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OPTIMIZATION OF PREPARATION CONDITIONS FOR ACTIVATED CARBON FROM *MUSA ACUMINATA* PSEUDO-STEM: A NEW PRECURSOR USING BOX–BEHNKEN DESIGN

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ABSTRACT

Musa Acumınata pseudo-stem (MAPS) was evaluated as a new precursor for the preparation of activated carbon via zinc chloride ($ZnCl_2$) activation. The preparation conditions were optimized through Box–Behnken design (BBD) to maximize iodine number (IN). A single quadratic model was developed to correlate the preparation variables namely; activation temperature, impregnation ratio and activation time for IN responses. A total of 17 individual experiments was conducted and the results showed that the response surface methodology (RSM based on BBD is very applicable to optimize preparation conditions activated carbon from MAPS. The predicted optimum conditions for the preparation of AC from MAPS via $ZnCl_2$ activation was 557 °C reaction temperature, 30 min reaction time and 1:1 $ZnCl_2$–MAPS ratio, resulting in IN of 1062 mg/g. Porosity parameters and Scanning Electron Microscopy (SEM) were used to evaluate the textural properties and morphology of the AC. The results revealed that MAPS could be recommended as a promising precursor for the production of activated carbon via $ZnCl_2$ activation due to its high IN.

Keywords: Activated carbon; Box-Behnken; Banana pseudo-stem; Iodine number

INTRODUCTION

Banana contributes about 17% of the world's total fruit production, and is cultured over 130 countries [1]. The most popular varieties are Cavendish (*Musa acuminata L*. cv cavendishii) and Dream [*Musa acuminata* Colla (*M. acuminata*) AAA cv Berangan] banana [2]. In tropical countries such as Malaysia, the harvesting activity of banana leaves behind a large amount of pseudo-stem residue. It has been estimated that banana plant produced agriculture waste about 88% by weight in terms of the leaf and the pseudo-stem or trunk after harvesting [3]. Another study [4] claimed that the residue to the product ratio for banana is about 2.4:1. This undeniably causes disposal issues which can lead to severe environmental pollutionand and ecological problems. On the contrary, these enormous amounts of agriculture by product are known as a highly valuable raw material for the production of activated carbon (AC) due to its abundance, low cost, excellent properties and special structure [5, 6]. To prepare AC, activation process has been claimed as the most important routes which help to create or increase porosity on the surface of carbon materials [7].

AC can be prepared either by physical or chemical activation [8]. According to Vargas et al [9], the most studied chemical activation parameters are types of activating agent, time, temperature, and impregnation ratio (activating agent/precursor). Thus, in this study the preparation conditions were optimized through Box–Behnken design (BBD) to maximize the iodine number (IN) of prepared AC. The IN is defined as the milligrams of iodine adsorbed by 1.0 g of carbon when the iodine concentration of the filtrate is 0.02 N. This is a simple and quick test which gives an indication of the internal surface area of ACs. BBD is a three-level factorial design for three factors with selected points from a system arrangement. The advantage of this design is that it can reduce the number of runs and can be used for a large number of factors in one process. Furthermore, mathematical model can be easily generated and it accurately describes the overall process in addition to analyze the effects of independent variables [10]. Hence, in this present study, the main objective was to optimize the preparatıon condıtıons (activation temperature, activation time and imprenation ratio) for production of actıvated carbon from *Musa Acuminata* pseudo-stem usıng BBD. The effectiveness of the preparation conditions was evaluated based on IN in order to characterize the quality of the produced AC.

EXPERIMENTAL

Musa acuminata pseudo-stem (MAPS) was collected from a local banana farm in Arau, Malaysia and used as the precursor. The air dried MAPS were ground and sieved to a particle size range of 2–0.4 mm. Zinc chloride (HmBG, 97.0%) was used as the chemical activator. Other chemicals used were iodine pearl (HmBG, 99.9%), sodium thiosulphate-5-hydrate (HmBG, 99.0%), starch (HmBG, 98.0%), hydrochloric acid (Fisher, 37.0%), potassium iodate (HmBG, 99.9%) and potassium iodide (HmBG, 99.9%). All the chemicals were used without any further purification. In this work, the following synthesizing parameters were studied: (A) activation temperature, (B) the activation time and (C) impregnation ratios. The low, middle and high levels of each variable are designated as -1, 0, +1. These three variables together with their respective ranges were chosen based on the literature. These factors along with their values are summarized in Table 1.

