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Adsorption and thermodynamic studies of hazardous azocoumarin dye from an aqueous solution onto low cost rice straw based carbons

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ABSTRACT

A new hazardous azocoumarin dye has been synthesized and characterized using different spectroscopic techniques. The adsorption of hazardous azocoumarin dye onto low cost rice straw based carbons (RSC) was investigated in an aqueous solution in a batch system with respect to initial dye concentration, contact time, solution pH and temperature. Surface modification of rice straw using scanning electron microscopy (SEM) was obtained. The surface area and pore volume of RSC were determined by nitrogen adsorption/desorption experiments at 77 K and found to be 67.4 $m^2\ g^{-1}$ and 0.134 $cm^3\ g^{-1}$, respectively. Experimental data indicated that the adsorption capacity of RSC for azocoumarin dye was higher in acidic rather than in basic solutions. Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were determined. The activation energy of adsorption was also evaluated and found to be +15.56 kJ mol^{-1} indicating that the adsorption is physisorption. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data. The dynamic data fitted the pseudo-second-order kinetic model well. The thermodynamics of the adsorption indicated spontaneous and exothermic nature of the process. The results indicate that RSC could be employed as low-cost material for the removal of acid dyes from an aqueous solution.

1. Introduction

Dyes are widely used in industrial fields such as textile, printing, paper-making, plastic, coating, food, plastic, pesticide, paint, pigments and pharmaceutical industry [1–3]. Over 10,000 different commercial dyes and pigments exist and more than 7×10^5 tons is produced annually worldwide [4]. Approximately 12% of synthetic dyes are lost during manufacturing and processing operations and 20% of these lost dyes enter the industrial wastewaters [5]. Because the dye effluent may cause damage to aquatic biota and human by mutagenic and carcinogenic effects, the removal of dye pollutants from wastewater is of great importance [6]. Various removal methods, including adsorption [7,8], coagulation [9], membrane filtration [10] and advanced oxidation [11] have been employed to eliminate dyes from wastewaters. Among them, adsorption has been recognized as a promising technique due to its high efficiency, simplicity of design, ease of operation as well as the wide suitability for diverse types of dyes [12,13]. In recent years, the search for low-cost adsorbents that have dye-binding capacities has intensified. This has led many workers to search for cheaper alternates such as coal, fly ash, silica gel, wool wastes, agricultural wastes, wood wastes and clay minerals [14–16]. Activated carbons is perhaps the most widely used adsorbent in the adsorption processes due to its high specific surface area and high adsorption capacity. Equilibrium data are known as adsorption isotherms, Langmuir, Freundlich, etc., are the main requirements for the design of adsorption systems. Obtaining equilibrium data for a specific sorbate/sorbent system can be carried out experimentally, with a time-consuming procedure that is incompatible with the growing need for adsorption systems design [17].

Activated carbon adsorption is one of the most often used technologies for the removal of natural or synthetic organic compounds in water. The Egyptian Environmental protection Agency regarded activated carbon adsorption as the best available technology for the removal of organic contaminants limited in the environmental regulations. In Egypt, rice straw is an easily available agricultural waste material, produced in large quantities as a by-product of rice milling and creates potential environmental problems. The waste products which are the main contributors to biomass burning are wheat residue and rice straw. Rice straw is a lignocellulosic agricultural by-product containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%) [18]. The disposal of rice straw by open-field burning frequently causes serious air pollution, hence new economical technologies for rice straw disposal and utilization must be developed. In recent years, attention has been focused on the utilization

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of native agricultural by-products as sorbent [19–21]. In order to improve the sorption capacity of these biomaterials, the low cost agricultural by-products were converted to activated carbon [22,23].

Coumarin (2-oxo-2*H*-chromene) and its derivatives represent one of the most important classes of compounds possessing numerous biological activities. Some of these compounds have proven to be active as antibacterial, antifungal [24], anti-inflammatory [25], and anticoagulant [26]. Coumarin derivatives are widely used as additives in food and cosmetics [27], pharmaceuticals and optical brighteners [28] and fluorescent dyes [29]. They are of special interest as yellowish-green fluorescent dyes [30].

In continuation to our interest in the study on dye adsorption onto low cost biomaterials [31,32], we synthesize and characterize a new hazardous azocoumarin dye, and investigate its adsorption onto low cost rice straw based carbons as adsorbent. Physical and chemical characteristics of the adsorbent (RSC) were evaluated with N_2 adsorption/desorption experiments at 77 K. The influences of adsorption parameters such as initial dye concentration, contact time, solution pH and temperature on the adsorption performance of azocoumarin dye were investigated. The kinetic and thermodynamic parameters were also calculated to determine rate constants and adsorption mechanism. The experimental data were fitted into Langmuir and Freundlich equations to determine which isotherm gives the best correlation to experimental data.

