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Dye biosorption onto pistachio by-product: A green environmental engineering approach

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ABSTRACT

Wastes from different sources can be utilized as effective materials in wastewater bioremediation. From this point of view, this study was aimed to investigate the possibility of using pistachio shell, a non-conventional cheap biosorbent, obtained as agricultural solid waste for removal of a reactive-azo dye from water. The batch biosorption studies were carried out as a function of dye concentration and contact time. The experimental results showed that the biosorption process was very rapid (nearly 10 min) and the percent yield of biosorption decreased with an increase in dye quantity. Two- and three-parameter biosorption models were employed to describe the experimental kinetic and isotherm data. The results revealed that the biosorption data were best fitted by the pseudo-second-order and Sips models. The maximum biosorption capacity was found to be 109.535 mg g^{-1}. The magnitude of standard Gibbs free energy change was calculated as −5.184 kJ mol^{-1} showing that physical forces were involved in the spontaneous biosorption of dye onto the biosorbent. This research suggests that the pistachio by-product can be an effective and low-cost material for the removal of such hazardous dyes from water.

1. Introduction

Water pollution by synthetic dyes has become one of the most serious environmental problems in the last decades. Dyes are introduced into the aquatic systems significantly as a result of various industrial sources. Numerous dyes are known to be toxic. The presence of these toxic substances in the environment may be harmful to humans and living species even at low concentration [1]. The removal of dyes from wastewater is significant in the protection of the ecosystem and human health.

Wastewaters containing dyes are very difficult to treat because of recalcitrant, resistant and stable nature of these pollutants [2]. Many physicochemical methods are available for dye removal from aqueous solution, including coagulation, flocculation, ion exchange, membrane filtration and advanced oxidation processes. Long operation time, high sludge production, low efficiency, high cost and in some cases, the production of toxic by-products make these technologies impractical and expensive to operate [3].

Biotechnological approaches are economical alternatives to eradicate dyes in wastewaters when compared with above processes. In this context, biosorption is emerging as a growing alternative technique for decolorization of dye containing effluents because it has significant advantages, especially from economical and environmental viewpoints. Biosorption has been proven as an effective and cheap process, especially when using bio-wastes and agricultural by-products as biosorbent [3,4]. Although the use of activated carbon for dye removal has been found to be successful, the application of activated carbon has been limited because of its high cost and regeneration difficulties [5,6]. Currently, there is a growing interest in using low-cost and non-conventional alternative biosorbents instead of traditional materials. The prominent and emerging trend of subjecting biosorbents in the biosorption technology is mainly because of their natural existence, abundance, renewable, biodegradable and economic features [7]. The usage of agricultural residues or industrial by-product as alternative biosorbent to activated carbon has therefore received considerable attention [4,5]. Recently, many industrial, agricultural and forestry sources are used as biosorbents including, olive stone, rice bran, shrimp shell, corn husk and *Ageratum conyzoides* leaf powder [2,3,5,8,9]. To make the biosorption process more attractive and feasible, novel low-cost biosorbents with higher biosorption capacities are required.

The genus *Pistacia* is a member of the *Anacardiaceae* family and consists of eleven or more species. However, pistachio, *Pistacia vera* L., is the only cultivated and commercially noteworthy species of this genus [10]. Pistachio is one of the most important tree nuts of the world. Iran, USA and Turkey are the top three producers of pistachio, and its global production increases steadily [11]. Pistachio nuts are mainly used as a snack food, both raw and toasted, and are a confectionery ingredient in fermented meats, ice cream, bread, sauces and pudding manufacturing [12]. Considering the shell/pistachio ratio (~45%), high amount of pistachio shell is produced as a by-product of the pistachio industries [13]. Mainly, this by-product is directly incinerated for heating purpose

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because it has no important industrial use. Using raw pistachio shell as biosorbent is more economical and environmental option. This presents the pistachio industry an opportunity to make valuable use of the huge quantities of pistachio shell generated every year. Thus, the aim of this study is to investigate the possibility of pistachio shell as a non-conventional low-cost biosorbent for the treatment of dye contaminated water. According to literature data, the natural form of this biomass was only used in the removal of Remazol Red dye from aqueous solution [14]. It was also utilized in activated carbon and modified forms for methylene blue removal [15,16]. There are several types of dyes including anionic (reactive, acid and direct dyes), cationic (basic dyes) and nonionic (disperse dyes). As the brightest class of soluble dyes, anionic dyes pose serious health and environmental risks [17]. The removal of these dyes is a very important aspect of water treatment before discharge. Hence, C.I. Reactive Red 238 was selected as model anionic dye system. It is a water soluble azo dye used extensively in the textile industry as a staining agent. Any study dealing with the removal of C.I. Reactive Red 238 by biosorption using biological by-product is not available in the literature. Thus, this study is the first attempt on use of the raw form of pistachio shell for a hetero-bireactive dye removal from aqueous solution. The effects of some operating variables including dye concentration and contact time on the dye biosorption were investigated in batch mode. Kinetic and equilibrium parameters were defined to understand the biosorption mechanism. Finally, FTIR and SEM characterizations were performed to elucidate the removal mechanism of C.I. Reactive Red 238 dye molecules by the biosorbent.

