# Optimization of Pink Guava (*Psidium guajava*) Waste-based Activated Carbon Preparation Conditions for Methylene Blue Dye Removal

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Abstract- The optimal conditions for preparation of guava waste based activated carbon (GWAC) for removal of Methylene Blue (MB) dye from aqueous solution were investigated and the performance of GWAC on adsorption capacity were evaluated. The GWAC was prepared using simple thermo-chemical activation method. Central composite design (CCD) was used to determine the optimum preparation conditions for GWAC with response to the GWAC yield and MB percentage removal. Two quadratic models were developed to correlate the preparation variables for both responses. The significant factors on each experimental design response were identified from the analysis of variance (ANOVA). The optimum GWAC preparation conditions were obtained using 550°C activation temperature, 1.93 hour activation time and 1.00 impregnation ratio resulting in 71.71% of GWAC yield and 54.58% of MB removal. From the analysis, activation temperature was found to have the greatest effect on carbon vield. On the other hand, activation temperature and impregnation ratio were found to have significant effects on MB removal. The adsorption performance of GWAC was then conducted using the batch adsorption study to determine the adsorption capacity. The adsorption study was carried out at different initial concentrations of MB (50 - 500 mg/L) at temperature of 30°C for 5 hours. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models followed by kinetics study. The experimental data for GWAC were fitted well with Langmuir isotherm with a maximum monolayer adsorption capacity of 250.00 mg/g. The kinetic study on adsorption of MB obeyed the peudo-second order kinetics with good correlation. The results demonstrated that GWAC is an effective adsorbent for removal of MB and has potential to replace the commercial activated carbon for removal of dyes from wastewater.

Keywords- Adsorption Isotherms; Guava Waste Activated Carbon; Methylene Blue; Thermo-chemical Activation

# I. INTRODUCTION

Textile industry is one of the industries that produce great income to economic growth in several countries around the world. Dyeing is a fundamental operation during textile fiber processing. This operation causes the production of more or less colored wastewater, depending on the degree of fixation of the dyestuffs on the substrates, which varies with the nature of the substances, the desired intensity of coloration, and the application method. There are more than 100,000 commercially available dyes with 700,000 tonnes of dyestuff production annualy [1]. From this amount, about 10% of the dyes used in industry were lost in the industrial effluents. In Malaysia, textile dyeing is a major industry that consumes large quantity of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes [2].

MB is the most commonly used substance for dying cotton, wood and silk. It 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, mental confusion and methemoglobinemia [3–5]. Therefore, it is necessary to remove such dye from industrial effluents before discharging into the water stream.

Various conventional methods of color removal from wastewater have been used. These include biological and physicalchemical process. However, these processes are difficult to handle and are not always effective and economical. The adsorption technique appears to offer the best prospects over others and proved itself as one of an effective and attractive process for the treatment of dye containing wastewater [6]. For the last few years, adsorption process by commercial activated carbon is very effective and the most frequently used treatment method for removal of dyes from wastewater.

Activated carbon is powerful adsorbent because it has a large surface area and pore volume, which allows the removal of organic compounds, heavy metal ions and colors [7]. Although activated carbon adsorption is considered as the best available technologies, but it is still considered highly expensive according to the market price of commercial activated carbon available. Thus, it has provoked the search for alternatives and low cost adsorbents to replace the commercial activated carbon. In recent years, agricultural wastes have gained a significant interest among researches and being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient seem to be possible option for dye removal. Studies reveal that various agricultural waste materials such as seed hulls [8], bamboo [9], garlic peel [10], pistachio shell [11], coconut shell and rice husk [12], palm kernel [13], fir wood [14] and tamarind wood [15] have been found to be suitable precurcors owing to their high carbon and low ash contents.

Guava is one of the most popular tropical fruit and widely growth which Malaysia has the largest pink guava's plantation in the world. Golden Hope Food & Beverages Sdn. Bhd. Malaysia is the largest pink guava producer in Asia with over 500 hectares guava planted that produced 10,000 tons of fruits for pink guava juice for exports to Japan, USA, Australia, Philippines, Korea, Canada, Singapore and New Zealand. From the 10,000 tons of fruits, about 10% (100 tons) of the fruits are considered decanter waste (scrubs and seeds). Thus, it is considered worthwhile to utilize this waste material for production of activated carbon for dye removal because of their availability in abundance at a low price and large adsorption capacities.

