OPTIMIZATION OF SYNTHESIS AND CHARACTERIZATION OF PALM SHELL-BASED BIO-CHAR AS A BY-PRODUCT OF BIO-OIL PRODUCTION PROCESS

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In this study the optimum preparation conditions of bio-char were achieved as a by-product of the bio-oil production process from oil palm shell as an agricultural waste material. To investigate the possibility of utilizing bio-char as an adsorbent for wastewater treatment and other applications, a central composite design was applied to investigate the influence of carbonization temperatures, nitrogen flow rates, particle sizes of precursor, and duration on the bio-char yield and methylene blue adsorption capacity as the responses. Methylene blue was chosen in this study due to its wide application and known strong adsorption onto solids. Two quadratic models were developed for the responses and to calculate the optimum operating variables providing a compromise between yield and adsorption. From the analysis of variance, temperature was identified as the most influential factor on each experimental design response. The predicted yield and adsorption capacity was found to agree satisfactorily with the experimental values. A temperature of 400°C, nitrogen flow of 2.6 L/min, particle size of 1.7 mm and time of 61.42 min were found as the optimum preparation conditions and near to the optimal bio-oil production variables.

Keywords: Palm shell; Bio-oil; Bio-char; Wastewater treatment; Optimization; Adsorption

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INTRODUCTION

Production of bio-oil as a renewable fuel from biomass resources is a potentially attractive area of research. The significant advantage in utilizing this oil is the positive contribution to the environment, such as decreasing CO_2 level of the atmosphere and consequently the greenhouse effect (Ertaş and HakkI Alma 2010; Peng et al. 2009; Xu et al. 2009; Zheng et al. 2008). Moreover, biomass sources as a raw material for bio-oil production are easy to obtain in various forms and are capable of re-generating themselves in a suitably short period of time (Ertaş and HakkI Alma 2010).

The characteristics of bio-oil depend on the composition of biomass feedstock and the type of pyrolysis process used to form it. Pyrolysis is the most popular thermal conversion process by which biomass can be converted into liquid fuels. In practice, up to 75 wt % of the biomass (on dry basis) is converted into bio-oil by using fast pyrolysis (Mauviel et al. 2009). Fast pyrolysis is mainly used for maximizing the liquid product yield using the preparation conditions of high heating and heat transfer rate, finely grounded biomass feed (to minimize the water in the product liquid oil), carefully controlled temperature (around 500 °C), short vapor residence time (less than 2 seconds), and rapid cooling of the pyrolysis vapors (Tsai et al. 2006).

Bio-char as a porous material is the most important by-product of the pyrolytic process, and it can be used as an adsorbent in other applications. Besides having a high surface area and micropore volume, a favorable pore size distribution makes this group of adsorbents suitable for a variety of applications such as separation, storage, and purification of gasses and adsorption of solutes from an aqueous solution (Lillo-Ródenas et al. 2007). For some considerable time, bio-char products have been used as adsorbents in applications where impurities have to be removed in low concentrations. Adsorption is the ideal method because it is non-specific (Molina-Sabio and Rodríguez-Reinoso 2004). It is therefore understandable that extensive research has been undertaken to develop bio-char to optimum pore-size distributions that meet the broad range of industrial requirements. As the applications become more specific, a more specific pore-size distribution is required, which depends on the preparation method and the carbon precursor (Bansal et al. 1988; Ehrburger et al. 1992).

Similar to bio-oil production processes, preparation variables have a very important role in development and characteristics of the produced bio-char. In both bio-oil and bio-char production process, higher obtained yield of final products at lower operating and energy cost is desirable for the producer, but care should be taken to not overlook other requirements from the end-users, such as high surface area, appropriate porosity, and high bulk density.

Table 1. Analysis of Oil Palm Shell *

Proximate analysis (wt %)		Elemental analysis (wt %)		Ligninocellulosic contents (wt %)	
Fixed Carbon	13.8	C	54.7	Cellulose	29.7
Moisture	4.7	H	7.49	Hemicellulose	16.9
Ash	7.2	N	2.03	Lignin	53.4
Volatile	74.3	O	35.6		

* (Arami-Niya et al. 2010)

Additionally, the selection of precursor is a very important factor in production of bio-oil and bio-char. Malaysia, as the major producer of oil palm in the world, generates more than 2.4 million tons of palm shell waste annually. It is estimated that the amount of waste is equal to 45.84 PJ (peta or 10^{15} joule) which is important as renewable energy (Abnisa et al. 2011). In general, these agricultural by-products are not used and have to be disposed. Usually, to reduce the amount of disposal, the waste of palm shell is burned without energy recovery or used to cover the surface of the roads in the plantation areas. However, the conversion of palm shell to bio-oil with a thermal process provides more benefit and potency to be used as biomass energy to substitute for fossil fuels. In addition, any cheap material with high carbon and low inorganic content can be used as a raw material for the preparation of activated carbon. Although coal and wood are mostly used as precursors for activated carbon, agricultural waste products would be a better choice in some applications and they can reduce the pressure on mines and forests (Do 1998; Mozammel et al. 2002). Because of the inherent characteristics of oil palm shell such as high carbon content, low ash, and almost negligible sulfur content, this agricultural waste is considered to be a good quality and attractive precursor for the preparation of bio-char. An elemental analysis and the lingocellulosic contents of oil palm shell is shown in Table 1 (Arami-Niya et al. 2010).

The objective of this study was to find the optimum production conditions of bio-char as a by-product of the bio-oil production process from oil palm shell by simultaneously considering the carbonization temperature, nitrogen flow rate, particle size of raw materials, and carbonization time. Desirable production outputs based on yield and adsorption were considered as responses. In addition, the optimum condition to obtain the highest amount (quantity) of bio-oil by a pyrolysis process was compared to that of the produced bio-char. No known study has been conducted on optimizing the bio-char production from oil palm shell as a by-product of the bio-oil production process using the response surface methodology (RSM). In this work, effects of different preparation variables on the production yield and methylene blue adsorption capacity of the prepared bio-char were studied.

