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Full Length Article

Synthesis of low-cost adsorbent from rice bran for the removal of reactive dye based on the response surface methodology

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ABSTRACT

Rice bran is a major by-product of the rice milling industry and is abundant in Taiwan. This study proposed a simple method for modifying rice bran to make it a low-cost adsorbent to remove reactive blue 4 (RB4) from aqueous solutions. The effects of independent variables such as dye concentration (100–500 ppm), adsorbent dosage (20–120 mg) and temperature (30–60 °C) on the dye adsorption capacity of the modified rice bran adsorbent were investigated by using the response surface methodology (RSM). The results showed that the dye maximum adsorption capacity of the modified rice bran adsorbent was 151.3 mg g^{-1} with respect to a dye concentration of 500 ppm, adsorbent dosage of 65.36 mg, and temperature of 60 °C. The adsorption kinetics data followed the pseudo-second-order kinetic model, and the isotherm data fit the Langmuir isotherm model well. The maximum monolayer adsorption capacity was 178.57–185.19 mg g^{-1}, which was comparable to that of other agricultural waste adsorbents used to remove RB4 from aqueous solutions in the literature. The thermodynamics analysis results indicated that the adsorption of RB4 onto the modified rice bran adsorbent is an endothermic, spontaneous monolayer adsorption that occurs through a physical process.

1. Introduction

The colored wastewater discharged from diverse industries, such as the cosmetics, food, paper and textile industries, is a serious problem because it contains harmful or toxic dyes and organic substances [1]. Therefore, these environmental unfriendly substances need to be removed from the water to prevent the pollution of the natural water system. Several methods have been applied to remove the harmful substances, including adsorption, biodegradation, coagulation, flocculation, membrane filtration, ozonation, and photodegradation [2–4]. However, the adsorption process has been recognized as the most applied method due to its easy operational procedures, low cost, high efficiency, flexibility and insensitivity to harmful substances [5–8]. Active carbon is the most commonly used adsorbent due to the advantage of effective adsorption, but its weaknesses are its high material and regeneration costs [9]. Therefore, various low-cost, alternative adsorbents produced from agricultural waste or byproducts, such as coconut shells [10], orange peels [11], rice husks [12], rye straw [13], walnuts and poplar woods [14], have been studied and applied for the dye removal from wastewater.

Rice bran is a valuable material and a major by-product of the rice milling industry. Most of the rice bran produced is used as food for cattle and poultry, while a small portion (approximately 10%) is used for rice bran oil extraction [15]. The production of rice bran is prevalent in Taiwan. Any possible application of rice bran will yield environmental and economic benefits. Thus, the objective of this study was to propose a simple method to modify rice bran to make it a low-cost adsorbent and to evaluate its efficiency with respect to removing reactive blue 4 (RB4) from aqueous solutions. To enhance the efficiency of dye removal and reuse the adsorbent, base and magnetic treatments were used. Various control factors of the dye adsorption process, such as pH, adsorbent dosage, initial dye concentration and contact temperature, were investigated through batch adsorption experiments. Furthermore, the optimum operating conditions for the adsorption capacity of the adsorbent to be sufficient to remove dye were investigated via the response surface methodology (RSM) based on the central composite design (CCD). The adsorption kinetic and isotherm models were applied to evaluate the batch experimental data of RB4 adsorption onto the adsorbent. Finally, the thermodynamic parameters were determined from the isotherm data to explain the characteristics of the adsorption process.

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Table 1
Matrix for the CCD with the respective coded values.

Run	Independent variables (coded)			Responses
	X_1: dye concentration (ppm)	X_2: adsorbent dosage (mg)	X_3: temperature (°C)	Y: adsorption capacity (mg g^{-1})
1	300 (0)	20 (−1.68)	45 (0)	206.5
2	418.9 (1)	99.7 (1)	53.9 (1)	82.9
3	300 (0)	70 (0)	30 (−1.68)	85
4	300 (0)	70 (0)	45 (0)	83.9
5	181.1 (−1)	99.7 (1)	53.9 (1)	36.2
6	418.9 (1)	40.3 (−1)	36.1 (−1)	189.5
7	418.9 (1)	99.7 (1)	36.1 (−1)	82.9
8	181.1 (−1)	99.7 (1)	36.1 (−1)	35.8
9	181.1 (−1)	40.3 (−1)	53.9 (1)	89.5
10	500 (1.68)	70 (0)	45 (0)	139.0
11	300 (0)	70 (0)	45 (0)	85.3
12	300 (0)	70 (0)	45 (0)	84.4
13	100 (−1.68)	70 (0)	45 (0)	28.6
14	300 (0)	70 (0)	45 (0)	83.1
15	181.1 (−1)	40.3 (−1)	36.1 (−1)	89.3
16	418.9 (1)	40.3 (−1)	53.9 (1)	192
17	300 (0)	120 (1.68)	45 (0)	51.4
18	300 (0)	70 (0)	45 (0)	85.3
19	300 (0)	70 (0)	60 (1.68)	86.3
20	300 (0)	70 (0)	45 (0)	87.3

