green microalga contains high amount of protein and smaller amounts of carbohydrate, lipid, vitamin, and other biomolecules [12]. These compounds include a variety of functional groups such as carboxyl, hydroxyl, phosphate, sulfate, and other charged groups which can be responsible for dye binding [10]. Many studies have shown that *S. platensis* can effectively remove dyes and heavy metals from aqueous solutions [11,13–15].

The cultivation of *S. platensis* microalga is an effective process for obtaining several valuable pigment molecules such as *β*-carotene, chlorophyll a, and phycobiliproteins [16]. Phycocyanin is an accessory photosynthetic pigment of the phycobiliprotein family [17]. As a natural blue pigment, it has been used as a food colorant for chewing gum, ice sherbets, soft drinks, candies, and cosmetics including lipstick and eyeliners [18]. Another application of phycocyanin is as biochemical tracers in immunoassays due to its fluorescent property [17,18]. Besides, it has good therapeutic values such as antioxidant, anticancer, antiviral, anti-allergic, antimutagenic, anti-inflammatory, neuroprotective and hepatoprotective activities [16,19]. Phycocyanin has highly commercial uses, with a market value of around 10–50 million US$ per annum [17]. Therefore, *S. platensis* containing high amount of phycocyanin pigment has been widely used as a source for production of phycocyanin due to its numerous benefits mentioned above. On the other hand, the phycocyanin production from *S. platensis* microalga results in producing the waste alga biomass and causing negative environmental impact due to disposal problem. Thus, a sustainable approach is to utilize the waste biomass without phycocyanin content as a low-cost biosorbent for dye removal. However, up to now, there have no reported studies in literature on the removal of dye using waste *S. platensis* biomass.

In the present study, the possible use of waste *S. platensis* biomass as an alternative inexpensive biosorbent for C.I. Basic Red 46 (C.I. BR 46) dye removal was investigated. C.I. BR 46 was chosen as a model azo dye because of its wider use in industrial applications. The equilibrium and kinetic aspects of removal of C.I. BR 46 by the biosorbent were examined. The waste algal biomass was characterized by Fourier transform infrared (FT-IR) spectroscopy. This is an effective and economical method for bioremediation of contaminated water with dye.

2. Materials and methods

2.1. Dye solution

C.I. Basic Red 46 (C.I. BR 46) dye was obtained from a local source. It was of commercial quality and used without further purification. Stock dye solution at a concentration of 500 mg L^{-1} was prepared by dissolving appropriate amount of the dye in distilled water. The experimental concentrations were obtained by the dilution of this solution. 0.1 M HCl or 0.1 M NaOH was used for pH adjustment of the working solutions.

2.2. Preparation and characterization of biosorbent

S. platensis (strain M2) cultures (Plankton Laboratory, University of Cukurova, Adana, Turkey) were grown in climate chamber (Snijders Scientific, UK) at 40 μmol photons m^{-2} s^{-1} under a 12 h light/12 h dark photoperiod. The microalga was cultivated in the medium of Schlösser [20] at 30˚C and pH 9.5. Illumination was provided by daylight type 36 W fluorescent lamps vertically mounted behind thermal glass on both sides of the cabinet. Temperature was maintained stable using a temperature sensor and controller. The initial biomass concentration of algal culture was 0.12 g L^{-1}. The biomass amount of *S. platensis* was determined by measuring the optical density at 670 nm [21]. After nearly 7 d of cultivation, the algal biomass was harvested by centrifugation at 10,000 rpm for 15 min. It was thoroughly washed with distilled water for the removal of residual materials. *S. platensis* biomass obtained was then subjected to phycocyanin extraction process. The extraction was performed by sonication method using sodium phosphate buffer solution (pH 7.0) in ultrasonic cell crusher with a frequency of 20 kHz [22]. After phycocyanin extraction, the residual biomass was obtained by centrifugation at 10,000 rpm for 30 min. This biomass was dried at 70˚C for 24 h and then crushed, milled, and sieved. The particles in range of 125–250 μm were selected for biosorption experiments. The final product as biosorbent was stored in an airtight container until use. The infrared spectrum of waste *S. platensis* biomass was obtained using a FT-IR spectrometer equipped with an attenuated total reflection accessory (Spectrum 400, PerkinElmer, USA) to define the functional groups present on the biosorbent. A scanning electron microscope (SEM) image of biosorbent was obtained by a SEM (JSM-6390, JEOL, USA) for the identification of its surface morphology.

