

Optimization of basic dye removal by oil palm fibre-based activated carbon using response surface methodology

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Abstract

Oil palm fibre was used to prepare activated carbon using physiochemical activation method which consisted of potassium hydroxide (KOH) treatment and carbon dioxide (CO₂) gasification. The effects of three preparation variables: the activation temperature, activation time and chemical impregnation (KOH:char) ratio on methylene blue (MB) uptake from aqueous solutions and activated carbon yield were investigated. Based on the central composite design (CCD), a quadratic model and a two factor interaction (2FI) model were respectively developed to correlate the preparation variables to the MB uptake and carbon yield. From the analysis of variance (ANOVA), the significant factors on each experimental design response were identified. The optimum activated carbon prepared from oil palm fibre was obtained by using activation temperature of 862 °C, activation time of 1 h and chemical impregnation ratio of 3.1. The optimum activated carbon showed MB uptake of 203.83 mg/g and activated carbon yield of 16.50%. The equilibrium data for adsorption of MB on the optimum activated carbon were well represented by the Langmuir isotherm, giving maximum monolayer adsorption capacity as high as 400 mg/g at 30 °C.

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Keywords: Oil palm fibre activated carbon; Methylene blue; Central composite design; Optimization; Langmuir isotherm

1. Introduction

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 dyeing cotton, wood and silk. MB can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, diarrhea, gastritis, mental confusion and methemoglobinemia [4,5]. Thus, the removal of MB from industrial effluents has become one of the major environmental concerns.

Removal methods of dyes in industrial effluents may be traditionally divided into three main categories: physical, chemical and biological processes. Physical adsorption is generally considered to be the most efficient method for quickly lowering the concentration of dissolved dyes in an effluent [6]. Commercial activated carbon is the preferred adsorbent for dye removal, but its widespread use is restricted due to its high cost [7]. This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications [8]. Therefore, in recent years, this has prompted a growing research interest in the use of alternative non-conventional waste materials from industry and agriculture as the starting materials to produce activated carbons, such as waste apricot [9], rubber seed coat [10], jute fiber [11], coconut husk [12–14], plum kernel [15], apricot shell [16], rice straw [17,18], corncob [19], bamboo [20], rattan sawdust [21], sunflower seed hull [22], coconut shell [23], rubberwood sawdust [24] and *Ceiba pentandra* hulls [25].

Malaysia, the world's leading palm oil producing country has produced 11.9 million tonnes of palm-pressed mesocarp fibre (*Elaeis guineensis*) in 2005 [26]. Traditionally, the fibre is mixed with kernel shell and being utilized as solid fuel to

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generate electricity for the mill. The excess fiber is then transported to the plantation for field mulching. To make better use of this cheap and abundant waste, it is proposed to make it into activated carbon. Conversion of oil palm fibre to 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, there are limited studies reported on the utilization of oil palm fibre to produce activated carbon. In our previous work [27], oil palm fibre has been shown to be a feasible precursor for preparing activated carbon. Some other relevant studies found in the literature were utilization of sulphuric acid and heat-treated oil palm fibre for adsorption of Cr (VI) [28], preparation and characterization of char from oil palm fibre [29] and sorption of copper by dye-treated oil palm fibres [30]. The most important characteristic of an activated carbon is its adsorption performance which is highly influenced by the preparation conditions. Experimental design technique is a very useful tool for this purpose as it provides statistical models which help in understanding the interactions among the parameters that have been optimized [31]. Response surface methodology (RSM) has been found to be a useful tool to study the interactions of two or more variables [32]. 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 [33], Luscar char [34], Turkish lignite [32] and coconut husk [12,13]. As far as known, no study has been done on preparation of activated carbon from oil palm fibre by applying RSM approach.

Therefore, the focus of this research was to carry out a statistical optimization to determine the optimum preparation conditions for activated carbon from oil palm fibre, which gave high activated carbon yield and high MB uptake from aqueous solutions. The effects of three numerical activated carbon preparation variables: activation temperature, activation time and chemical impregnation (KOH:char) ratio, were studied simultaneously on the two responses using a central composite design (CCD). Empirical models correlating the MB uptake and the activated carbon yield to the three variables were then developed.