Response Surface Mechanism (RSM) is a collection of statistical and mathematical techniques that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions which are useful for developing, improving and optimizing processes. In this work, a standard RSM design, known as central composite design (CCD) was applied to study the variables for preparing the activated carbons from guava waste. The aim of this study was to optimize the GWAC preparation variables; activation temperature, activation time and NaOH:char impregnation ratio for the removal of MB dye from aqueous solution. Laboratory batch adsorption studies were conducted to evaluate the adsorption capacity of the optimized GWAC adsorbent. Effects of contacts time and initial MB concentration have been investigated. Langmuir and Freundlich isotherm models were tested for their applicability with the experimental data followed by adsorption kinetics study.

# II. MATERIALS AND METHODS

#### A. Adsorbate

MB (MB),  $C_{16}H_{18}CIN_3S \cdot 3H_2O$  supplied by Sigma Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate. The stock solution of 1000 mg/L was prepared by dissolving 1 g of powdered MB with 1 L distilled water in a volumetric flask.

#### B. Adsorbent

The guava waste used in this research was collected from Golden Hope Food and Beverages Sdn. Bhd., Sungkai, Perak. It was used as raw material for preparation of activated carbon in this research.

#### C. Preparation of Guava Waste Activated Carbon

Guava waste was cleaned by washing it with water to remove any impurities and contaminants. After that, the guava was dried in the oven at  $110^{\circ}$ C for 48 hours. The dried guava were crushed with a blender and sieved to a size smaller than 500 µm. Then, the sieved guava was carbonized at 400°C for 1 hour in a muffle furnace in order to produce charcoal.

The charcoal that was obtained by the process of carbonization was subjected impregnation in Sodium hydroxide (NaOH) solution by weight ratio at 70°C for 24 hours. Equation (1) shows the calculation of impregnation ratio of NaOH with char. The solution was then placed inside the incubator shaker to ensure the solution have mixed well. After that, the solution was dried in the oven at 110°C for 24 hours. The resulted sample was further activated in a muffle furnace at fixed activation temperature and time.

$$IR = \frac{w_{NaOH}}{w_{char}} \tag{1}$$

where:

 $w_{NaOH}$  = Dry weight of NaOH pellets (g)

 $w_{char} =$ Dry weight of char (g)

After cooling process, the sample was washed successfully several times with 1 M Hydrochloric acid (HCl) and followed by hot water until the pH become neutral (pH 7). The washed sample was dried in the oven at 110°C to obtain activated carbon as the final product. The activated carbon yield is calculated by using Equation (2). These preparation steps were used in preparation of 20 samples with different impregnation ratio, activation temperature and activation time according to Response Surface Mechanism (RSM) analysis.

$$Yield (\%) = \frac{w_{ac}}{w_{char}} x \ 100 \tag{2}$$

where:

 $w_{ac}$  = Dry weight of final activated carbon (g)

 $w_{char} =$ Dry weight of char (g)

#### D. Experimental Design and Optimization (RSM Analysis)

Response Surface Mechanism (RSM) is a tool to study the interaction of two or more factors. In this work, a central composite design (CCD) was applied to study the variables for preparing the activated carbons from guava waste. This method can reduce the number of experimental trials needed to evaluate multiple parameters and their interactions. Generally, the CCD consists of  $2^n$  factorial runs, 2(n) axial runs and six center runs, where n is the number of factors.

In the present study, the activated carbons were prepared using thermo-chemical activation method where the variables studied were activation temperature  $(x_1)$ , activation time  $(x_2)$  and NaOH:char impregnation ratio  $(x_3)$ . These three variables together with their respective ranges were chosen based on the literature and preliminary studies as given in Table I. For each categorical variable, a  $2^3$  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 for this procedure for each precursor.

