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The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste

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ABSTRACT

The efficacy of pistachio hull powder (PHP) prepared from agricultural waste was investigated in this study as a novel adsorbent for the elimination of dye molecules from contaminated streams. Removal of methylene blue (MB) as a cationic model dye by PHP from aqueous solution was studied under different experimental conditions. The selected parameters were solution pH (2–10), PHP dosage (0.5–3 g/L), MB concentrations (100–400 mg/L), contact time (1–70), and solution temperature (20–50 °C). The experimental results indicated that the maximum MB removal could be attained at a solution pH of 8. The dosage of PHP was also found to be an important variable influencing the MB removal percentage. The removal efficiency of MB improved from 94.6 to 99.7% at 70 min contact time when the MB concentration was decreased from 300 to 100 mg/L at a pH and PHP dosage of 8 and 1.5 g/L, respectively. The kinetic analysis showed that the pseudo-second-order model had the best fit to the experimental data. The Langmuir equation provided the best fit for the experimental data of the equilibrium adsorption of MB onto PHP at different temperatures. In addition, the maximum adsorption capacity increased from 389 to 602 mg/g when the temperature was increased from 20 to 50 °C. The thermodynamic evaluation of MB adsorption on PHP revealed that the adsorption phenomenon under the selected conditions was a spontaneous physical process. Accordingly, pistachio hull waste was shown to be a very efficient and low-cost adsorbent, and a promising alternative for eliminating dyes from industrial wastewaters.

Keywords: Cationic dye; Methylene blue; Waste materials; Adsorption; Pistachio hull

1. Introduction

Dyes are synthetic organic compounds that are increasingly being produced and used as colorants in many industries worldwide, including textile, plastic, paper, etc. (Crini, 2006; Wu and Tseng, 2008). The wastewater generated by the processes of these industries usually contains up to around 10% of used dye (Forgacs et al., 2004). Most of the dyes are toxic and carcinogenic compounds; they are also recalcitrant and thus stable in the receiving environment, posing a serious threat to human and environmental health (Crini, 2008). Accordingly, to protect humans and the receiving ecosystem from contamination, the dyes must be eliminated from the dye-contained wastewaters before being released into the environment.

Because dye molecules are resistant to biodegradation (Ravi Kumar et al., 1998), biological processes are not useful or efficient methods for the removal of dyes from effluents. Although different chemical advanced oxidation processes (AOPs) have been shown to be efficient for the degradation of several classes of dyes, they are expensive and economically non-attractive. Adsorption is one of the promising alternative techniques used for the removal of dyes from water and wastewater (Gupta and Suhas, 2009), and activated carbon is the most widely used adsorbent (Wu et al., 2005). However, the production of activated carbon is complex and expensive, making this technology economically non-efficient. Accordingly, the critical challenge for applying the adsorption method to dye removal is finding a low-cost adsorbent that is profoundly available with high removal capacity so adsorption can successfully compete with other dye removal techniques. This is the driving force behind further studies attempting to find an efficient low-cost adsorbent. Waste

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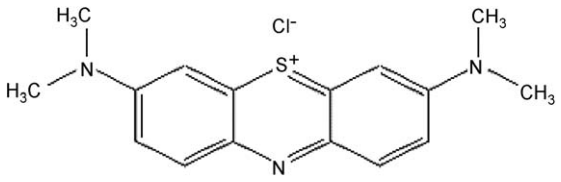

Fig. 1 – The structure of methylene blue dye.

materials have recently been viewed as potential low-cost adsorbents, and many reports have been published showing their ability to adsorb various contaminants including dyes (e.g., Wu and Tseng, 2008; Gupta and Suhas, 2009; Rafatullah et al., 2010). Pistachio hull, an agriculture waste, is proposed as a no-cost and profoundly accessible potential dye adsorbent.

