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Elimination of anionic dye by using nanoporous carbon prepared from an industrial biowaste

Fuat Güzel [a,*], Hasan Sayğılı [b], Gülbahar Akkaya Sayğılı [a], Filiz Koyuncu [a]

[a] Department of Chemistry, Faculty of Education, Dicle University, 21280 Diyarbakır, Turkey
[b] Department of Chemistry, Faculty of Science & Arts, Batman University, 72060 Batman, Turkey

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ABSTRACT

The preparation of nanoporous carbon from tomato waste (TWNC), and its ability to remove Orange II (OII) dye were reported. The TWNC was characterized by Fourier Transform Infrared Spectroscopy (FTIR), Brunauer Teller surface area (BET), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). The effects of initial concentration, solution pH, adsorbent dosage and temperature were investigated. The kinetic data followed a pseudo-first order model. The mechanism of the process was determined from the intraparticle diffusion model. The isotherm analysis indicated that the adsorption data could be represented by the Langmuir model. The maximum monolayer adsorption capacity was determined as 312.5 mg g^{-1} under determined optimum conditions of variables (pH 2.0, adsorbent dosage 0.1 g L^{-1}, contact time 180 min and temperature 50 °C). Thermodynamic study showed that the adsorption was spontaneous and endothermic. The results indicate that TWNC can be employed as low-cost alternative to expensive commercial activated carbon for treatment of industrial wastewater containing OII.

1. Introduction

The discharge of dye effluents from textile, leather, paper, and plastic industries into the environment causes severe problems to many forms of life [1]. Azo dyes are the synthetic dyes that are used in many textile industries. Azo dyes have azo group band (–N=N–) and because of their low cost, solubility and stability, they are widely used in many textile industries. Azo dyes and their intermediate products are toxic, carcinogenic and mutagenic to aquatic life [2].

Acid Orange II (*p*-(2-hydroxy-1-naphthylazo)-benzene sulfonic acid) (OII) is a popular water-soluble monoazo dye that is used for dyeing a variety of materials such as , cosmetics, wool, silk, cotton and paper industries. Like most of other azo dyes, it tends to be disposed in industrial wastewater and poses a severe health threat to humans [3–5]. It is highly toxic, and its ingestion can cause eye, skin, mucous membrane, and upper respiratory tract irritations; severe headaches; nausea; water-borne diseases such as dermatitis; and loss of the bone marrow leading to anemia. It has now been well determined that the main cause of its chronic toxicity is the electron-withdrawing character of the azo group, which develops an electron deficiency and becomes reduced to carcinogenic amino compounds. Its consumption can be fatal, as it is carcinogenic in nature and can lead to tumors [6,7]. Hence, removal of dyes from such wastewaters is a major environmental problem and it is necessary because dyes are hazardous even at low concentrations.

Color removal from industry or domestic effluents has drawn considerable attention in the last few years because of their toxicity and visibility. Various conventional technologies including chemical oxidation, biological treatment, coagulation–flocculation, and membrane processes are currently effective methods for reducing dye concentrations in wastewater. However, these treatment processes are costly and cannot effectively be used to treat a wide range of dye containing wastewater. Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants than other conventional methods. As a powerful adsorbent, activated carbon (AC) has been widely used for various applications owing to its high surface area and porous features, such as purification of drinking water, treatment of exhaust gas and wastewater, support of catalyst, gas storage, and electrochemical capacitor and so on. As a result of environmental compliance in many countries, the need for AC will continue growing [8]. However, due to their high production costs, these materials tend to be more expensive than other adsorbents. This has led a growing research interest in the production of ACs from renewable and cheaper precursors. The choice of precursor largely depends on its availability, cost, and purity, but the manufacturing process and intended applications of the product are also important considerations [9,10]. Therefore, in recent years, various kinds of AC have been prepared from low-cost precursor materials, which are predominantly vegetable wastes, such as orange peels, melon seeds [11], coir pith [12], coconut coir [13], bamboo dust, coconut shell, groundnut shell, rice husk, and straw [14], corncob [15], almond shell [16], palm shell [17], and coconut shells [18,19]. In this paper we report the adsorption study of nanoporous carbon that is prepared from tomato waste

* Corresponding author. Tel.: +90 412 2488377; fax: +90 412 2488257.
E-mail address: fguzel@dicle.edu.tr (F. Güzel).

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(TW). Tomato is a very abundant and inexpensive material in Mediterranean countries. According to the records of the United Nations Food and Agriculture Organization (FAO), tomato is the most widely grown product in fresh vegetables around the world with a production of 145.6 million tons. Turkey ranks fourth with the production of 10 million tons of tomato in the world [20].

In this study, we prepared nanoporous carbon from TW as a low-cost and abundantly available precursor, which is a waste of tomato juice and paste factories, with chemical activation by zinc chloride as a dehydrating agent. Optimum adsorption conditions are determined as a function of pH, TWNC dose, initial OII concentration, contact time, and temperature. The adsorption mechanisms are also evaluated in terms of kinetic, equilibrium isotherm and thermodynamic parameters.

2. Materials and methods

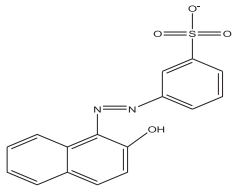
2.1. Materials

TW was collected from tomato paste factory in Adana city of Turkey. Firstly, the TW was washed and dried in an air oven at 70 °C for 24 h and then crushed and sieved to the desired particle size (between 177 μm and 400 μm) for using in the chemical activation experiment. Zinc chloride (purchased from Sigma-Aldrich) of purity 99.9% was used as chemical activator in preparation of TWNC. OII (purchased from Fluka) was used as adsorbate. The general characteristics are given in Table 1 [21]. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 1000 mg L^{-1}. The experimental solutions of the desired concentrations were obtained by successive dilutions. All chemicals used were of analytical grades.

