



ORIGINAL ARTICLE

Removal of hazardous Rhodamine dye from water by adsorption onto exhausted coffee ground



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Abstract Exhausted coffee ground powder (CGP) was proved to be an efficient adsorbent for the removal of Rhodamine dyes (i.e. Rhodamine B and Rhodamine 6G) from aqueous solutions by batch adsorption experiments. The morphology, chemical structure as well as the surface property of the as-prepared CGP adsorbent were investigated by using SEM, FT-IR and contact angle meter analytical techniques. The adsorption kinetics and isotherm behaviors of Rhodamine molecules onto CGP were studied and compared using pseudo-1st, pseudo-2nd and Langmuir/Freundlich models, respectively. The maximum adsorption capacities of Rh B and Rh 6G were calculated at 5.255 and 17.369 $\mu\text{mol g}^{-1}$ by Langmuir model fitting. The effects of temperature, ionic strength, solution volume and the co-existing anions on the sorption behavior were also investigated. Furthermore, the adsorption mechanism responsible for the efficient removal of dyes is discussed in terms of adsorption process caused by electrostatic and intermolecular forces.

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1. Introduction

The textile industry is one of the major sources, which discharges large amounts of industrial waste water. The discharge of such contaminated water into public streams is a great environmental challenge not only due to its treatment for reuse but

also its toxicity to human beings and animals by contaminating underground water reservoirs [1]. The Rhodamine dye is one of fresh peach of synthetic dyes and it is widely used as a colorant in the manufacturing of textiles and food stuffs. It has been medically proven that drinking water contaminated with Rhodamine dyes could lead to subcutaneous tissue borne sarcoma which is highly carcinogenic [2]. In addition, others kinds of toxicity such as reproductive and neurotoxicity have been widely and intensively investigated and proved as well by exposure to these dyes [2].

Various natural or wasted materials have been extensively explored and investigated for the adsorption removal of different contaminants from aqueous solutions [3–6]. Coffee beans are now produced and used in significant quantities worldwide.

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According to the data reported by United States Department of Agriculture (USDA), the annual global production capacity of coffee beans in the year 2012/2013 was estimated as exceeding 150 million of 60 kg bags and in future more production and waste of coffee ground are expected [7]. Therefore, the efficient utilization of the waste of coffee grounds has attracted considerable attention as millions of posts of coffee are brewed and millions of pounds of wet grounds are thrown every day all around the world. The carbonized form of coffee grounds has been attempted for soil remediation, adsorption removal of hazardous molecules from aqueous or gas phases or waste water desalination [8–10].

In this work, exhausted coffee ground powder (CGP) was used directly as a zero-cost adsorbent for the application of adsorption removal of series of Rhodamine dyes like Rhodamine B (Rh B) and Rhodamine 6G (Rh 6G) from aqueous solutions. The crystal and chemical structures of the as-prepared CGP were examined to understand the possible adsorption mechanism for removal of dyes. In addition, the adsorption kinetic, isotherm behaviors were compared and the thermodynamic parameters were calculated as well. Furthermore, the adsorption mechanism responsible for the efficient adsorption removal behavior is discussed in terms of adsorption caused by electrostatic and intermolecular forces.

2. Experimental

2.1. Materials

The coffee powders were purchased from local market in Saudi Arabia. To obtain the final CGP product, each 5 g of coffee powders was washed with 200 mL of boiled deionized water 3 times to get rid of any impurities. Salts of KCl and K₂SO₄ were purchased from BDH chemicals (Poole England) and K₂HPO₄ was purchased from Sigma–Aldrich (USA). The Rh B and Rh 6G dyes were purchased from Lambda Physik (USA) and Merck (Germany), and their properties are listed in Table 1. All the chemical reagents are of analytical grade and used without further purification.

2.2. Characterization

The crystal structure of the as-prepared CGP adsorbent was investigated by X-ray diffractometer (XRD, Bruker D8 ADVANCE) with 2θ scope of 10–90° using Cu-Kα X-ray source

(λ = 0.15418 nm). The morphology of the as-prepared CGP was studied by a scanning electron microscope (SEM, FEI inspect F50). Fourier transform infrared spectra (FTIR) were recorded at room temperature using a FTIR spectrophotometer (NEXUS 670). The zeta potentials of the as-prepared adsorbent at different pHs were determined by a zeta potential instrument (Malvern, Great Britain). The water contact angle was measured by a contact angle meter (SL200B, Shanghai) at ambient conditions.

2.3. Batch adsorption experiments

Batch adsorption experiments were conducted to examine the adsorption kinetics, adsorption isotherm, the effect of temperature, solution pH and the ionic strength on the adsorption process as well as desorption and regeneration. A certain amount of CGP was mixed with Rhodamine dye aqueous solutions with a known initial concentration, and the mixture was stirred in a stir machine at a constant stirring speed and temperature. The mixture was centrifuged at 4000 rpm in a centrifugation machine after batch adsorption experiments so that the absorbance of Rh B and Rh 6G can be measured at 554 and 526 nm by means of UV–vis spectrophotometer (JASCO, V-570), respectively. The concentrations of the solutions were determined using linear regression equation.

2.3.1. Kinetics [11]

Two kinetic models were used to fit the experimental data at different temperatures. The pseudo-first-order rate expression of Lagergren model is generally expressed as follows:

$$\frac{dq}{dt} = k_1(q_{eq} - q) \quad (1)$$

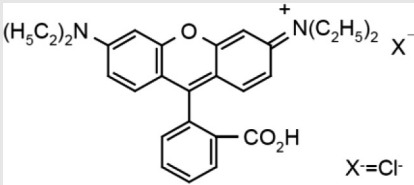
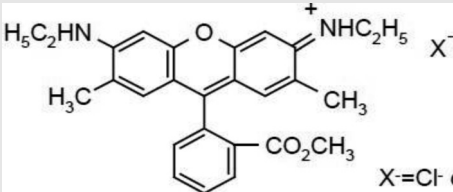
where q_{eq} and q are the amounts of adsorbed dye onto the CGP at equilibrium and at time t , respectively. k_1 is the rate constant of first-order adsorption. The integrated form of Eq. (1) is:

$$\frac{1}{q} = \frac{k_1}{tq_{eq}} + \frac{1}{q_{eq}} \quad (2)$$

The plots of $1/q$ against $1/t$ for the pseudo-first-order equation give a linear relationship and k_1 and q_{eq} values can be determined from the slope and intercept of this equation, respectively.

The pseudo-second-order kinetic rate equation is expressed as:

Table 1 Selected properties of Rh B and Rh 6G.

Dyes	Rh B	Rh 6G
Structure	 <p>(H₅C₂)₂N⁺ N(C₂H₅)₂ X⁻ X = Cl⁻</p>	 <p>H₅C₂NH⁺ NHC₂H₅ X⁻ X = Cl⁻</p>
Chemical formula	C ₂₈ H ₃₁ N ₂ O ₃ ·Cl	C ₂₇ H ₂₉ ClN ₂ O ₃
M _w	479.02	464.98

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