To evaluate the adsorption potential of pistachio hull wastes for removing dyes from wastewater, methylene blue (MB) was selected as a model cationic dye; several waste materials have been studied using MB as the model dye. Rafatullah et al. (2010) recently reviewed the works published on MB removal by adsorption onto different low-cost adsorbents and reported a wide range of adsorption capacity from 2 to 915 mg/g, which is comparable to that of commercial activated carbon. Among the waste materials tested over the past decade, some materials like papaya seeds (Hameed, 2009a) and grass waste (Hameed, 2009b) have shown considerable adsorption capacity. However, the applications of these materials are limited practically because the adsorbent is not available in great enough amounts. In the other words, despite having a significant capacity for dye adsorption, most of these materials are not produced in a central location in one country; therefore, they are not available in sufficient bulk to be commercialized for full scale application. Indeed, a candidate material that can act an alternative to activated carbon must both have a high adsorption capacity and be profoundly available in bulk at no or low cost. In this context, the pistachio hull, an agricultural waste, was proposed to be investigated for its potential to adsorb MB. Pistachio hulls are a waste generated in pistachio peeling factories and are accessible in bulk at no cost. Therefore, it is very interesting to test the capability of pistachio hull waste to eliminate dyes from wastewater. The main purpose of the present study was to explore the capability of pistachio hull waste to remove a basic model dye, MB, from liquid media under different experimental conditions. The effects of main parameters, i.e., solution pH, mass of adsorbent, dye concentration, contact time, and solution temperature, were studied for MB removal. The kinetics, isothermics and thermodynamics of MB adsorption under optimal experimental conditions were also evaluated.

2. Materials and methods

2.1. Materials

MB, a model of cationic dyes with a molecular formula of $C_{16}H_{18}N_3ClS$, was purchased from a local market. The structure of MB is shown in Fig. 1. The MB used in the present study has a molecular weight of 319.85 with its maximum absorbance at a wavelength of 665 nm. A powder made from pistachio hulls, hereafter referred to as pistachio hull powder (PHP), was used as an adsorbent. The characteristics of PHP have been given elsewhere (Moussavi and Barikbin, 2010). In summary, PHP is a micropore adsorbent with a BET surface area of 1.04 m^2/g and containing –OH, –CH, C=O, and –CO groups on its surface (Moussavi and Barikbin, 2010). Distilled water was used for the preparation of dye solutions. All other chemicals were of analytical grade and purchased from Merck.

2.2. Procedure of adsorption and equilibrium experiments

The ability of PHP to adsorb MB was tested at different conditions (Table 1) using a series of batch tests in a shaker-incubator instrument (IKA® KS4000i). For each test, 100 mL of dye solution with the desired composition (pH and dye concentration as given in Table 1), was poured into an Erlenmeyer flask, the given amount of PHP was added, the temperature of the incubator was adjusted to the desired level, and the instrument was used to stir the mixture at 100 rpm for a preset time. When mixing was completed, the suspension was filtered through a 0.2 μm fiberglass filter; the filtrate was then analyzed for its maximum absorbance at a wavelength of 665 nm. The concentration of MB was calculated from the calibration curve prepared by measuring the absorbance of the serial dilutions of dye at 665 nm, and then plotting the concentration versus absorbance.

Five flasks were used to evaluate the MB adsorption equilibrium on PHP; 100 mL of 400 mg/L MB solution with optimum pH of 8 (see Section 3.1) was poured into each of them and a different mass of PHP (0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 g) was then added to flasks and put on the shaker for mixing for 12 h. We assumed the mixtures would reach equilibrium. At the end of the shaking time, the residual concentration of MB was measured in the filtrate (as described above) and the adsorption capacity (mg/g) was calculated as the mass of MB adsorbed onto PHP divided by the amount of PHP added to the flask. The adsorption equilibrium of MB onto PHP was examined at various temperatures between 20 and 50 °C under conditions given in Table 1. To ensure the repeatability of the data, all tests were conducted in duplicate and the mean of values was used for data analysis.

2.3. Data analysis

The effect of the experimental operational parameters of pH, dye concentration, PHP dose, mixing time, and temperature on MB removal from the dye solution was analyzed by plotting the fraction of MB remaining in the solution versus the investigated variable. After finding the optimum conditions of the tested variables where the residual dye in the solution was minimal (maximum dye removal), the kinetics, equilibrium, and thermodynamics of MB adsorption onto PHP were evaluated. To assess the adsorption kinetics, the results of the effect of MB concentration and contact time were analyzed using pseudo-first-order and pseudo-second-order models (Gómez et al., 2007), as well as the intraparticle diffusion model (Weber and Morris, 1963). The linear form of these models for boundary conditions of $q = 0$ at $t = 0$ and $q_t = q_e$ at $t = t_e$ are presented in "Equations and nomenclature" section. The Langmuir, Freundlich, and Dubinin–Radushkevich models were used to evaluate the MB adsorption equilibrium for PHP. The linear forms of these equations (Hameed, 2009c) are given in "Equations and nomenclature" section. The thermodynamics of MB adsorption were assessed based on the data of the designated experiments (Table 1) using the changes of Gibbs free energy of adsorption (ΔG°), standard enthalpy change (ΔH°) and stan-