2.2. Preparation of TWNC

30 g of TW (on a dry basis) was impregnated with 30 g zinc chloride (TW/$ZnCl_2$ weight ratio of 1:1) and 5 mL of distilled water was added to this mixture for obtained slurry. Then, this slurry was dried at 105 °C for 12 h in an air oven. The impregnated sample was placed in a stainless-steel horizontal reactor (7 cm diameter and 100 cm length), and then heated to the activation temperature of 500 °C for 1 h under nitrogen atmosphere (99.99%) flow (100 mL min^{-1}) at a heating rate of 10 °C min^{-1}. It was cooled down to room temperature under nitrogen flow and then carbonized product was added on 0.2 N 500 mL hydrochloric acid solution and boiled for 1 under reflux. This mixture was filtered and washed with hot distilled water at several times to remove residual chemicals and chlorine until filtrated solution did not give any reaction with 0.1 N silver nitrate. The yield was calculated as the ratio of the dry weight of resultant activated carbon to the weight of the air-dried of the raw precursor. The obtained TWNC was dried at 105 °C for 12 h and ground and sieved between 177400 μm. Finally, the TWNC was stored in desiccators for further use in adsorption experiments.

Table 1
General characteristics of Orange II dye.

Chemical structure			
			
Molecular formula	$C_{16}H_{11}N_2NaO_4S$	Molecular weight (g/mol)	350.32
C.I. number	15510	Molecular volume (Å^3)	232
C. I. name	Acid Orange II	Molecular surface area (Å^2/molecule)[a]	279
Chemical class	Anionic dye	Width (Å)[a]	7.3
Chromophore	Monoazo	Length (Å)[a]	13.6
Ionization	Acidic	Depth (Å)[a]	2.3
Dye content (%)	85		
λ_{max} (nm)	485		

[a] By referenced [21].

2.3. Characterization of TWNC

The physical and chemical characteristics of the activated carbon, including: proximate and ultimate analysis, total pore volume, mesopore volume, micropore volume, surface area, average pore diameter, point of zero charge (pH_{pzc}), and surface functional group analyses were determined using standard analytical procedures.

The proximate analysis was conducted according to ASTM D3173-3175 standards [22] and the results were expressed in terms of moisture, ash, volatile matter, and fixed carbon contents. The Elemental Analyzer (Thermo Scientific Flash 2000, CHNS Analyzer, Italy) was used for ultimate analysis, and the results were expressed in terms of carbon, nitrogen, hydrogen and sulfur element contents. The content of oxygen was calculated as difference to 100%.

The surface physical morphologies of TW and TWNC before and after OII adsorption were identified by using SEM technique (JEOL JSM-6335F, USA).

The XRD patterns of the TW and TWNC were collected on an X-ray powder diffractometer (Bruker, D8 Discovery EVA, Germany). Textural characteristics were determined by N_2 adsorption–desorption isotherms measured at −196 °C (Micromeritics, ASAP 2020). Prior to the measurement, the TWNC was outgassed at 320 °C under nitrogen flow for 6 h. The nitrogen adsorption–desorption data were recorded at liquid nitrogen temperature (−196 °C) and was measured over a relative pressure (P/P_o) range from approximately 10^{-6} to 1. The specific surface area (S_{BET}) was determined by means of the standard BET equation [23,24] applied in the relative pressure range from 0.05 to 0.35 [25]. This study assumes that the cross-sectional area of a nitrogen molecule is 0.162 nm^2. The external surface area (including only mesopore, S_{ext}), micropore volume (V_μ) and micropore area (S_μ) were calculated by t-plot method. The total pore volume (V_T) was estimated by converting the amount of nitrogen gas adsorbed (expressed in cm^3g^{-1} STP) at a relative pressure of 0.95 to liquid volume of the nitrogen adsorbate [26]. The mesopore volume (V_m) was determined by subtracting the micropore volume from the total pore volume while the microporosity fraction (V_μ (%) = V_μ / V_T) and mesoporosity fraction (V_m (%) = V_m / V_T) were based on the total pore volume. The average pore diameter (D_p) was estimated from the BET surface area and total pore volume ($D_p = 4V_T / S_{BET}$) assuming an open-ended cylindrical pore model without pore networks [27]. This study assumes that micropores are less than 2 nm wide, mesopores are 2–50 nm wide and macropores are more than 50 nm wide [25,26]. The pore size distribution was determined by using Barrett–Joyner–Halenda (BJH) method (Harkins and Jura model, FAAS corrections) [28].

The surface chemistry of TWNC was analyzed by FTIR spectroscopy, Boehm's titration, and pH of the point of zero change (pH_{pzc}) methods. Surface functional groups were detected using the pressed potassium bromide (KBr) pellets containing 5% of carbon sample by FTIR spectrometer (PerkinElmer spectrum 100, USA) in the scanning range of 4000–450 cm^{-1}. The quantification of the basic and acidic groups on the surface of the TWNC was performed according to the Boehms titration method [29] using analytical grade reagents. The combined influence of all the functional groups of activated carbon determines pH_{pzc}, i.e., the pH at which the net surface charge on carbon was zero. The pH_{pzc} of the TWNC was determined by the method described by Preethi and Sivasamy [15]. The difference between the initial pH (pH_i) and ΔpH ($pH_i - pH_f$) values was plotted against the pH_i. The point of intersection of the resulting curve with abscissa, where pH was zero, gives the pH_{pzc}.

Adsorptive properties of the TWNC were preliminarily characterized by measuring both iodine and methylene blue numbers. The iodine number and methylene blue number tests were conducted as described