

Optimization Study of Preparation Eucalyptus Trees Activated Carbon for Removal of Methylene Blue Dye from Aqueous Solution

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Abstract

Mesoporous activated carbon were prepared from eucalyptus trees stalks (ES) using physiochemical activation method, which consisted of potassium hydroxide (KOH) treatment and carbon dioxide (CO₂) gasification. Based on the central composite design (CCD), two factor interaction (2FI) and quadratic models were respectively employed to correlate preparation of the activated carbon with these variables. The effects of the activation temperature, activation time and chemical impregnation ratios on the carbon yield and methylene blue removal were investigated. From the analysis of variance (ANOVA), the most influential factor on each experimental design response was identified. The optimum conditions for preparing activated carbon from eucalyptus stalks were found to be activation temperature of 650 oC, activation time of 0.5 h and chemical impregnation ratio of 2.5. The carbon yield was found to be 22.3% while the removal of methylene blue was found to be 89%.

Keywords: Eucalyptus stalks; Optimization; Activated carbon; Adsorption; Methylene blue.

1. Introduction

Dyes are used in many industries in order to color their products such as textile industry. The presence of dyes in effluents is a major concern due to their adverse effect to many forms of life. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons [1]. Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk. Though MB is not strongly hazardous, it can cause some harmful effects where acute exposure to MB will cause increased heart rate, vomiting, shock, cyanosis, jaundice, quadriplegia and tissue necrosis in humans [2]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on the receiving waters. Adsorption onto activated carbon has been found to be superior compared to other techniques for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of adsorbate and its simplicity of design [3].

Activated carbon (AC) obtained from various from agricultural wastes, such as oil palm frond [4], oil palm fiber [5], durian shell [6], oil palm shell [7], banana stalk [8], Olive stones [9], jute fiber carbon [10], coconut husk [11], pistachio nut shell [12], Cassava peel [13], date seed [14], mangos teen peel [15], willow tree legs [16], and eucalyptus wood (which is an abundant and low-cost material). Eucalyptus is the most valuable and widely planted hardwood in the world.

It was found that using response surface methodology (RSM) has been to be a useful tool to study the interactions of two or more variables in production of activated carbon for different applications. The adsorption capacity and activated carbon yield are highly influenced by the preparation conditions [17]. This research was mainly focus on the optimization of the experimental conditions to prepare high yield eucalyptus trees branches activated carbon for high removal of methylene blue dye (MB) from aqueous solutions at the optimum conditions using central composite design (CCD) software.

2. Experiment

2.1. Materials

Methylene blue (MB) supplied by Sigma–Aldrich was used as an adsorbate and was not purified prior to use. Distilled water was used to prepare all solutions. Table 1 listed the properties of Methylene blue (MB) dye used.

Table 1: Some properties of the MB used

Properties	
Chemical formula	C ₁₆ H ₁₈ ClN ₃ S.3H ₂ O
Molecular weight	373.9 g/mol
Type	Basic dye
Solubility	Soluble in water
Solution pH	6.5
Wave length	668 nm

2.2 Preparation and characterization of activated carbon

Eucalyptus trees stalks (ES) used as precursors for preparation of activated carbon. The precursor was firstly cutting into pieces (1-2 cm), washed to remove dirt from its surface and was then dried overnight at 105 °C . The dried precursors was crushed and screened to particle size of 1-3 mm and carbonized at 300 ° C under purified nitrogen (99.995%) flow of 150 cm³/min for 2 h in a stainless steel vertical tubular reactor placed in a tube furnace. The heating rate was fixed at 10 °C/min. The char produced was then soaked in potassium hydroxide (KOH) solution with different impregnation (KOH: char) ratio, according to CCD software results. The mixture was then dehydrated in an oven overnight at 105 ° C to remove moisture and was then activated under the same condition as carbonization, but to a different final temperature. Once the final temperature was reached, the nitrogen gas flow was switched to CO₂ and activation was held for different period of time. The eucalyptus trees stalks activated carbon produced (ESAC) was then cooled to room temperature under nitrogen flow and then washed with warm distilled water and 0.1 molar hydrochloric acid until the pH of the washing solution reached 6–7.