2. Materials and methods

2.1. Preparation of activated carbon

Oil palm fibre used for preparation of activated carbon was obtained from United Palm Oil Mill, Nibong Tebal, Malaysia. The procedure used to prepare the activated carbon was referred to our previous work [27]. The pre-treated precursor was loaded in a stainless steel vertical tubular reactor placed in a tube furnace. Carbonization of the precursor was carried out by ramping the temperature from room temperature to 700 °C with heating rate of 10 °C/min and hold for 2 h. Throughout the carbonization process, purified nitrogen (99.995%) was flown through at

flow rate of 150 cm³/min. The char produced was mixed with KOH pellets with different KOH:char impregnation ratio (IR), calculated using the following equation:

$$IR = \frac{w_{\text{KOH}}}{w_{\text{char}}} \quad (1)$$

where w_{KOH} is the dry weight (g) of KOH pellets and w_{char} is the dry weight (g) of char. Deionized water was then added to dissolve all the KOH pellets.

The mixture was then dehydrated in an oven overnight at 105 °C to remove moisture and was then activated under the same condition as carbonization, but to a different final temperature. Once the final temperature was reached, the nitrogen gas flow was switched to CO₂ and activation was held for different period of time. The activated product was then cooled to room temperature under nitrogen flow and then washed with hot deionized water and 0.1 M hydrochloric acid until the pH of the washing solution reached 6–7.

2.2. Design of experiments

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions [31]. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables [33]. A standard RSM design called a 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 [34]. Generally, the CCD consists of a 2ⁿ factorial runs with 2n axial runs and n_c center runs (six replicates).

The dependant variables selected for this study were (i) x_1 , CO₂ activation temperature; (ii) x_2 , CO₂ activation time and (iii) x_3 , KOH:char impregnation ratio. A statistical optimization was conducted by using CCD. For each categorical variable, a 2³ full factorial CCD for the three variables, consisting of 8 factorial points, 6 axial points and 6 replicates at the center points were employed, indicating that altogether 20 experiments were required, as calculated from the following equation [34]:

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

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

The center points are 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 (± α, 0, 0), (0, ±α, 0) and (0, 0, ±α) where α is the distance of the axial point from center and makes the design rotatable. In this study, the α value was fixed at 1.682 (rotatable). Table 1 shows the complete design matrix of the experiments carried out, together with the results obtained. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The two responses were MB uptake

(Y_1) and activated carbon yield (Y_2). Each response was used to develop an empirical model which correlated the response to the three activated carbon preparation variables using a second-degree polynomial equation as given by the following equation [35]:

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \left(\sum_{i=1}^n b_{ii} x_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (3)$$

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

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

2.4. Adsorption 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 373.9 g/mol, which corresponds to MB hydrochloride with three groups of water.

Batch adsorption was performed in 20 sets of 250 ml Erlenmeyer flasks where 100 ml of MB solutions with initial concentration of 200 mg/l was placed in each flask. The pH of the solution was natural without any pH adjustment. 0.1 g of each of the prepared activated carbon, with particle size of 200 μ m, was added to each flask and kept in an isothermal shaker of 120 rpm at 30 °C until equilibrium was attained. The equilibration time was taken as the time when the MB concentration was constant. All aqueous 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 solutions before and after adsorption were determined using a double beam UV–vis spectrophotometer (UV-1601 Shimadzu, Japan) at its maximum wavelength of 668 nm. The MB uptake at equilibrium, q_e (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (4)$$

where C_0 and C_e (mg/l) are the liquid-phase concentrations of MB at initial and at equilibrium, respectively. V is the volume of the solution (l) and W is the mass of dry adsorbent used (g).

2.5. Activated carbon yield

The activated carbon yield was calculated based on the following equation:

$$\text{Yield (\%)} = \frac{w_c}{w_0} \times 100 \quad (5)$$

where w_c and w_0 are the dry weight of final activated carbon (g) and dry weight of precursor (g), respectively.