TABLE I INDEPENDENT VARIABLES AND THEIR CODED LEVELS FOR THE CENTRAL COMPOSITE DESIGN

Variables (factors)	Code	Codo Unita		Coded variable levels						
variables (factors)	Coue	Units	-α	-1	0	+1	+α			
Activation temperature	$x_I$	°C	348.87	400.00	475.00	550.00	601.13			
Activation time	$x_2$	h	0.66	1.00	1.50	2.00	2.34			
Impregnation ratio	<i>X</i> 3	-	0.32	1.00	2.00	3.00	3.68			

The center points are used to determine the experimental error and the reproducibility of the data. The axial points are located at  $(\pm \alpha, 0, 0)$ ,  $(0, \pm \alpha, 0)$  and  $(0, 0, \pm \alpha)$  where  $\alpha$  is the distance of the axial point from center and makes the design rotatable. In this study,  $\alpha$  value was fixed at 1.682 (rotatable). The experimental sequence was randomized in order to minimize the effects of the uncontrolled factor. The two responses were activated carbon yield  $(Y_1)$  and MB removal  $(Y_2)$ . Table II shows the experimental design matrix for preparation of guava waste activated carbon. 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 Equation (3):

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

where:

- Y = Predicted response
- $b_o = \text{Constant coefficient}$

 $b_i$  = Linear coefficients

- $b_{ii}$  = Interaction coefficients
- $b_{ii}$  = Quadratic coefficients

 $x_i$ ,  $x_j$  = Coded values of the activated carbon (AC) preparation variables.

		Activated carbon preparation variable						
Run	Туре	Activation	Activation	Impregnation				
		temperature, x <sub>1</sub> (°C)	time, $x_2$ (h)	ratio, x3				
1	Fact	400.00	1.00	1.00				
2	Fact	550.00	1.00	1.00				
3	Fact	400.00	2.00	1.00				
4	Fact	550.00	2.00	1.00				
5	Fact	400.00	1.00	3.00				
6	Fact	550.00	1.00	3.00				
7	Fact	400.00	2.00	3.00				
8	Fact	550.00	2.00	3.00				
9	Axial	348.87	1.50	2.00				
10	Axial	601.13	1.50	2.00				
11	Axial	475.00	0.66	2.00				
12	Axial	475.00	2.34	2.00				
13	Axial	475.00	1.50	0.32				
14	Axial	475.00	1.50	3.68				
15	Center	475.00	1.50	2.00				
16	Center	475.00	1.50	2.00				
17	Center	475.00	1.50	2.00				
18	Center	475.00	1.50	2.00				
19	Center	475.00	1.50	2.00				
20	Center	475.00	1.50	2.00				

TABLE II EXPERIMENTAL DESIGN MATRIX FOR PREPARATION OF GUAVA WASTE ACTIVATED CARBON

III. THEORY OF ADSORPTION ISOTHERM AND KINETICS

# A. Isotherm Models

#### 1) Langmuir isotherm:

Langmuir model is based on the assumption that adsorption energy is constant and independent of surface coverage where the adsorption occurs on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs when the surface is covered by a monolayer of adsorbate [16].

(7)

The linear form of Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{mon}} + \frac{C_e}{q_{mon}} \tag{4}$$

where:

 $q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g)

 $C_e$  = Equilibrium adsorbate concentration (mg/L)

 $K_L$  = Equilibrium constants of Langmuir equation (L/g)

 $q_{mon}$  = Maximum adsorption capacity corresponding to complete monolayer coverage (mg/g)

The linear form can be used for linearization of experimental data by plotting  $C_e/q_e$  against  $C_e$  yields a straight line with slope,  $\alpha_L/K_L$ , and intercept  $1/K_L$ . The ratio  $\alpha_L/K_L$  indicates the theoretical monolayer saturation capacity,  $q_{mon}$ , mg/g. The shape of the isotherm can determine whether the adsorption is favourable or not.

The favourable nature of adsorption can be expressed in terms of the dimensionless separation factor of the equilibrium parameter, which is defined by Equation (5).

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$

The value of  $R_L$  indicates the type of isotherm: irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ).

2) Freundlich isotherm:

Freundlich expression is an empirical equation applicable to non-ideal sorption on heterogeneous surface as well as multilayer sorption [17]. The well known logarithm Freundlich equation is given as:

$$\ln q_e = \ln K_F + b_F \ln C_e \tag{6}$$

where:

 $q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g)

 $K_F$  = Freundlich isotherm constant (mg/g) (L/mg)<sup>1/n</sup>

 $C_e$  = Equilibrium concentration of adsorbate (mg/L)

n = Freundlich heterogeneity factor

By plotting log  $q_e$  versus log  $C_e$ , constant  $K_F$  and exponent 1/n can be calculated.

