PREPARATION OF MESOPOROUS ACTIVATED CARBON FROM WILLOW LEGS: OPTIMIZATION STUDY ON REMOVAL OF METHYLENE BLUE USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Mesoporous activated carbon was prepared from willow tree legs (WL) using physiochemical activation (potassium hydroxide treatment and carbon dioxide gasification). Based on the central composite design (CCD), two factor interaction (2 FI) and quadratic models were respectively employed to correlate the activated carbon preparation variables. The effects of the activation temperature, activation time and chemical impregnation ratios on the carbon yield, methylene blue (MB) 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 willow legs were found to be activation temperature of $650.5^{\circ}C$, activation time of 1.5 h and chemical impregnation ratio of 1.65. The carbon yield was found to be 17% while the removal of methylene blue was found to be 91.46%.

Key words: Willow trees, Activated carbon, Methylene blue, Central composite design, Adsorption.

INTRODUCTION

Dyes are widely used by textile industries to color their products. One of the major problems concerning textile wastewaters is colored effluent. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms[1]. Methylene blue (MB) dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. Therefore the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters[2].

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Adsorption processes using activated carbons are widely used to remove pollutants from wastewaters[3]. However, commercially available activated carbon is expensive. In the last years, special emphasis on the preparation of activated carbons from several agricultural by-products has been given due to the growing interest in low cost activated carbons from renewable, copious, especially for application concerning treatment of wastewater. Researchers have studied the production of activated carbon from palm-tree[4], cassava peel[5], bagasse[6], date pits[7], olive stones[8], fir woods, pistachio shells[9] and jute fiber[10]. The advantage of using agricultural by-products as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to manufacture.

The focus of the research is to evaluate the adsorption potential of willow tree legs - based activated carbon for methylene dye due to the fact that the willow tree is a very abundant and inexpensive material. MB was chosen in this study because of its known strong adsorption onto solids and is often serves as a model compound for removing organic contaminants and colored bodies from aqueous solutions. MB which is the most commonly used material for dying cotton, wood, and silk has a molecular weight of 373.9 g/mol^{-1}, which corresponds to methylene blue hydrochloride with three groups of water. The equilibrium data of adsorption studies were processed to understand the adsorption mechanism of the dye molecules onto the activated carbon.

EXPERIMENTAL

Material and methods

Adsorbate

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 MB dye used.

Table 1: Some properties of the MB used

Chemical formula	$C_{16}H_{18}ClN_3S.3H_2O$
Molecular weight	373.9 g/mol
Type	Basic dye
Solubility	Soluble in water
Solution pH	6.5
Wave length	668 nm

Preparation and characterization of activated carbon

Willow tree legs (WL) used as precursors for preparation of willow tree legs activated carbon (WLAC). The precursor was first into pieces (1-3 cm) washed to remove dirt from its surface and was then dried in an oven at $75^{\circ}C$ for three days. The dried precursors was crushed and screened to particle size of 1-4 mm and carbonized at $400^{\circ}C$ under nitrogen flow for 2 h using stainless steel vertical tubular reactor placed in a tube furnace. The char produced was mixed with KOH pellets with different impregnation ratio (IR), as calculated using equation (1):

$$IR = \frac{w_{KOH}}{w_{char}} \qquad \ldots(1)$$

Where w_{KOH} is the dry weight (g) of KOH pellets and w_{char} is the dry weight (g) of char. Distilled water was then added to dissolve all the KOH pellets. The mixture was then dehydrated in an oven overnight at $100^{\circ}C$ 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 CO_2 and activation was held for different period of time. The activated product was then cooled to room temperature under nitrogen flow and then washed with hot distilled water and 0.1 M hydrochloric acid until the pH of the washing solution reached 6-7 [11].

Characterization of the prepared activated carbon

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

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[12]. 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[13]. Generally, the CCD consists of a 2^n 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 (x_1) activation temperature; (x_2) activation time and (x_3) 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[14]. 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 (2):

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \qquad \ldots(2)$$

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 as given by equation (3)[15].

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \qquad \ldots(3)$$

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 CO_2. The parameters involved in the preparation were varied using the response surface methodology (RSM). The three variables studied were x_1, activation temperature, x_2, activation time and x_3, 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[16]. 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 Y_1 activated carbon yield, Y_2 removal of MB.

Activated carbon yield

The experimental activated carbon yield was calculated based on the following equation (4):

$$\% \text{ Yield} = \frac{w_c}{w_o} \times 100 \qquad \qquad \ldots(4)$$

Where w_c and w_o are the dry weight of final activated carbon (g) and dry weight of precursor (g), respectively.

