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Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology

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Abstract

Coconut husk was used to prepare activated carbon using physiochemical activation method, consisted of potassium hydroxide (KOH) treatment and carbon dioxide (CO_2) gasification. The effects of the preparation variables which were activation temperature, activation time and chemical impregnation (KOH:char) ratio on the adsorption capacity on methylene blue dye and carbon yield were investigated. Based on the central composite design (CCD), a two factor interaction (2FI) model and a quadratic model were respectively developed to correlate the preparation variables to the adsorption capacity and yield. From the analysis of variance (ANOVA), the most influential factor on each experimental design response was identified. The predicted adsorption capacity and yield after process optimization was found to agree satisfactory with the experimental values. The optimum conditions for preparing activated carbon from coconut husk were found as follows: activation temperature of 816 °C, activation time of 1 h and KOH:char ratio of 3.9.

Keywords: Coconut husk; Activated carbon; Methylene blue; Central composite design; Optimization

1. Introduction

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]. Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents [2]. It is estimated that more than 100,000 commercially available dyes with over 7×10^5 tonnes of dye-stuff produced annually [3]. Methylene blue (MB) is the most commonly used substance for dying 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, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans [4]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on the receiving waters.

In general, dyes are poorly biodegradable or resistant to environmental conditions [5]. Therefore it is necessary to treat the wastewaters or industrial effluents containing dyes before being discharged into the waterways. A number of chemical and physical processes such as flocculation, chemical coagulation, precipitation, ozonation and adsorption have been widely used to treat dye bearing wastewaters [6]. However, the 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 adsorbates and its simplicity of design. However, commercially available activated carbons are still considered expensive. This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications [7,8]. Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products, such as palm seed coat [9], rubber seed coat [10], jute fiber [11], rubber wood sawdust [12], pecan shell [13], corncob [14], bamboo [15], rattan sawdust [16] and oil palm fiber [17].

Coconut husk is the mesocarp of coconut and a coconut is consists of 33–35% of husk. In Malaysia, about 151,000 ha of

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land was being used for coconut plantation in year 2001. It was estimated that 5280 kg of dry husks were become available per hectare per year. At present, coconut husks are used as fuel for coconut processing, as a domestic fuel and as a source of fiber for rope and mats.

To make better use of this cheap and abundant agricultural waste, it is proposed to convert coconut husk into activated carbon. Conversion of coconut husk into activated carbon will serve a double purpose. First, unwanted agricultural waste is converted to useful, value-added adsorbents and second, the use of agricultural by-products represents a potential source of adsorbents which will contribute to solving part of the wastewater treatment problem in Malaysia. However, not many studies have been done on converting coconut husk into activated carbon. Some of the relevant studies found in the literature were preparation of copper impregnated coconut husk carbon for adsorption of arsenic [18], preparation of activated carbon from digested sewage sludge with the additive coconut husk using $ZnCl_2$ as activating agent [19] and production of activated carbon from coconut fiber using CO_2 and phosphoric acid activation for removal of phenol, acid red 27 dye and Cu^{2+} ions [20]. Kavitha and Namasivayam [21] has carried out a study on adsorption of methylene blue using coir pith carbon which was only subjected to carbonization and they reported that the adsorption capacity of the prepared carbon was 5.87 mg/g. The above studies have shown that coconut husk is a feasible starting material which can be used to produce activated carbons applicable in adsorbing various pollutants.

A challenge in activated carbon production is to produce very specific carbons which are suitable for certain applications. The most important characteristic of an activated carbon is its adsorption capacity which is highly influenced by the preparation conditions. In assessing the effect of treatments on quality attributes, the use of an adequate experimental design is particularly important. Response surface methodology (RSM) has been found to be a useful tool to study the interactions of two or more variables [22]. Optimization of experimental conditions using RSM was widely applied in various processes, however, its application in activated carbon production is very rare. Some of the previous studies found in applying RSM in preparation of activated carbons were using precursors such as olive-waste cakes [23], Luscar char [24] and Turkish lignite [22]. As far as known, no study has been done on preparation of activated carbon from coconut husk with physiochemical activation method consisting of KOH treatment and CO_2 gasification, by using RSM approach.

