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Removal of disperse dye from aqueous solution using waste-derived activated carbon: Optimization study

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ABSTRACT

The purpose of this work is to obtain optimal preparation conditions for activated carbons prepared from rattan sawdust (RSAC) for removal of disperse dye from aqueous solution. The RSAC was prepared by chemical activation with phosphoric acid using response surface methodology (RSM). RSM based on a three-variable central composite design was used to determine the effect of activation temperature (400–600 °C), activation time (1–3 h) and H_3PO_4:precursor (wt%) impregnation ratio (3:1–6:1) on C.I. Disperse Orange 30 (DO30) percentage removal and activated carbon yield were investigated. Based on the central composite design, quadratic model was developed to correlate the preparation variables to the two responses. The most influential factor on each experimental design responses was identified from the analysis of variance (ANOVA). The optimum conditions for preparation of RSAC, which were based on response surface and contour plots, were found as follows: temperature of 470 °C, activation time of 2 h and 14 min and chemical impregnation ratio of 4.45.

1. Introduction

Activated carbons, with their high porosity, are extensively used in industrial purification and chemical recovery operations. This is due to their extended specific surface area between 500 and 2000 m^2/g, their high pore volume and the presence of surface functional groups, especially oxygen groups [1]. Activated carbons are materials having complex porous structures with associated energetic as well as chemical inhomogeneities. Their structural heterogeneity is a result of existence of micropores, mesopores and macropores of different sizes and shapes. The main application of this adsorbent is for separation and purification of gaseous and liquid-phase mixtures [2].

A challenge in activated carbon production is to produce very specific carbons with a given pore size distribution from low-cost materials at low temperature. Precursors used for the production of activated carbons are organic materials that are rich in carbon, such as coal, lignite, and wood. Although coal is the most commonly used precursor, agricultural waste in certain condition is a better choice [3]. Many agricultural by-products such as coconut shell [4], grain sorghum [5], coffee bean husks [6], rubber wood sawdust [7], chestnut wood [8], fruit stones [9] and bamboo waste [10] have been discovered to be suitable precursors for activated carbon due to their high carbon and low ash contents. Agricultural wastes are considered to be very important feedstock because of two basic facts: they are renewable sources and low-cost materials [11].

There are two processes for preparation of activated carbon: chemical activation and physical activation. Chemical activation is a single step method of preparation of activated carbon in the presence of chemical agents while physical activation involves carbonization of carbonaceous materials followed by activation of the resulting char in the presence of activating agents such as CO_2 or steam. The chemical activation usually takes place at a temperature lower than that used in physical activation; this results in an improvement of pore development in the carbon structure because of the effect of chemicals. The carbon yields of chemical activation are higher than physical one [12].

Rattan (Palmae/Arecaceae family) is spiny climbing plant belonging to the palm family. It is considered to be the most important non-wood forest product in Peninsular Malaysia. There are about 600 species in the world, of which 106 species are found in Peninsular Malaysia. Only 21 of these species, however, are utilized and marketed. Rattan also plays an important role in the manufacture of household commodities in many rural areas. In addition, value added rattan are utilized as furniture, walking sticks, rattan balls, baskets, toys and mats. Consequently considerable amount of sawdust are generated as residues. Currently most of these residues are used as boiler fuel. To make better use of rattan sawdust, it is proposed to convert it to an activated carbon. The advantage of using non-wood forest products as raw materials for manufacturing activated carbon is renewable and potentially less expensive [13]. Furthermore, preparation and characterization of adsorbent

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Table 1
Independent variables and their coded levels for the central composite design.

Variables (factors)	Code	Unit	Coded variable levels				
			$-\alpha$	−1	0	+1	$+\alpha$
Temperature	X_1	(°C)	331.820	400	500	600	668.179
Activation time	X_2	(h)	0.318	1	2	3	3.681
Impregnation ratio (IR)	X_3	–	1.977	1:3	1:4.5	1:6	7.022

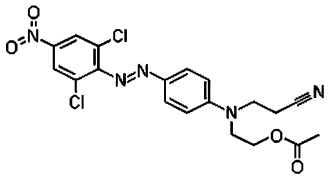
from rattan sawdust with H_3PO_4 activation are not available in the scientific literature.