2.3 Characterization of the prepared activated carbon

Scanning electron microscopy (SEM) analysis was carried out on the prepared AC under optimum conditions, to study its surface texture and the development of porosity. Brunauer, Emmett and Teller (BET) suggested to determine the pore size distributions, the surface area and pore characteristics of AC using Micromeritics (Model ASAP 2020, US).

2.4 Design of experiments for preparation of activated carbon

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables [18]. A standard design called a central composite design (CCD) was applied in this work to study the variables for preparing the activated carbons. 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 [19]. Generally, the CCD consists of a 2ⁿ factorial runs with 2n axial runs and n_c center runs (six replicates). The activated carbons were prepared using physiochemical activation method by varying the preparation variables using the CCD. The activated carbon preparation variables studied were (x₁) activation temperature; (x₂) activation time and (x₃) KOH: char impregnation ratio. These three variables together with their respective ranges were chosen based on the literature and preliminary studies. Activation temperature, activation time and impregnation ratio are the important parameters affecting the characteristics of the activated carbons produced [20]. The number of experimental runs from the central composite design (CCD) for the three variables consists of eight factorial points, six axial points and six replicates at the centre points indicating that altogether 20 experiments were required, as calculated from equation 1:

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \quad (1)$$

where *N* is the total number of experiments required and *n* is the number of process variables. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. Each response (*Y_i*) for carbon yield and MB removal was used to develop an empirical model which correlated the response to the three preparation process variables using a second degree polynomial equation (equation 2) [21].

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

where *Y* is the predicted activated carbon yield or MB removal response, *b_o* 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 or MB removal variables. The activated carbon was derived from these precursors by physiochemical activation method which involved the use of KOH treatment and followed by gasification with CO₂. The parameters involved in the preparation were varied using the response surface methodology (RSM). The three variables studied were *x₁*, activation temperature, *x₂*, activation time and *x₃*, KOH/char impregnation ratio (IR). These three variables together with their respective ranges were chosen based on the literature and the results obtained from the preliminary studies where the activation temperature, activation time and IR were found to be important parameters affecting the characteristics of the activated carbon produced [22]. The most important characteristic of an activated carbon is its adsorption uptake or its removal capacity which is highly influenced by the preparation conditions. Besides, activated carbon yield during preparation is also a main concern in activated carbon production for economic feasibility. Therefore, the responses considered in this study were *Y₁* activated carbon yield, *Y₂* removal of MB.

2.5 Activated carbon yield

The experimental activated carbon yield was calculated based on the following equation (3):

$$\%Yield = \frac{w_c}{w_o} \times 100 \quad (3)$$

where w_c and w_o are the dry weights of final AC and precursor (g), respectively.

2.6 Adsorption studies

Batch adsorption was performed in 20 sets of 250 mL Erlenmeyer flasks. In a typical adsorption run, 100 mL of methylene blue solution with initial concentration of 100 mg/L was placed in a flask. 0.30 g of the prepared activated carbon (ESAC), with particle size of 2 mm, was added to the flask and kept in an isothermal shaker (120 rpm) at 30 °C until equilibrium was attained. The concentrations of dye solution before and after adsorption were determined using a double beam UV-Vis spectrophotometer (UV-1700 Shimadzu, Japan). The maximum wavelength of the methylene blue was found to be 668 nm. The percentage removal of dye at equilibrium was calculated by the following equation (4):

$$\% Removal = \frac{(C_o - C_e)}{C_o} \times 100 \quad (4)$$

where C_o and C_e (mg/L) are the concentration of dye at initial and at equilibrium, respectively [23].

3. Results and discussion

3.1 SEM and BET analysis

The surface morphology of the prepared activated carbon (ESAC) was examined using scanning electron microscope (Model Leo Supra 50VP Field Emission, UK). Figure 1 show the SEM image (magnification $\times 1000$) of activated carbon prepared under optimum conditions. It can be seen that the surface of activated carbon prepared contains a well-developed pores where there is a good possibility for dye to be absorbed into the surface of the pores. The (BET) surface area was 806 m²/g using Micromeriticsue (Model ASAP 2020, US).