EXPERIMENTAL

Raw Material

Oil palm shell waste was obtained from the Malaysian oil palm shell (MOPS). The samples were ground and sieved to different particle sizes ranging from 0.5 < dp < 0.85, 0.85 < dp < 1.4, 1.4 < dp < 1.7, 1.7 < dp < 2 mm, and dp > 2. It was then washed with distilled water several times to remove dust and impurities and then dried at 105°C for 24 h to remove any surface moisture.

Experimental Procedure

The pyrolysis experiments were performed on 150 g of the dried palm shell in a 304 stainless steel tubular reactor with a length of 127 cm and an internal diameter of 2.5 cm with a sweep gas (nitrogen) connection. The reactor was heated externally by an electric vertical furnace with a programmable controller (Carbolite VST 12/900). The system can be run up to a maximum temperature of 1200°C. A K-type thermocouple was used to control the temperature inside the reactor. The four parameters temperature, N_2 flow rate, reaction time, and particle size were chosen for investigation in this study. To control the N_2 gas flow rate, a flow controller (BROOKS mass flow sensor, 5860i series) was utilized. In a typical pyrolysis run, palm shell with particle sizes of 0.5 to 2.5 mm was placed on a metal mesh located at the middle of the reactor and was degassed under N_2 flow of 5 L/min. After 15 minutes of degassing, the N_2 flow was set at desired flow rate (1-5 L/min) and the furnace started to heat the sample at a rate of 10°C/min. The temperature of the reactor was increased until it reached the desirable temperature of 400 to 800°C. The sample was kept at this temperature for 30 to 150 min under a flow of N_2 gas and the unit was then left to cool down to room temperature. Following pyrolysis, the condensable liquid products were collected and weighed in a series of condensers maintained at 0.5°C. After pyrolysis, the bio-char was removed from inside the reactor and weighed. The product's yield was calculated using the following equation,

$$Yield(\%) = \frac{W_f}{W_0} \times 100 \tag{1}$$

where W_f and W_o are the dry weight (g) of produced bio-char or bio-oil and dry weight (g) of precursor (palm shell) as a feed for process, respectively.

Table 2. Independent Variables and their Coded Levels for the CCD

Variables	Code	Coded variable level -1	 0	 1
Temperature (°C)	x_1	500	600	700
Flow (L/min)	x_2	2	3	4
Size (mm)	x_3	1	1.5	2
Time (min)	x_4	60	90	120

Experimental Design

It is important to evaluate the performance of the systems to increase the yield of the processes without increasing the cost. The method used for this purpose is called optimization. Therefore, standard response surface methodology (RSM) design using a central composite design (CCD) was applied for the production of bio-oil and bio-char from oil palm shell. The CCD method that was chosen as the experimental design is appropriate for fitting a quadratic surface with a minimum number of experiments in order to optimize the effective process parameters. In addition, this method helps to analyze the interaction between these parameters (Azargohar and Dalai 2005). With this method, a core factorial is created that forms a cube with sides that are two coded units in length (from -1 to +1 as noted in Table 2). Table 2 shows the ranges and the levels of the variables examined in this study, which were thermal process temperature (X_1), nitrogen flow rate (X_2), precursor particle size (X_3), and thermal process time (X_4). These four variables and their respective ranges were chosen based on the literature and our preliminary studies. Process temperature, nitrogen flow rate, precursor particle size, and time were found to be important parameters affecting both the bio-oil production yield and characteristics of the produced bio-char (Stavropoulos and Zabaniotou 2005; Tay et al. 2001; Wu and Tseng 2006).

The CCD (N as a number of experiments) consists of 2n axial runs with 2^n factorial runs and n_c centre runs where n is the number of independent variables (Eq. 2).

$$N = 2^n + 2n + n_C \tag{2}$$

Table 3. Experimental Design Matrix and Response Results

Run	Type	Temperature(°C), X_1	Flow (L/min), X_2	Size (mm), X_3	Time(min), X_4	Yield, Y_1	Adsorption, Y_2
1	Fact	500	4	2	120	29.7	24.27
2	Fact	500	4	1	60	28.9	36.35
3	Center	600	3	1.5	90	30	21.59
4	Axial	600	3	1.5	30	28.9	21.17
5	Axial	600	3	1.5	150	27.2	16.46
6	Fact	500	2	2	60	32.3	29.34
7	Fact	500	4	2	60	30.8	28.19
8	Fact	700	2	2	60	26.7	20.01
9	Axial	400	3	1.5	90	34.3	53.53
10	Center	600	3	1.5	90	29.7	23.16
11	Fact	500	2	1	120	29.9	26.98
12	Fact	500	4	1	120	29.2	30.22
13	Fact	700	4	2	60	26.4	16.96
14	Center	600	3	1.5	90	31	20.02
15	Fact	500	2	2	120	31.13	23.36
16	Fact	700	4	2	120	24.6	21.26
17	Axial	600	3	2.5	90	27.6	26.37
18	Axial	600	3	0.5	90	25.4	29.19
19	Center	600	3	1.5	90	30	20.9
20	Fact	500	2	1	60	30.33	34.556
21	Center	600	3	1.5	90	30.7	21.59
22	Axial	600	1	1.5	90	27.9	14.046
23	Fact	700	4	1	60	23.6	16.46
24	Fact	700	2	1	120	24.2	18.64
25	Axial	800	3	1.5	90	22.6	29.84
26	Axial	600	5	1.5	90	27.4	11.22
27	Fact	700	2	2	120	24.3	20.82
28	Fact	700	2	1	60	23.9	18.07
29	Fact	700	4	1	120	24.4	20.37
30	Center	600	3	1.5	90	30.2	21.59

For the four variables, a 2^4 full factorial CCD for each categorical variable that consists of 16 factorial points, 8 axial points, and 6 replicates at the centre points were employed. The centre points are used to estimate the experimental error and the duplicability of the data. Where the low and high levels are coded as −1 and +1, the independent variables are coded to the (−1, 1) interval, respectively. The axial points are placed at (±α, 0, 0, 0), (0, ± α, 0, 0), (0, 0, ± α, 0) and (0, 0, 0, ± α) where the distance of the axial point from centre is α. The value of α depends on the number of points in the factorial portion of the design. In fact, the value of α can be calculated by Equation 3 (Montgomery 2001).