2. Materials and methods

2.1. Physical measurements

C, H and N were determined on Automatic Analyzer CHNS Vario ELIII, Germany. Spectroscopic data of the azocoumarin dye were obtained using the following instruments: FT-IR spectra (KBr discs, 4000–400 cm^{-1}) by Jasco-4100 spectrophotometer; the ^1H NMR spectrum by Bruker WP 300 MHz using DMSO-d_6 as a solvent containing TMS as the internal standard; Mass spectrum by Shimadzu GC-MS-QP2010 Plus instrument. The SEM results of the RSC sample before and after the adsorption processes were obtained using (JEOL-JSM-6510 LV) scanning microscope to observe surface modification. UV-visible spectrophotometer (Perkin-Elmer AA800 Model AAS) was employed for absorbance measurements of samples. An Orion 900S2 model digital pH meter and a Gallenkamp Orbital Incubator were used for pH adjustment and shaking, respectively. N_2 adsorption/desorption isotherms on RSC at 77 K were measured on a Quantachrome Nova Instruments version 10, from which the Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore volume were calculated.

2.2. Synthesis of azocoumarin dye

4-(2-(3,3′-dicyano-2-(2-oxo-2H-chromen-3-yl)-1-((4-sulfophenyl)diazenyl)allylidene) hydrazinyl)benzenesulfonic acid (Fig. 1) was prepared using a method describes in the literature [33]. An aqueous solution of sulfanilic acid diazonium chloride (0.02 mol) was added gradually with constant stirring to 4-(2-(3,3′-dicyano-2-(2-oxo-2H-chromen-3-yl) (0.01 mol) in aqueous ethanol containing sodium acetate (5 g) at −5 °C. The reaction mixture was left for 30 min and the yellow solid precipitate was collected by filtration and crystallized from ethanol. Yield 60%; yellow solid; mp = 177–179 °C; Anal.: Calcd. for $C_{26}H_{16}N_6O_8S_2$ (604): C, 51.65; H, 2.67; N, 13.90; S, 10.61. Found: C, 51.63; H, 2.68; N, 13.90; S, 10.59. FT-IR spectrum IR (KBr) (v cm^{-1}): 1609 (C═N) and 1720 (C═O), 2230, 2248 (two CN), 3113 (NH) and 3436 (OH) cm^{-1}. ^1H-NMR spectrum in d_6-DMSO, ppm: 12.60 (s, 1H, NH), 9.01 (s, 1H, OH), 9.07 (s, 1H, OH), and 7.35–8.4 (m, 13H, ArH^+ coumarin H-4). Mass spectrum, MS *m/z* 604 (M^+).

2.3. Preparation of rice straw based carbons

Rice straw based carbon (RSC) as adsorbent was collected from Tammy Amdid, Dakahlia, Egypt Biogas Factory. The concept is based on the burning of waste rice straw in a special incinerator at the temperature of 1000–1200 °C. During the burning process the hydrocarbons are converted to carbon oxides, hydrogen, methane, propane and other gases. The carbon waste was left to cool down. In our laboratory the rice straw based carbon waste (RSC) was crushed, ground and sieved through a 200 μm sieve and washed several times with bidistilled water. The adsorbent sample was dried at 120 °C for 48 h. preserved in the desiccators over anhydrous $CaCl_2$ for further use.

2.4. Dye adsorption experiments

The adsorption experiments of azocoumarin dye were carried out in batch equilibrium mode. A 0.1–0.9 g sample of RSC with 100 ml aqueous solution of 30–100 mg·L^{-1} sodium salt of azocoumarin dye solution at

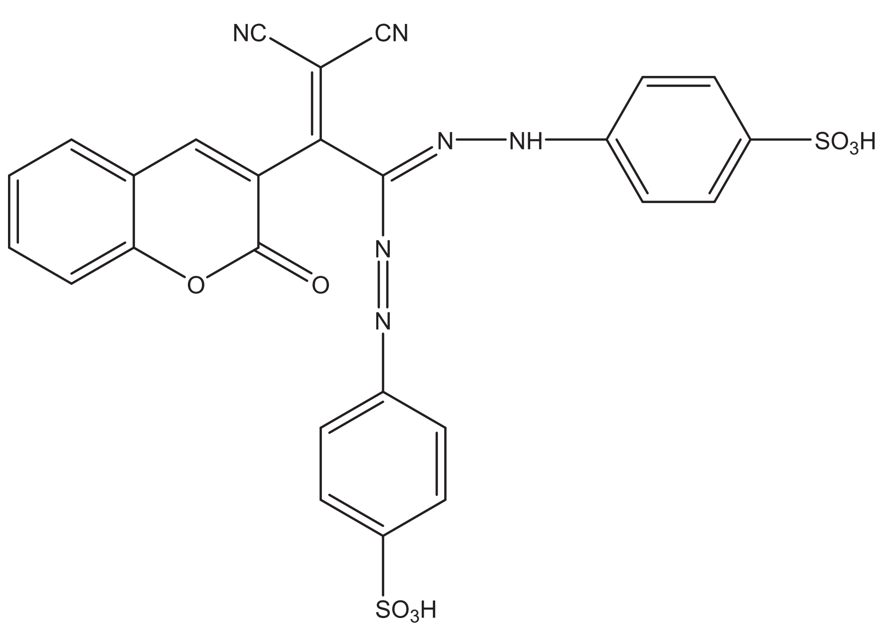

Fig. 1. The structure of azocoumarin dye.