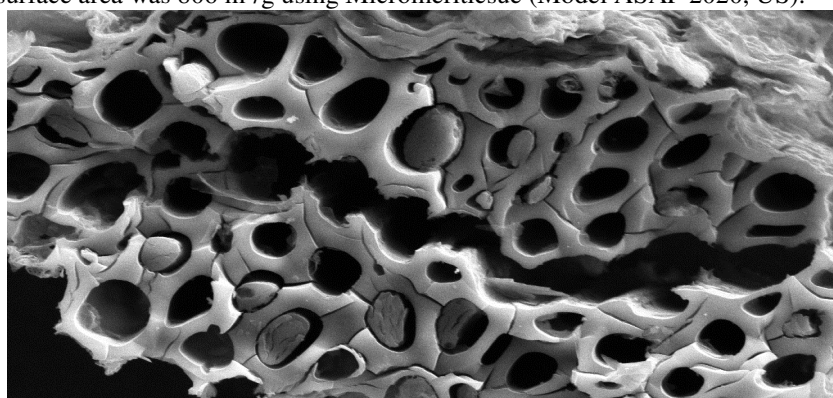


Fig. 1: SEM image (magnification $\times 1000$) of activated carbon prepared (ESAC)

3.2 Preparation of (ESAC) using DOE

The complete design matrix for the yield response of activated carbon prepared from stalks of eucalyptus trees (ESAC) with the removal of methylene blue solution from the experimental works include 20 runs, five runs from them at the center point were conducted to determine the experimental error and the reproducibility of the data. The yield of activated carbon and the removal of methylene blue were influenced not only by the preparation variables, but also depended on the type and nature of the original precursors as different precursors would have different physical and chemical characteristics.

3.3 Stalks of eucalyptus trees activated carbon yield

The experimental data revealed that the activation time have the greatest effect on the ESAC yield response and gave the highest F value of 26.38. The Analysis of variance (ANOVA) results shows the interaction between activation temperature and impregnation ratio has more effect on the prepared activated carbon ESAC yields. Figure 2 (a, b and c) shows the interaction effects between the parameters considered on the yield of ESAC. It depicts the effect of activation temperature and activation time on the response with IR being fixed at zero level (IR=1.75). Figure 2 b depicts the effect of activation temperature and IR on the same response with activation time fixed at zero level (time=1.0), while Figure 2c depicts the effect of activation time and IR on the same response with activation temperature fixed at zero level (temp. = 600 °C). In general, the ESAC yield was found to decrease with increasing activation temperature, activation time and chemical impregnation ratio. The increase in activation temperature would increase the removal of volatiles and impurities from the sample due to thermal decomposition and carbon

monoxide emission via C-CO₂ reaction. The development of porosity of the activated carbons by KOH activation is associated with gasification reaction. It is assumed that KOH is reduced to metallic potassium during the preparation process. The yield was strongly affected by the chemical impregnation ratio where an increased impregnation ratio decreased the yield and the carbon burn off increased. This was because when higher impregnation ratio was used, the weight losses were due to increase of volatile products release as a result of intensification in the dehydration and elimination reactions [23, 24].