$$\alpha = (2^n)^{0.25} \tag{3}$$

In this study, the α value was fixed at 2, and four variables were investigated coded as follows: process temperatures (500 to 700 °C) (X_1), N_2 gas flow rate (2 to 4 L/min) (X_2), particle size of precursor (1 to 2 mm) (X_3) and process duration (60 to 120 min) (X_4) while the bio-oil production yield percentage (Y_1) and amount of percentage of methylene blue removal (Y_2) were taken as the process responses. All experiments were done in a randomized order to reduce the effect of unexplainable variance in the observed responses due to unrelated factors (Sumathi et al. 2009). It was assumed that the responses to be affected by the relation between the four independent variables and the production yield and experimental methylene blue adsorption data follow a quadratic equation as given by Eq. 4 (Gönen and Aksu 2008),

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \tag{4}$$

where Y is the predicted response, X_i to X_j are coded variables, b_0 is the constant coefficient, b_i is the linear term coefficient, b_{ij} is the interaction coefficient, b_{ii} is the quadratic coefficient, and n is the number of bio-char preparation variables.

Design expert software (version 7.1.6, Stat-Ease, Inc., Minneapolis, USA) was used to improve the mathematical model and estimate the subsequent regression analysis, analysis of variance (ANOVA) and the response surfaces (Montgomery 2001). The complete design matrices of the experiments performed, together with the results obtained, are shown in Table 3.

Batch Equilibrium Studies

Methylene blue was chosen in this study due to its wide application and strong adsorption onto solids. Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water.

Adsorption experiments of methylene blue on produced bio-char were carried out at fixed weighted (2 g/L) amounts of each sample with 100 mL solution of methylene blue (initial concentration of 300 mg/L). The aqueous methylene blue solutions were prepared by dissolving a known amount of corresponding methylene blue in 1 L of distilled water. Analytical-grade reagents were used in all cases. The stock solution was diluted as required to obtain standard solutions of concentrations ranging between 100 and 300 mg/L. The experiments were performed in a thermal shaker at a controlled temperature of 30 °C for a period of 24 h at 120 rpm using 250 mL Erlenmeyer flasks containing 100 mL of different methylene blue concentrations at room temperature. In order to reduce the error of the adsorption data, each sample was tested three times, and the average was reported. Samples were taken out at regular intervals and the residual concentration in the solution was analyzed using a double beam UV–visible spectrophotometer (Perkin Elmer) at 616.5 nm after filtering the adsorbent with Whatman filter paper (0.2 µm) to make it carbon free. The batch process was used so that there was no need for volume correction. The experiments were carried out at different initial concentrations and adsorbent dosages. The methylene blue concentration retained in the adsorbent phase was calculated according to Equation 5,

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{5}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of lead solution, respectively, V is the volume (L), and W is the weight (g) of the adsorbent. Two replicates per sample were done and the average results are presented.

By knowing the methylene blue concentration at initial concentrations and equilibrium concentrations, the efficiency of adsorption of methylene blue by bio-char can be calculated by using the following equation:

$$Adsorption(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{6}$$

Characterization

The characterization of bio-char samples was carried out using N_2 adsorption/ desorption at -196°C using Micromeritics ASAP 2020 surface area analyzer to assess the pore morphology of the produced bio-char. The BET surface area, micropore and total pore volume, and pore size distribution were obtained by analyzing N_2 adsorption-desorption profiles. The specific surface areas were determined according to the BET method at the relative pressure in the range of 0.05 to 0.30 (Sing 1998). Pore volume was directly calculated from the volume of nitrogen held at the highest relative pressure ($p/p_o = 0.99$). The volume of micropore was estimated using the Dubinin-Radushkevich (DR) equation (Rouquerol et al. 1999). Pore size diameters were determined using the Dollimore-Heal adsorption pore distribution method.

Proximate analyses were carried out according to ASTM D 7582-10, and the results are expressed in terms of moisture, volatile content, and fixed carbon and ash contents. The sample was heated from room temperature to 110°C in a nitrogen atmosphere until complete dehydration for the determination of the moisture content was achieved. Then the temperature was increased rapidly to 950°C and held for 7 min. Volatile matter was determined gravimetrically after dehydration. The temperature was then decreased to 650°C and the atmosphere was changed to oxygen gas. Weight loss during the oxidation stage shows carbon content and ash constituted the remaining mass at the end of the analysis. Ultimate analysis was carried out using a CHNS/O Analyzer model 2400 to determine the fixed carbon, hydrogen, nitrogen, and oxygen content of the samples.

RESULTS AND DISCUSSION

Development of Regression Model Equation

To improve the correlation between the preparation variables of bio-char to the production yield and adsorption capacity of methylene blue, a Central Composite Design (CCD) was used. Six experiments were run at the centre point to determine the experimental error. According to the sequential model sum of squares, the models were selected based on the highest order polynomials, where the additional terms were significant and the models were not aliased. For both yield and methylene blue adsorption capacity of the produced bio-char, a quadratic model was selected, as suggested by the software. The design of this experiment, together with the experimental results, is presented in Table 2. To fit the response function of bio-char yield and methylene blue adsorption, regression analysis was performed. The quadratic model for yield and methylene blue adsorption capacity in terms of coded factors, after excluding the insignificant terms is represented as Eq. (7) and (8), where the variables represent bio-char yield (Y_1) and adsorption of methylene blue (x_2) as a function of temperature (x_1), flow rate (x_2), particle size (x_3), and carbonization time (x_4):

$$Y_1 = 30.27 - 2.82x_1 - 0.26x_2 + 0.66x_3 - 0.37x_4 + 0.31x_1x_2$$
$$-0.47x_3x_4 - 0.48x_1^2 - 0.68x_2^2 - 0.96x_3^2 - 0.58x_4^2 \tag{7}$$

$$Y_2 = 21.475 - 5.336x_1 - 0.96x_3 - 0.98x_4 + 1.78x_1x_3$$
$$+2.07x_1x_4 + 4.87x_1^2 - 2.39x_2^2 + 1.39x_3^2 - 0.85x_4^2 \tag{8}$$