## B. Kinetics Models

### 1) The pseudo-first order model:

The kinetics data of adsorption was analyzed by the pseudo-first order equation of Lagergren and Svenska is generally expressed as [18];

 $\ln(q_e - q_t) = \ln q_e - k_1 t$ 

where:

 $q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g)

 $q_t$  = Amount of solute adsorb per unit weight of adsorbent at time (mg/g)

 $k_1$  = Rate constant of pseudo-first order sorption (1/min)

t = Time (min)

2) The pseudo-second order model:

If the rate of sorption is a second order mechanism, the pseudo second order chemisorption kinetic rate equation is expressed as [16]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{8}$$

where:

- $q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g)
- $q_t$  = Amount of solute adsorb per unit weight of adsorbent at time (mg/g)
- $k_2$  = Rate constant of pseudo-second order sorption (g/min.mg)

t = Time (min)

### IV. RESULTS AND DISCUSSION

#### A. Development of Regression Model Equation

In this study, the central composite design was used to develop a polynomial regression equation in order to analyze the correlation between the activated carbon preparation variables to the activated carbon yield and MB removal. 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. Run 15-20 at the center point were conducted to determine the experimental error and the reproducibility of the data. Table III shows the complete design matrixes together with both response values obtained from the experimental work. Activated carbon yield and MB removal were found to range from 44.69 to 78.31% and 24.66 to 72.08%, respectively.

				Activated c	arbon preparat		MD			
Run		Level		Level		Activation temperature,	Activation time,	time, r <sub>2</sub> Impreg- nation ratio,		removal, $Y_2$
				$(^{\circ}C)$	(h)	<i>x</i> <sub>3</sub>		(%)		
1	-1	-1	-1	400.00	1.00	1.00	56.23	67.61		
2	+1	-1	-1	550.00	1.00	1.00	78.31	45.29		
3	-1	+1	-1	400.00	2.00	1.00	62.58	40.01		
4	+1	+1	-1	550.00	2.00	1.00	67.92	67.62		
5	-1	-1	+1	400.00	1.00	3.00	62.04	67.62		
6	+1	-1	+1	550.00	1.00	3.00	72.47	47.12		
7	-1	+1	+1	400.00	2.00	3.00	62.14	46.49		
8	+1	+1	+1	550.00	2.00	3.00	62.32	71.06		
9	-1.682	0	0	348.87	1.50	2.00	44.69	72.08		
10	+1.682	0	0	601.13	1.50	2.00	65.86	57.12		
11	0	-1.682	0	475.00	0.66	2.00	50.56	37.38		
12	0	+1.682	0	475.00	2.34	2.00	52.39	24.69		
13	0	0	-1.682	475.00	1.50	0.32	75.79	42.83		
14	0	0	+1.682	475.00	1.50	3.68	53.05	24.66		
15	0	0	0	475.00	1.50	2.00	49.11	30.45		
16	0	0	0	475.00	1.50	2.00	49.11	29.21		
17	0	0	0	475.00	1.50	2.00	49.11	29.21		
18	0	0	0	475.00	1.50	2.00	49.11	29.21		
19	0	0	0	475.00	1.50	2.00	49.11	29.21		
20	0	0	0	475.00	1.50	2.00	49.11	29.21		

TABLE III EXPERIMENTAL DESIGN MATRIX AND RESULTS

The quadratic model was suggested by the software for activated carbon yield, as well as the linear and quadratic models were suggested by the software for MB removal. The final empirical formula models for activated carbon yield ( $Y_1$ ) and MB removal ( $Y_2$ ) in terms of coded factors are represented by Equations (9) and (10), respectively.