Table 1
Experimental design matrix and results

Run	Activated carbon preparation variables			MB uptake, Y_1 (mg/g)	Carbon 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)	22.64	21.28
2	900.00 (+1)	1.00 (−1)	1.00 (−1)	131.96	17.08
3	750.00 (−1)	3.00 (+1)	1.00 (−1)	24.67	20.38
4	900.00 (+1)	3.00 (+1)	1.00 (−1)	209.94	8.47
5	750.00 (−1)	1.00 (−1)	3.90 (+1)	195.28	15.40
6	900.00 (+1)	1.00 (−1)	3.90 (+1)	213.62	15.00
7	750.00 (−1)	3.00 (+1)	3.90 (+1)	180.44	15.20
8	900.00 (+1)	3.00 (+1)	3.90 (+1)	213.81	7.27
9	698.87 (−1.682)	2.00 (0)	2.45 (0)	12.90	20.66
10	951.13 (+1.682)	2.00 (0)	2.45 (0)	213.76	13.42
11	825.00 (0)	0.32 (−1.682)	2.45 (0)	130.65	21.42
12	825.00 (0)	3.68 (+1.682)	2.45 (0)	204.56	15.78
13	825.00 (0)	2.00 (0)	0.01 (−1.682)	0.07	22.49
14	825.00 (0)	2.00 (0)	4.89 (+1.682)	204.64	15.43
15	825.00 (0)	2.00 (0)	2.45 (0)	132.12	17.57
16	825.00 (0)	2.00 (0)	2.45 (0)	202.35	16.49
17	825.00 (0)	2.00 (0)	2.45 (0)	202.49	16.78
18	825.00 (0)	2.00 (0)	2.45 (0)	144.55	17.00
19	825.00 (0)	2.00 (0)	2.45 (0)	201.79	16.60
20	825.00 (0)	2.00 (0)	2.45 (0)	202.70	16.85

Table 2
Analysis of variance (ANOVA) for response surface quadratic model for MB uptake

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model	1.00×10^5	9	11122.49	11.44	0.0004
x_1	34268.35	1	34268.35	35.26	0.0001
x_2	2633.89	1	2633.89	2.71	0.1307
x_3	42068.41	1	42068.41	43.28	< 0.0001
x_1^2	5068.12	1	5068.12	5.21	0.0455
x_2^2	2.75	1	2.75	0.0028	0.9586
x_3^2	7382.00	1	7382.00	7.60	0.0203
x_1x_2	1034.40	1	1034.40	1.06	0.3266
x_1x_3	7374.37	1	7374.37	7.59	0.0203
x_2x_3	1119.87	1	1119.87	1.15	0.3083
Residual	9719.48	10	971.95	–	–

3. Results and discussion

3.1. Development of regression model equation

A polynomial regression equation was developed by using CCD to analyze the factor interactions by identifying the significant factors contributing to the regression model. The complete design matrix together with both the response values obtained from the experimental works are given in Table 1. Runs 15–20 at the center point were used to determine the experimental error. MB uptake was found to range from 0.07 to 213.81 mg/g, whereas the activated carbon yield obtained ranged from 7.27 to 22.49%.

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 uptake, the quadratic model was selected as suggested by the software. For carbon yield, the two factor interaction (2FI) model was found to best fit the experimental data. The final empirical models in terms of coded factors after excluding the insignificant terms for MB uptake (Y_1) and carbon yield (Y_2) are shown in Eqs. (6) and (7), respectively.

$$Y_1 = 180.21 + 50.09x_1 + 13.89x_2 + 55.50x_3 - 18.75x_1^2 + 0.44x_2^2 - 22.63x_3^2 + 11.37x_1x_2 - 30.36x_1x_3 - 11.83x_2x_3 \quad (6)$$

$$Y_2 = 16.53 - 2.68x_1 - 1.97x_2 - 1.92x_3 - 1.90x_1x_2 + 0.97x_1x_3 + 0.20x_2x_3 \quad (7)$$

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^2 value for Eq. (6) was 0.912 and 0.842 for Eq. (7). This indicated that 91.2 and 84.2% of the total variation in the MB uptake and carbon yield, respectively, was attributed to the experimental variables studied. The closer the R^2 value to unity, the better the model will be as it will give predicted values which are closer to the actual values for the response. The R^2 of 0.912 for Eq. (6) was considered relatively high, indicating that there was a good agreement between the experimental and the predicted MB uptake from this model. However, the R^2 of 0.842 for Eq. (7) was considered as moderate to validate the fit, which might lead to larger variation in the carbon yield predicted from the model.