2. Material and methods

2.1. Chemicals

All chemicals reagents used were of analytical grades. C.I. Reactive Red 238 dye was provided from a textile plant located in Gaziantep (Turkey). It is a dark red powder with molecular formula of $C_{29}H_{15}O_{13}S_4ClFN_7Na_4$ and molecular weight of 944.2 g mol^{-1}. The chemical structure of dye was not disclosed by the manufacturing company (CIBA). An accurately weighed quantity of the dye was dissolved in distilled water to prepare a stock solution (1 g L^{-1}). The working solutions were prepared from the stock solution to the desired concentrations through successive dilutions using distilled water.

2.2. Biosorbent

Pistachio shell was kindly supplied by a local pistachio processing factory (Gaziantep, Turkey). It was first washed with tap water, followed by several washings with distilled water to remove extraneous materials. The biomass was dried at 70 °C in an oven until a constant weight was achieved. The dried biomass was then grounded in a domestic mixing grinder. The resulting material was sieved and the particles in the range of 63–125 μm were chosen for the study. The microstructure and surface properties of biosorbent were characterized using a scanning electron microscope (SEM, ZEISS, EVO LS 10). Fourier transformed infrared spectrometer (FTIR, PerkinElmer, Spectrum 400) was used to identify the functional groups (possibly involved in the dye biosorption process) on the biosorbent in the range of 450–4000 cm^{-1}.

2.3. Experimental studies

Biosorption experiments were performed using 0.1 g biosorbent in a batch system to investigate and optimize the effects of dye concentration and reaction time on the efficiency of dye removal at a fixed dye solution volume of 100 mL, natural pH of dye (~6.4) and 30 °C. The effect of dye concentration on the biosorption process was evaluated in the range of 50–200 mg L^{-1}. The influence of contact time was performed by varying the time from 0 to 120 min. After each biosorption experiment, the solutions were centrifuged for thorough separation and the supernatant liquids were analyzed for residual dye concentrations using a UV–visible spectrophotometer at the maximum wavelength for the dye (540 nm). The same procedures were employed to investigate biosorption isotherms and kinetics.

Dye biosorption capacity (q_t or q_e, mg g^{-1}) and yield (BY, %) of biosorbent were calculated by the following equations:

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{2}$$

$$BY = \frac{C_0 - C_t}{C_0} \times 100 \tag{3}$$

where C_0, C_t and C_e (mg L^{-1}) are the concentrations of dye at the initial, a time t and equilibrium, respectively. V (L) is the volume of aqueous dye solution and M (g) is the mass of biosorbent.

All the model parameters and constants were evaluated by non-linear regression using SigmaPlot 12.0 software. The suitability, accuracy and precision of these models were tested by the determination coefficient (R^2) and standard error (SE). For the best model, it is desired a high R^2 and low SE value.

3. Results and discussion

3.1. Contribution of functional groups in biosorption process

Pistachio shell is a lignocellulosic material including cellulose, hemicellulose and lignin as main components. A FTIR study was carried out to obtain information on possible interactions between the reactive groups of this biomass and dye molecules. The FTIR spectra of biosorbent before and after dye biosorption are presented Fig. 1. A broad characteristic band at 3327 cm^{-1} corresponds to the stretching vibrations of *O*—H and *N*—H groups [4]. The peak at 2908 cm^{-1} shows the stretching vibration of aliphatic *C*—H [9]. The bands in 1750–1500 cm^{-1} are attributed to CO and CC the stretching vibrations [1,16]. The peaks in 1450–1310 cm^{-1} are assigned to the bending vibrations of *O*—H and *C*—H groups [9]. The bands in 1300–1100 cm^{-1} indicate C—O stretching vibration. A strong peak at 1028 cm^{-1} can be attributed to C—*O*—C, *P*—O or P—OH stretching. The band at 895 cm^{-1} can be due to the bending vibration of *C*—H group [4]. Fig. 1(b) reveals significant changes in the peak intensities of some functional group bands such as 3327, 1730, 1416, 1234 and 1152 cm^{-1} due to the dye biosorption. These findings implied that several functional groups on the surface of pistachio shell were likely involved in the biosorption of C.I. Reactive Red 238.

3.2. Topographical analysis of biosorbent

SEM images of unloaded and dye loaded biosorbent are indicated in Fig. 2. An irregular surface morphology and a high number of pores can be seen from the SEM micrographs of pistachio shell. These surface characteristics will provide an increase in the dye uptake capacities of biosorbents from aqueous solution due to the trapping of pollutants on their irregular surfaces [3,8]. Besides, The SEM figure of dye loaded biosorbent clearly shows that the surface binding sites of pistachio shell are occupied by the dye molecules.

3.3. Effects of time and dye concentration on biosorption efficiency

The influence of contact time on the dye biosorption was studied in the range of 0–120 min (Fig. 3). The experimental results indicated that a contact time of about 10 min was generally sufficient to achieve equilibrium and the removal of dye did not change significantly with further