

## PROCESS VARIABLES OPTIMIZATION FOR PREPARATION AND CHARACTERIZATION OF NOVEL ADSORBENT FROM LIGNOCELLULOSIC WASTE

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In this study, powdered activated carbon (PAC) was produced from agricultural waste biomass of kenaf (*Hibiscus cannabinus* L.) core or stalk, and the process variables were optimized by applying central composite design (CCD). The influences of carbonization temperature, duration of activation, and impregnation ratio on removal percentage of copper Cu(II) ions from aqueous solution and carbon yield were investigated. A quadratic model for adsorption percentage and a 2FI model for carbon yield were developed. The models were used to determine optimum process variables for production of activated carbon from the woody core of kenaf. From the analysis of variance (ANOVA), the most significant factor on each response of adsorption capacity and yield were identified. An activation temperature of  $(568\pm 1)^\circ\text{C}$ , activation time of 2.02 hours, and impregnation ratio of 1.75 were found as optimum production conditions. The experimental results showed excellent agreement with the predicted results obtained from a designed experiment that included the variables and responses of sorption capacity and yield. Textural properties of the prepared activated carbons were determined. The performance of the prepared activated carbon was further evaluated by fitting the equilibrium data with regression equations of Langmuir, Freundlich, and Temkin models at different temperatures. The research concluded that the prepared sorbent has good potential to remove Cu (II) ions from waste water.

*Key words:* Adsorption; Biomass; Central composite design; Equilibrium; Optimization

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### INTRODUCTION

Activated carbon comprises a wide range of amorphous carbonaceous materials that are widely used for purification of waste water. The effectiveness of activated carbon as a versatile adsorbent is due to its unique surface characteristics, including a highly developed internal surface area between 500 and 2000 m<sup>2</sup>/gm, favorable pore size, and a high degree of surface reactivity. Their structure is complex and heterogeneous due to the presence of micropores, mesopores, and macropores of different sizes and shapes (Ahmad *et al.* 2009). By applying restricted oxidation or activation technique, the presence of carboxylate and phenol groups on the surface of activated carbon particles can be enhanced. These groups act as essential binding groups for divalent cations. The

adsorption uptake of an activated carbon is highly dependent on its production conditions and the nature of the starting materials. The range of preparation variables of temperature, activation time, activating gas, impregnating agent, and impregnation ratio will extensively modify its surface area, pore volume, and pore size distribution, including the percentages of micro and mesopores. For a commercial scale production, these points should be considered carefully to get maximum output of the process. Particularly, the development of the preparation method for an activated carbon for a specific purpose typically is based on the trial and error approach guided by the background review of literature. The successful resolution to this challenge fundamentally depends upon the development of proper adsorbents with specific properties followed by subsequent exploitation in small scale as well as large scale filtering units. Commercially available activated carbons are produced from coal, lignite, and peat, which are non-renewable resources. However, the widespread application of commercial activated carbon for waste water treatment is constrained by its high production cost. This has initiated growing research interest toward production of activated carbon that can be derived from renewable, abundant, and low cost materials originated from ligno-cellulosic biomass due to their high carbon and low ash content (Egila *et al.* 2011). Many agricultural waste residues, such as digested sewage sludge and coconut husk (Tay *et al.* 2001), cassava peel (Sudaryanto *et al.* 2006), palm shell (Adinata *et al.* 2007), olive seed waste (Stavropoulos and Zabaniotou 2005), oil palm fiber (Hameed *et al.* 2008), rubber wood sawdust (Srinivasakannan and Bakar 2004), turkish lignite (Karacan *et al.* 2007), bamboo waste (Ahmad *et al.* 2010), waste rapeseed (Tofan *et al.* 2011), oil palm ash (Chowdhury *et al.* 2011a,c), and rattan sawdust (Ahmad *et al.* 2009) have been utilized to produce activated adsorbent.

The above review of the literature reflects that, until now, no attempts have been made to produce activated carbon from agricultural waste residues of kenaf core or stalk obtained from the kenaf crop plantation process and consequently explores the feasibility of its use for removal of inorganic contaminants like copper from waste water. Kenaf (*Hibiscus cannabinus* L.) is a tropical or subtropical plant that grows abundantly in Malaysia (Chowdhury *et al.* 2011b). To date, nine varieties of kenaf have been introduced in Malaysia as a potential crop to replace tobacco. This plant has a single, straight and branchless stalk that is made up of an inner woody core and an outer fibrous bark surrounding the core. After extraction of the bast fiber, the woody core or stalk is left as waste materials. Thus, from an environmental view, innocuous disposal of these agro residues is immensely important. It was observed from the above-mentioned literature that most of the agricultural residues were converted to activated carbon by using response surface methodology (RSM) to eliminate organic compound from waste water. Only few studies have recently attempted to remove inorganic contaminants like heavy metals from an aqueous solution by applying the RSM technique (Zahangir *et al.* 2008; Chowdhury *et al.* 2011b).

The objectives of this study were to determine the optimum production conditions for preparing activated carbon from kenaf core, an agricultural waste. In this study, a central composite design (CCD) based on response surface methodology (RSM) was selected to study the individual, as well as cumulative effects of activation temperature, time, and impregnation ratio on the removal percentage of copper and production yield.

To examine the applicability of the prepared activated carbon, the experimental data were fitted with Langmuir, Freundlich, and Temkin isotherm models. The significant feature of core based activated carbon that makes it unique and a potential adsorbent is that it can be produced from renewable sources of agricultural waste materials. Optimization of the production parameters involved with the conversion of core materials to activated carbon provides an environmentally safe, innovative, and economically feasible solution to the problem of waste disposal.