2. Materials and methods

2.1. Materials

Rice bran, produced by milling rice grain (Tainan 11), was purchased from the local grinding mill in Taichung County, Taiwan. Methanol (purity ≥ 99.9%), ammonia hydroxide (purity ≥ 99.9%), and sodium hydroxide (purity ≥ 97%) were purchased from Fisher Chemical (USA). Ferric chloride (purity ≥ 98%) and ferrous chloride (purity ≥ 98%) were purchased from Acros Organics (Belgium). All chemicals were analytical grade and used without further purification. Reactive blue 4 (RB4) (35%) was purchased from Sigma-Aldrich (USA). The dye aqueous solution was prepared by dissolving a certain amount of RB4 in distilled water to give an initial dye concentration for the dye removal experiments.

2.2. Adsorbent preparation

The rice bran was washed with distilled water to remove the impurity and dried at 373.15 K for 24 h. Afterward, 5 g of rice bran was immersed in 125 ml of methanol at 50 °C for 2 h at an agitation rate of 100 rpm in a shaker with a thermostatic water bath. After pretreatment, the rice bran was washed and dried at 100 °C for 24 h to obtain the adsorbent, which was designated PRB. Subsequently, the magnetite PRB was prepared by using the chemical co-precipitation method [16] with minor modification. Briefly, 6 g of PRB, 12 g of ferric chloride and 5 g of ferrous chloride were dissolved in 300 ml of distilled water. Then, different amounts of ammonia hydroxide were added slowly to the mixture to adjust the pH value at 85 °C for 1 h in a shaker that was maintained at 100 rpm. The amount effect of ammonia hydroxide on the preparation of the adsorbent was investigated by conducting adsorption experiments. After washing and drying, the magnetite PRB (MPRB) was obtained and soaked in an aqueous ammonia solution (50%) with a ratio of 40 g L^{-1}. After 24 h, the base treatment mixture (BMPRB) was filtered, washed and dried at 100 °C for 8 h.

2.3. Characterization

The synthesized adsorbent was characterized by using SEM/EDX (Hitachi S-3000H, Japan) and FTIR (Perkin Elmer Spectrometer, USA). A Genesys^{TM} UV–vis spectrophotometer (10S UV-VIS, Germany) was used to monitor the dye adsorption behavior of the adsorbent. The magnetic property of the adsorbent was analyzed by using a Superconducting Quantum Interference Device Vibrating Sample Magnetometer (SQUIDVSM, MPMS7, USA). A gas sorption system (Micromeritics, Model ASAP 2020, USA) was used to determine the surface area and porosity property of the adsorbent.

2.4. Experimental design and statistical analysis

The RSM is often used to optimize variables simultaneously and evaluate the influence of variables to attain the best response with a reduced number of experiments. In this study, the central composite design (CCD) was employed to evaluate the effects that three variables, viz. dye concentration (X_1: 100–500 ppm), adsorbent dosage (X_2: 20–120 mg), and temperature (X_3: 30–60 °C), have on the dye adsorption capacity of the adsorbent (Y: adsorption capacity). This design requires five levels (−α, −1, 0, 1, +α) of each variable, and 20 experimental runs were conducted. There is a relation between the variables that can be expressed by a polynomial equation. Analysis of variance (ANOVA) was performed to judge the significance of each term in the polynomial equation and the validation of the determined model. The Design Expert software (version 10.0) was used for the experimental matrix design, optimization procedure, regression model evaluation, and response surface graphs representation.

2.5. Batch adsorption experiments

The adsorption of RB4 dye onto the adsorbents was carried out via a batch adsorption process. The adsorption experiments were conducted, based on the CCD design matrix (Table 1), in a shaker at a constant speed of 100 rpm. After 6 h, the samples were taken from the shaker, and then the RB4 dye contents in the adsorbent were determined by using a UV/VIS spectrophotometer (Thermo Scientific, Germany) at a wavelength of 596 nm. The adsorption capacity (q) of the adsorbent for RB4 was calculated by solving the following equation:

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium dye concentrations, respectively, V is the volume of the dye solution and W is the dosage of the adsorbent used.