Analysis of variance (ANOVA) was further carried out to justify the adequacy of the models. The ANOVA for the quadratic model for MB uptake is listed in Table 2. From the ANOVA for response surface quadratic model for MB uptake, the Model F -value of 11.44 and Prob > F of 0.0004 implied that the model was significant. For the model terms, values of Prob > F less than 0.05 indicated that the model terms were significant. In this case, activation temperature (x_1), chemical impregnation ratio (x_3), x_1^2 , x_3^2 , x_1x_3 were significant model terms whereas activation time (x_2), x_2^2 , x_1x_2 and x_2x_3 were all insignificant to the response.

The ANOVA for the 2FI model for activated carbon yield is listed in Table 3. From the ANOVA for response surface 2FI model for carbon yield, the Model F -value of 11.56 and Prob > F of 0.0001 implied that the model was significant as well. In this

Table 3
Analysis of variance (ANOVA) for response surface 2FI model for activated carbon yield

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model	238.48	6	39.75	11.56	0.0001
x_1	98.17	1	98.17	28.54	0.0001
x_2	53.08	1	53.08	15.43	0.0017
x_3	50.32	1	50.32	14.63	0.0021
x_1x_2	29.03	1	29.03	8.44	0.0123
x_1x_3	7.57	1	7.57	2.20	0.1619
x_2x_3	0.31	1	0.31	0.09	0.7680
Residual	44.71	13	3.44	–	–

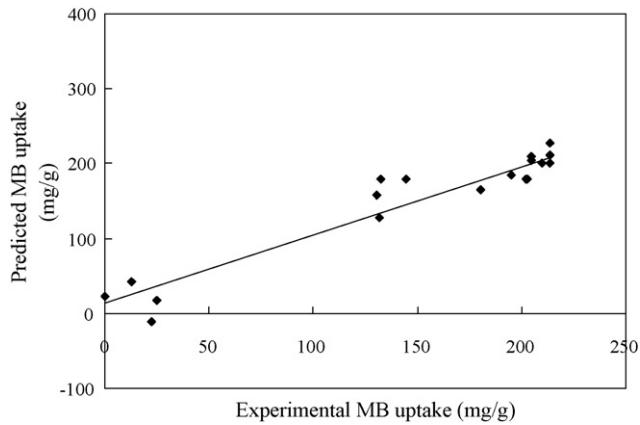


Fig. 1. Predicted vs. experimental methylene blue uptake.

case, x_1 , x_2 , x_3 and x_1x_2 were significant model terms whereas x_1x_3 and x_2x_3 were insignificant to the response. From the statistical results obtained, it was shown that the above models were adequate to predict the MB uptake and the carbon yield within the range of variables studied. Figs. 1 and 2 show the predicted values versus the experimental values for MB uptake and carbon 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 two responses.

3.2. MB uptake

Based on the ANOVA results obtained, both activation temperature and chemical impregnation ratio were found to have significant effects on the MB uptake, with chemical impregnation ratio imposing the greatest effect on MB uptake of the activated carbons prepared. Activation time on the other hand imposed the least effect on the response. The quadratic effects of activation temperature and chemical impregnation ratio as well as the interaction effects between x_1 and x_3 were considered moderate. Fig. 3 shows the three-dimensional response surfaces which were constructed to show the most important two variables (activation temperature and chemical impregnation ratio) on the MB uptake (Y_1). The activation time was fixed at zero

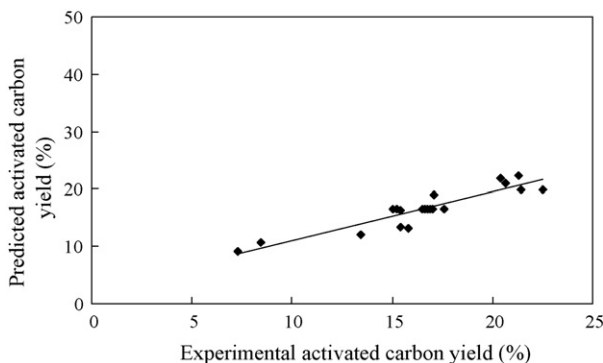


Fig. 2. Predicted vs. experimental activated carbon yield.