The chemical activation was performed with $ZnCl_2$ as the activating reagent. 50 g of air-dried MAPS were mixed, by stirring with a required solution of $ZnCl_2$ to obtain the desired ratio of $ZnCl_2$ (dry basis). Later the mixture was then dried at 105 °C for 24 h to remove excess water. Then, the impregnated MAPS were packed into 100 ml crucibles and placed in an electrical muffle furnace (Carbolite) and heated 50 °C/min to the desired temperature. IN was determined using the ASTM D4607-94 method [11]. The Design Expert® software based on the BBD was applied to optimize ACs preparation based on their IN. The number of experiments (N) required for the development of BBD is defined as N = 2k (k-1) + C_0 (where k is the number of factors and C_0 is the number of central points). With three factors, the BBD model by default consists of 12 factorial design runs and 5 replicates at the central point, for a total of 17 experiments. AC produced at optimum condition was characterized by N_2 adsorption at -196 °C with an automatic adsorption instrument (ASAP 2010, Micromeritics) and the surface morphology was examined using a desktop scanning electron microscope (SEM, Phenom Pro X).

Table 1: Factors with their levels for AC preparation

Factors	Unit	Code	Levels		
			−1	0	+1
Activation temperature	°C	A	400	600	800
Activation time	min	B	30	60	90
Impregnation ratio	-	C	1.00	3.00	5.00

RESULTS AND DISCUSSION

Statistical analysis.

In the present work, the relationship between the response (IN) and three independent factors (activation temperature, activation time and impregnation ratios) were studied. The experimental results at each point were obtained based on the designed variables as suggested in Table 2. The experimental sequence was randomized to minimize the effects of the uncontrolled factors. Regression analysis is the general approach to fit the empirical model with the collected response variable data. Table 2 also represents the BBD matrix measured and predicted response of IN. The coefficients of the full regression model equation and their statistical significance were determined and evaluated using Design-Expert 9.0.2 software from State-Ease Inc. The final model in terms of actual value is given in Eq. (1).

Iodine Number =

$$1015.06 + 37.00A + 0.46B + 14.14C - 53.54A^2 + 29.89B^2 + 21.88C^2 + 12.54AB + 47.23AC + 7.64BC \quad (1)$$

where *A, B* and *C* are the coded terms for the three variables that have been selected, i.e. reaction temperature, reaction time and impregnation ratios. A positive sign in front of the terms indicates synergistic effect, whereas negative sign resembles the antagonistic effect. The results obtained were analyzed by analysis of variance (ANOVA). The significant quadratic models and the corresponding significant model term for all responses are tabulated in Table 3.

Table 2: BBD design of independent variables, matrix measured and predicted response of IN for process optimization

Std	Run	Factor 1 Temp (°C)	Factor 2 Time (min)	Factor 3 Ratio	Iodine Number (mg/g) Experimental	Predicted
10	1	600.00	90.00	1.00	1034	10
3	2	400.00	90.00	3.00	950	3
5	3	400.00	60.00	1.00	983	5
17	4	600.00	60.00	3.00	1049	17
2	5	800.00	30.00	3.00	1008	2
13	6	600.00	60.00	3.00	1001	13
1	7	400.00	30.00	3.00	972	1
16	8	600.00	60.00	3.00	1020	16
7	9	400.00	60.00	5.00	896	7
14	10	600.00	60.00	3.00	1002	14
4	11	800.00	90.00	3.00	1035	4
9	12	600.00	30.00	1.00	1050	9
12	13	600.00	90.00	5.00	1098	12
6	14	800.00	60.00	1.00	977	6
11	15	600.00	30.00	5.00	1084	11
8	16	800.00	60.00	5.00	1078	8
15	17	600.00	60.00	3.00	1003	15

Referring Table 3, it was observed that the quadratic term of reaction temperature of (A^2) has a large significant effect on the IN due to the high F-value (28.07). Furthermore, linear term of reaction temperature (A), the interaction between reaction temperature and impregnation ratios (AC) and quadratic term of reaction time (B^2) had greatly affected the IN with an F-value of 25.47, 20.75 and 8.75 respectively. In order to test the fit of the model, the regression equation and determination coefficient (R^2) were determined. For the IN, the value of the determination coefficient (R^2 = 0.9288) indicates that the sample variation of 92.88% for IN is attributed to the independent variables and only 7.12% of the total variations could not be explained by the model. A higher value of the correlation coefficient justified an excellent correlation between the independent variables.

Figure 1 shows the correlation between experimental values and predicted values of IN. The value of the adjusted determination coefficient (Adj. R = 0.8374) is relatively high to support for a high significance of the model. It could be found that in the scattering between the data points and the diagonal line showed adequate agreement between the actual and predicated data obtained by the model. It indicated that the predicted models were proved appropriate to navigate the design space defined by the BBD.