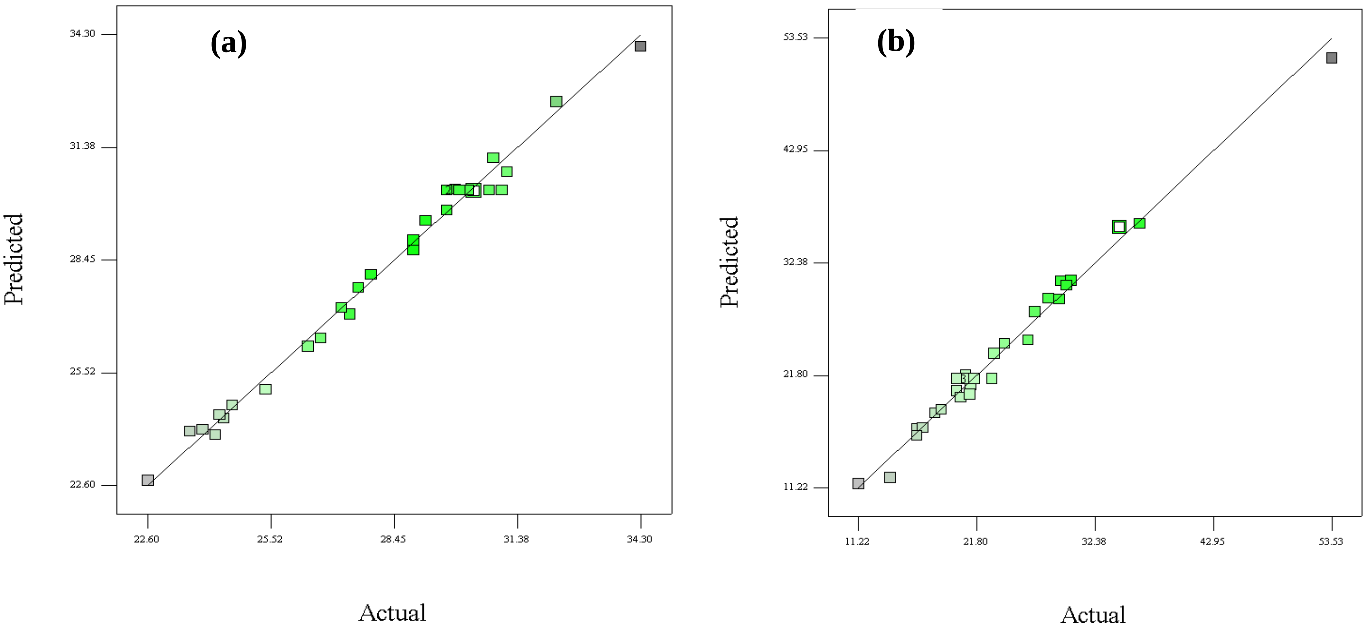

Fig. 1. Predicted vs. Actual value of **(a)** production yield (%) and **(b)** methylene blue adsorption capacity

Positive and negative signs in front of the terms indicates synergistic and antagonistic effects, respectively. The multiple regression analysis technique that is included in the RSM was used to estimate the model's coefficient for the response. Fit quality of the models was judged from their coefficients of correlation and determination. The predicted bio-char yield and methylene blue adsorption capacity by using Eq. 7 and 8 are given in Fig. 1(a) and Fig. 1(b) along with the experimental value. As seen in these figures, the points or point clusters are placed very close to the diagonal line, indicating the capability of developed quadratic models to satisfactory adjust to the experimental data.

Statistical Analysis

The coefficients of the empirical model (Eq. (2)) and their statistical analyses were assessed using the Design Expert Software. The models have been used to visualize the effects of experimental factors on bio-char yield percentage and methylene blue adsorption capacity responses in Figs. 2(a) and (b). The quadratic correlations between the carbonization temperature, nitrogen flow rate, particle size, and time of carbonization, as well as the fitted model, are given in Tables 4(a) and (b). The statistical significance of the quadratic model equations that are shown in these two tables was evaluated by the F-test analysis of variance (ANOVA). The statistical significance shows that these regressions are statistically significant at a 95% confidence level. The models presented high determination coefficients (R^2) that are close to unity, showing that both of the models fit the experimental data. When the regression coefficient value (R^2) is close to 1, the model can give a predicted value that is near the actual value for the response. This shows that the predicted value for both Y_1 and Y_2 would be very accurate and close to their actual value.

The suitability of the models was further justified through analysis of variance (ANOVA). The ANOVA for the quadratic models for bio-char yield percentage and methylene blue adsorption capacity are listed in Tables 4(a) and (b), respectively. Regression coefficients, the significance, and standard error of each coefficient were determined by F-value and Prob > F-value. From the ANOVA for response surface quadratic models for bio-char yield percentage (Y_1) and methylene blue adsorption capacity (Y_2), the model F-value of 103.9859 and 86.84 implies that the models are significant. Values of "Prob > F" less than 0.05 indicates that the model terms are significant, while values of ''Prob > F'' greater than 0.1 indicates the model terms are not significant. For the case of bio-char yield percentage (Y_1), carbonization temperature (X_1), particle size (X_3), carbonization time (X_4), interaction effect between carbonization temperature, and flow rate (X_1X_2), interaction effect between particle size and carbonization time (X_3X_4), square effect of carbonization temperature (X_1^2), square effect of flow rate (X_2^2), square effect of particle size (X_3^2) and square effect of carbonization time (X_4^2) were significant model terms. Additionally, carbonization temperature (X_1) particle size (X_3), carbonization time (X_4), X_1X_3, X_1X_4, X_1^2, X_2^2, X_3^2, and X_4^2 were significant model terms in the methylene blue adsorption capacity model (Y_2). Therefore, from the statistical results obtained, it can be verified that the mentioned models are accurate enough to predict the yield and the adsorption capacity within the range of variables studied.