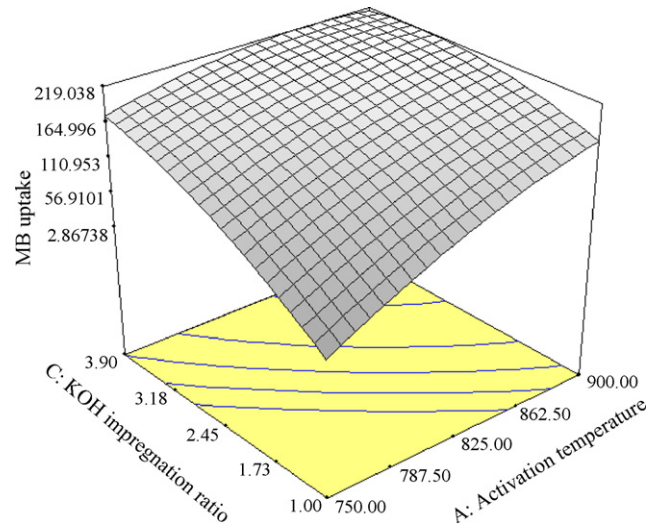


Fig. 3. Three-dimensional response surface plot of methylene blue uptake (effect of activation temperature and chemical impregnation ratio, $t = 2$ h).

level ($t = 2$ h). As can be seen from Fig. 3, MB uptake increases with increase in activation temperature and chemical impregnation ratio. The highest MB uptake was obtained when both the variables were at the maximum point within the range studied.

The results obtained were in agreement with our previous works on preparation of activated carbons from coconut husk for adsorption of MB and 2,4,6-trichlorophenol [12,13]. Sudaryanto et al. [36] also reported that activation time gave 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. [37] 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, Yang and Lua [38] observed that activation temperature and dwell time were important parameters that affected the characteristics of the activated carbons prepared from pistachio-nut shells by CO_2 activation. In this work, all the three variables studied were found to have synergistic effects on the MB uptake 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 [33,38–40]. 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 [41].

As chemical impregnation ratio increased, the catalytic oxidation also caused the widening of micropores to mesopores, therefore increasing the MB adsorption capacity as well [42]. At high KOH impregnation ratio, the microporosity development is mostly due to the intercalation of potassium metal in the carbon structure [36]. 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 [43]. 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) on the other hand, activation temperature was found to have the greatest effect on it, while activation time and chemical impregnation ratio showed almost similar effects on the response, which were less significant compared to activation temperature. 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).