The preparation of activated carbon is influenced by many factors such as temperature, time, and impregnation ratio. Therefore, it is important to study the effect of these factors on activated carbon production in order to determine the most important ones and their regions of interest [14]. Response surface methodology (RSM) is a useful tool to study the interactions of two or more factors. RSM is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. It usually contains three stages: (i) design and experiments, (ii) response surface modeling through regression, (iii) optimization [15]. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions [16]. In the last few years, RSM has been applied to optimize and evaluate interactive effects of independent factors in numerous chemical and biochemical processes. These applications are the preparation of activated carbons from olive-waste cakes by physical activation [17], sewage sludge by chemical activation [18] and Turkish lignite by chemical activation [14]. The focus of this research was to optimize the preparation conditions of activated carbon for removal of Disperse Orange 30 (DO30). A central composite design (CCD) was selected to study simultaneously the effects of three numerical activated carbon preparation variables: temperature, activation time and chemical impregnation ratio, on the two responses; percentage removal of DO30 and carbon yield.

2. Experimental

2.1. Adsorbate

C.I. Disperse Orange 30 (DO30), 4-((2,6-dichloro-4-nitrophenyl) azo)-N-(cyanoethyl)-N-(acetoxyethyl) supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate. Distilled water was used to prepare all solutions. DO30 has a chemical formula of $C_{19}H_{17}Cl_2N_5O_4$, with molecular weight of 450.27 g/mol. The chemical structure of DO30 is as follows:



2.2. Preparation of activated carbon

The rattan sawdust was collected from a local furniture factory Penang, Malaysia. It was washed with hot distilled water to remove dust like impurities, dried at 105 °C until constant weight of the sample was reached and the material was finally sieved to discrete sizes. Chemical activation method using phosphoric acid (purity 85% Merck, Germany) was used to activate the raw material. 40 g of raw material was impregnated by certain amount of 40 wt% concentration phosphoric acid with occasional stirring. The amount of phosphoric acid solution used was adjusted to give a certain impregnation ratio (weight of activating agent:weight of precursor) of 3:1, 4:1, 5:1, and 6:1. The impregnation ratio is given by

$$\text{impregnation ratio (IR)} = (\text{weight of } H_3PO_4 \text{ in solution}) : (\text{weight of precursor}) \quad (1)$$

After impregnation, the solution was filtered to take the residual acid. Subsequently, impregnated samples were air dried under sunlight for 3 days. Activation of phosphoric acid impregnated precursor was carried out at temperatures (400–600 °C) with a carbonization time of 1–3 h under nitrogen flow (150 cm^3/g) at a heating rate of 10 °C/min. After activation, the samples were cooled to room temperature under nitrogen flow and were washed sequentially several times with hot distilled water (70 °C) until the washing solution attained pH of 6–7. Finally, the samples were oven dried at 110 °C for 24 h and then stored in plastic containers.

2.3. Design of experiment (DOE)

The RSM has several classes of designs, with its own properties and characteristics. Central composite design (CCD), Box–Behnken design and three-level factorial design are the most popular designs applied by the researchers. The CCD was used to study the effects of the variables towards their responses and subsequently in the optimization studies [19]. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters. In order to determine if there exist a relationship between the factors and the response variables investigated, the data collected must be analyzed in a statistically manner using regression. A regression design is normally employed to model a response as a mathematical function (either known or empirical) of a few continuous factors and good model parameter estimates are desired [19]. In developing the regression equation, the test factors were coded according to Eq. (2):

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

where x_i is the coded value of the ith independent variable, X_i the natural value of the ith independent variable, X_i^x the natural value of the ith independent variable at the center point, and ΔX_i is the value of step change.

Each response was used to develop an empirical model that correlated the response to the activated carbon preparation variables using a second-degree polynomial equation as given by Eq. (3) [19]:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (3)$$

where Y is the predicted response, b_0 the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and x_i, x_j are the coded values of the activated carbon preparation variables.

The ranges and the levels of the variables investigated in the study are given in Table 1. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The responses were percentage removal on DO30 (Y_1) and activated