Table 4 (a). Analysis of Variance (ANOVA) for Response Surface Quadratic Model for of Yield of Bio-Char

Source	**Sum of Squares**	**Degree of Freedom**	**Mean of Square**	***F*-Value**	**p-value Prob > *F***	**Remarks**
Model	250.073	14	17.862	103.985	< 0.0001	significant
X_1	190.198	1	190.198	1107.241	< 0.0001	significant
X_2	1.582	1	1.582	9.213	0.0083	significant
X_3	10.533	1	10.537	61.345	< 0.0001	significant
X_4	3.298	1	3.298	19.2	0.0005	significant
X_1X_2	1.539	1	1.539	8.961	0.0091	significant
X_1X_3	0.005	1	0.005	0.032	0.8602	
X_1X_4	0.03	1	0.03	0.179	0.6776	
X_2X_3	0.03	1	0.03	0.179	0.6776	
X_2X_4	0.224	1	0.224	1.309	0.2704	
X_3X_4	3.456	1	3.456	20.123	0.0004	significant
X_1^2	6.253	1	6.253	36.402	< 0.0001	significant
X_2^2	12.588	1	12.588	73.285	< 0.0001	significant
X_3^2	25.54	1	25.54	148.684	< 0.0001	significant
X_4^2	9.146	1	9.146	53.247	< 0.0001	significant
Residual	2.576	15	0.171	-	-	
Lack of Fit	1.383	10	0.138	0.579	0.783	
Pure Error	1.193	5	0.238	-	-	
Cor Total	252.649	29	-	-	-	
R-Squares	0.989					

Bio-Char Yield

In the case of bio-char yield percentage (Y_1), it can be seen in Table 4(a) that all the factors had a significant effect on it. By comparing F-values of the studied factors, carbonization temperature (X_1) with the highest F-value of 1107.24 was found to have the greatest effect on carbonization yield (Y_1). This is in agreement with previous studies (Acharya et al. 2009; Tan et al. 2008). After carbonization temperature (X_1), the highest effect on carbonization yield belongs to particle size of raw material (X_2) with an F-value of 61.34, while carbonization time (X_3) and nitrogen flow rate (X_4) with F values of 19.2 and 9.2, respectively, showed a less significant effect. Although carbonization temperature (X_1) showed the highest F value, the quadratic effect of particle size of raw material (X_2^2) on carbonization yield was more significant compared to other factors

Table 4 (b). Analysis of Variance (ANOVA) for Response Surface Quadratic Model for of Adsorption of Methylene Blue

Source	Sum of Squares	Degree of Freedom	Mean of Square	*F*-Value	p-value Prob > *F*	Remarks
Model	1861.265	14	132.947	86.838	< 0.0001	significant
X_1	683.264	1	683.264	446.295	< 0.0001	significant
X_2	0.467	1	0.467	0.305	0.5889	
X_3	22.187	1	22.187	14.492	0.0017	significant
X_4	22.885	1	22.885	14.948	0.0015	significant
X_1X_2	3.316	1	3.316	2.165	0.1618	
X_1X_3	50.609	1	50.609	33.056	< 0.0001	significant
X_1X_4	68.873	1	68.873	44.986	< 0.0001	significant
X_2X_3	4.004	1	4.004	2.615	0.1267	
X_2X_4	6.677	1	6.677	4.361	0.0542	
X_3X_4	1.229	1	1.229	0.803	0.3843	
X_1^2	649.752	1	649.752	424.406	< 0.0001	significant
X_2^2	157.446	1	157.446	102.84	< 0.0001	significant
X_3^2	53.061	1	53.0614	34.658	< 0.0001	significant
X_4^2	19.834	1	19.834	12.955	0.0026	significant
Residual	22.964	15	1.53			
Lack of Fit	17.637	10	1.763	1.655	0.3009	
Pure Error	5.326	5	1.065			
Cor Total	1884.229	29				
R-Squares	0.987					

(X_1^2, X_3^2, and X_4^2) that displayed similar effects. On the other hand, most of the interaction effects between the variables were not significant, and only X_1X_2 and X_3X_4 exhibited significant interaction effects.

The three-dimensional (3D) response surfaces in Fig. 2(a) and (b) show the effects of the bio-char preparation variables on the carbon yield percentage (Y_1). Figure 2(a) shows the effect of carbonization temperature and nitrogen flow rate, while Fig. 2(b) displays the effect of particle size of raw material and carbonization time on the yield. These figures imply that carbon yield decreases with increasing carbonization temperature, precursor's particle size and carbonization time. These figures visualize the obtained results in Table 4(a). It can be seen that carbonization temperature with the highest *F*-value causes sharp changes in carbonization yield, while nitrogen flow rate with the lowest *F*-value cannot have major effects on it.

The presented results are also in agreement with the study by Uzun et al. (2010). They found that carbonization temperature plays an important role in the yield of bio-char and that this factor is the most effective element affecting carbonization yield. In addition, they mentioned that an increase in temperature causes a release of volatiles as a result of intensifying dehydration and elimination reactions, thus resulting in a decrease in carbonization yield.