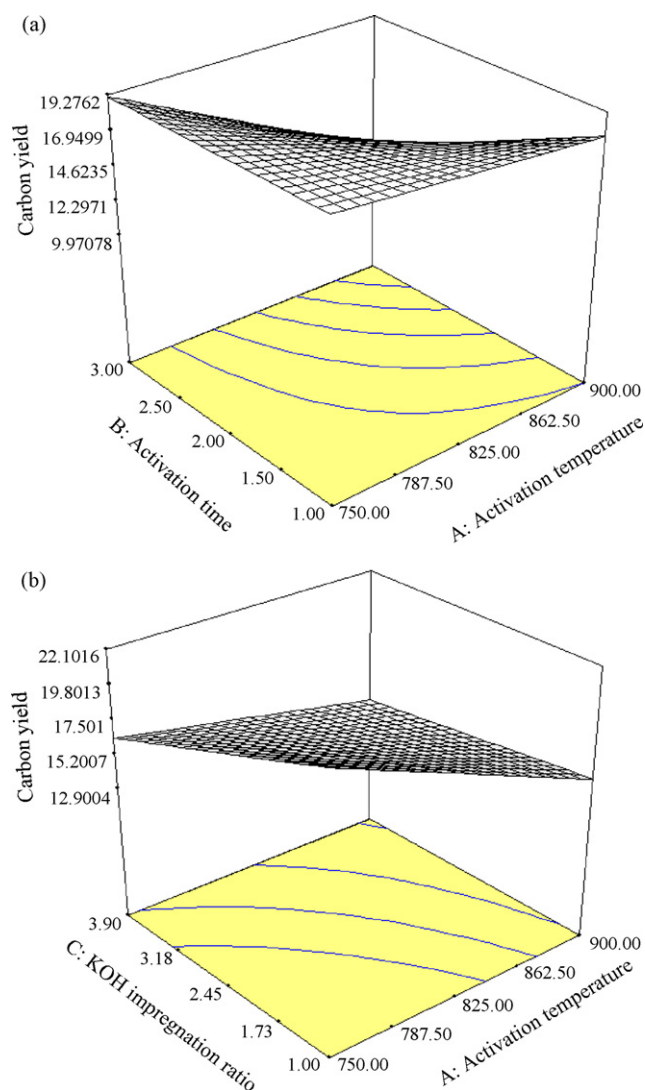


Fig. 4. (a) Three-dimensional response surface plot of activated carbon yield (effect of activation temperature and activation time, chemical impregnation ratio = 2.45). (b) Three-dimensional response surface plot of activated carbon yield (effect of activation temperature and chemical impregnation ratio,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

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.

Similar trend was observed in our previous works on preparation of activated carbons from coconut husk [12,13]. Sudaryanto et al. [36] found that activation temperature played 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–CO₂ reaction rate, thereby resulting in a higher carbon burnoff and decreasing yield [38,40,42]. 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 [33]. Şentorun-Shalaby et al. [37] 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 structure. The yield for activated carbon prepared from fir wood was also found to decrease gradually with increase in duration of CO₂ gasification [41]. The yield was strongly affected by the chemical impregnation ratio where increasing impregnation ratio decreased the yield and increased the carbon burnoff. 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 [42]. 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 [36].

3.4. Process optimization

In the production of commercial activated carbons, relatively high product yields are expected for economical feasibility and the most important property of activated carbon is its adsorption performance. Therefore, the activated carbon produced should have a high carbon yield and also a high adsorption MB uptake 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 experimental conditions with the highest desirability were selected to be verified. The activated carbon was prepared under the experimental conditions given in Table 4, together with the predicted and experimental values for MB uptake and carbon yield. The optimum activated carbon prepared from oil palm fibre was obtained by using acti-

Table 4
Model validation

CO ₂ activation temperature, x_1 (°C)	862
CO ₂ activation time, x_2 (h)	1
KOH impregnation ratio, x_3	3.1
MB uptake (mg/g)	
Predicted	200.06
Experimental	203.83
Activated carbon yield (%)	
Predicted	17.39
Experimental	16.50

vation temperature of 862 °C, activation time of 1 h and chemical impregnation ratio of 3.1. The optimum activated carbon showed MB uptake of 203.83 mg/g and activated carbon yield of 16.50%. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors between the predicted and the actual values, which were only 1.85 and 5.39%, respectively for MB uptake and carbon yield.

3.5. Adsorption isotherm of MB on activated carbon prepared under optimum conditions

The MB adsorption capacity of the activated carbon prepared under optimum conditions were determined by performing adsorption tests in a set of 250 ml Erlenmeyer flasks where 100 ml of MB solutions with initial concentrations of 50–500 mg/l were placed in these flasks. Other operating parameters such as activated carbon dosage, solution temperature and agitation speed were similar as the adsorption studies carried out for determining the MB uptake. The concentrations of the MB solutions were similarly measured and the amount of adsorption at equilibrium, q_e (mg/g) was calculated using Eq. (4). The adsorption data obtained were then fitted to the Langmuir isotherm model to determine the MB adsorption capacity of the activated carbon prepared. The Langmuir isotherm model was used to fit the data based on our previous findings that the Langmuir isotherm was the best model to describe the adsorption equilibrium of MB on oil palm fibre-based activated carbon [27]. Besides, from the literatures, most of the equilibrium data obtained for adsorption of dyes on activated carbons were found to be best represented by the Langmuir model [20,21,39,44,45].

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 [46]. The linear form of Langmuir isotherm equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (8)$$

where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 (mg/g) is the maximum amount of the adsorbate per unit weight of the adsorbent to form a complete monolayer on the surface whereas b (l/mg) is Langmuir con-

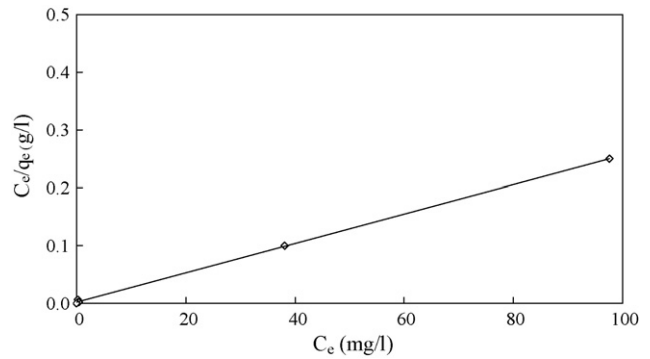


Fig. 5. Langmuir adsorption isotherm of MB on oil palm fibre-based activated carbon at 30 °C.