Therefore, the focus of this research was to optimize the preparation conditions of activated carbon with high carbon yield and adsorption capacity on methylene blue (MB) dye. A central composite design (CCD) was selected to study simultaneously the effects of three numerical activated carbon preparation variables: activation temperature, activation time and chemical impregnation (KOH:char) ratio, on the two responses. Empirical models correlating the MB adsorption capacity and the activated carbon yield to the three variables were then developed.

2. Materials and methods

2.1. Preparation of activated carbon

Coconut husk used for preparation of activated carbon was obtained locally. The precursor was first washed to remove dirt from its surface and was then dried overnight at 105 °C. The dried husk was crushed to desired mesh size (1–2 mm) and then carbonized at 700 °C under purified nitrogen (99.995%) flow of 150 cm^3/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. The mixture was then dehydrated in an oven overnight at 105 °C to remove moisture and 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 carbon dioxide (CO_2) and activation was held for different period of time. The activated product was then cooled to room temperature and washed with hot deionized water and hydrochloric acid of 0.1 M until the pH of the washing solution reached 6–7 [17].

2.2. Design of experiments

The parameters for preparing the activated carbon was studied with a standard response surface methodology (RSM) design called a central composite design (CCD). This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, and also to analyze the interaction between the parameters [24]. 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 [25]. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c center runs (six replicates).

In this study, the activated carbons were prepared using physiochemical activation method by varying the preparation variables using the CCD. The variables studied were (i) x_1, activation temperature; (ii) x_2, activation time and (iii) x_3, KOH impregnation ratio. These three variables together with their respective ranges were chosen based on the literature and some preliminary studies. Activation temperature, activation time and chemical impregnation ratio were found to be important parameters affecting the characteristics of the activated carbons produced [19,26–29].

For each categorical variable, a 2^3 full factorial central composite design for the three variables, consisting of 8 factorial points, 6 axial points and 6 replicates at the centre points were employed, indicating that altogether 20 experiments were required, as calculated from Eq. (1) [24]:

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

where N is the total number of experiments required and n is the number of factors.

Table 1
Experimental design matrix and results

Run	Activated carbon preparation variables			Adsorption capacity, Y_1 (mg/g)	Yield, Y_2 (%)
	Activation temperature, x_1 (°C)	Activation time, x_2 (h)	KOH impregnation ratio, x_3		
1	750.00 (−1)	1.00 (−1)	1.00 (−1)	39.68	23.09
2	900.00 (+1)	1.00 (−1)	1.00 (−1)	370.37	17.36
3	750.00 (−1)	3.00 (+1)	1.00 (−1)	107.53	21.74
4	900.00 (+1)	3.00 (+1)	1.00 (−1)	370.37	6.79
5	750.00 (−1)	1.00 (−1)	3.90 (+1)	454.55	16.57
6	900.00 (+1)	1.00 (−1)	3.90 (+1)	588.24	9.54
7	750.00 (−1)	3.00 (+1)	3.90 (+1)	370.37	17.40
8	900.00 (+1)	3.00 (+1)	3.90 (+1)	384.62	6.73
9	698.87 (−1.682)	2.00 (0)	2.45 (0)	68.97	21.90
10	951.13 (+1.682)	2.00 (0)	2.45 (0)	526.32	3.23
11	825.00 (0)	0.32 (−1.682)	2.45 (0)	140.85	21.54
12	825.00 (0)	3.68 (+1.682)	2.45 (0)	357.14	13.25
13	825.00 (0)	2.00 (0)	0.01 (−1.682)	21.55	23.42
14	825.00 (0)	2.00 (0)	4.89 (+1.682)	416.67	18.82
15	825.00 (0)	2.00 (0)	2.45 (0)	303.03	16.66
16	825.00 (0)	2.00 (0)	2.45 (0)	312.50	18.43
17	825.00 (0)	2.00 (0)	2.45 (0)	333.33	18.25
18	825.00 (0)	2.00 (0)	2.45 (0)	357.14	17.87
19	825.00 (0)	2.00 (0)	2.45 (0)	357.14	17.65
20	825.00 (0)	2.00 (0)	2.45 (0)	322.58	18.30