2.3. Biosorption studies

The batch biosorption experiments were carried out with 0.05 mg of the biosorbent with 50 mL of C.I. BR 46 dye solutions of desired concentration at pH 6 in a series of 100 mL conical flasks. The samples were agitated at a constant speed in a temperature-controlled water bath at 30°C for the required time periods. The flasks were withdrawn from the bath at prefixed time intervals and the residual dye concentrations in the solutions were analyzed by centrifuging the mixtures and then measuring the absorbance of supernatants using a UV–visible spectrophotometer at the maximum wavelength of dye. The concentration of C.I. BR 46 was calculated by comparing absorbance to the dye calibration curve previously obtained. The biosorption capacity of biosorbent, q (mg g^{-1}) was calculated as:

$$q = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where C_0 (mg L^{-1}) is the initial dye concentration, C_t (mg L^{-1}) is the residual dye concentration at time t (min), V (L) is the volume of dye solution, and M (g) is the amount of biosorbent used. The q value is equal to q_t at time t and q_e at equilibrium, respectively. In the same way, the C_t value is equal to C_e at equilibrium.

2.4. Biosorption data evaluation

In this study, each experiment was repeated twice at the same conditions and the arithmetical average values obtained from these experiments were used to give results. The parameters of kinetic and isotherm models with statistical evaluation data were defined by nonlinear regressions using the software OriginPro (ver. 8.0, OriginLab Co., USA). The statistical analyses used were chi-square (χ^2), determination coefficient (R^2) and standard deviation (SD).

3. Results and discussion

3.1. Biosorbent characterization

The main vibrational bands and their respective assignments based on FT-IR analysis for the biosorbent used are revealed in Table 1. As we previously described in more detail [23], the biomass profile of *S. platensis* alga was produced and this is shown in Table 2. The algal biomass was composed of different biomolecules. These compounds contain a variety of functional groups such as carboxyl, hydroxyl, phosphate, sulfate, and other charged groups which can be responsible for dye binding [10–12]. Thus, FT-IR results suggest that the waste *S. platensis* biomass can be considered as a potential biosorbent for the dye biosorption.

Table 1
Main biosorbent bands and their respective assignments obtained by FT-IR analysis

Band (cm^{-1})	Assignment
3394.74	O–H and N–H stretching
2932.66	CH stretching
1651.67	C=O stretching (Amide I)
1537.98	C–N stretching (Amide II)
1404.50	COO– stretching
1240.57	–NH bending (Amide III)
1154.70, 1081.28	C–O stretching
1023.88, 931.24, 706.18	P–O, S–O and C–H stretching

Table 2
Biomass profile of *S. platensis* microalga

Biomolecule groups	Value (mg g^{-1})[a]
Protein	641.25 ± 3.5
Carbohydrate	104.22 ± 2.6
Chlorophyll	16.49 ± 4.1
Carotenoid	5.52 ± 3.0
Phycocyanin	67.10 ± 2.1
Phenolic compounds	6.32 ± 3.9

[a]Mean value ± standard error in triplicate as dry basis.

SEM image of the waste *S. platensis* is shown in Fig. 1. The figure clearly revealed the presence of rough and irregular surface morphology of the waste microalga biomass. This may be a good possibility for the dye molecules to be trapped and biosorbed.

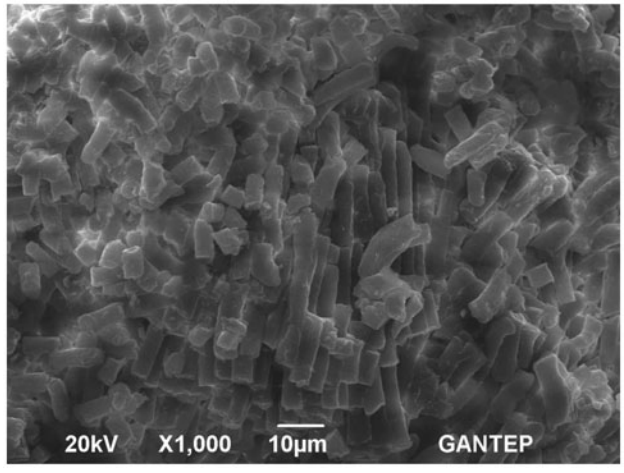

Fig. 1. SEM image of waste *S. platensis*.

3.2. Biosorption equilibrium

The biosorption isotherms represent the equilibrium relationship between the synthetic dye concentration in the liquid phase and that on the biosorbent surface at a given condition. A number of isotherm models have been developed to describe the equilibrium relationship [24]. Freundlich and Langmuir models are the most widely used to describe the biosorption isotherm. Thus, the biosorption equilibrium data for C.I. BR 46 dye removal by the waste *S. platensis* biomass were analyzed by nonlinear Freundlich and Langmuir isotherm models. Freundlich model [25] which assumes biosorption onto heterogeneous solid surface and biosorption energy sites of exponential type is represented as:

$$q_e = K_f C_e^{1/n_f} \quad (2)$$

where K_f (mg g^{-1} (L mg^{-1})$^{1/n}$) and n_f are Freundlich isotherm constants related to biosorption capacity and intensity, respectively. Freundlich model was not able to describe well the biosorption equilibrium based on the statistical data as seen in Table 3.