$$Y_{1} = 48.85 + 5.39x_{1} - 0.81x_{2} - 3.24x_{3} + 3.86x_{1}^{2} + 2.52x_{2}^{2} + 7.09x_{3}^{2} - 3.37x_{1}x_{2} - 2.10x_{1}x_{3} - 0.75x_{2}x_{3}$$
(9)

$$Y_2 = 29.01 - 1.16x_1 - 1.74x_2 - 1.38x_3 + 15.11x_1^2 + 3.24x_2^2 + 4.20x_3^2 + 11.87x_1x_2 - 0.15x_1x_3 + 1.01x_2x_3$$
(10)

The coefficient with one factor represent the effect of the particular factor, while the coefficients with two factors and those with second-order terms represent the interaction between two factors and quadratic effect, respectively. The positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the models developed was evaluated based on the correlation coefficients,  $R^2$  value. In fact, the models developed seems to be the best at high  $R^2$  statistics which is closer to unity as it will give predicted value closer to the actual value for the responses [19]. In this experiment, the  $R^2$  values for Equations (9) and (10) were 0.8108 and 0.8508, respectively. This indicated that 81.08% and 85.08% of the total variation in the activated carbon yield and MB removal, respectively, were attributed to the experimental variables studied.

### B. Statistical Analysis

The results of the surface quadratic model in the form of analysis of variance (ANOVA) are given in Tables IV and V for activated carbon yield and MB removal, respectively. ANOVA is required to justify the significance and adequacy of the models. The mean squares were obtained by dividing the sum of the squares of each of the variation sources, the model and the error variance, by the respective degrees of freedom. If the value of Prob.>*F* less than 0.05, the model terms are considered as significant [20]. From Table 4, the model *F*-value of 4.99 and Prob.>*F* of 0.0096 implied that this model was significant. In this case,  $x_1$ ,  $x_1^2$  and  $x_3^2$  factors were significant model terms whereas  $x_2$ ,  $x_3$ ,  $x_2^2$ ,  $x_1x_2$ ,  $x_1x_3$  and  $x_2x_3$  were insignificant to the response.

FABLE IV ANALYSIS OF VARIANCE (ANOVA) FOR	OR RESPONSE SURFACE QUADRATIC MODEL FOR ACTIVATED CARBON YIELD
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Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> -value	Prob.>F	Comment
Model	1584.81	9	176.09	4.99	0.0096	significant
$x_I$	397.01	1	397.01	11.26	0.0073	
<i>x</i> <sub>2</sub>	8.88	1	8.88	0.25	0.6266	
<i>X</i> 3	143.79	1	143.79	4.08	0.0710	
$x_1^2$	214.72	1	214.72	6.09	0.0332	
$x_2^2$	91.26	1	91.26	2.59	0.1387	
$x_{3}^{2}$	725.08	1	725.08	20.56	0.0011	
$x_1x_2$	91.06	1	91.06	2.58	0.1391	
$x_1x_3$	35.32	1	35.32	1.00	0.3405	
$x_2 x_3$	4.52	1	4.52	0.13	0.7279	
Residual	352.59	10	35.26	-	-	

TABLE V ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE QUADRATIC MODEL FOR MB REMOVAL

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> -value	Prob.>F	Comment
Model	4650.10	9	516.68	6.33	0.0040	significant
$x_l$	18.28	1	18.28	0.22	0.6461	
<i>x</i> <sub>2</sub>	41.48	1	41.48	0.51	0.4921	
$x_3$	25.88	1	25.88	0.32	0.5857	
$x_1^2$	3289.15	1	3289.15	40.32	< 0.0001	
$x_2^2$	151.32	1	151.32	1.86	0.2031	
$x_{3}^{2}$	254.04	1	254.04	3.11	0.1081	
$x_1x_2$	1128.13	1	1128.13	13.83	0.0040	
$x_1x_3$	0.19	1	0.19	2.281E-03	0.9628	
$x_2 x_3$	8.16	1	8.16	0.10	0.7583	
Residual	815.68	10	81.57	-	-	

From Table V, the model *F*-value of 6.33 and Prob.>*F* of 0.0040 indicated that the model was significant. In this case,  $x_1^2$  and  $x_1x_2$  were significant model terms whereas  $x_1$ ,  $x_2$ ,  $x_3$ ,  $x_2^2$ ,  $x_3^2$ ,  $x_1x_3$  and  $x_2x_3$  were insignificant to the response. From the statistical results obtained, it was shown that the both models which are Equations (9) and (10) were adequate to predict the activated carbon yield and MB removal within the range of variables studied. In addition, Figs. 1 and 2 show the predicted values versus the experimental values for activated carbon yield and MB removal, respectively. It can be seen that the models developed were successful in capturing the correlation between the activated carbon preparation variables to the response when the predicted values obtained were quite close to the experimental values.