The centre points were used to determine the experimental error and the reproducibility of the data. The independent variables are coded to the (−1, 1) interval where the low and high levels are coded as −1 and +1, respectively. The axial points are located at ($\pm\alpha$, 0, 0), (0, $\pm\alpha$, 0) and (0, 0, $\pm\alpha$) where α is the distance of the axial point from centre and makes the design rotatable. The α value was fixed at 1.682 (rotatable). The complete design matrix of the experiments carried out, together with the results obtained, are shown in Table 1. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The responses were adsorption capacity on methylene blue (Y_1) and activated carbon yield (Y_2). Each response was used to develop an empirical model that correlated the response to the activated carbon preparation variables using a second-degree polynomial equation as given by Eq. (2) [30]:

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

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

2.3. Model fitting and statistical analysis

Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used for regression analysis of the experimental data to fit the equations developed and also for evaluation of the statistical significance of the equations.

2.4. Batch equilibrium studies

Methylene blue (MB) supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate and was not purified prior to use. Deionized water was used to prepare all the solutions and reagents. MB was chosen in this study due to its wide application and known strong adsorption onto solids. MB has a chemical formula of $C_{16}H_{18}N_3SCl$, with molecular weight of 319.86 g/mol, which corresponds to methylene blue hydrochloride with three groups of water. Chemical structure of MB is shown in Appendix A.

Adsorption tests were performed in a set of 43 Erlenmeyer flasks (250 ml) where 100 ml of MB solutions with initial concentrations of 50–500 mg/l were placed in these flasks. Equal mass of 0.1 g of the prepared activated carbon with particle size of 200 μm was added to each flask and kept in an isothermal shaker of 120 rpm at 30 °C for 48 h to reach equilibrium. The pH of the solutions was natural at 6.5. Aqueous samples were taken from the solution and the concentrations were analyzed. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. The concentrations of MB in the supernatant solution before and after adsorption were determined using a double beam UV-Visible spectrophotometer (Shimadzu, Japan) at 668 nm. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (3)$$

where C_o and C_e (mg/l) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (l) and W is the mass of dry adsorbent used (g).

The adsorption data obtained were then fitted to Langmuir isotherm model to determine the adsorption capacity of each activated carbon prepared. Langmuir isotherm model was used to fit the data because from the literature and also the preliminary studies carried out, most of the equilibrium data obtained for adsorption of dyes on activated carbons were found to be best represented by this model [15–17,26,31,32]. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [33]. The linear form of Langmuir isotherm equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \qquad (4)$$

where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_o and b are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

2.5. Activated carbon yield

The carbon yield was calculated based on the following equation:

$$\text{yield}\,(\%) = \frac{w_c}{w_o} \times 100 \qquad (5)$$

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

3. Results and discussion

3.1. Development of regression model equation

Central composite design (CCD) was used to develop correlation between the activated carbon preparation variables to the adsorption capacity and yield. The complete design matrix together with both the responses values obtained from the experimental works are given in Table 1. The maximum monolayer adsorption capacity on MB was found to range from 21.55 to 588.24 mg/g, whereas the carbon yield obtained ranged from 3.23 to 23.42%. Runs 15–20 at the center point were used 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 MB adsorption capacity, the linear and two factor interaction (2FI) models were suggested by the software, however the 2FI model was selected in this case due to the higher order polynomial. For carbon yield in the other hand, the quadratic model was selected as suggested by the software. The final empirical models in terms of coded factors after excluding the insignificant terms for MB adsorption capacity (Y_1) and carbon yield (Y_2) are shown in Eqs. (6) and (7), respectively:

$$Y_1 = 310.15 + 110.61x_1 + 10.53x_2 + 115.28x_3 - 23.41x_1x_2 - 55.70x_1x_3 - 44.46x_2x_3 \qquad (6)$$

$$Y_2 = 17.93 - 5.11x_1 - 2.04x_2 - 1.94x_3 - 2.31x_1^2 - 0.60x_2^2 + 0.72x_3^2 - 1.61x_1x_2 + 0.37x_1x_3 + 1.24x_2x_3 \qquad (7)$$

Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the model developed was evaluated based on the correlation coefficient value. The R value for Eqs. (6) and (7) was 0.922 and 0.978, respectively. Both the R values obtained were relatively high (close to unity), indicating that there was a good agreement between the experimental and the predicted values from the models. The R^2 value for Eq. (6) was 0.851 and 0.957 for Eq. (7). This indicated that 85.1% and 95.7% of the total variation in the adsorption capacity and yield, respectively, was attributed to the experimental variables studied. The standard deviations for the two models were 73.00 and 1.63, respectively, for Eqs. (6) and (7). The closer the R^2 value to unity and the smaller the standard deviation, the better the model will be as it will give predicted value which is closer to the actual value for the response. This indicated that the predicted value for Y_2 would be more accurate and closer to its actual value, compared to Y_1.

The adequacy of the models was further justified through analysis of variance (ANOVA). The ANOVA for the 2FI model for MB adsorption capacity is listed in Table 2. From the ANOVA for response surface 2FI model for MB adsorption capacity, the Model F-value of 12.36 implied that the model was significant. Values of Prob > F less than 0.05 indicated that the model terms were significant. In this case, activation temperature (x_1) and chemical impregnation ratio (x_3) were significant model terms whereas activation time (x_2) and the interaction terms (x_1x_2, x_1x_3, x_2x_3) were all insignificant to the response.

The ANOVA for the quadratic model for activated carbon yield is listed in Table 3. From the ANOVA for response surface

Table 2
Analysis of variance (ANOVA) for response surface 2FI model for adsorption capacity

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
Model	3.95×10^5	6	65852.25	12.36	0.0001
x_1	1.67×10^5	1	1.67×10^5	31.36	<0.0001
x_2	1514.25	1	1514.25	0.28	0.6030
x_3	1.82×10^5	1	1.82×10^5	34.06	<0.0001
x_1x_2	4384.69	1	4384.69	0.82	0.3809
x_1x_3	24818.81	1	24818.81	4.66	0.0502
x_2x_3	15810.87	1	15810.87	2.97	0.1087
Residual	69274.33	13	5328.79	–	–

Table 3
Analysis of variance (ANOVA) for response surface quadratic model for yield

Source	Sum of squares	Degree of freedom (DF)	Mean square	F-Value	Prob > F
Model	591.69	9	65.74	24.75	<0.0001
x_1	356.53	1	356.53	134.23	<0.0001
x_2	56.76	1	56.76	21.37	0.0009
x_3	51.33	1	51.33	19.33	0.0013
x_1^2	76.88	1	76.88	28.94	0.0003
x_2^2	5.22	1	5.22	1.97	0.1911
x_3^2	7.37	1	7.37	2.77	0.1268
x_1x_2	20.67	1	20.67	7.78	0.0191
x_1x_3	1.11	1	1.11	0.42	0.5325
x_2x_3	12.35	1	12.35	4.65	0.0565
Residual	26.56	10	2.66	–	–

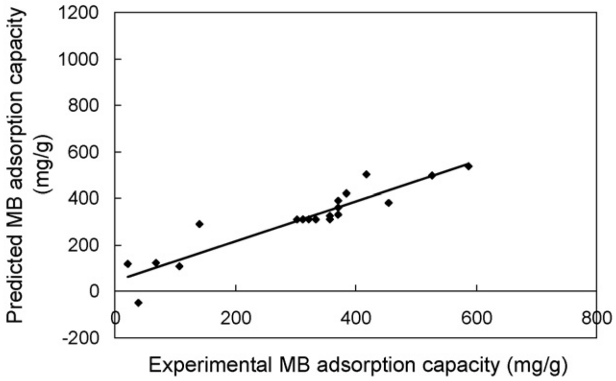

Fig. 1. Predicted vs. experimental adsorption capacity on methylene blue.

quadratic model for yield, the Model F-value of 24.75 implied that the model was significant as well. In this case, x_1, x_2, x_3, x_1^2 and x_1x_2 were significant model terms. From the statistical results obtained, it was shown that the above models were adequate to predict the adsorption capacity and the yield within the range of variables studied. Figs. 1 and 2 show the predicted values versus the experimental values for adsorption capacity and yield, respectively. As can be seen, the predicted values obtained were quite close to the experimental values, indicating that the models developed were successful in capturing the correlation between the activated carbon preparation variables to the adsorption capacity and yield.

