Dye Removal Potential of Red Pine Cone from Synthetic Wastewater under Optimized Conditions

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Abstract

Synthetic dyes are extensively used in many industrial applications like textile, leather and cosmetics. The release of various harmful dyes from these industries into the environment has attracted great attention worldwide in recent years. Biosorption is a very effective dye removal technique from aqueous system. In this research, the biosorption performance of cone of red pine for C.I. Basic Red 46 as a model azo dye from synthetic wastewater under optimized biosorption conditions was investigated. The equilibrium data were evaluated with Freundlich, Langmuir and Dubinin-Radushkevich isotherm models. The biosorption equilibrium was successfully described through Langmuir isotherm. This displayed the monolayer coverage of dye molecules on the biosorbent surface. The pseudo-first-order, pseudo-second-order, logistic and intra-particle diffusion models were used for the kinetic evaluation. The logistic model presented the best fit to the experimental results. Thus, this forestry waste biomass can be employed as a cheap biosorbent for the dye removal.

Key words: Red pine; cone; azo dye; biosorption

1. Introduction

Synthetic dyes are extensively used in many industrial applications including textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries [1]. The release of various harmful dyes from these industries into the environment has attracted great attention worldwide in recent years. Dyes usually have a synthetic origin and complex chemical structure that make them persistence to light, oxidation and biodegradable process. As well known, the presence of dyes in water sources can cause reduction of light penetration, photosynthetic activity and gas solubility in addition to visual pollution. Also many dyes and their degradation derivatives are toxic at even carcinogenic in nature [2]. It is necessary to remove these harmful dyes from contaminated water for a better ecosystem quality.

Several technologies such as membrane filtration, oxidation, coagulation, reverse osmosis and ion-exchange have been examined for removal of synthetic dyes from aqueous system. However, most of these methods require high capital and operating costs, and may result in large volumes of solid wastes. In addition, they have other restrictions like short half-life, formation of by-products and release of aromatic amines [3]. On the other hand, biosorption is a very effective dye removal technique and now it is noted to be superior to other methods for water treatment with regard to ease of operation, cost economics, eco-compatibility, high efficiency, simplicity of design and insensitive to toxic substances [4, 5]. A considerable number of low-cost biosorbents have been recently applied for removal of dyes [6]. As

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compared to activated carbon, most of these materials have low biosorption potential. Thus, the search for excellent and efficient biosorbent is still going on.

Calabrian pine (*Pinus brutia* Ten.) is a characteristic species of the eastern Mediterranean. It is widely extended in Turkey and far Eastern Greece, secondarily in the Crimea, Caucasus coast, Azerbaijan, Iraq, Syria, Lebanon, Crete and Cyprus [7]. Calabrian pine is an economically important forest tree in Turkey, providing both timber resources and amenity, used widely in afforestation and reforestation programs [8]. Its forests represent about 27% of the country's forest area, which totals at 5,854,673 ha in 2012 [9]. Pine tree cones are produced in large quantities at forest industries as a litter. Utilization of these cones has been limited to domestic fuel in some rural areas, extraction of essential oils for therapeutic purposes when they are still unripe, and on seasonal decoration [10]. These forest residues are potential lingo-cellulosic biomaterials for dye biosorption. They are very cheap, renewable and great availability. New usage of them as biosorbent is an attractive alternative from both environmental and economic aspects. In addition, it can provide additional income for forest landowners.

The main objective of this study is to investigate the biosorption performance of raw cone shell of Calabrian pine for C.I. Basic Red 46 as a model azo dye from aqueous system under optimized biosorption conditions. The isotherm models of Freundlich, Langmuir and Dubinin-Radushkevich were used for the equilibrium data analysis. The kinetic data were analyzed using the pseudo-first-order, pseudo-second-order, logistic and intra-particle diffusion models.

