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Removal of hazardous azopyrazole dye from an aqueous solution using rice straw as a waste adsorbent: Kinetic, equilibrium and thermodynamic studies

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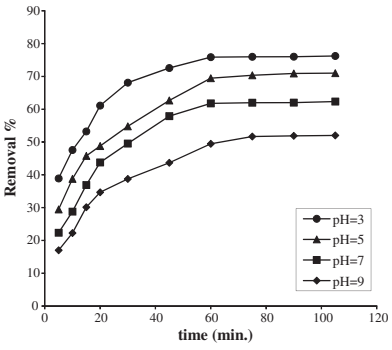
HIGHLIGHTS

- We use rice straw as a waste adsorbent for the removal of hazardous azopyrazole dye.
- The equilibrium data fitted well with the Freundlich model.
- The kinetic data tends to fit well in the pseudo-second-order kinetics model with high correlation coefficients.
- The thermodynamics of the adsorption indicated spontaneous and exothermic nature of the process.
- Results are of marked significance to the water treatment industries.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, activated carbonmade from rice straw (ACRS) was synthesized simply by a low cost and nontoxic procedure and used for the adsorption of hazardous azopyrazole dye. The effect of different variables in the batch method as a function of solution pH, contact time, concentration of adsorbate, adsorbent dosage and temperature were investigated and optimal experimental conditions were ascertaine. Surface modification of ACRS using scanning electron microscopy (SEM) was obtained. More than 75% removal efficiency was obtained within 75 min at adsorbent dose of 0.5 g for initial dye concentration of 30–100 mg L^{-1} at pH 3. The experimental equilibrium data were tested by the isotherm models namely, Langmuir and Freundlich adsorption and the isotherm constants were determined. The kinetic data obtained with different initial concentration and temperature were analyzed using a pseudo-first-order and pseudo-second-order equations. The activation energy of adsorption was also evaluated and found to be +13.25 kJ mol^{-1} indicating that the adsorption is physisorption. The thermodynamics of the adsorption indicated spontaneous and exothermic nature of the process. The results indicate that ACRS could be employed as low-cost material for the removal of acid dyes from aqueous solution.

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Introduction

Over the years, azo compounds constitute one of the largest classes of industrially synthesized organic compounds, potent in drug and cosmetics [1,2]. Of all classes of dyestuffs, azo dyes have attained the widest range of usage because variations in chemical structures are readily achievable and methods of application are generally not complex [3]. In fact, 60–70% of all dyes stuff in use and production fall in this group [4]. According to a statistical data survey, one million tons of such dyes are produced annually worldwide [5,6]. It can simply be defined as any class of artificial dyes that contains the azo group (—N=N—). When describing a dye molecule, nucleophiles are referred to as auxochromes, while the aromatic groups are called chromophores. Together, the dye molecule is often described as a chromogen [7]. Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophiles. Amino- and hydroxy-groups are commonly used coupling components [8]. The traditional application field of the synthetic azo dyes still remains the textile industry, and the finishing of fibrous materials. The emergence of diverse classes of synthetic dyes including azo dyes occurred due to constant effort to find specific dye for application in diverse materials of industrial importance which include, but not limited to textile fabric [9], leather, aluminium sheet, ink-jet printer, paper, electro-optical devices [10]. They are among the compounds which are suitable for biocidal treatment of textile materials due to the fact that some of them exhibit biological activity, as a result of the presence of some bioactive templates that form a definite type of bonding with the molecules of the fibrous material [11].

The industrial wastewater usually contains a variety of organic compounds and toxic pulp mills and dyestuff manufacturing discharge highly colored wastewater which have provoked serious environmental concerns all over the world [12,13]. Several methods including adsorption [14,15], coagulation [16], membrane filtration [17] and advanced oxidation [18] 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 [19,20]. 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 [21].

Activated carbons is perhaps the most widely used adsorbent in the adsorption processes due to its high specific surface area and high adsorption capacity [22,23]. Recently, increasing attention was paid on the development of highly effective and low cost adsorbents. In this respect, renewable biological adsorbents are attractive, because of low cost, easy availability and low toxicity. Activated carbon made from rice straw is one of the most often used technologies for the adsorption of natural or synthetic organic compounds in water [24,25]. 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 create potential environmental problems. The waste products which are the main contributors to biomass burning are wheat residue and rice straw. 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 order to improve the sorption capacity of these biomaterials, the low cost agricultural by-products were converted to activated carbon.

The aim of this study is to investigate the adsorption of hazardous azopyrazole dye onto rice straw as a waste adsorbent. Effects of different parameters such as initial adsorbate concentration, adsorbent dosage, contact time, solution pH and temperature were studied. 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.

Materials and methods

Physical measurements

C, H and N were determined on Automatic Analyzer CHNS Vario ELIII, Germany. Spectroscopic data of the azopyrazole 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 ACRS 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 ACRS at 77 K was 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.

Synthesis of azopyrazole dye

4-((4-methoxyphenyl)diazenyl)-2-(5-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenol (Fig. 1).

A well stirred solution of p-anisidine **1** (0.1 mol) in 2N hydrochloric acid (125 ml) was cooled in an ice-bath and diazotized with 0.1N sodium nitrite solution (100 ml). The mixture was stirred at −5 °C for 1 h. The above cold diazonium solution was added

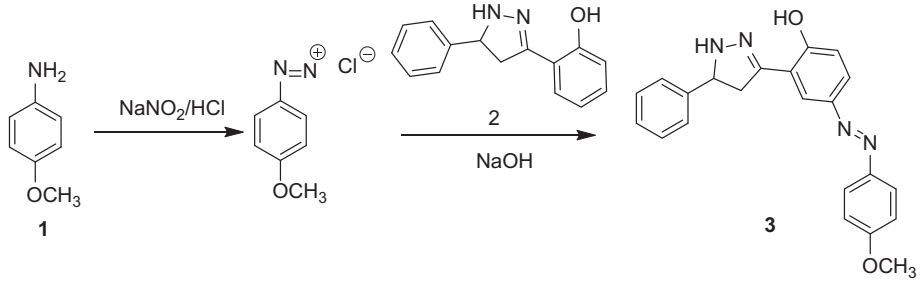

Fig. 1. Structure of azopyrazoledye (**3**).