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, 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 (5):

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \qquad \qquad \ldots(5)$$

Where C_o and C_e (mg/L) are the concentration of dye at initial and at equilibrium, respectively[17].

RESULTS AND DISCUSSION

SEM and BET analysis

The surface morphology of the prepared activated carbon was examined using scanning electron microscope (Model Leo Supra 50VP Field Emission, UK). Fig. 1 shows the SEM image (magnification × 500) 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.
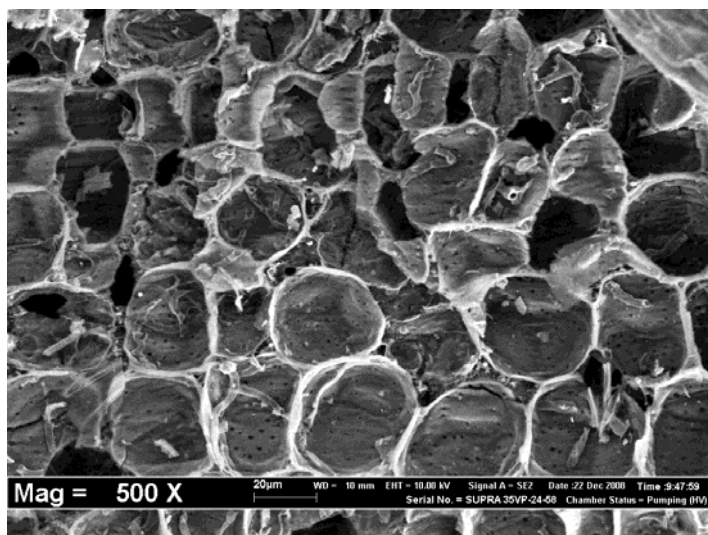

Fig. 1: SEM micrographs willow tree legs -based activated carbon (500×)

The Brunauer-Emmett-Teller (BET) surface area and the average pore diameter were 806.6 m^2/g and 2.35 nm, respectively using Micromeriticsue (Model ASAP 2020, US).

Preparation of willow tree legs activated carbon using DOE

The complete design matrix for the yield response of activated carbon prepared from willow tree legs 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.

Willow tree legs activated carbon yield

The experimental data revealed that the activation time have the greatest effect on the WLAC yield response and gave the highest F value of 14.25. The information presented in Table 2 gave indication that activation time and IR have effect on the activated carbon yield.

**Table 2: ANOVA for response surface quadratic model for WLAC yield**

Source	Sum of squares	Degree of freedom	Mean square	F Value	Prob > F
Model	16.08	9	1.79	14.25	0.0001
X_1	0.16	1	0.16	1.28	0.2839
X_2	0.84	1	0.84	6.66	0.0274
X_3	8.51	1	8.51	67.89	< 0.0001
X_1^2	0.24	1	0.24	1.90	0.1979
X_2^2	4.13	1	4.13	32.93	0.0002
X_3^2	2.88	1	2.88	22.95	0.0007
X_1X_2	0.080	1	0.080	0.64	0.4430
X_1X_3	0.080	1	0.080	0.64	0.4430
X_2X_3	0.000	1	0.000	0.000	1.0000

The quadratic effect of quadratic effects of activation time and IR on the yield of WLAC was higher compared to the activation temperature on the same response. It appears that the interaction between activation temperature and time have more effect on the WLAC yields. Fig. 2(a), (b) and (c) shows the three-dimensional response and the interaction effects between the parameters considered on the yield of WLAC. In the case of Fig. 2(a), it depicts the effect of activation temperature and activation time on the response with IR being fixed at zero level (IR = 1.50). Fig. 2(b) depicts the effect of activation temperature and IR on the same response with activation time fixed at zero level (time = 1.65 h), while Fig. 2(c) depicts the effect of activation time and IR on the same response with activation temperature fixed at zero level (temperature = 650°C).