2. Materials And Methods

2.1. Preparation Of Biosorbent And Dye Solution

The pine cone shells were collected from a plantation in Gaziantep, Turkey. After washing with distilled water to eliminate dust and other residues, the shells were dried at 80 °C and then crushed, milled and sieved. The fractions of particle between 63 and 500 μm were selected for biosorption studies. These were then stored in an airtight plastic container to use as biosorbent without any further pre-treatments.

As a model azo dye, C.I. Basic Red 46 was obtained from a local source. It was of commercial quality and used without further purification. A 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. The pH values of working solutions were adjusted by the addition of 0.1 M HCl and 0.1 M NaOH solutions whenever necessary.

2.2. Experimental Setup

The batch biosorption experiments were carried out with 0.05 mg of the biosorbent with 50 mL of dye solutions of desired concentration at pH 8 in a series of 100 mL conical flasks. The samples were agitated at a constant speed in a temperature-controlled water bath at 25 °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 dye concentration was calculated by comparing absorbance to the dye calibration curve previously obtained.

2.3. Biosorption Data Evaluation

The dye biosorption amount of biosorbent, q (mg g^{-1}), was calculated as [11]:

$$q = \frac{(C_o - C_t)V}{M} \quad \text{........................ (1)}$$

where C_o (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.

Each experiment for this biosorption study was repeated twice at the same conditions and the arithmetical average values obtained from these experiments were used to give the research 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).

3. Results And Discussion

3.1. Effect Of Biosorption Factors On Dye Removal

Fig. 1 shows the effect of each factor studied on the dye removal. Fig. 1a displays that the biosorption capacity of cone shell increased with increase in the initial dye concentration. This may be due to the high driving force for mass transfer at a high initial dye concentration. In addition, if the dye concentration in solution is higher, the active sites of biosorbent are surrounded by much more dye molecules and the biosorption occurs more efficiently [12]. As can be observed in Fig. 1b, the dye removal decreased with enhancing the biosorbent particle size. The higher dye biosorption efficiency with smaller particles can be due to the fact that smaller biosorbent particles provide a larger surface area and better accessibility of dye into active pores [13]. The biosorption capacity of pine cone shell increased with increase in contact time as shown in Fig. 1c. It may be attributed to more vacant active sites being available on the biosorbent surface for further dye biosorption until equilibrium [14].

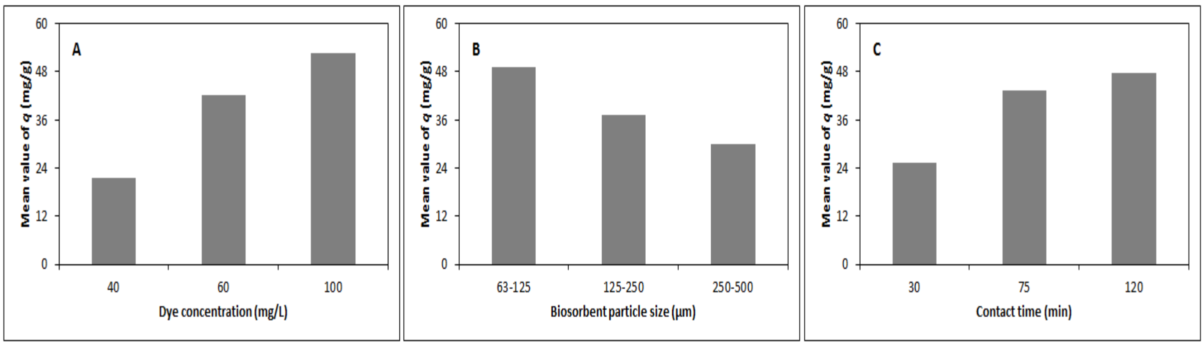

Fig. 1. Effect of each factor studied on biosorption of dye

3.2. Biosorption Equilibrium

Biosorption isotherms describe how dye molecules interact with biosorbent material. They are critical for optimization of biosorption mechanism pathway, expression of surface property and capacity of biosorbent and effective design of biosorption system [15, 16]. Thus, the equilibrium data obtained from the biosorption experiments were evaluated at the optimized dye removal conditions with Freundlich, Langmuir and Dubinin-Radushkevich isotherm models.