Figure 2a, 2b and 2c show the contour plot and responses for the effect of reaction temperature, reaction time and impregnation ratios respectively on IN of prepared AC from MAPS. Figure 2a and 2c, showed that the combination effect of reaction temperature and reaction time (AB) and reaction time and impregnation ratio (BC) had no significant effect on the IN. However referring on Figure 2b, it can be seen that the influence of temperature on IN was highly affected by the amount of $ZnCl_2$ used. It was observed that the IN increased with an increase in the reaction temperature as well as impregnation ratios. At a lower temperature of 400 °C and higher impregnation ratio of $ZnCl_2$ (5:1), the IN was relatively lower (920 mg/g).

Table 3: ANOVA for the regression model and respective model term for iodine number

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F	Remarks
Model	39295.45	9	4366.16	10.15	0.0029	significant
A-Temp	10951.39	1	10951.39	25.47	0.0015	
B-Time	1.69	1	1.69	3.930E-003	0.9518	
C-Ratio	1598.52	1	1598.52	3.72	0.0952	
AB	629.29	1	629.29	1.46	0.2656	
AC	8922.35	1	8922.35	20.75	0.0026	
BC	233.30	1	233.30	0.54	0.4853	
A^2	12071.78	1	12071.78	28.07	0.0011	
B^2	3762.37	1	3762.37	8.75	0.0212	
C^2	2016.56	1	2016.56	4.69	0.0671	
Residual	3010.07	7	430.01			
Lack of Fit	1299.65	3	433.22	1.01	0.4745	not significant
Pure Error	1710.42	4	427.60			
Cor Total	42305.52	16				

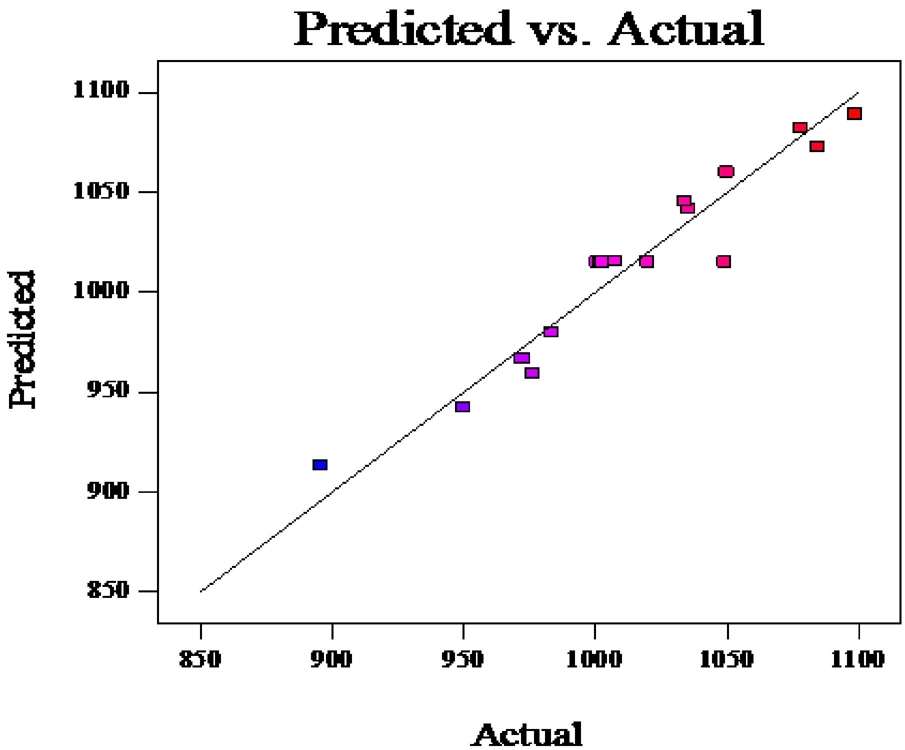

Figure 1: Relationship between predicted and actual values of IN (Eq. (1))

On the contrary, at the higher reaction temperature of 800 °C and higher impregnation ratio of $ZnCl_2$ (5:1), the IN raised up significantly to 1070 mg/g. However, at similar temperature the IN gradually decreases with a decreasing in the impregnation ratio of $ZnCl_2$ (from 5:1 to 1:1). This would be due to that activating agent reacted with the precursor and volatile matter which then diffused quickly out of the surfaces of particles during the activation process [12]. Therefore, with a high activating agent content, the gasification of surface carbon atoms became predominant, leading to an increase in the weight loss, corresponding to the new pore generation and pore opening/widening and thereby resulting in high surface area (high IN). Similar finding was also has been reported by Kumar and Mohan [13] who studied the activation of lignin by with $ZnCl_2$.

Optimization analysis.