Fig. 1 Predicted versus experimental activated carbon yield

Fig. 2 Predicted versus experimental MB removal

#### C. Activated Carbon Yield

The activation temperature was found to have the greatest effect on activated carbon yield with the highest *F*-value of 11.26, while activation time and impregnation ratio were considered as moderate effect on this response. The quadratic effect of activation temperature and activation time showed almost similar effects on the response. This interaction effects between the variables were insignificant. Fig. 3 demonstrates the effect of activation temperature and activation time on activated carbon yield, with impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00), whereas Fig. 4 demonstrates the effect of activation temperature and impregnation ratio at zero level (2.00).

the chemical that has been used which was sodium hydroxide (NaOH) was accumulated with the activated carbon. A contravene trend was shown in the studied by Yang and Qiu (2010) which found that the activation temperature has a negative effect on activated carbon yield [21]. This is because at higher temperature, more volatiles are released, resulting in a lower yield.



Fig. 3 Three-dimensional response surface plot of activated carbon yield – effect of activation temperature and activation time (impregnation ratio = 2.00)



Fig. 4 Three-dimensional response surface plot of activated carbon yield – effect of activation temperature and impregnation ratio (activation time = 1.50 h)

# D. Removal of MB

The impregnation ratio and activation temperature were found to have significant effects on the MB removal of guava waste activated carbon, whereas the activation time showed the least significant effect on this response. Among all the factors being considered, impregnation ratio was found to impose the high effect on the MB removal, as it showed the higher *F*-value. Besides, the quadratic effects of impregnation ratio and activation temperature as well as the interaction effects between both variables were considered moderate. Figure 5 shows the three-dimensional response surface which was constructed to show the interaction effects on the impregnation ratio and activated temperature on the MB removal. For this plot, the activation time was fixed at zero level (1.5 h). As can be seen from Fig. 5, the MB removal generally increased with increased in the two variables studied. A similar trend has been reported in the studied by Sudaryanto *et al.*, (2006) [22].



Fig. 5 Three-dimensional response surface plot of MB removal – effect of activation temperature and impregnation ratio (activation time = 1.50 h)

### E. Process Optimization

Central composite design has been used to optimize the parameters affecting the activated carbon yield and MB removal responses. In this case, it is difficult to optimize both responses because the interest region of factors is different. When activated carbon yield increases, MB removal will decrease and vice versa. Therefore, the function of desirability was applied using Design-Expert software (STAT-EASE Inc., Minneapolis, USA) in order to compromise between these responses. In this optimum analysis, the target criteria was set as maximum values for both responses while the values of the variables were set in the ranges being studied.

Activated carbon was reproduced based on the optimum condition parameters. The predicted and experimental results of activated carbon yield and MB removal at optimum conditions are shown in Table VI. The optimum activated carbon was obtained by using activation temperature of 550°C, activation time of 1.93 hours and impregnation ratio of 1.00. The optimum activated carbon showed activated carbon yield of 71.7% and MB removal of 54.58% based on adsorption studied. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors, which were only -3.22 and 2.73%, respectively for activated carbon yield and MB removal.

Model	<b>X</b> 1	<b>X</b> 1	<b>X</b> 1	<b>X</b> 1	<b>X</b> <sub>2</sub>			AC yield (%)			MB removal (%	)
desirability	(°C)	°C) (h)	(h) X <sub>3</sub>	Predicted	Experimental	Error (%)	Predicted	Experimental	Error (%)			
0.726	550	1.93	1.00	69.46	71.70	-3.22	56.11	54.58	2.73			

## TABLE VI MODEL VALIDATIONS

#### F. Effect of Initial Concentration and Contact Time

Effects of initial concentration of MB,  $C_o$  and contact time on the adsorption capacity,  $q_t$  for GWAC is shown in Fig. 6. From the result, the amount of MB adsorbed per unit weight of adsorbent (mg/g) increases with increases in initial concentrations.



