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Optimization of comparative removal of two structurally different basic dyes using coal as a low-cost and available adsorbent

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ABSTRACT

In the present work, response surface methodology (RSM) was employed to study the effects of operational parameters on the removal of two dyes (C.I. Basic Blue 3 (BB3) and C.I. Basic Yellow 2 (BY2)) using coal as low-cost and available adsorbent. Quadratic central composite design (CCD) was used for experiments designing, process modeling and optimization. The investigated variables were dye initial concentration (10–50 mg/L), adsorbent dosage (0.4–2 g/L), temperature (12–60 °C) and contact time (5–45 min). The significance of the model and regression coefficients were tested by the analysis of variance (ANOVA), residuals analysis and *t*-test statistics. The obtained models were highly significant at confidence level of 99%. The results predicted by the models were found to be in good agreement with those obtained by performing experiments (R^2 = 0.923 and 0.964 and Adj-R^2 = 0.865 and 0.933 for BY2 and BB3, respectively). For both dyes, the adsorption process was mainly influenced by the initial concentration of the dyes and adsorbent dosage, whereas the other factors showed lower effects. Different color removal efficiencies were obtained for the dyes with different chemical structures. The optimum initial concentration of dye, adsorbent dosage, temperature and contact time were found to be 30 mg/L, 1.5 g/L, 25 °C and 10 min. Under optimal conditions, high removal efficiency of dyes (97.08% and 91.29% respectively for BY2 and BB3) was obtained.

1. Introduction

Synthetic dyes are a relatively large group of organic chemicals and are mostly aromatic compounds which can be divided into groups like non-ionic, cationic and anionic dyes. Such substances with considerable coloring capacity are widely used in the printing, paper, textile, electroplating, pulp mill, cosmetics and food industries [1]. The discharge of dye-containing effluent into the water bodies is undesirable. Dyes possess direct toxicity to the microbial populations through growth inhibition, obstruct light penetration, decelerate photosynthetic activity and cause oxygen deficiency in water bodies [2]. Most of dyes also disturb human health, have carcinogenic effect or cause allergies, dermatitis or skin irritation. The adverse effects of dyes in aquatic environments arise from their synthetic nature and aromatic structure with delocated electrons and various functional groups which make them considerably resistant to degradation [3,4].

Basic dyes are a group of water-soluble cationic dyes which are employed in leather, paper preparing, printing and textile fibers dyeing. The principle use of basic dyes is the dyeing of acrylics [5]. BY2 and BB3 are two cationic dyes with oxazine and diarylmethane structures, respectively. Although BY2 and BB3 are not extremely toxic, they may cause some harmful effects on aquatic organisms and may produce discomfort of the eyes in direct human exposure. Therefore, the treatment of dye-containing effluent prior to disposal is necessary.

Among various methods available for removal of dyes from industrial effluents, such as biotreatment [6–8], adsorption [9–11], flocculation–coagulation [12], photocatalytic degradation [13–15], chemical oxidation [1,16,17] and *etc.*, adsorption has been proven to be the most promising alternative due to its simplicity, availability of different low-cost adsorbents and high performance [18]. Many researchers have tested different adsorbents efficiency such as activated carbon [19–21], clay minerals [22–24], zeolite [25], silica [26], chitin [27,28] and coal [29] for lowering the dye concentration in wastewater. In this regard, because of its availability and cheapness, coal is one of the best options with excellent adsorption capacity toward dyes. Coal, resulted from plants degradation, is composed primarily of carbonaceous materials along with minerals (chiefly hydrogen, sulfur, oxygenand nitrogen). Sorption of dye

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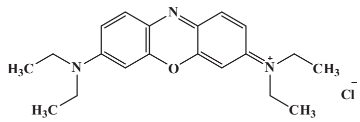
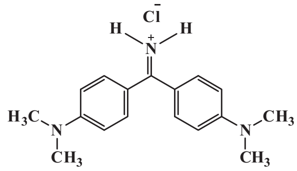
Table 1
Characteristics of C.I. Basic Blue 3 and C.I. Basic Yellow 2.

C.I. name	Chemical structure	Molecular formula	M_w (g/mol)	λ_{max} (nm)	Class
Basic Blue 3 (BB3)		$C_{20}H_{26}N_3OCl$	359.89	654	Oxazine
Basic Yellow 2 (BY2)		$C_{17}H_{22}ClN_3$	303.83	432	Diarylmethane

molecules is attributed to the presence of various functional groups on the surface of coal [30,31].

