Journal of Hazardous Materials 181 (2010) 666–672

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (Reactive Red 195) onto *Pinus sylvestris* L.

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ARTICLE INFO

Article history:
Received 9 November 2009
Received in revised form 13 May 2010
Accepted 14 May 2010
Available online 11 June 2010

Keywords:
Elovich equation
Intraparticle diffusion
Kinetic
Pinus sylvestris L.
Reactive Red 195
Thermodynamic

ABSTRACT

This study investigated the biosorption of Reactive Red 195 (RR 195), an azo dye, from aqueous solution by using cone biomass of *Pinus sylvestris* Linneo. To this end, pH, initial dye concentration, biomass dosage and contact time were studied in a batch biosorption system. Maximum pH for efficient RR 195 biosorption was found to be 1.0 and the initial RR 195 concentration increased with decreasing percentage removal. Biosorption capacity increased from 6.69 mg/g at 20 °C to 7.38 mg/g at 50 °C for 200 mg/L dye concentration. Kinetics of the interactions was tested by pseudo-first-order and pseudo-second-order kinetics, the Elovich equation and intraparticle diffusion mechanism. Pseudo-second-order kinetic model provided a better correlation for the experimental data studied in comparison to the pseudo-first-order kinetic model and intraparticle diffusion mechanism. Moreover, the Elovich equation also showed a good fit to the experimental data. Freundlich and Langmuir adsorption isotherms were used for the mathematical description of the biosorption equilibrium data. The activation energy of biosorption (*Ea*) was found to be 8.904 kJ/mol by using the Arrhenius equation. Using the thermodynamic equilibrium coefficients obtained at different temperatures, the study also evaluated the thermodynamic constants of biosorption (ΔG^o, ΔH^o and ΔS). The results indicate that cone biomass can be used as an effective and low-cost biosorbent to remove reactive dyes from aqueous solution.

1. Introduction

Dyes are extensively used in many industries including textile, leather, pulp and paper, food and plastics. They are classified as acid and reactive dyes, cationic-basic dyes, non-ionic-disperse dyes, and anionic direct dyes [1,2]. Amongst the most commonly used ones are reactive dyes which present medium to high fastness for cellulose fibres [3]. Approximately 700,000 tones and 10,000 different types of dyes and pigments are being produced annually across the world and a significant proportion of these dyes enter the environment in wastewater [4]. There are some reports about the negative effects of these dyes. For example, reactive dyes are toxic for several organisms and constitute a threat to ecosystems mainly because they block out the sunlight and thus reduce photosynthesis and dissolved oxygen concentration [5,6]. Besides, many dyes or their metabolites have carcinogenic, teratogenic and mutagenic effects on humans and other life forms [7,8]. Therefore, removal of dyes before disposal of the wastewater is extremely important. Several methods such as photochemical oxidation, membrane filtration, ozone treatment, activated carbon adsorption, reverse osmosis and coagulation have been developed to remove dyes from wastewater [9–11]. However, they are ineffective, especially for the removal of brightly coloured, water-soluble reactive and acid dyes. In addition, most of these methods require high costs and are difficult to operate particularly on a great scale. Conversely, biosorption has attracted increasing interest owing to its lower cost, its effectiveness in producing less sludge and its environmental friendliness [12–14].

Over the last few decades, there has been an increase in the use of plant waste products for dye removal by biosorption from wastewater because of their natural availability and the high degree of dye removal achieved under laboratory conditions [15]. These alternative biosorbents include *Enteromorpha prolifera* [8], *Azadirachta indica* [12], *Posidonia oceanica* fibres [15], *Eriobotrya japonica* [16], wheat bran [17], *Botrytis cinerea* [18], *Penicillium restrictum* [19] and *Pinus sylvestris* [20].

Cone biomass is a waste itself and a readily available biosorbent. The ovulate cone is the well known cone of the *Pinus* and other conifers. Each cone is composed of an axis upon which are borne, in a spiral fashion, a large number of woody scales. Two megasporangia in ovules develop on the upper surface of each scale. Upon maturity they become seeds; the ovulate cone is, therefore, a seed-bearing cone. The scales of the mature cone are composed of epidermal and sclerenchyma cells which contain cellulose, hemicellulose, lignine, rosin and tannins in their cell walls [21,22].

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doi:10.1016/j.jhazmat.2010.05.064

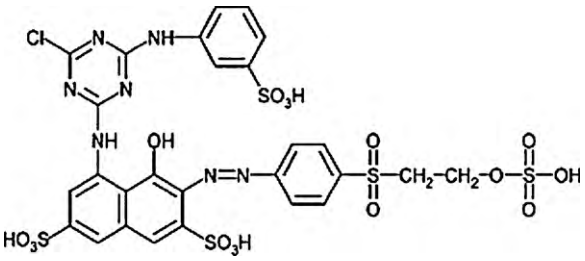

Fig. 1. Chemical structure of Reactive Red 195.