Fig. 6 Effect on initial concentration and contact time on adsorption of MB by GWAC

When the initial concentrations of adsorbate increase from 50 to 500 mg/L, the adsorption capacity of MB for GWAC was increased from 37.11 to 202.46 mg/g. A similar trend has been reported by Raposo *et al.*, [23]. It is because the initial concentration plays an important role which provides the necessary driving force to overcome the resistance to the mass transfer of MB between the aqueous and solid phase [24]. The interaction between adsorbates and both adsorbent also enhances with the increasing of the initial concentration. Hameed, [25] reported the range of adsorption capacity of MB using papaya seeds which was from 16.42 to 99.30 mg/g.

Aqueous MB with different initial concentration were kept in contact with the adsorbent for five hours. The adsorption result revealed that the uptake of the adsorbate was fast at the initial stage of the contact period, and then it became slower near to the equilibrium. The initial rapid phase was due to an increase in the number of vacant sites available at the initial stage [25]. In other words, the number of adsorption sites available is higher and the driving force for the mass transfer is greater. Therefore, it is much easier for the adsorbate to reach the adsorption site. After a lapse time, number of active sites becomes less and the adsorbent becomes crowded inside the particles.

#### G. Isotherm Analysis

Adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. The adsorption isotherm of MB onto GWAC was fitted by well-known isotherm models which are Langmuir and Freundlich to assess their utility. Both models also were used for more in-depth interpretation of the adsorption data. Generally, the Langmuir model is obtained under the ideal consumption of a

totally homogeneous adsorption surface, whereas the Freundlich model is suitable for a highly heterogeneous surface. In this work, both models were used to describe the relationship between the amount of MB adsorbed and its equilibrium concentration.

Fig. 7 and Fig. 8 show Langmuir and Freundlich isotherms of MB onto GWAC, respectively. The applicability of both isotherms was compared by judging the correlation coefficients,  $R^2$  as shown in Table VII.  $R^2$  value for Langmuir was greater than Freundlich. A similar result was reported by the adsorption of MB onto rejected tea waste [26].



Fig. 8 Freundlich isotherm of MB onto GWAC

TABLE VII LANGMUIR AND FREUNDLICH PARAMETERS OF MB ADSORPTION ONTO GWAC ADSORBENT

Adsorbent		Lang	muir	Freundlich			
	q <sub>mon</sub> (mg/g)	$K_L$ (L/g)	$R^2$	$R_L$	$\frac{K_F (\mathrm{mg/g})}{(\mathrm{L/mg})^{1/n}}$	n	$R^2$
GWAC	250.00	0.0147	0.9980	0.1198	11.7170	1.912	0.951

The plots of  $C_e/q_e$  versus  $C_e$  for the adsorption of MB onto GWAC in Fig. 7 were employed to obtain the values of maximum monolayer adsorption capacity,  $q_{mon}$  and Langmuir constant,  $K_L$ . Both Langmuir parameters were calculated by slope and intercept of the plot from this isotherm and their values are presented in Table 7. The maximum monolayer adsorption capacity,  $q_{mon}$  for GWAC was 250.00 mg/g. Thus, it was observed that the performance of GWAC in this study was comparable with the commercial activated carbon available.

The adsorption data were described well by Langmuir isotherm model with  $R^2$  values of 0.998 and the dimensionless separation factor,  $R_L$  values was 0.1198. This confirmed that GWAC are favourable for adsorption of MB dye.

The Freundlich isotherm was applicable for non-ideal adsorption on heterogeneous surface as well as multilayer adsorption. The plot of Log  $q_e$  versus Log  $C_e$  for the adsorption of MB onto GWAC as shown in Fig. 8 was employed to obtain the slope of 1/n and intercept value of  $K_F$ . Values of n,  $K_F$  and  $R^2$  are given in the Table 7. In this study, the value of n for GWAC was 1.912. This value shows that the adsorption was favourable condition because the value of n was exceeding 1 [27]. The low

correlation coefficients,  $R^2$  of 0.951 show poor agreement of Freundlich isotherm with the experimental data compared to Langmuir isotherm.