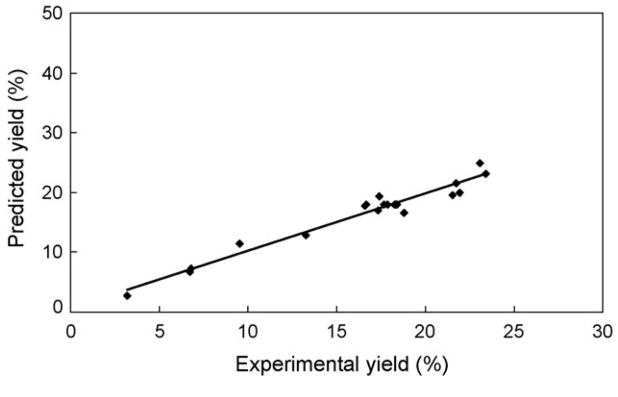

Fig. 2. Predicted vs. experimental activated carbon yield.

3.2. Adsorption capacity on methylene blue

Based on the F values (Table 2), both activation temperature and chemical impregnation ratio were found to have significant effects on the adsorption capacity whereas activation time showed the least effect on adsorption capacity of the activated carbon prepared. The interaction effects between x_1 and x_3, as well as x_2 and x_3 were moderate. Fig. 3 shows the three-dimensional response surfaces which was constructed to show the effects of the activated carbon preparation variables (activation temperature and chemical impregnation ratio) on the MB adsorption capacity (Y_1). The effects of activation temperature and chemical impregnation ratio were studied as they were found to have significant effects on the response. The activation time was fixed at zero level. As can be seen from Fig. 3, MB adsorption capacity increases with increase in activation temperature and chemical impregnation ratio. The highest adsorption capacity value was obtained when both the variables were at the miximum point within the range studied.

The results obtained were in agreement with the works by Sudaryanto et al. [27] which reported that activation time gave

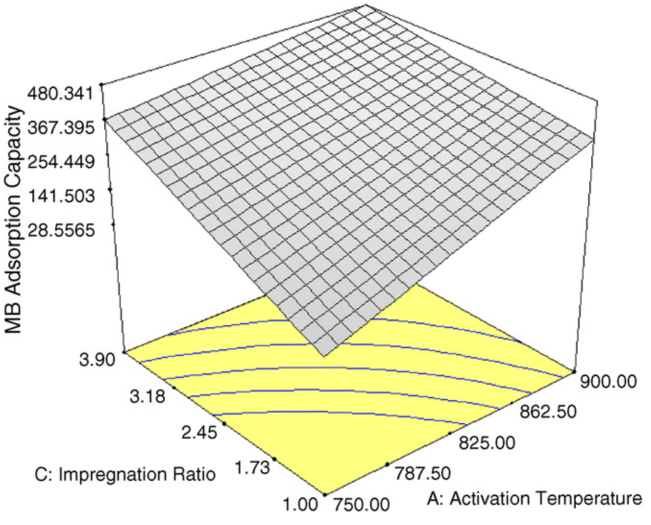

Fig. 3. Three-dimensional response surface plot of adsorption capacity on methylene blue (effect of activation temperature and chemical impregnation ratio, $t = 2$ h).

no significant effect on the pore structure of activated carbon produced from cassava peel, and the pore characteristics changed significantly with the activation temperature and also the KOH impregnation ratio. Şentorun-Shalaby et al. [28] also found that activation time did not show much effect on the surface area obtained for activated carbons prepared from apricot stones using steam activation. However, in this work, all the three variables studied were found to have synergistic effects on the adsorption capacity of the activated carbons prepared. This was expected as the progressive temperature rise and longer activation time would increase the C-KOH and C-CO_2 reaction rates, resulting in increasing devolatilization which further developed the rudimentary pore structure in the char and also enhanced the existing pores and created new porosities. The increase in activation temperature and time entailed an opening and enlargement of the pores, which enhanced the adsorption of MB [23,26,34]. Besides, the increase in temperature also caused the CO_2 and the surface metal complex to further gasify the carbon, leading to widening of micropore to mesopore [29]. As chemical impregnation ratio increased, the catalytic oxidation also caused the widening of micropores to mesopores, therefore increasing the MB adsorption capacity as well [35]. At high KOH impregnation ratio, the microporosity development is mostly due to the intercalation of potassium metal in the carbon structure [27]. Indeed, MB 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 [36]. This meant that when more mesopores were developed, more MB molecules could be adsorbed by the activated carbons, therefore enhancing the adsorption capacity of the activated carbons.