Langmuir model [26] which proposes monolayer coverage and identical sites with the same biosorption energy on the biosorbent surface is given by:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

The effect of isotherm shape on whether the biosorption process is suitable or unsuitable can be exhibited by the separation factor (R_L) as [9]:

$$R_L = \frac{1}{1 + b C_0} \quad (4)$$

where b (L mg^{-1}) is the constant related to the energy of biosorption and q_m (mg g^{-1}) is the maximum biosorption capacity of the biosorbent. The statistical results showed in Table 3 present that Langmuir model was more adequate to represent the data of biosorption equilibrium. Fig. 2 also presents that this isotherm model points were quite close to the experimental points during the biosorption period. The value of R_L obtained as 0.47 shows a suitable biosorption system [9]. These results revealed the monolayer C.I. BR 46 coverage on the homogeneous surface of the biosorbent. The biosorption capacity of waste *S. platensis* biomass was obtained as 23.06 mg g^{-1} for the dye. This value was very close to that of the virgin alga (25.46 mg g^{-1}). These findings showed that *S. platensis* not only can be used as a potential material for the phycocyanin production, but also has potential for dye removal by its residual biomass which is considered to be a problem for environmental protection after phycocyanin extraction.

Furthermore, Dubinin–Radushkevich (D–R) model [27] was employed to determine the nature of dye removal process as:

$$q_e = q_m \exp^{-B\varepsilon^2} \quad (5)$$

The mean free energy, E (kJ mol^{-1}), can be defined based on D–R model by [28]:

$$E = \frac{1}{(2B)^{1/2}} \quad (6)$$

where B (mol^2 kJ^{-2}) is a constant related to the mean free energy of biosorption, ε is the Polanyi potential which is equal to RTln (1 + (1/C_e)). R (J mol^{-1} K^{-1}) is the universal gas constant and T (K) is the absolute temperature. The mean energy value for the biosorption of C.I. BR 46 dye by the waste *S. platensis* biomass was found to be 5.04 kJ mol^{-1}, which reveals that

Table 3
Equilibrium isotherm model parameters

Freundlich				
K_f mg g^{-1} (L mg^{-1})$^{1/n}$	n_f –	χ^2	R^2	SD
0.03	5.53	14.471	0.783	3.804
Langmuir				
q_m (mg g^{-1})	R_L –	χ^2	R^2	SD
23.06	0.47	2.154	0.973	1.467
D–R				
q_m (mg g^{-1})	E (kJ mol^{-1})	χ^2	R^2	SD
35.21	5.04	9.240	0.862	3.040

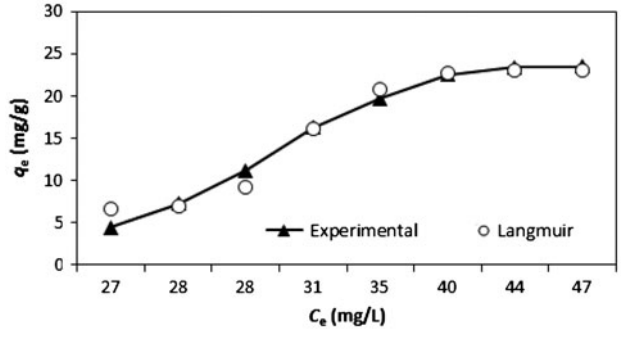

Fig. 2. Equilibrium isotherm models.

C.I. BR 46 was probably to be removed mainly via physical biosorption [28].

3.3. Kinetics of biosorption

The biosorption kinetics provides valuable insights of the biosorption reaction mechanisms and kinetic studies are necessary to design biosorption systems [29]. To investigate details of the biosorption process of C.I. BR 46 on the waste microalga biomass, we analyzed the biosorption kinetics using several models such as the nonlinear pseudo-first-order, pseudo-second-order, and logistic kinetic models. The pseudo-first-order model [30] is frequently used in biosorption studies. It is generally expressed as:

$$q_t = q_e(1 - \exp^{-k_1 t}) \quad (7)$$

The initial biosorption rate, h_0 (mg g^{-1} min^{-1}), is defined by [31]:

$$h_0 = k_1 q_e \quad (8)$$

where q_t and q_e (mg g^{-1}) represent dye biosorption amounts for the biosorbent at time t and at equilibrium, respectively. k_1 (min^{-1}) is the biosorption rate constant of pseudo-first-order model. As seen in Table 4, this model was not suitable for describing the biosorption behavior of biosorbent for C.I. BR 46 based on the statistical results.