The current study investigated the biosorption of Reactive Red 195 (RR 195) ions from aqueous solution by using cone biomass of *P. sylvestris* L. This dye is largely used for textile dying in Turkish cloth industry. To investigate the mechanisms of RR 195 biosorption, the characteristic constants of biosorption were determined using a pseudo first- and second-order equation, the Elovich equation and intraparticle diffusion equation, respectively. The Langmuir and Freundlich isotherms were used to describe equilibrium isotherms. The biosorption mechanisms of RR 195 onto cone biomass were also evaluated in terms of thermodynamics and kinetics. The magnitude of the heat effect for the biosorption process is the most important criterion to develop a thermodynamic and kinetic relationship for the dye–biosorbent interaction process. The relative binding affinity of the biosorbent and the main mechanism for biosorption are also discussed.

2. Materials and methods

2.1. Materials

The biosorbent used in this study, *P. sylvestris* cones, was collected in July 2007. The cones were washed repeatedly with deionized water to remove the adhering dirt and soluble impurities, dried at 80 °C for 24 h and crushed. The dried biomass was ground in a mortar to a very fine powder and sieved through a 400-mesh copper sieve. The powdered biosorbent was stored in glass bottles prior to use.

The textile dye, Reactive Red 195 (RR 195), was obtained from Dystar, Turkey and used without further purification. Its chemical composition is shown in Fig. 1. By dissolving RR195 in deionized water, the dye containing stock solution (1000 mg/L) was obtained. The other required concentrations (50–200 mg/L) were prepared by diluting the stock solution of RR 195. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted to desired values with dilute HCl or NaOH.

2.2. Batch biosorption studies

The experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL of dye solutions. The effect of biomass concentration on RR 195 biosorption was determined using biomass sampling amounts ranging from 5.0 to 40 g/L. To determine the effect of initial dye concentration of RR 195, dye concentrations ranging from 50 to 200 mg/L were prepared and used. The batch experiments were performed under shaking at 200 rpm at 20 °C, pH 4.0 for 180 min. The effect of temperature on RR 195 biosorption was increased from 20 to 50 °C. The effect of pH on the biosorption process was determined at different pH values ranging from 1.0 to 6.0.

After the biosorption process, the solution was centrifuged for 5 min at 4500 rpm and supernatants were analyzed for remaining dye concentration using a spectrophotometer (540 nm) (Shimadzu UV-160A).

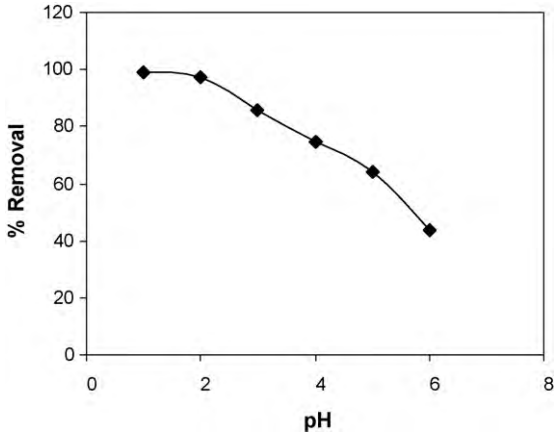

Fig. 2. Effect of pH on % Removal of *P. sylvestris* for RR 195 (C_0 = 100 mg/L; T = 25 °C; m = 20 g/L).

3. Results and Discussion

3.1. Effect of initial pH

pH is an important parameter for biosorption studies and affects not only the biosorption capacity, but also the colour and solubility of dye solutions [19]. The effect of initial solution pH on the biosorption amount of cone biomass was investigated in the pH range between 1-6 (which was adjusted with HCl or NaOH at the beginning of the experiment and not controlled afterwards) at a constant temperature of 20 °C and 100 mg/L initial Reactive Red 195 concentration. It was observed that the solution pH affects the amount of dye biosorbed.

As seen in Fig. 2, the biosorption of RR 195 was at its maximum amount at the initial pH of 1.0, but decreased with pH up to 6.0. The biosorption capacity for RR 195 onto cone biomass increased from 43.59% to 98.80% when the solution pH decreased from 6.0 to 1.0. A similar observation has been reported in the literature, suggesting that reactive dye biosorption decreases with increasing pH [23,24]. Reactive dyes are also called anionic dyes because of the negative electrical structure of the chromophore group [8]. The increase in OH^- ions with increasing pH also results in a competition with dye anions for biosorption sites, leading to a decrease in biosorption. As pH decreases, the number of positively charged sites on the biosorbent surface increases; as a result, dye biosorption also increases due to the electrostatic attractions between negatively charged dyes anions and positively charged biosorbent surface [25]. In the initial experiments, the optimum pH value was obtained at pH 1.0. However, in the following experiments, the pH value was fixed at 4.0, which was the native pH value of solution.

3.2. Effect of biosorbent dosage

The influence of initial biosorbent concentration on the biosorption capacity of cone biomass was studied for a dye concentration of 100 mg/L and a biosorbent content of 5–40 g/L at 20 °C temperature (figure not shown). The increase in biosorbent dose resulted in an increase in biosorption efficiency. Biosorption efficiency increased from 57.78% to 74.67% as the biosorbent dose increased from 5 to 20 g/L. Further increases in biosorbent dosage reduced the maximum removal of RR 195. This can be explained by aggregate formation during biosorption, which takes place at high biosorbent concentrations causing a decrease in the effective biosorption area. The increase in the percentage of dye removal with biosorbent dosage could be attributed to an increase in the biosorbent surface areas, augmenting the number of biosorption sites avail-