Desalination 268 (2011) 117–125

Contents lists available at ScienceDirect

Desalination

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

Adsorption of textile dyes on *Pine Cone* from colored wastewater: Kinetic, equilibrium and thermodynamic studies

Niyaz Mohammad Mahmoodi [a], Bagher Hayati [b], Mokhtar Arami [b,*], Christopher Lan [c]

[a] *Department of Environmental Research, Institute for Color Science and Technology, Tehran, Iran*
[b] *Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran*
[c] *Department of Chemical & Biological Engineering, University of Ottawa, Ottawa, Canada*

ARTICLE INFO

Article history:
Received 22 August 2010
Received in revised form 28 September 2010
Accepted 2 October 2010
Available online 1 November 2010

Keywords:
Adsorption
Textile dyes
Pine Cone
Kinetics
Equilibrium
Thermodynamic

ABSTRACT

In this paper, the adsorption of Acid Black 26 (AB26), Acid Green 25 (AG25) and Acid Blue 7 (AB7) onto *Pine Cone* (PC) was investigated in aqueous solution. Surface study of PC was investigated using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). The effect of operational parameters such as adsorbent dosage, dye concentration, inorganic anion (salt), pH and temperature onto dye removal was studied. The intraparticle diffusion model, the pseudo-first order and the pseudo-second order were used to describe the kinetics data. Equilibrium isotherms were analyzed using Langmuir, Freundlich and Tempkin adsorption models. Thermodynamic parameters of dye adsorption were obtained. The experimental data fitted well to the pseudo-second order kinetics model for dyes. The results indicated that isotherm data of AB26 and AG25 followed Langmuir isotherm and isotherm data of AB7 followed Freundlich isotherm models. The thermodynamic data indicated that the adsorption was endothermic process. Dye desorption studies in aqueous solution at pH 12 showed that maximum desorption of 93%, 97% and 94.5% were achieved for AB26, AG25 and AB7, respectively. It can be concluded that PC could be effectively employed as an effective biosorbent for the removal of dyes.

1. Introduction

Dyes have been used as colorants at different industries such as textile, food, paper, cosmetic, etc. [1]. More than 0.7 million tons of synthetic dyes are produced annually worldwide. In addition, over 10,000 different dyes and pigments have been applied in those industries. Researches indicate that approximately 15% of produced synthetic dyes per year have been lost during processing operations that involve the production and handling with many organic compounds hazardous to human health [2]. Wastewaters of dye production and application industries present an environmental problem because of the aesthetic nature due to the fact that the color is visible even in a low dye concentration.

The textile industry consumes large quantities of water at its different steps of dyeing and finishing, among other processes. The non-biodegradable nature of dyes and their stability toward light and oxidizing agents complicate the selection of a suitable method for their removal [3,4]. In addition, toxicity bioassays have demonstrated that most of them are toxic.

Several methods such as membrane [5], electrochemical [6], coagulation/flocculation [7], biological [8–10], etc. have been used for dye removal from wastewater. Among the treatment methods, adsorption is considered to be relatively superior to other techniques because of low cost, simplicity of design, availability and ability to treat dyes in more concentrated form [11,12]. The research of the recent years mainly focuses on utilizing agricultural natural materials as low cost and available adsorbents [13–21] (Table 1).

A literature review showed that *Pine Cone* was not used to remove dyes from colored wastewater. In this study, *Pine Cone* was used as an agricultural natural adsorbent to remove Acid Black 26 (AB26), Acid Green 25 (AG25) and Acid Blue 7 (AB7) from aqueous solution. Effective parameters such as adsorbent dosage, dye concentration, inorganic anion (salt), pH and temperature were investigated on dye removal. Kinetic, isotherm and thermodynamic studies were conducted to evaluate the adsorption capacity of *Pine Cone*.

2. Experimental

2.1. Chemicals and materials

Pine Cone (PC) was obtained from a local fruit field in the Iran. The PC was first washed to remove the adhering dirt and then were dried, crushed, and sieved. After drying, they were sieved through a

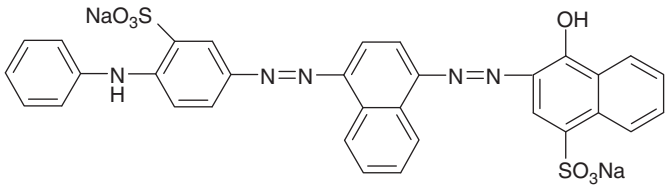
* Corresponding author. Tel.: +98 21 64542614; fax: +98 21 66400245.
E-mail addresses: nm_mahmoodi@aut.ac.ir (N.M. Mahmoodi), arami@aut.ac.ir (M. Arami).