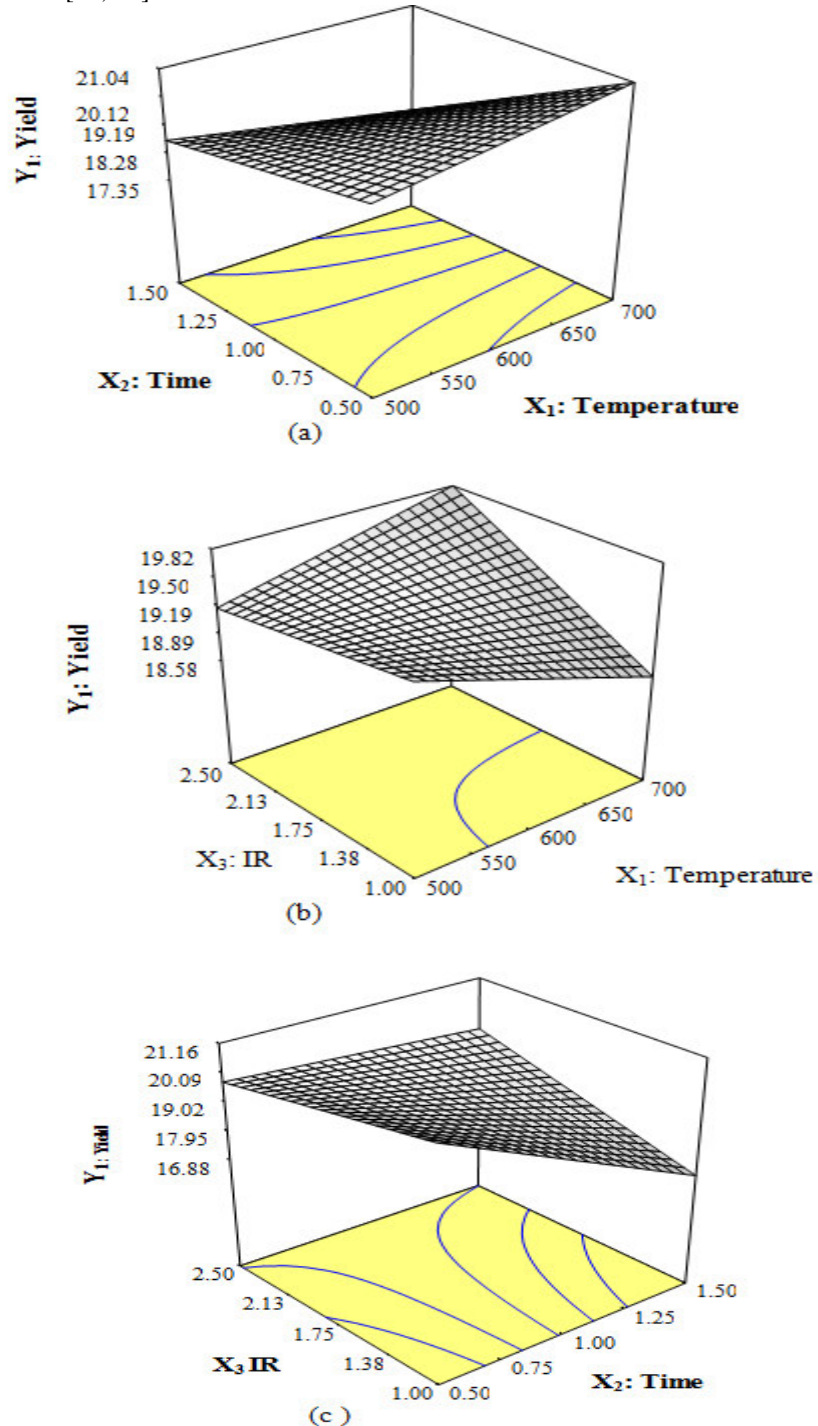


Figure 2: Three-dimensional response on the yield of ESAC, (a) the variables activation temperature and activation time, (b) the variables activation temperature and IR and (c) activation time and IR.

Methylene blue removal onto prepared activated carbon

The experimental results obtained for the removal of methylene blue onto prepared ESAC give indication that the

activation time and IR have significant effects, while IR have the significant for the quadratic effect. The interaction effect between activation temperature with activation time and activation time with IR were significant. However, the interaction effects between activation temperatures with IR were insignificant. Figure 3 (a, b and c), shows the three-dimensional response and the interaction effects between the variables activation temperature, activation time and IR on the MB removals. It would be observed from these figures that the removal of MB on BPAC generally increase with increase of activation temperature and IR.