3.3. *Activated carbon yield*

For carbon yield (Y_2) in the other hand, activation temperature was found to have the greatest effect on it, with the highest *F* value (Table 3) of 134.23, while activation time and chemical impregnation ratio showed almost similar effects on the response, which were less significant compared to activation temperature. The quadratic effect of activation temperature on yield was also larger compared to activation time and chemical impregnation ratio. However, the interaction effects between the variables were less significant. The effects of activation temperature, activation time and chemical impregnation ratio on yield were studied as they were found to have significant effects on the response. Fig. 4(a) and (b) shows the three-dimensional response surfaces which were constructed to show the effects of the activated carbon preparation variables on the carbon yield (Y_2). Fig. 4(a) shows the effect of activation temperature and activation time on yield (KOH impregnation ratio was fixed at zero level) whereas Fig. 4(b) shows the effect of activation temperature and chemical impregnation ratio on the yield (activation time was fixed at zero level). The carbon yield was found to decrease with increasing activation temperature, activation time and chemical impregnation ratio. The highest yield was obtained when all the three variables were at the minimum point within the range studied.

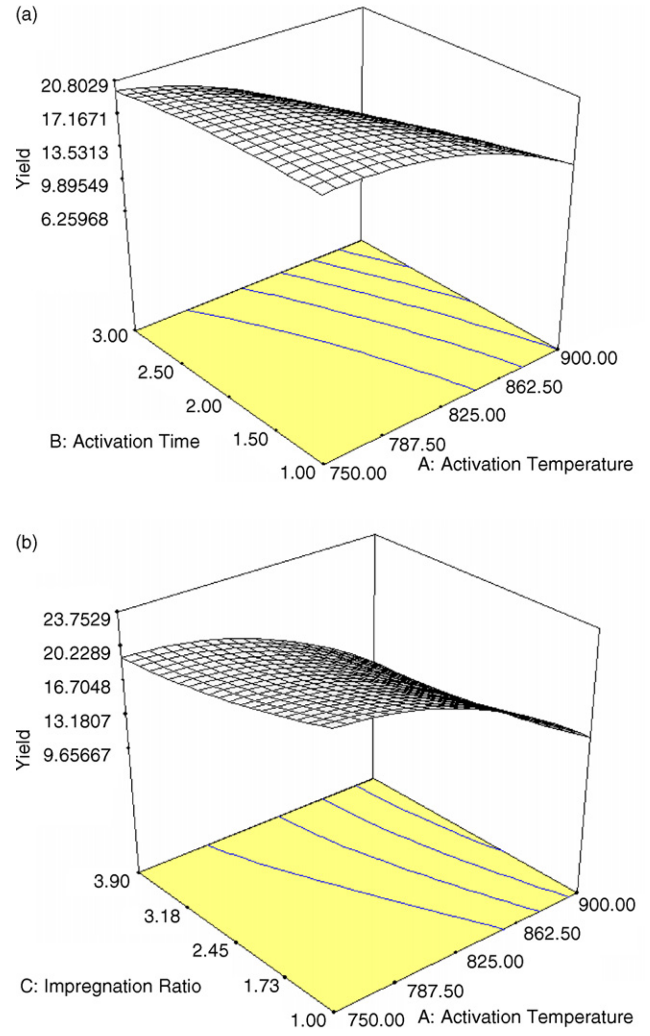

Fig. 4. (a) Three-dimensional response surface plot of activated carbon yield (effect of activation temperature and activation time, chemical impregnation ratio = 2.45). (b) Three-dimensional response surface plot of activated carbon yield (effect of activation temperature and chemical impregnation ratio, $t = 2$ h).

