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Equilibrium, kinetic and thermodynamic studies of Acid Orange 52 dye biosorption by *Paulownia tomentosa* Steud. leaf powder as a low-cost natural biosorbent

Fatih Deniz *, Saadet D. Saygideger

Department of Biology, Faculty of Arts and Science, Gaziantep University, 27310 Gaziantep, Turkey

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ABSTRACT

The biosorption of Acid Orange 52 onto the leaf powder of *Paulownia tomentosa* Steud. was studied in a batch adsorption system to estimate the equilibrium, kinetic and thermodynamic parameters as a function of solution pH, biosorbent concentration, dye concentration, biosorbent size, temperature and contact time. The Langmuir, Freundlich and Temkin isotherm models were used for modeling the biosorption equilibrium. The experimental equilibrium data could be well interpreted by the Temkin and Langmuir isotherms with maximum adsorption capacity of 10.5 mg g^{-1}. In order to state the sorption kinetics, the fits of pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion kinetic models were investigated. It was obtained that the biosorption process followed the pseudo-second order rate kinetics. Thermodynamic studies indicated that this system was exothermic process. The results revealed that *P. tomentosa* leaf powder could be an efficient biosorbent for the treatment of wastewater containing Acid Orange 52.

1. Introduction

Increasing environmental pollution caused by toxic dyes is a matter of great concern. Even small traces of the non-biodegradable and highly toxic dyes can be harmful to the mankind. Effluents from dye production and dying mills are highly objectionable if discharged into open water without any proper treatment. The presence of coloring material in water system also reduces penetration of light and photosynthetic activity. Dyes are also major component of the laboratory wastes, which are then led into the soil and water bodies (Mittal et al., 2007). So, these dyes need to be removed.

Removal of toxic dyes from industrial wastewater has been practiced for several decades. The conventional physico-chemical removal methods such as chemical precipitation, electroplating, membrane separation, evaporation and resin ionic exchange are usually expensive and sometimes, not effective. Therefore, there is a need for an alternative technique, which is efficient and cost-effective. Biosorption, based on living or non-living microorganisms or plants, is a promising potential alternative to conventional processes for the removal of dyes (King et al., 2008). The main attractions of biosorption are high selectivity and efficiency, cost effectiveness and good removal performance (Aksu and Tezer, 2005).

In Gaziantep, a city of Turkey, main roads, parks and schools have planted *Paulownia tomentosa* Steud. A lot of *P. tomentosa* leaf felled in autumn and often are collected as waste by cleaners. This research is needed to develop an alternative technology for utilizing these leaves. Several researchers reported the usage of plant-leaf to adsorb dyes from solution (Han et al., 2007; Ponnusami et al., 2008), but no research was reported about dye adsorption onto *P. tomentosa* leaf. In the present study, the leaf of *P. tomentosa* has been used as an adsorbent for the removal of Acid Orange 52 (AO 52) from aqueous solution. AO 52 is selected as a model dye for evaluating the potential of the leaf to remove dye from wastewaters. AO 52 is a water-soluble azo dye, which is widely used in the textile, paper manufacturing, printing, pharmaceutical, food industries and also in research laboratories. Biosorption process was optimized by investigating pH, dye concentration, temperature, contact time, biosorbent concentration and biosorbent size. The equilibrium biosorption data were evaluated by Langmuir, Freundlich and Temkin isotherm models. The pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion kinetic models were used for determining of the adsorption kinetics. The thermodynamic parameters (ΔG°, ΔH° and ΔS°) and activation energy (E_a) were also determined.

* Corresponding author. Tel.: +90 342 3171948; fax: +90 342 3171032.
E-mail addresses: fdeniz@gantep.edu.tr, f_deniz@windowslive.com (F. Deniz).

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2. Methods

2.1. Preparation of biosorbent

The green leaves of *P. tomentosa* used in the present investigation were collected from the campus of Gaziantep University (Gaziantep, Turkey) in October 2008. The collected materials were washed with distilled water for several times to remove all the dirt particles. The washed materials were then completely dried in an oven at 70 °C until constant weight. Then the dried leaves were powdered using domestic grinder and the powder was sieved for the particle size of 63–500 μm. Then, the obtained powder was used as biosorbent without any pretreatment for AO 52 adsorption.

2.2. Chemical and reagents

The azo dye, AO 52 (C.I.13025, $C_{14}H_{14}N_3NaO_3S$), HCl and NaOH were obtained from Merck with analytical grade. Chemical structure of AO 52 was shown in Fig. 1. The stock dye solution was prepared by dissolving appropriate amount of AO 52 in 500 mL distilled water. The working solutions were obtained by diluting the dye stock solution to the required concentrations. The pH of solutions was adjusted with 0.1 M concentrations of HCl and NaOH, using a pH-meter (Hanna, pH 211).