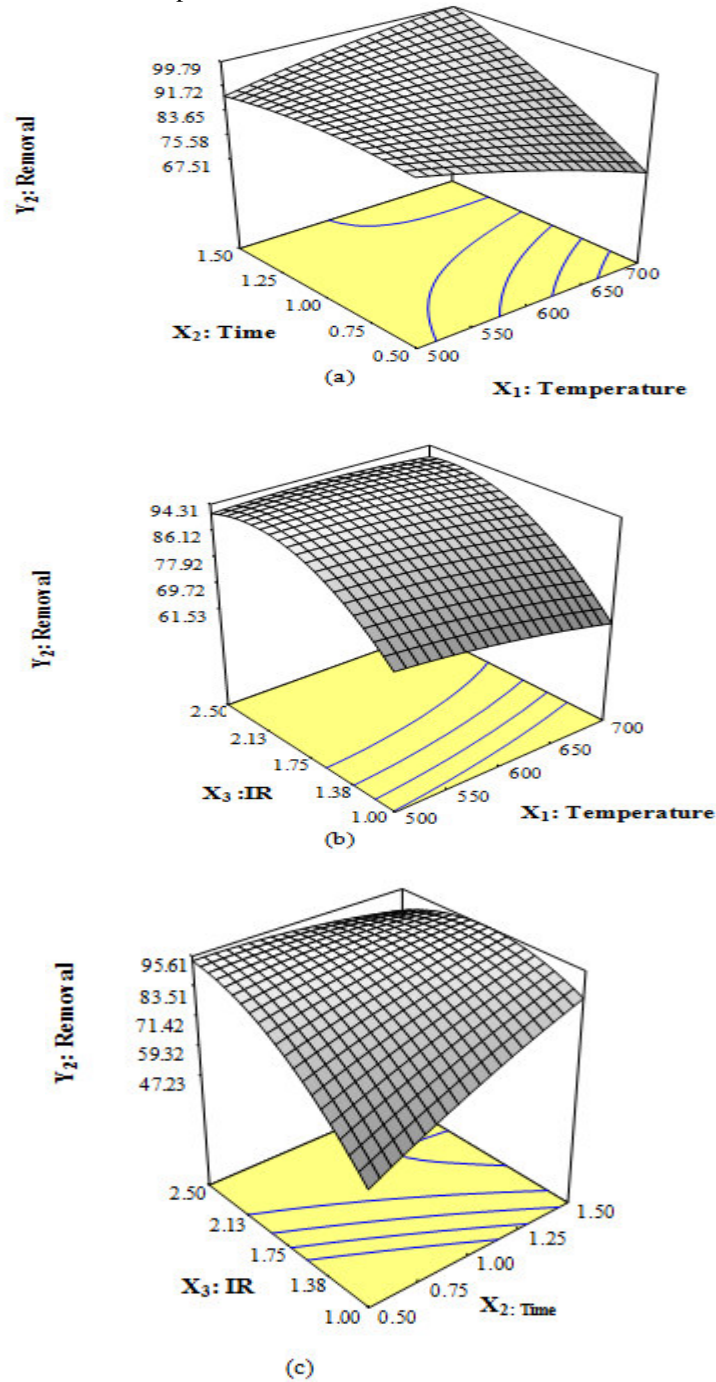


Figure 3: Three-dimensional response between the variables activation temperature, time and IR for the removals of methylene blue onto ESAC, (a) the variables activation temperature and activation time, (b) the variables activation temperature and IR and (c) the variable activation time and IR.

Optimization of operation parameters

In order to optimize the preparation conditions for activated carbons used for methylene blue removal, the targeted criteria was set as maximum values for the two responses of activated carbon yield (Y₁) and MB removal (Y₂)

while the values of the three variables (activation temperature, time and IR) were set the within the range of values studied. It was found that the optimum preparation activation temperature, activation time and IR needed were 600 °C, 1.0 h and 1.75 respectively, which gave ESAC yield and MB removal of 19.3 and 90.2% respectively.

Conclusion

Eucalyptus trees stalks (ES) were used as precursor to prepare mesoporous activated carbon with sufficient yield of carbon and high methylene blue dye removal. A central composite design was conducted to study the effects of three activated carbon preparation variables, which were the activation temperature, activation time and chemical impregnation ratio on the activated carbon yield and the removal of methylene blue. It was found that the ESAC yield decrease with increasing activation temperature, activation time and chemical impregnation ratio. The optimum conditions for prepare ESAC was obtained using 600 °C activation temperature, 1.0 h activation time and 1.75 KOH: char impregnation ratio.

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