0011-9164/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2010.10.007

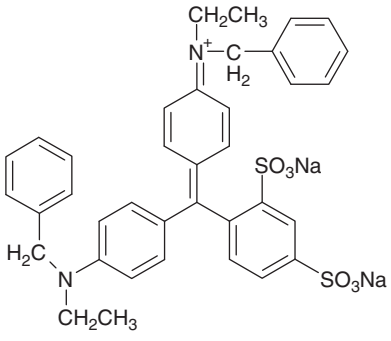
Table 1
Adsorption capacities of natural adsorbents to remove of cationic dyes.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Ref.
Canola hull	Basic Blue 41	67.6	[15]
Canola hull	Basic Red 46	49.0	[15]
Canola hull	Basic Violet 16	25.0	[15]
Tamarind hull	Basic red 18	65.5	[17]
Tamarind hull	Basic violet 16	46.1	[17]
Soy meal hull	Direct Red 81	120.5	[19]
Soy meal hull	Acid Blue 92	114.9	[19]
Soy meal hull	Acid Red 14	109. 9	[19]
Orange peel	Direct Red 23	10.7	[21]
Orange peel	Direct Red 80	21.0	[21]
Pine cone	Acid Black 26	62.9	Present study
Pine cone	Acid Green 25	43.3	Present study
Pine cone	Acid Blue 7	37.4	Present study

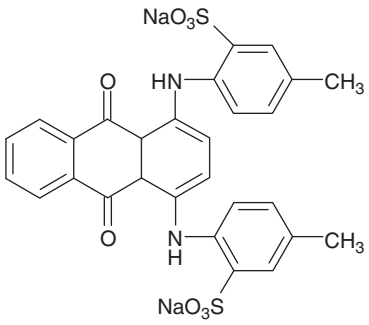
3.36 mm mesh. Acid dyes (Acid Black 26 (AB26), Acid Green 25 (AG25) and Acid Blue 7 (AB7)) were used. Dyes were obtained from Ciba Ltd. The chemical structure of dyes was are shown in Fig. 1. Other chemicals were Analar grade from Merck. The pH of the solutions was adjusted using H_2SO_4 or NaOH.



AB26



AB7



AG25

Fig. 1. The chemical structure of dyes.

2.2. Adsorption tests

The adsorption measurements were conducted by mixing various amounts of PC (0.1–0.3 g) for AB26 and (0.2–0.6 g) for AG25 and AB7 in jars containing 200 mL of dye solutions (50 mg/L) at various pH values (2–12). The pH of the solution was adjusted using H_2SO_4 or NaOH. Adsorption experiments were carried out at different dye concentrations using optimum amount of PC (1 g/L adsorbent for AB26 and 2 g/L adsorbent for AG25 and AB7) at pH 2 and 25°C for 30 min. The dye removal was monitored and determined at certain time intervals (2.5, 5, 10, 15, 20, 25 and 30 min) during the adsorption processes. A CECIL 2021 UV–vis spectrophotometer was used to determine the dye concentration. To investigate the inorganic anion (salt) effect on dye removal efficiency, different salts such as NaCl, Na_2SO_4, $NaHCO_3$, and K_2CO_3 were added to dye solution. At the end of the adsorption experiments, the samples were centrifuged and the dye concentration was determined. For thermodynamic studies, dyes adsorptions at different temperatures (25–65°C) were performed.

2.3. Surface studies

The FTIR spectrum of PC was achieved by Perkin-Elmer Spectrophotometer Spectrum One in the range of 450–4000 cm^{-1}. Scanning Electron Microscope (SEM) LEO 1455VP was used to obtain the SEM images of original PC and dye adsorbed PC. The experiments were conducted with 200 mL dye solutions (50 mg/L dye concentration, pH 2, 1 g/L PC for AB26 and 2 g/L for AG25 and AB7). After the mixing, PC was separated from the solutions by centrifugation and dried for 120 min at 50°C.

2.4. Desorption studies

The adsorbent that was used for the adsorption of dye solution was separated from solution by centrifugation and then dried. It was agitated with 200 mL of distilled water at different pH values (2–12) for the predetermined equilibrium time of the adsorption process. The desorbed dye was determined.

3. Results and discussion

3.1. Surface characteristics

In order to investigate the surface characteristic of PC, FTIR of PC was studied (Fig. 2). The FTIR of PC shows that the peak positions are at 3383.78, 2923.4, 2845.41, 1690.81, 1444.32 and 1048.65 cm^{-1}. The band at 3383.78 cm^{-1} is due to O–H and N–H stretching. While the bands at 1690.81 and 1523.51 cm^{-1} reflect the carbonyl group stretching (amide) and N H bending, respectively. Bands at 1305.59 and 1168.67 cm^{-1} correspond to C–H bending and C–O stretching, respectively [22,23].

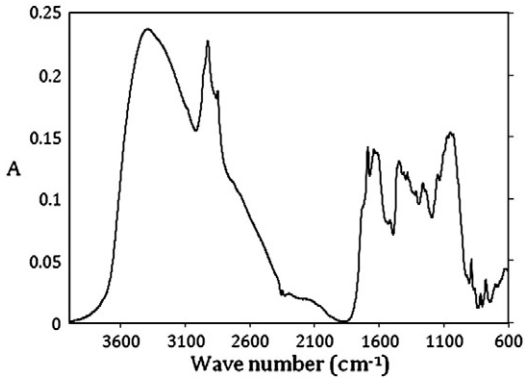


Fig. 2. The FTIR spectrum of PC.