In general, the WLAC 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 $C-CO_2$ reaction, this resulted into a decrease in sample weight[16]. 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[17,18]. Similar trend was observed in the previous works on preparation of activated carbons from coconut husk, the carbon yield was found to decrease with increasing activation temperature, activation time and chemical impregnation ratio[19,20]. The highest yield was obtained when all the three variables were at the minimum point within the range studied[21].
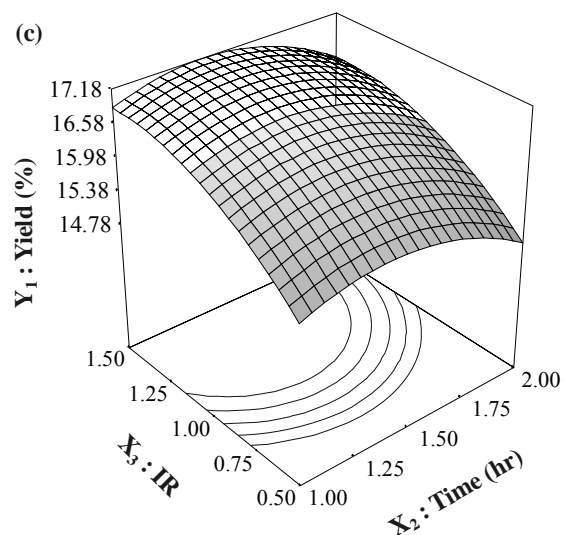
DESIGN-EXPERT Plot

(a)

(b)
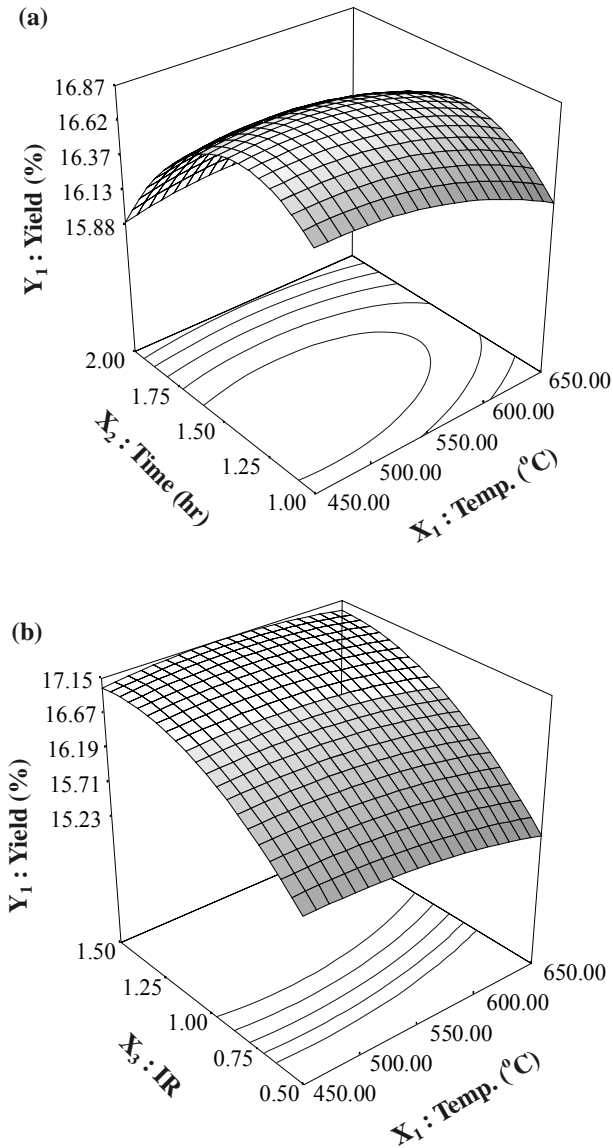
**Fig. 2: Three-dimensional response on the yield of WLAC
(a) the variables activation temperature and activation time (IR = 1.65),
(b) the variables activation temperature and IR (time = 1.5 h) and
(c) activation time and IR (temp. = 650°C)**

Methylene blue removal onto prepared activated carbon

The experimental values obtained for the removal of methylene blue and its response revealed that the activation temperature and IR have significant effects, while IR have the significant for the quadratic effect. The interaction effect between activation temperature with activation time was significant. However, the interaction effect between activation temperature with IR and between activation times with IR were insignificant as shown in Table 3.

Table 3: ANOVA results for MB removal by WLAC

Source	Sum of squares	Degree of freedom	Mean square	F Value	Prob > F
Model	1843.81	9	204.87	14.77	0.0001
X_1	414.38	1	414.38	29.87	0.0003
X_2	0.83	1	0.83	0.060	0.8119
X_3	1002.34	1	1002.34	72.25	0.0001

Cont…

Source	Sum of squares	Degree of freedom	Mean square	F Value	Prob > F
X_1^2	16.84	1	16.84	1.21	0.2964
X_2^2	0.56	1	0.56	0.040	0.8448
X_3^2	164.55	1	164.55	11.86	0.0063
X_1X_2	220.50	1	220.50	15.89	0.0026
X_1X_3	0.50	1	0.50	0.036	0.8532
X_2X_3	32.00	1	32.00	2.31	0.1598

Fig. 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 WLAC generally increase with increase of activation temperature and IR.

