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## Removal of a hazardous azo dye (Basic Red 46) from aqueous solution by princess tree leaf

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### ARTICLE INFO ABSTRACT

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Batch biosorption experiments were carried out for the removal of Basic Red 46 (BR 46) from aqueous solution by using princess tree leaf (PTL) as a potential biosorbent. The effects of solution pH, biosorbent dosage and size, dye concentration, temperature and contact time on the biosorption of BR 46 onto the PTL were investigated. The experimental results showed that maximum pH for efficient BR 46 biosorption was about 8.0. The equilibrium was attained in 70 min. The amount of BR 46 sorbed onto the PTL increased with the increase of dye concentration, in contrary, it decreased with increases of temperature, biosorbent dosage and size. The equilibrium sorption was best described by the Langmuir isotherm model. The maximum monolayer sorption capacity was found as 43.10 mg  $g^{-1}$  at 25 °C. Kinetic studies indicated that the pseudosecond order model fitted to the experimental data well. Thermodynamic parameters demonstrated that the biosorption process was spontaneous and exothermic. The results revealed that the PTL could be used as a low-cost alternative biosorbent for the dye removal from wastewater.

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#### 1. Introduction

In the 21st century, environmental pollution is one of the major threats to human life. Among the different types of pollution, waste water stream is one of the major problems due to a large amount of water used in our daily life. Waste water containing dye is the major source of water pollution [\[1\].](#page--1-0) Dyes are extensively used as coloring agents in many industries such as textile, leather, plastic, cosmetic, food and pharmaceutical [\[2\]](#page--1-0). Among these various industries, textile ranks first in usage of dyes for coloration of fiber. As a result, they generate a considerable amount of colored wastewater [\[3\].](#page--1-0) The presence of dyes in water, even at very low concentrations, is highly visible and undesirable [\[4\]](#page--1-0). These dyes are primarily of synthetic origin and have complex aromatic structures, which make them more stable to light, heat and oxidizing agents, and are usually biologically non-degradable [\[5\]](#page--1-0). Besides, many dyes or their metabolites have carcinogenic, teratogenic and mutagenic effects on humans and other life forms [\[6\].](#page--1-0) Thus, it is necessary to remove dyes from wastewater before it is discharged.

During the past years, several methods such as coagulation, flocculation, ion exchange, membrane separation and advanced oxidation have been reported and attempted for the removal of dyes from effluents. Most of these techniques may be efficient for the

removal of dyes, but they are costly and lead to generation of sludge or formation of byproducts [\[7\]](#page--1-0). In recent years, the development of biosorption technology has represented a powerful alternative for the removal of dyes from wastewaters with the advantages of low-cost, greater profitability, ease of operation and greater efficiency [\[8\].](#page--1-0) Over the last few decades, there has been an increase in the use of plant waste products for dye removal by biosorption from wastewater. Some of these alternative biosorbents are neem leaf powder, loquat seed biomass, bean waste biomass, Thuja orientalis cone biomass, palm kernel fiber, durian peel and hazelnut shells [8–[14\]](#page--1-0). However, the biosorption capacities of most of the above were still limited. New economical, locally available and highly effective biosorbents are still under development.

Princess tree (Paulownia tomentosa Steud.) is cheap and easily available plant in many countries and is commonly planted as ornamentals in parks, roads, schools and gardens. Princess tree falls in autumn and its leaf is often collected as waste by cleaners. Although the princess tree leaf (PTL) is a widely available waste material, its application for the dye removal has been reported by only one work so far [\[15\]](#page--1-0). Thus, the PTL as a low-cost and abundant biosorbent could be an alternative for the removal of dyes from wastewater.

In this study, Basic Red 46 (BR 46) was used as a model compound. It is a synthetic azo dye which is used widely in the textile industry. Azo dyes are a class of dyes characterized by the presence of the azo group. Due to high usage of these dyes, large volumes of colored effluents are discharged into environmental water sources. The release of azo dyes into the environment is of concern due to their

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toxic, mutagenic and carcinogenic characteristics of the dyes and their biotransformation products [\[16\]](#page--1-0). Hence, removal of azo dyes from wastewater is a major environmental issue.

The main object of this study was to examine the feasibility of using the PTL as a biosorbent for the removal of BR 46 from the aqueous solution. Effects of different parameters including solution pH, biosorbent dosage and size, dye concentration, temperature and contact time were studied to optimize the biosorption process. The isotherm, kinetic and thermodynamic parameters were explored to describe the experimental data.