Freundlich model assumes biosorption onto heterogeneous solid surface and biosorption energy sites of exponential type [17]. Based on the statistical information in Table 1, Freundlich model did not properly characterize the biosorption equilibrium. On the other hand, the value of n_f was found to be 3.3796 for C.I. Basic Red 46 biosorption by the pine cone shell. This represents a suitable biosorption [18].

Langmuir model proposes monolayer coverage and identical sites with the same biosorption energy on the biosorbent surface [19]. As can be seen in Table 1, with more suitable statistical results, Langmuir model fitted better to the biosorption data than Freundlich model. This shows the monolayer coverage of C.I. Basic Red 46 dye molecules on the cone shell surface. On the other hand, for Langmuir-type biosorption system, the effect of isotherm shape on whether a biosorption process is favorable or unfavorable can be predicted by the separation factor, R_L [20]. The R_L value was obtained as 0.3861 for the removal of C.I. Basic Red 46 by the biosorbent. The values of R_L between 0 and 1 reflect a favorable biosorption [21].

Dubinin-Radushkevich model is generally applied to express the nature of biosorption as physical and chemical [22]. In Dubinin-Radushkevich isotherm, the mean free energy, E (kJ mol^{-1}), shows the mechanism by which biosorption takes place [23]. A value of mean free energy below 8 kJ mol^{-1} displays physical biosorption while a value between 8 and 16 kJ mol^{-1} indicates chemical biosorption [24]. The mean free energy value for C.I. Basic Red 46 biosorption by the pine cone shell was found to be 3.2686 kJ mol^{-1} as shown in Table 1. This presents that the predominant mechanism of the biosorption of dye by the cone shell was likely physical biosorption. To support this information, the standard Gibbs free energy change, $\Delta G°$ (kJ mol^{-1}), was determined by [25]:

$$\Delta G° = -RT\ln K_c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where K_c is the distribution coefficient (C_s/C_e). C_s and C_e (mg L^{-1}) are the equilibrium dye concentrations on biosorbent and in solution, respectively. The standard Gibbs free energy change for the biosorption of C.I. Basic Red 46 by the cone shell was calculated as -6.6536 kJ mol^{-1}. A value of the change of free energy between -20 and 0 kJ mol^{-1} indicates a physical biosorption [26]. This result agrees well with that from the Dubinin-Radushkevich isotherm model.

Table 1. Data of isotherm models

Model	Equation	Parameter	Value	R^2	*SD*
Freundlich	$q_e = K_f C_e^{1/n_f}$	K_f	23.0384	0.6823	10.8889
		n_f	3.3796		
Langmuir	$q_e = \frac{q_L b C_e}{1+bC_e}$	q_L	66.0207	0.9782	3.0842
	$R_L = \frac{1}{1+bC_o}$	R_L	0.3861		
Dubinin-Radushkevich	$q_e = q_{DR} \exp^{-B_{DR}\varepsilon^2}$	q_{DR}	69.5042	0.9654	3.5914
	$E = \frac{1}{(2B_{DR})^{1/2}}$	E	3.2686		

SD: standard deviation, K_f (mg g^{-1}) (L mg^{-1})$^{1/n}$: a constant related to biosorption capacity, n_f: a constant related to biosorption intensity, q_L (mg g^{-1}): maximum monolayer biosorption capacity, b (L mg^{-1}): a constant related to energy of biosorption, R_L: separation factor, q_{DR} (mg g^{-1}): maximum biosorption capacity, B_{DR} (mol^2 kJ^{-2}): a constant related to mean free energy of biosorption, ε: Polanyi potential, E (kJ mol^{-1}): mean free energy.