## H. Adsorption Kinetics

The pseudo-first order and pseudo-second order rate constant for MB adsorption were evaluated from the linear plots of ln  $(q_e - q_t)$  versus t and  $t/q_t$  versus t as shown in Fig. 9 as well as Fig. 10, respectively. The correlation coefficients,  $R^2$  calculated from these models for GWAC are listed in Tables VIII.



Fig. 9 Pseudo-first order kinetics for adsorption of MB by GWAC



Fig. 10 Pseudo-second order kinetics for adsorption of MB by GWAC

Initial concen- tration (mg/L)	q <sub>e,exp</sub> (mg/g)	Pseudo-first order				Pseudo			
		<i>k</i> 1 (1/min)	q <sub>e,cal</sub> (mg/g)	$R^2$	∆ <b>q (%)</b>	<i>k</i> <sub>2</sub> (g/ min.mg)	q <sub>e,cal</sub> (mg/g)	$R^2$	∆ <b>q</b> (%)
50	37.11	0.0553	69.34	0.906	38.84	0.0011	47.62	0.979	12.67
100	73.26	0.0645	159.96	0.862	52.93	0.0007	90.92	0.980	10.78
200	129.84	0.0668	293.09	0.851	56.23	0.0004	166.67	0.981	12.69
300	164.49	0.0737	419.76	0.832	69.40	0.0003	200	0.981	9.65
400	184.11	0.0806	537.03	0.809	85.73	0.0003	250	0.982	16.00
500	202.46	0.0852	641.21	0.807	96.92	0.0003	250	0.983	10.50

TABLE VIII KINETIC PARAMETERS OF THE PSEUDO-FIRST ORDER AND PSEUDO-SECOND ORDER MODELS FOR ADSORPTION OF MB BY GWAC

The pseudo-first order and pseudo-second order parameters for GWAC was calculated by slope and intercept of the plots. The correlation coefficient,  $R^2$  values for pseudo-first order of GWAC were slightly lower compared to the values for pseudo-second order which seen to be more accurate. The ranges of correlation coefficient,  $R^2$  for pseudo-first order by GWAC was 0.807 to 0.906. This phenomenon agree with Ho and McKay, [28] that suggest the first order equation of Lagergren does not

fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption process in many cases. This result proved that the adsorption of MB onto GWAC was not a pseudo first order kinetic.

On the other hand, the range of correlation coefficient,  $R^2$  for pseudo-second order was 0.979 to 0.983 indicating that the adsorption of MB on GWAC were fitted well to this model at all concentration. Similar trend was observed in the MB adsorption on activated carbon prepared from Posidonia oceanica (L.) dead leaves: Kinetics and equilibrium studies [29]. Moreover, the different in calculated equilibrium adsorption capacity,  $q_{e,cal}$  with experimental equilibrium adsorption capacity,  $q_{e,exp}$  were shown to be more consistent in pseudo-second order because the values were lower compared to pseudo-first order. Thus, it can be concluded that MB adsorption on GWAC follows the pseudo-second order rate equation. This suggested that chemisorptions might be the rate-limiting step that controlled the adsorption process [30].

### V. CONCLUSIONS

The optimum guava waste activated carbon (GWAC) preparation conditions were obtained using 550°C activation temperature, 1.93 hour activation time and 1.00 impregnation ratio resulting in 71.71% of activated carbon yield and 54.58% of MB removal. From the RSM analysis, activation temperature was found to have the greatest effect on carbon yield. On the other hand, activation temperature and impregnation ratio were found to have significant effects on MB removal.

The adsorption of MB dye from aqueous solutions on GWAC was studied in a batch system at initial concentration (100-500mg/L) at temperature 30°C. The experimental data of adsorption studies of GWAC adsorbent were described well by Langmuir adsorption isotherm model with correlation coefficient,  $R^2$  of 0.998. This indicates that the MB adsorption onto GWAC was monolayer adsorption with maximum adsorption capacity of 250.00 mg/g, respectively. The kinetic adsorption study on MB using GWAC was best described by pseudo-second order model. The results of the present study indicated that GWAC could be employed as an alternative to commercial activated carbon for the removal of MB from aqueous solutions.

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