#### 2. Materials and methods

#### 2.1. Preparation of biosorbent material and dye solution

The princess tree leaf (PTL) used in this study was collected from the campus of Gaziantep University, Gaziantep, Turkey in October 2008. It was firstly washed with distilled water, dried at 70 °C for 24 h, crushed in a domestic grinder and sieved to obtain particle size in the range of 63–500 μm. The powdered biosorbent was stored in an airtight container until use. No other chemical or physical treatments were used prior to biosorption experiments.

Basic Red 46 (BR 46) was supplied by a local textile factory and used without further purification. The dye was of commercial purity (Type: Cationic,  $M_w$ : 322 g mol<sup>-1</sup>,  $\lambda_{\text{max}}$ : 530 nm). The chemical structure is shown in Fig. 1. A stock solution of 500 mg  $L^{-1}$  was prepared by dissolving accurately quantity of the dye in distilled water. The test solutions were prepared by diluting the stock solution to the desired concentrations. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted to the desired values with dilute HCl or NaOH using a pH-meter (Hanna, pH 211).

#### 2.2. Batch biosorption experiments

All experiments were carried out with the biosorbent sample in 100 mL conical flasks containing 50 mL BR 46 solutions in a water bath to elucidate the optimum values of the experimental parameters including solution pH (2–10), biosorbent dosage (1–5 g  $L^{-1}$ ) and size (63–500  $\mu$ m), dye concentration (20–100 mg L<sup>-1</sup>), temperature (25– 45 °C) and contact time (0–90 min). After each biosorption study, the samples were centrifuged (5000 rpm, 10 min) for solid–liquid separation and the residual dye concentration in solution was analyzed by a UV–Vis spectrophotometer (GBC, Cintra 202) at 530 nm. The equilibrium, kinetic and thermodynamic studies were performed by determining optimum biosorption conditions.

The amount of biosorption,  $q \pmod{g^{-1}}$ , was calculated by:

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

where  $C_0$  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 biosorbent used (g).



Fig. 1. Chemical structure of BR 46.

#### 3. Results and discussion

#### 3.1. Effect of solution pH

The pH of the dye solution affects not only the surface charge of the biosorbent, the degree of ionization of the materials and the dissociation of functional groups on the active sites of the biosorbent, but also the structure of the dye molecule [\[17\].](#page--1-0) The results of the pH studies at different pH values are shown in Fig. 2. Biosorption capacity of the PTL for BR 46 increased with increasing pH and reached a maximum level at the pH of 8.0. Then, it started to decrease. Similar pH trends were also reported by other researchers for kaolin [\[1\]](#page--1-0) and Polygonum orientale [\[18\].](#page--1-0) The lower biosorption of BR 46 at low pH values may be explained by the competition of excess  $H^+$  ions with the dye cation for active biosorption sites [\[19\].](#page--1-0) However, it did not explain the slight decrease of the dye biosorption at higher pH values.

#### 3.2. Effect of biosorbent dose and size

The effect of biosorbent dose ranging from 1 to 5 g  $L^{-1}$  on BR 46 biosorption is given in [Fig. 3.](#page--1-0) As seen from [Fig. 3a](#page--1-0), biosorption capacity for BR 46 decreased with the PTL dosage increasing. This may be due to the decrease in the total sorption surface area available to BR 46 resulting from overlapping or aggregation of sorption sites [\[20\].](#page--1-0) Similar behaviour for the effect of biosorbent dosage on the dye biosorption capacity was observed and discussed in the literature for different types of biosorbents [\[21,22\]](#page--1-0).

Biosorption of BR 46 was studied at three different particle sizes (63–125, 125–250 and 250–500 μm) of the PTL. The results shown in [Fig. 3](#page--1-0)b led to the conclusion that biosorption increases with decreasing particle size. This may be due to the fact that the smaller biosorbent particles have shortened diffusion paths, such that the ability of the dye to penetrate all internal pores of the biosorbent is higher [\[23\]](#page--1-0).

#### 3.3. Effect of dye concentration

The effect of initial dye concentration in the range of 20 to 100 mg  $L^{-1}$  on biosorption of the BR 46 was investigated and is shown in [Fig. 4](#page--1-0). The biosorption capacity of the PTL increased from 3.04 to 46.13 mg  $g^{-1}$  with increasing of the initial dye concentration. This is probably due to the increase in the driving force of the concentration gradient, as an increase in the initial dye concentration. Similar results were reported by other researchers for coniferous pinus bark powder [\[24\]](#page--1-0) and tea [\[25\].](#page--1-0)

#### 3.4. Effect of temperature

The effect of temperature on the removal of BR 46 by the PTL was investigated in the temperature range of 25–45 °C. The temperature



Fig. 2. Effect of solution pH on BR 46 sorption (biosorbent dose: 1 g L<sup>-1</sup>, dye concentration: 40 mg L−<sup>1</sup> , particle size: 125–250 μm and temperature: 25 °C).

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