2.3. Batch biosorption experiments

The batch biosorption studies were carried out at various pH (2–10), dye concentration (20–100 mg L^{-1}), temperature (25–45 °C), contact time (0–180 min), biosorbent concentration (0.1–0.5 g L^{-1}) and biosorbent size (63–500 μm) with 30 mL AO 52 solution in a water bath to elucidate the optimum conditions of biosorption. After each biosorption process, the dye solution was separated from the biosorbent by centrifugation at 5000 rpm for 10 min. Then, supernatants were analyzed for remaining dye concentration by a UV–vis spectrophotometer (GBC, Cintra 202) monitoring the changes in the absorbance values at 520 nm. The amount of AO 52 adsorbed onto the leaf, q (mg g^{-1}), was obtained by the following equation, Eq. (1):

$$q = \frac{(C_o - C_e)V}{M} \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations of dye (mg L^{-1}), respectively. V is the volume of the solution (L) and M is the amount of adsorbent used (g).

3. Results and discussion

3.1. Determination of optimum biosorption conditions

3.1.1. The effect of solution pH on biosorption

The pH of aqueous solution is an important controlling parameter in the biosorption process (Nuhoglu and Oguz, 2003). To analyze the influence of pH on the biosorption capacity of *P. tomentosa* leaf for AO 52 dye, the experiments were carried out at different initial solution pH values varying from 2 to 10. The results were presented in Fig. 2a showed that the biosorption capacity decreased significantly with an increase in the solution pH and the maximum adsorption level was determined as 0.57 mg g^{-1} at pH 2. It is well known that at lower pH, more protons will be available to protonate the adsorbent surface, thereby increasing the electrostatic attractions between negatively charged dye anions and positively charged adsorption sites and causing an increase in the dye adsorption (Chiou and Chuang, 2006). Hence, all the succeeding investigations were performed at pH 2.

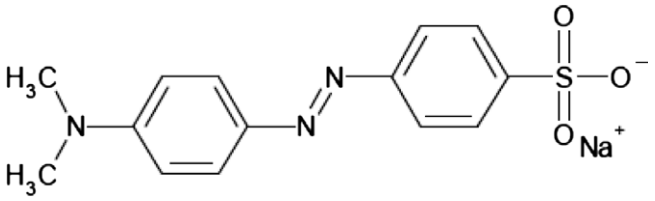

Fig. 1. Chemical structure of AO 52.

3.1.2. The effect of leaf dose on biosorption

The effect of biosorbent dose on the dye adsorption was investigated in the range of 0.1–0.5 g L^{-1} and the results were shown in Fig. 2b. The adsorbed AO 52 concentration increased from 1.6 to 1.8 mg L^{-1} while the adsorbed AO 52 amount per unit biomass weight, q (mg g^{-1}) decreased from 0.48 to 0.11 mg g^{-1} by increasing the biosorbent concentration from 0.1 to 0.5 g L^{-1}. Increase in biosorption with the biosorbent dose could be attributed to increased surface area and the availability of more adsorption sites. The decrease in q value may be due to the decrease in solute transfer rate onto the adsorbent surface, i.e., the amount of solute adsorbed onto unit weight of adsorbent gets splitted with increasing biomass concentration (Vasanth Kumar et al., 2005). Finally, biosorbent dose of 0.1 g L^{-1} was chosen for the other biosorption studies.

3.1.3. The effect of initial dye concentration on biosorption

Biosorption of AO 52 onto the leaf powder was carried out at different initial dye concentrations (20, 40, 60, 80 and 100 mg L^{-1}). The results were given in Fig. 2c. It was showed that dye adsorption capacity of the biosorbent was increased with an increase in the initial dye concentration. Initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases. Hence, a higher initial dye concentration of dye will enhance the adsorption process (Donmez and Aksu, 2002; Banat et al., 2003). The amount of dye adsorbed increased from 0.7 to 20.8 mg g^{-1} with an increase in initial dye concentration from 20 to 100 mg L^{-1}. The effect of initial dye concentration on the biosorption capacity has been found to be of considerable significance for the dye used. So, all the succeeding adsorption studies were performed at dye concentration of 100 mg L^{-1}.

3.1.4. The effect of particle size on biosorption

The effect of particle size of the biosorbent on the AO 52 adsorption capacity of the biosorbent was investigated in the range of 63–500 μm and the results were indicated in Fig. 2d. As seen in figure, the equilibrium dye adsorption changed insignificantly by the particle size. An increase in the particle size from 63–125 to 125–250 μm leads to an increase in the adsorption capacity from 20.12 to 21.66 mg g^{-1} for the biosorbent. When the particle size further increased to 250–500 μm, dye adsorption value was detected as 20.82 mg g^{-1}. The variations in adsorption capacity values due to particle size may be assumed negligible. Finally, all other adsorption experiments were carried out at 125–250 μm.

3.1.5. The effect of temperature on biosorption

The effect of temperature on adsorption capacity of the biosorbent was studied at 25, 35 and 45 °C and the results were shown in Fig. 2e. Slight decrease in the biosorption of AO 52 with the increasing temperature suggested that biosorption between the leaf and AO 52 dye was an exothermic process and the mechanism was mainly physical adsorption which is dominant at lower temperatures. Similar results were also mentioned by some