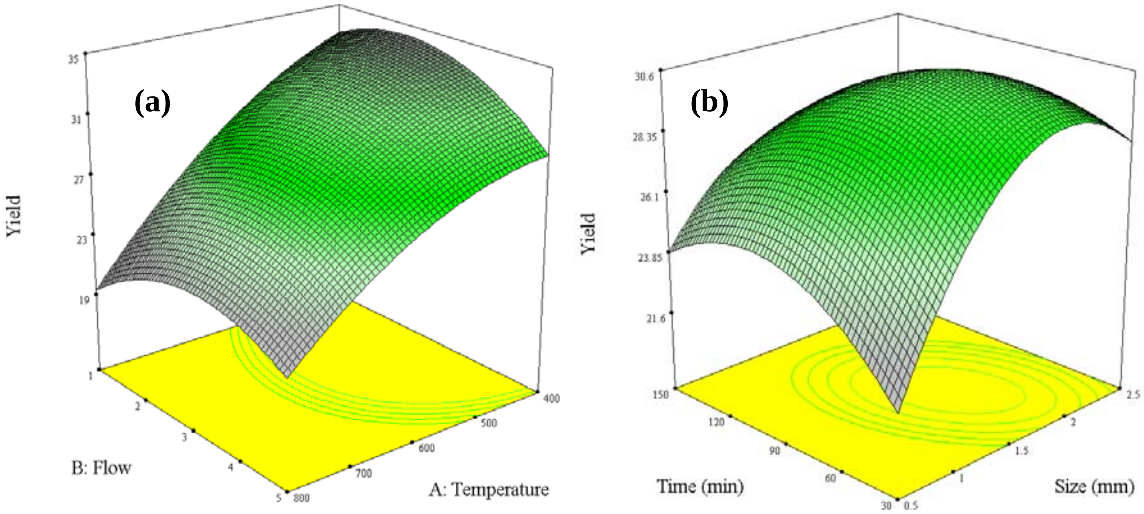

Fig. 2. The three-dimensional response surfaces **(a)** the effect of temperature and nitrogen flow rate **(b)** the effect of particle size of raw material and carbonization time on the yield

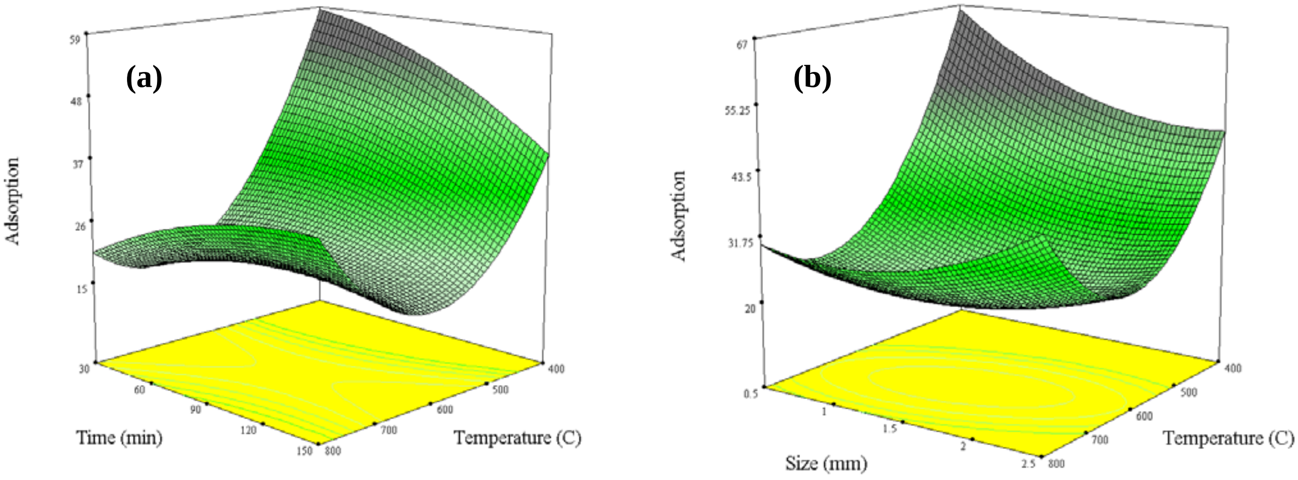

Fig. 3. The three-dimensional response surfaces **(a)** the effect of temperature and nitrogen flow rate **(b)** the effect of particle size of raw material and carbonization time on the methylene blue adsorption capacity

The effect of carbonization time on yield of bio-char is shown in Fig. 3(a). Increasing the carbonization time enhances the activity of secondary reactions (formation of secondary char, permanent gases, and light organic compounds). As a result, there would be acceleration in development of the carbon porosity and decrease in yield.

On the other hand, by grinding the precursor to smaller particle size, the surface of the solid will increase. By increasing the solid surface, there would be more active sites to be attacked during the carbonization process. Therefore, when the precursor becomes smaller in size, the gas molecule gains more access to the amorphous components and volatile matters, resulting in more weight loss and higher carbonization yield.

Although the flow rate of nitrogen during the carbonization process showed the lowest *F*-Value, this parameter has a significant effect on carbonization yield percentage (Table 4 (a)). Flow rate of the source gas as one of the deposition conditions was also mentioned as one of the effective factors affecting the type of microstructures in pyrolytic carbons according to IUPAC Definitions (Fitzer et al. 1995). The obtained results were in agreement with Uzun et al. (2010), affirming that an increase in nitrogen flow rate during the carbonization process enhances the release of volatiles and rate of bio-char formation.

Adsorption Capacity on Methylene Blue

Table 5 shows the results of the methylene blue adsorption experiments on the produced bio-char. Based on the *F*-values that are mentioned in this table, carbonization temperature, particle size of precursor, and duration of carbonization were found to have significant effects, whereas flow rate of nitrogen showed an insignificant effect on adsorption capacity of the synthesized bio-char. The interaction effects between X_1 and X_3, as well as X_1 and X_4 and the quadratic effect of all the factors (X_1^2, X_2^2, X_3^2 and X_4^2) were significant. Figures 3(a) and 3(b) show the three-dimensional response surfaces, which were constructed to show the effects of the bio-char synthesis variables (temperature, particle size, and duration) on the methylene blue adsorption capacity (Y_2). The effect of temperature was studied as it was found to have the highest significant effect on the response. As can be seen from Figs. 3(a) and 3(b), methylene blue adsorption capacity decreases with the increase in carbonization temperature and process time.

An explanation of the carbon structure is the best described by focusing on its porous structure. The devolatilization of biomass materials developed porosity in the chars, resulting in particles with an essentially micro–macropore structure. Carbon deposition also occurs as a result of the breaking down of some of the materials which collide with the pore walls (Kamishita et al. 1977).