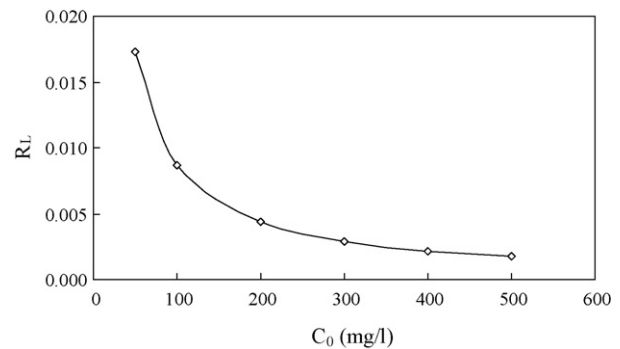


Fig. 6. Effect of MB initial concentration on separation factor R_L .

stant related to the affinity of the binding sites. When C_e/q_e was plotted against C_e , a straight line with slope of $1/Q_0$ was obtained, as shown in Fig. 5. The value obtained for Q_0 and b was 400 mg/g and 1.136 l/mg, respectively. The correlation coefficient, R^2 value of 0.9997 indicated that the adsorption data of MB on the activated carbon prepared were well represented by the Langmuir isotherm.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called separation factor or equilibrium parameter, R_L , defined as [46]:

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

The parameter R_L indicates the shape of isotherm as follows:

Value of R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Fig. 6 represents the calculated R_L values versus the MB initial concentration at 30 °C. All the R_L values were between 0 and 1, indicating that the adsorption of MB on the prepared activated carbon was favourable at the conditions being studied. However, as the MB initial concentrations increased, the R_L values decreased. This indicated that adsorption was more favourable at higher initial concentration.

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

Adsorbents	Maximum monolayer adsorption capacity, Q_0 (mg/g)	References
Oil palm fibre-based activated carbon	400.00	This work
Sewage sludge-based activated carbon	139.40	[45]
Bamboo dust-based activated carbon	143.20	[44]
Groundnut shell-based activated carbon	164.90	[44]
Dehydrated wheat bran carbon	122.00–222.20	[5]
Jute fiber-based activated carbon	225.64	[11]
Olive-seed waste residue-based activated carbon	190.00–263.00	[39]
Rattan sawdust-based activated carbon	294.14	[21]
Coconut husk-based activated carbon	434.78	[14]
Commercial activated carbon Filtrasorb F300	240.00	[39]

The maximum monolayer MB adsorption capacity, Q_0 obtained for the optimal activated carbon prepared was as high as 400 mg/g. This result agreed with the work done by Baçaoui et al. [33] where the optimum 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. In our previous work, we found that the optimum activated carbon from coconut husk was obtained using 816 °C activation temperature, 1 h activation time and 3.9 KOH:char impregnation ratio, which resulted in 15.5% of carbon yield and 434.78 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 mg/g on MB. 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 oil palm fibre.

4. Conclusions

The effects of three activated carbon preparation variables: activation temperature, activation time and chemical impregnation (KOH:char) ratio, on the MB uptake and activated carbon yield were studied by conducting a CCD. A quadratic model and a 2FI model were respectively developed to correlate the preparation variables to the MB uptake and carbon yield. Through analysis of the response surfaces derived from the models, activation temperature and chemical impregnation (KOH:char) ratio were found to have significant effects on the MB uptake, with chemical impregnation ratio imposing the greatest effect on this response. Activation temperature was found to have the greatest effect on carbon yield. The optimum activated carbon prepared from oil palm fibre was obtained by using activation temperature of 862 °C, activation time of 1 h and chemical impregnation ratio of 3.1. The optimum activated carbon showed MB uptake of 203.83 mg/g and activated carbon yield of 16.50%. The equilibrium data were well represented by the Langmuir isotherm, giving maximum monolayer adsorption capacity as high as 400 mg/g.

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