This result was also in agreement with the work done by Sudaryanto et al. [27] where activation temperature was found to play an important role on the yield of activated carbon whereas activation time did not show much effect on the carbon yield. The increase in temperature would release increasing volatiles as a result of intensifying dehydration and elimination reaction and also increased the C-KOH and C-CO_2 reaction rate, thereby resulting in decreasing yield [34,35]. Indeed, the increase in activation temperature quickens the gasification reactions of carbon and therefore, the attack of the amorphous components which obstruct the pores causes a decrease in the carbon yield [23]. Şentorun-Shalaby et al. [28] observed that at higher activation temperature, activation of apricot stones became more extensive and resulted in a lower solid yield with a more widened porous stucture. The yield for activated carbon prepared from fir wood was also found to decrease gradually with increase in duration of CO_2 gasification [29]. The yield was strongly affected by the chemical impregnation ratio

Table 4
Model validation

Activation temperature, x_1 (°C)	Activation time, x_2 (h)	KOH impregnation ratio, x_3	MB adsorption capacity (mg/g)		Carbon yield (%)	
			Predicted	Experimental	Predicted	Experimental
816	1	3.9	449.78	434.78	17.25	15.50
811	1	3.9	445.36	416.67	17.38	19.20

where increasing impregnation ratio decreased the yield and increased the carbon burn-off. This was because when higher impregnation ratio was used, the weight losses were due to increasing release of volatile products as a result of intensifying dehydration and elimination reactions [35]. KOH would promote the oxidation process, therefore with high impregnation ratio, the gasification of surface carbon atoms was the predominant reaction, leading to increase in the weight loss of carbon [27].

3.4. Process optimization

In the production of commercial activated carbons, relatively high product yields are expected and the most important property of activated carbon is its adsorption capacity. Therefore, the activated carbon produced should have a high carbon yield and also a high adsorption capacity for economical viability. However, to optimize both these responses under the same condition is difficult because the interest region of factors are different. When Y_1 increases, Y_2 will decrease and vice versa. Therefore, in order to compromise between these two responses, the function of desirability was applied using Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA). The two experimental conditions with the highest desirability were selected to be verified. The activated carbons were prepared under the experimental conditions given in Table 4, together with the predicted and experimental values for adsorption capacity and yield. It was observed that the experimental values obtained were in good agreement with the values calculated from the models. The optimal activated carbon was obtained using 816 °C activation temperature, 1 h activation time and 3.9 KOH impregnation ratio, resulting in 15.5% of carbon yield and 434.78 mg/g of adsorption capacity on MB. This result agrees with the work done by Baçaoui et al. [23] where the optimal activated carbon from olive-waste cakes was obtained using 68 min activation time and 822 °C activation temperature which resulted in 15.8% of carbon yield and 426 mg/g of adsorption capacity on MB.

Table 5 lists the comparison of maximum monolayer adsorption capacity of MB on various adsorbents. The activated carbon prepared in this work had a relatively large adsorption capacity on MB compared to some other adsorbents reported in the literature, including commercial activated carbon, F300 which was reported to have adsorption capacity of 240.00 mg/g. This indicated that the preparation method and operating conditions applied in this study could be used to produce activated carbon with high adsorption performance on MB dye from coconut husk.

3.5. Surface morphology of the optimally prepared activated carbon

Fig. 5(a) and (b) respectively shows the scanning electron microscope (SEM) images of the precursor (raw coconut husk) and the activated carbon obtained under the optimum preparation conditions. As can be seen from Fig. 5(a), there was very little pores available on the surface of the precursor. However, after KOH treatment and CO_2 gasification under the optimum preparation conditions at 816 °C activation temperature, 1 h activation time and 3.9 KOH impregnation ratio, many large pores in a honeycomb shape were developed on the surface of the activated carbon, as shown in Fig. 5(b). This shows that KOH and CO_2 were effective in creating well-developed pores on the surfaces of the precursor, hence leading to the activated carbon with large surface area and porous structure which had high adsorption capacity on MB. Similar observations were reported by other researchers in their works of preparing activated carbons from jute and coconut fibers [20], apricot stones [28] and pistachio-nut shells [34].