A methylene blue molecule has a minimum molecular cross-section of about 0.8 nm, and it has been estimated that the minimum pore diameter it can enter is 1.3 nm. As long as the highest adsorption value is at 400 °C, it can be said that increase in temperature causes a decrease in micropore and mesopore volume. The obtained results were in agreement with the work by Wan Daud et al. (2000), in which carbonized oil palm shell showed a similar trend for micropore volume. The mentioned explanation also can be true for the decrease in methylene blue adsorption by increasing the particle size of precursor. Shrinkage of the particles and narrowing of pore entrance would take place to a greater degree in smaller particles.

Table 5. Results of the Model Evaluation (experiment 1 indicates the optimum bio-char yield conditions and high capacity of methylene blue adsorption)

Temperature (°C)	Flow (L/min)	Size (mm)	Time (min)	Yield (%)		Adsorption (mg/ml)	
				Experimental	Predicted	Experimental	Predicted
400	2.60	1.70	61.42	32.9	34.31	52.19	53.563

On the other hand, it can be seen that duration of the process was not very effective relative to the pore structure of the produced carbons. However, in this work, time was found to have a significant effect on the adsorption capacity of the bio-char prepared with the lowest *F*-value among other significant parameters.

Process Optimization

One of the most important aims in the economically viable production of commercial bio-char is to ensure relatively high product yields. In addition, the most important property of bio-char is its adsorption capacity. To find the optimum process parameters for a relatively high yield of bio-char as well as adsorption capacity, the response surface methodology was used. Thus, the synthesized bio-char should have a high carbon yield and a high adsorption capacity for economical feasibility. Design Expert software (version 7.1.6, Stat-Ease, Inc., Minneapolis, USA) was applied to optimize both of these responses under the same conditions and to compromise between these two responses. The two experimental conditions with the highest desirability were selected to be verified.

Table 5 shows the operating conditions suggested by the DOE model as the four variables for product yield and adsorption capacity. The experimental results together with those predicted by a regression model are presented in Table 5. The results show that the predicted data calculated from the models and the experimental data fit well. The deviation errors between experimental and predicted values were 95.89% and 97.45% for yield and methylene blue adsorption, respectively. These numbers show the statistical analysis is trustworthy to optimize the production of oil palm shell-based bio-char with high yield and methylene blue adsorption.

The maximum bio-oil production from palm shell has been reported as 47.3 wt% at the operation temperature of 500°C and 2 L/min N_2 flow rate for 60 min reaction time and particle size of 2 mm (Abnisa et al. 2011). The mentioned study investigated the maximum bio-oil production conditions at the same range of operation parameters that were studied in this work. It is noteworthy that the optimum preparation conditions of bio-char are very near those of the maximum bio-oil production. Therefore, the produced bio-char as the by-product of the determined palm shell based bio-oil preparation condition shows also high yield and methylene blue adsorption.

Scanning electron micrograph (SEM) images of the oil palm shell biomass and the corresponding char are shown in Fig. 4. As can be seen from Fig. 4(a), there were very small pores present on the surface of the precursor. However, after gasification under the optimum preparation conditions at 400 °C carbonization temperature, nitrogen flow rate of 2.6 mL/min, particle size of 1.7 mm, and 61.42 min carbonization time, the number of pores were increased on the surface of the bio-char, as shown in Fig. 4(b). This shows that thermal carbonization under the optimum conditions was effective in creating almost well-developed pores on the surfaces of the precursor, hence leading to an bio-char with narrow pore size distribution and porous structure which attains high adsorption capacity of methylene blue.

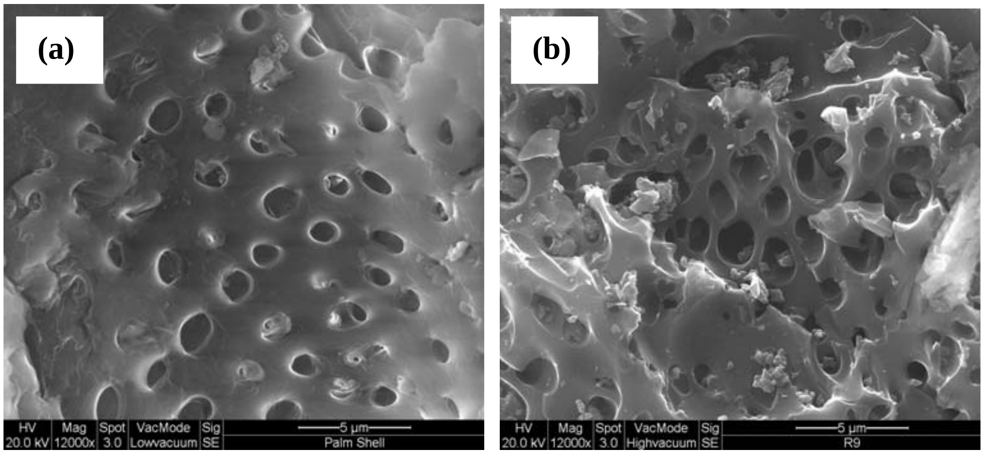

Fig. 4. SEM image of **(a)** raw palm shell (12000×). **(b)** palm shell-based bio-char synthesized under optimum conditions (12000×)

Characterization of Bio-char Synthesized under Optimum Conditions

Results of the proximate and ultimate analysis of the produced oil-palm shell based bio-char under the optimum preparation are given in Table 6. As mentioned before, the high fixed carbon and volatile contents of the palm shell make this material a good precursor for preparing bio-char. After the carbonization process at the optimum preparation conditions, the volatile content of the chars decreased from 74.3% to 45.5%, while the fixed carbon content increased from 13.8% to 42.9%. This behavior was due to the release of volatile matter during the carbonization process, which subsequently caused an increase in carbon content. These results are in agreement with our study on the production of activated carbon (Arami-Niya et al. 2010).