BBD was applied for the development of a polynomial regression equation to analyze IN results. It was found that IN of the prepared AC ranged from 895 to 1098 mg/g. The three replicate experiments yielded a good agreement with the predicted values. The experimental results verified the validity of the model and existence of an optimal point. This indicated that the RSM was a powerful tool for determining the exact optimal values of the individual factors. According to the BBD results, the optimal operating conditions for the maximum IN were found to be the activation temperature (A) of 557 °C, activation time (B) of 30 min, and impregnation ratio (C) of 1:1.

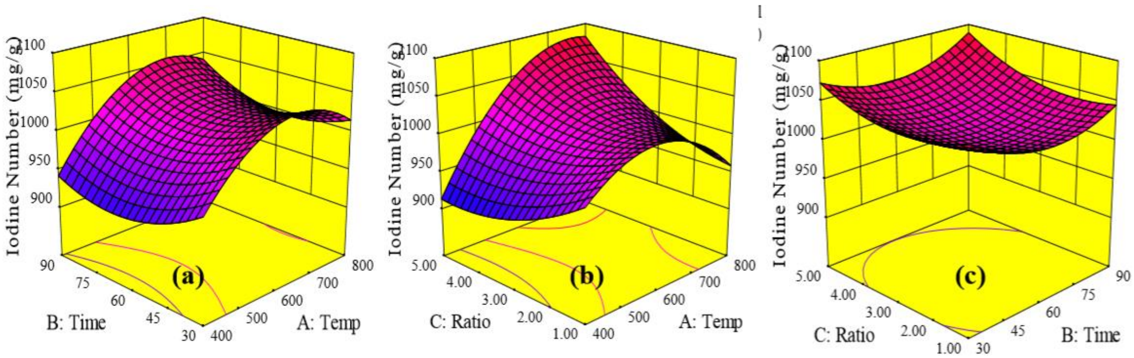

Figure 2: Response for the effect of (a) temperature and reaction time, (b) temperature and impregnation ratio and (c) reaction time and impregnation ratio on the IN of AC produced.

Activated Carbon Characterization.
BET surface area, total pore volume and pore diameters of the AC prepared from optimum condition were 1214.6 m^2/g, 1.0 cm^3/g and 3.7 nm respectively. Almost similar results were also reported by previous study [3, 9, 13]. SEM images of the MAPS and AC prepared from optimum conditions are shown in Figure 4. There are significant differences between surface morphology between MAPS and the AC obtained. The surface of the raw material (Figure 4 (a)) was almost even with some natural cracks and void. However, after activation with $ZnCl_2$ the AC (refer Figure 4 (b)) produced showed well established porous surface which indicates that the thick wall of precursor opened and created wider porosity during the activation. Consequently, the AC exhibited honeycomb-like pores and showed almost homogenous surface morphology.

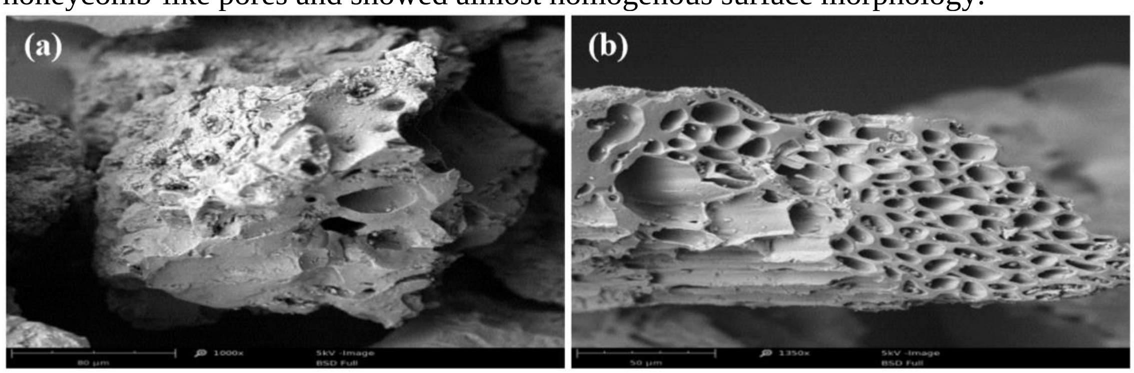

Figure 4: SEM images of (a) MAPS and (b) AC obtained in optimum condition at magnification of 3kX.

CONCLUSION

The preparation conditions have been optimized using the BBD. The optimal operating conditions suggested by the model were found to be the activation temperature (A) of 557 °C, activation time (B) of 30 min, and impregnation ratio (C) of 1:1. The F ratio and p values indicate that the activation temperature is the most important factors in the activation process. The increase in temperature favors the increase in the IN. Furthermore, the combination of all process parameters at optimum condition produced AC with IN of 1062 mg/g, which were in great agreement with the predicted values from the models. Based on the results obtained, MAPS can be a potential precursor material for producing activated carbon ith high IN.

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