Process optimization is a tool for discovering conditions in which the best possible response can be obtained. RSM is an empirical designing, modeling and optimizing technique for evaluating the influence of independent variables and their interaction effects on the response(s) with a reduced number of experiments [32,33]. Previously, the RSM approach has been successfully used to optimize the response efficiency and evaluate simple and combined effects of different variables on the response of several dye removal processes [34–39].

In the present study, the removal of two BY2 and BB3 dyes was investigated in a batch system using coal as adsorbent. Central composite design was used to recognize the relationship between process variables, including dye initial concentration, adsorbent dosage, temperature, contact time and response (color removal efficiency), as well as to optimize the process.

2. Materials and methods

2.1. Materials

Two cationic dyes used in this study, BY2 (1,1-bis(p-dimethylaminophenyl)methylenimine hydrochloride) and BB3 (phenoxazin-5-ium,3,7-bis(diethylamino) chloride), were obtained from Shimi-Boyakhsaz Company, Iran and used without any purification. The molecular structure and characteristics of the dyes are represented in Table 1. The coal was supplied from Aşkale coal mines in Turkey and air dried. The dried sample was ground and sieved to −180 + 400 mesh using standard sieves. All other chemicals used in this study were analytical grade and provided by Merck Co. Distilled water was used for the preparation of solutions.

2.2. Chemical and physical characterization of adsorbent

Chemical analyses of coal including moisture, ash yield, volatile matter and fixed carbon content (%) as well as elemental analyses were performed using ASTM standards and the mean values of duplicate tests are reported. The BET surface area of the coal was measured through N_2 adsorption at 77 K in the relative pressure range from 0.05 to 0.4 using Belsorp mini II Bel, Japan. The total pore volume, defined as the volume of liquid nitrogen corresponding to the adsorbed amount, was measured at a single point of $P/P_0 = 0.987$. The pore size distributions were deduced from N_2 adsorption isotherms using the Barrett–Joyner–Halenda (BJH) method [40]. Before measurements, the sample was degassed for 15 h at 100 °C in the degas port of the adsorption analyzer.

To identify the surface morphology of the coal, Quanta 400F field emission scanning electron microscopy (FE-SEM) (FEI Company, USA) was used.

The Fourier transform infrared (FT-IR) spectroscopy analyses, before and after dye adsorption process (in optimum conditions), were performed by a Bruker Tensor 27, Germany spectrometer instrument with potassium bromide (KBr) pellets. To prepare pellets, either dye-adsorbed or pure coal was dried and mixed with KBr and then ground in an agate mortar. FT-IR spectra were collected from wavelength range of 400–4000 cm^{-1}. The background spectrum of KBr was automatically removed from the sample spectrum.

2.3. Batch adsorption experiments

Dye stock solutions (1000 mg/L) were prepared by dissolving accurately weighed quantities of the dyes in distilled water. Dye solutions with different concentrations were prepared by diluting the stock solution with appropriate volume of distilled water. Batch experiments were carried out in 250 mL glass erlenmeyer flasks. Certain amount of coal was added into the flask containing 100 mL of dye solution. Flasks were placed in a shaking incubator (ISH 554 D, Fanavaran Sahand Azar Co., Iran) and shaken at different temperatures for a given time with constant frequency of 150 cycles per minute. At the end, suspension was centrifuged at 6000 rpm for 10 min and residual dye concentration was determined using a UV–vis spectrophotometer (WPA light wave S2000, UK) at dye maximum wavelength. Color removal (CR) efficiency (%) was calculated using the following equation:

$$CR(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final concentrations of dye (mg/L), respectively.

2.4. Design of experiments

CCD as the most accepted class of second-order designs in RSM, was used to design experiments and optimize the color removal process [41]. The effect of four experimental variables, initial concentration of dye (mg/L) (X_D), adsorbent dose (g/L) (X_A), temperature (°C) (X_T) and contact time (min) (X_t), on the removal efficiency of BY2 or BB3 (output variable or response) was investigated according to CCD at five levels ($\alpha = 2$). A total of 31 experiments were carried out in this work, including 16 experiments at factorial points, 8 experiments at axial point and 7 replications at central points. In this approach, to ease the statistical calculations, the variables (X_i) are being coded as x_i according to Eq. (2):

$$x_i = \frac{X_i - X_0}{\Delta X_i} \quad (2)$$

where X_0 is the value of X_i at the center point, and ΔX_i presents the step with maximum and minimum values of variable X_i.