3.3. Biosorption Kinetics

Kinetic studies are important to understand the biosorption dynamics in terms of order of the rate constant. The kinetic parameters provide information for designing and modeling the biosorption process [27]. The data of biosorption kinetics for dye onto the biosorbent were analyzed under optimal biosorption conditions obtained with various kinetic models including the pseudo-first-order [27, 28], pseudo-second-order [29], logistic [30] and intra-particle diffusion [31]. As can be shown in Table 2, the pseudo-first-order was not appropriate model for describing the biosorption kinetics based on the statistical evaluations. On the other hand, according to the statistical results presented in the table, the pseudo-second-order kinetic model provided a better fit to the experimental data obtained than the pseudo-first-order model. This confirms that the biosorption kinetics of dye onto the pine cone shell can be accurately described by the pseudo-second-order model.

The logistic model is mainly used for modeling of microbial growth and product formation [32, 33]. However, this model is slightly employed for explaining dye biosorption dynamics. The logistic model was used to define the biosorption kinetics of dye onto the cone shell and this model presented the best fit to the experimental results with the most suitable statistical outcomes as displayed in Table 2. Thus, these results reveals that the logistic model can be applied effectively for characterizing the removal kinetics of C.I. Basic Red 46 by the pine cone shell.

The effect of intra-particle diffusion as a potential rate-controlling step in the biosorption was evaluated by Weber and Morris intra-particle diffusion model. According to this model, if a linear line passing through the origin exists between q_t and $t^{1/2}$, the intra-particle diffusion is the sole rate-limiting step. But, if multi-linear plots are exhibited, two or more steps control the biosorption process [18]. The plot for dye biosorption by the biosorbent has three distinct regions (figure is not presented here). The initial region of the curve relates the biosorption on the external surface. The second stage corresponds to the gradual uptake presenting the intra-particle diffusion as rate-controlling step. The final plateau region indicates the surface biosorption and the equilibrium stage [12]. Hereby, the intra-particle diffusion was not the only rate-limiting step for the dye biosorption by the cone shell and also the other mechanism(s) may control the rate of biosorption or all of which may be operating simultaneously.

Table 2. Kinetic parameters

Model	Equation	Parameter	Value	R^2	*SD*
Pseudo-first-order	$q_t = q_e(1-\exp^{-k_1 t})$ $h_1 = k_1 q_e$	k_1 q_e h_1	0.0378 67.7251 2.5580	0.9827	2.5403
Pseudo-second-order	$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t}$ $h_2 = k_2 q_e^2$	k_2 q_e h_2	0.0011 69.9680 5.3844	0.9908	1.9973
Logistic	$q_t = \frac{q_e}{1+\exp^{-k(t-t_c)}}$	q_e k t_c	66.7553 0.0605 19.9207	0.9957	1.3725
Intra-particle diffusion	$q_t = k_p t^{1/2} + C$	k_p C	5.93564 9.08756	0.9431	4.6093

SD: standard deviation, k_1 (min^{-1}), k_2 (g mg^{-1} min^{-1}) and k_p (mg g^{-1} min$^{-1/2}$): biosorption rate constants, h_1 and h_2 (mg g^{-1} min^{-1}): initial biosorption rates, k (min^{-1}): maximum relative biosorption rate, t_c (min): time t pointing center of q_e (q_e/2), C (mg g^{-1}): a constant providing information about thickness of boundary layer.

Conclusion

The dye biosorption performance for the pine cone shell was successfully optimized using Taguchi experimental design model. This model provided reasonable predictive performance of dye biosorption (R^2: 0.9961). The dye concentration had the most significant impact on the dye removal with 51.571% contribution. Langmuir model fitted better to the biosorption data than Freundlich model. This showed the monolayer coverage of dye molecules on the biosorbent surface. The nature of biosorption of dye by the biosorbent was likely physical biosorption based on Dubinin-Radushkevich isotherm model and the standard Gibbs free energy change. The logistic model was found suitable in describing the biosorption kinetics. The kinetic parameters reflecting biosorption performance from the pseudo-second-order kinetics revealed an effective dye biosorption system. A design procedure for a single-stage batch dye biosorption system was also outlined. The study showed that the pine cone shell can be an efficacious biosorbent in the dye removal from water.

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