The pseudo-second-order kinetic model based on biosorption equilibrium capacity [32] is represented by:

$$q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t} \quad (9)$$

The initial biosorption rate, h_0 (mg g^{-1} min^{-1}), is calculated as [11]:

$$h_0 = k_2 {q_e}^2 \quad (10)$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant. The pseudo-second-order kinetic model gave a good fit to the kinetic data obtained as shown in Table 4. Many biosorption studies have reported that the pseudo-second-order model gives a reasonably good fit of data over the entire fractional approach to equilibrium. So, this model is extensively used to describe the kinetics of biosorption process [33,34].

On the other hand, the logistic model is mainly used for modeling of microbial growth and product formation [35,36]. However, this model is slightly employed for explaining dye biosorption kinetics. The sigmoidal logistic equation [37] can be expressed as:

$$q_t = \frac{q_e}{1 + \exp^{-k(t - t_c)}} \quad (11)$$

where k (min^{-1}) is the maximum relative biosorption rate constant and t_c (min) represents time t pointing center of q_e. The logistic model provided the best fit to the experimental data with the most suitable statistical results as seen in Table 4. It was found that the logistic points were very close to the experimental points over all the biosorption period as can be observed in Fig. 3. These findings present that this model can be used effectively for explaining the dynamics of dye biosorption process.

Weber and Morris intraparticle diffusion analysis [38] was also applied to experimental kinetic data

Table 4
Model parameters of biosorption dynamics

Pseudo-first-order					
k_1 (min^{-1})	q_e (mg g^{-1})	h_0 (mg g^{-1} min^{-1})	χ^2	R^2	SD
0.0293	27.96	0.82	0.940	0.988	0.970
Pseudo-second-order					
k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	h_0 (mg g^{-1} min^{-1})	χ^2	R^2	SD
0.0035	26.30	2.44	0.635	0.990	0.797
Logistic					
k (min^{-1})	q_e (mg g^{-1})	t_c (min)	χ^2	R^2	SD
0.0842	24.13	21.45	0.168	0.998	0.410
Intraparticle diffusion					
k_p (mg g^{-1} min$^{-1/2}$)	C (mg g^{-1})		χ^2	R^2	SD
3.4188	3.17		1.505	0.977	1.227

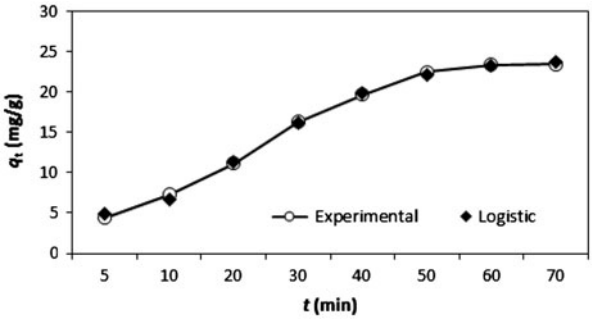

Fig. 3. Models of biosorption kinetics.

obtained for explaining the influence of mass transfer resistance on the binding of dye to the biosorbent by:

$$q_t = k_p t^{1/2} + C \quad (12)$$

where k_p (mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion rate constant and C (mg g^{-1}) is a constant providing information about the thickness of boundary layer. According to this model, the plot q_t versus $t^{1/2}$ shows multilinearity, and each portion represents a distinct mass transfer step. The first portion is the external mass transfer or instantaneous biosorption step. The second portion is the gradual biosorption step, where the intraparticle diffusion is rate controlling. The third portion is the final equilibrium [31,39]. The intraparticle diffusion plot for biosorption of C.I. BR 46 by the waste *S. platensis* biomass displayed the multilinearity with three distinct phases (plot not presented). Thus, the result revealed that this biosorption process was a complex process involving more than one mechanism [10,31].

4. Conclusions

Biosorption of C.I. BR 46 dye on the phycocyanin-extracted residual biomass of *S. platensis* was investigated in the study. FT-IR analysis showed that the waste biomass has various functional groups which can be responsible for dye binding. Langmuir model presented satisfactory fit with the experimental data and the maximum biosorption capacity was obtained as 23.06 mg g^{-1}. This value was very close to that of the virgin alga. The kinetic studies indicated that the logistic model could be used effectively for explaining the biosorption kinetics. Thus, this work revealed that *S. platensis* not only can be used as a potential material for the phycocyanin production, but also can be employed potentially for dye removal by its residual biomass after phycocyanin extraction.

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