The N_2 adsorption isotherm of the thermal bio-char under the optimum preparation conditions is shown in Fig. 5. The produced bio-char exhibits type I isotherms, characteristic of microporous adsorbent. Type-I isotherms reach a maximum value of adsorption without inflections and are characteristic of adsorbents containing microporosity only. The main increase in this type of isotherm is at low-pressure regions ($P/P_0 < 0.2$), which means nitrogen molecules are adsorbed mainly in the microporous structure. The adsorption in micropores was interpreted according to the pore filling mechanism, thus resulting in a highly adsorbed volume, however, at higher relative pressures ($P/P_0 > 0.2$), a smaller gas volume is adsorbed due to the increase in relative pressure. The gradual increase in adsorption after the initial filling of the micropores indicates a higher volume of wide micropores and the presence of small mesopores. The pore size distribution of this sample is also shown in Fig. 6. As it can be seen in this figure, the produced bio-char contains mostly pores with pore width less than 4 nm (the majority are between 2 and 4 nm). In addition, to maximize adsorption, it was found that the adsorbent for methylene blue has to be microporous with pores around 1.3 nm. Therefore, more methylene blue adsorption capacity in the bio-char sample can be the result of a high volume of micropores.

Surface area, total pore volume, micropore volume, and average pore diameter of bio-char are also obtained from N_2 adsorption isotherm (Table 6). The sample shows a high proportion of micropore volume (about 100% of total pore volume).

Table 6. Proximate and Ultimate Analysis, BET Surface Area, Total Pore and Micropore Volume of the Produced Bio-char under the Optimum Preparation Conditions

Proximate analysis (wt %)		Elemental analysis (wt %)			
Fixed Carbon	42.9	C	62.7	BET surface area (m^2/g)	58.3
Moisture	7.3	H	7.9	Pore volume (cm^3/g)	0.32
Ash	4.3	N	1.3	Micropore volume (cm^3/g)	0.29
Volatile	45.5	O	28.1	Average pore width (nm)	2.32

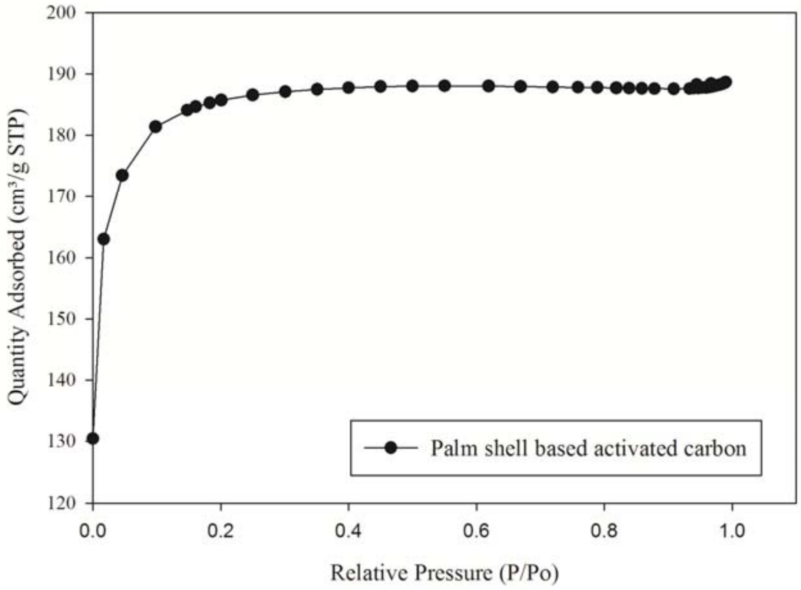

Fig. 5. N_2 adsorption isotherms of bio-char synthesized under optimum conditions

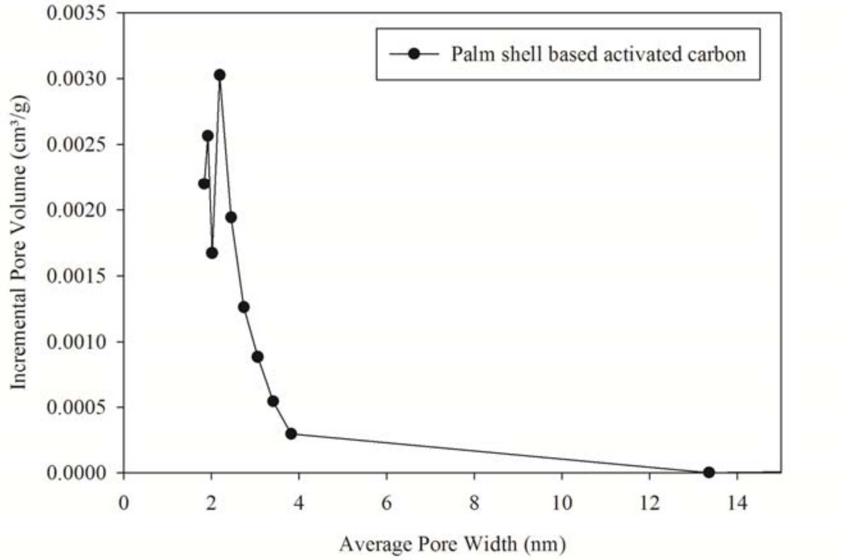

Fig. 6. Pore width vs. pore volume of bio-char synthesized under optimum conditions

CONCLUSIONS

In the present study palm shell-based bio-char as a by-product of the bio-oil production process was characterized by measuring the methylene blue dye adsorption capacity and bio-char production yield. A central composite design was conducted to study the effects of four variables of temperature, nitrogen flow rate, particle size, and carbonization time and to develop the models to correlate the variables to the responses. Based on the study, the following conclusions were drawn:

1. Temperature was identified as the most significant factor on each experimental design response of methylene blue dye adsorption capacity and bio-char production yield.
2. The optimization of condition was carried out and the carbonization temperature 400 °C, nitrogen flow rate of 2.6 L/min, particle size of 1.70 mm, and duration of 61.42 min was found as the optimized condition to have simultaneously high adsorption and production yield.
3. The deviation errors between experimental and predicted values were 95.89% and 97.45% (near to unity) for yield and methylene blue adsorption, respectively. Therefore, it can be conclude that the experimental values were found to agree satisfactory with the predicted values and near to that of bio-oil production.
4. After the carbonization process at the optimum preparation conditions, the fixed carbon content increased from 13.8% to 42.9% and the produced bio-char exhibited type I isotherms, characteristic of microporous adsorbent.

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