Table 5
Comparison of the maximum monolayer adsorption of MB on various adsorbents

Adsorbents	Maximum monolayer adsorption capacity (mg/g)	References
Coconut husk-based activated carbon	434.78	This work
Bamboo dust-based activated carbon	143.20	[31]
Groundnut shell-based activated carbon	164.90	[31]
Jute fiber-based activated carbon	225.64	[11]
Olive-seed waste residue-based activated carbon	190.00–263.00	[26]
Rattan sawdust-based activated carbon	294.14	[16]
Oil palm fiber-based activated carbon	277.78	[17]
Filtrasorb F300[a]	240.00	[26]

[a] Commercial activated carbon.

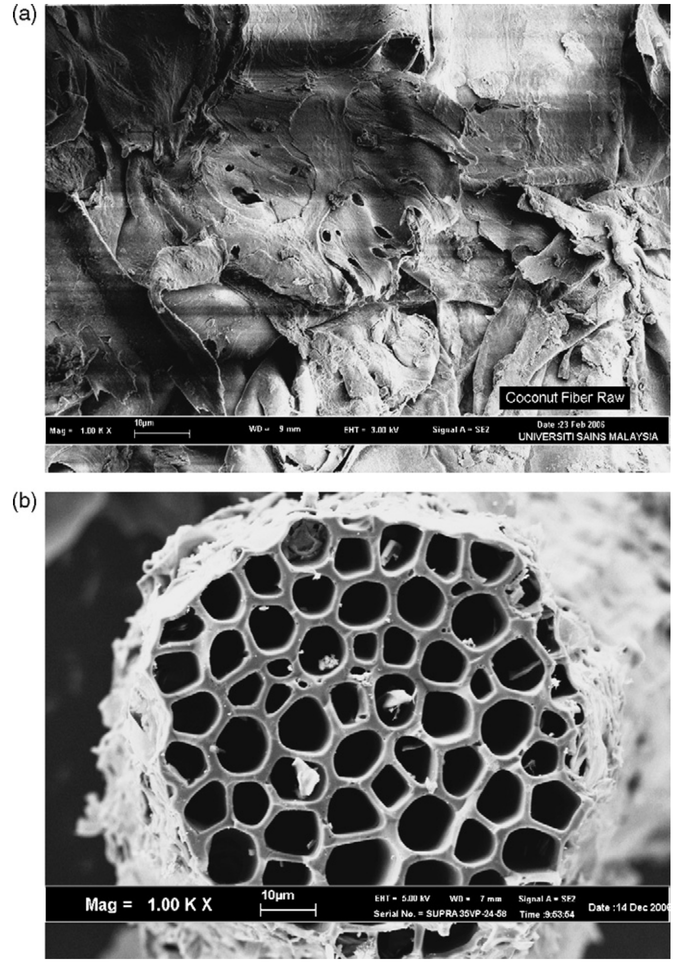

Fig. 5. (a) SEM image of raw coconut husk (1000×). (b) SEM image of coconut husk-based activated carbon prepared under optimum conditions (1000×).

4. Conclusions

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 (KOH:char) ratio, on the adsorption capacity on methylene blue dye and carbon yield. A 2FI model and a quadratic model were developed to correlate the preparation variables to the adsorption capacity and yield, respectively. Through analysis of the response surfaces derived from the models, activation temperature and KOH impregnation ratio were found to have significant effects on methylene blue adsorption capacity, compared to activation time whereas activation temperature showed the most significant effect on activated carbon yield. Process optimization was carried out and the experimental values obtained for the adsorption capacity and yield were found to agree satisfactory with the predicted values. The activated carbon prepared under the optimum conditions were found to have well-developed pores on its surface. Coconut husk-based activated carbon was shown to be a promising adsorbent for removal of methylene blue from aqueous solutions.

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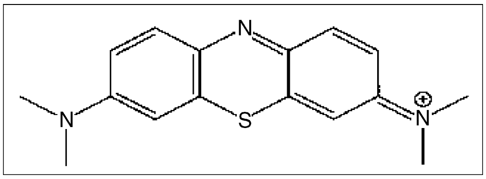
Appendix A. Chemical structure of methylene blue dye



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