Optimization of operation parameters

In order 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 (Y_1) and MB removal (Y_2) 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 650.5°C, 1.65 h and 1,5 respectively.
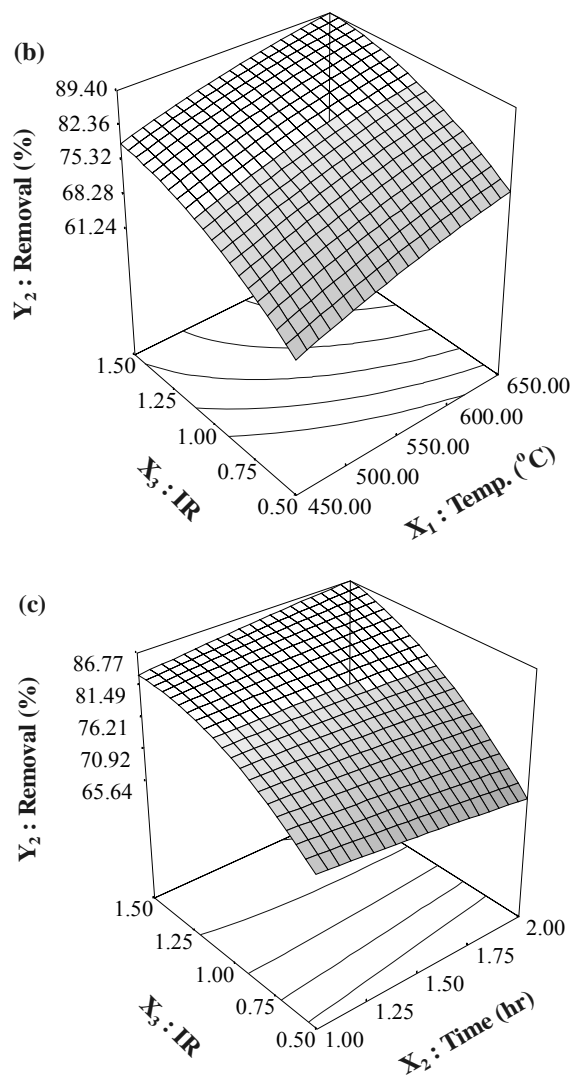

(a)

(b)

(c)
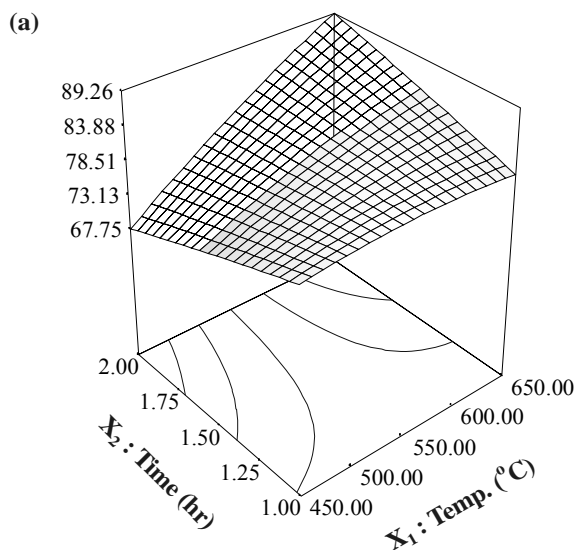
Fig. 3: Three-dimensional response between the variables activation temperature, time and IR for the removals of methylene blue onto WLAC, (a) the variables activation temperature and activation time (IR = 1.65), (b) the variables activation temperature and IR (time = 1.5 h) and (c) activation time and IR (temp= 650°C)

CONCLUSION

Willow tree legs were used as precursor to prepare mesoporous activated carbon with high surface area, sufficient yield of carbon and high 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. Through analysis of the response surfaces derived from the models, the WLAC yield was found to decrease with increasing activation temperature, activation time and chemical impregnation ratio. It was found that the removal of methylene blue increase with the increasing of activation temperature and IR The optimum conditions for prepare WLAC was obtained using 650°C activation temperature, 1.65 h activation time and 1.5 KOH: char impregnation ratio.

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