## EXPERIMENTAL

### Preparation of Precursors

The agricultural waste biomass of kenaf core or stalk (KC) was obtained from the Malaysian Agricultural Research and Development Institute (MARDI). The raw precursors were washed thoroughly to eliminate dust or other impurities. Then they were dried in an oven for 105 °C for 24 hours and cut into small pieces. Finally, they were sieved to the size of 1 to 2 mm.

### Preparation of Activated Carbon

Physio-chemical activation method which was explained in our previous studies (Chowdhury *et al.* 2011b) was used to produce powdered activated carbon (KCAC) from kenaf core (KC). The semi-carbonization, as well as activation steps were performed in a stainless steel vertical tubular reactor. At constant pressure, Nitrogen (N<sub>2</sub>) and CO<sub>2</sub> gases were passed inside the furnace. The pressure of gas flow was adjusted by using pressure regulators, and the flow rates of the gases were controlled by gas flow meters (Model Dwyer RMA-12-SSV, US). The two types of gas streams were combined by using a 3-way valve. The outlet from the valve was connected at the bottom of the reactor. All the connecting piping system inside and outside of the furnace was made up of stainless steel which were connected by stainless steel fittings to withstand high temperature and pressure. A stainless steel wire mesh was located at the bottom of the tubular reactor to protect the sample from falling outside. The reactor was placed inside a vertical tubular furnace. The furnace was equipped with a programmable system (Model Watlow Series 942, US) that controlled heating rate, final temperature, and residence time. The temperature within the sample bed in the reactor was measured with a K-type thermocouple having maximum temperature limit of 1000 °C. Another similar type of thermocouple was placed outside the reactor to measure the temperature of the tubular furnace.

Dried precursors (80 gm) were placed inside the tubular reactor. Purified nitrogen gas was used to evacuate oxygen and create the inert atmosphere through the reactor. The flow rate of nitrogen gas and the heating rate were maintained at 150 cm<sup>3</sup>/min and 10 °C/min, respectively, for the semi-carbonization step. The temperature was increased gradually from room temperature to 400 °C. Under inert atmosphere, this temperature was kept constant for 2 h to produce chars. The chars were cooled down to room temperature under nitrogen flow and then stored in air-tight containers for further treatment. A requisite amount of char was mixed with dried KOH pellets to maintain

definite impregnation ratio preselected by the design of the experiment. The impregnation ratio was calculated by using Equation (1):

$$\text{Impregnation ratio (IR)} = \frac{W_{\text{KOH}}}{W_{\text{Char}}} \quad (1)$$

Here,  $W_{\text{KOH}}$  is the dry weight of potassium hydroxide pellets and  $W_{\text{char}}$  is the dry weight of char (Chowdhury *et al.* 2011b). In this work, the KOH:char ratio was kept at 1.7. Then 69.2 g of dried KOH pellets were crushed and mixed with 250 mL water, into which 40 g of char were placed. The mixture was stirred to dissolve the KOH pellets completely. The impregnated sample was placed inside the oven (Model Memmert 600 Germany) overnight at 105 °C. This dehydrated the sample and left only KOH on the samples. Based on past studies, KOH was chosen as a chemical activating agent, as it can disrupt the graphite layer at high temperature in the presence of carbon dioxide and thereby finally increase the porosity of the prepared activated carbon (Salman and Hameed 2010). The KOH-impregnated chars were placed inside the same tubular reactor for activation.

The conditions of heating rate and nitrogen gas flow rate were the same as for the semi-carbonization step. The temperature was increased from room temperature to the desired activation temperature. Once the required activation temperature was reached, the nitrogen gas flow was switched off. At this stage, carbon dioxide (CO<sub>2</sub>) gas was passed into the reactor at the same flow rate and heating rate as the semi-carbonization step in order to initiate the activation process. According to the experimental requirement preset by the experimental design, the samples were kept inside for a certain period of time. After cooling the activated carbons at room temperature under nitrogen gas flow, the final samples were collected and washed with hot deionized water to recover unreacted KOH. The sample was washed several times with hot deionized water with addition of a few drops of hydrochloric acid (0.1 molar) until the pH of the washing solutions reached around 6 to 7. The washed activated carbons were then kept in an oven at 105 °C until the activated carbons were totally dried. The dried products were stored in air-tight containers for subsequent characterization and sorption studies.

## Experimental Design

The removal efficiency of copper, Cu(II) ions along with the highest possible yield can be increased by optimizing the production variables of activation temperature, activation time, and impregnation ratio. Therefore, a central composite design (CCD) based on response surface methodology (RSM) was applied to verify the influences of individual process variables and their interactive influences on the responses of yield and removal percentage (Azargohar and Dalai 2005; Wu and Tseng 2006). The removal percentage,  $Y_1$  was calculated by using Equation (2),

$$Y_1 = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where  $C_o$  and  $C_e$  (mg/L) represent the aqueous phase concentrations of Cu(II) ions at initial and equilibrium condition, respectively.

The response of activated carbon yield,  $Y_2$  was calculated by following Equation (3).

$$Y_2 = \frac{W_f}{W_o} \times 100 \quad (3)$$

Here,  $W_f$  (g) is the dry weight of the final activated carbon derived from kenaf stalk or core, and  $W_o$  (g) is the dry weight of the precursor.

Based on the central composite design, 20 experiments are required in order to analyze the influence of three variables. These experimental runs consist of 8 factorial points, 6 axial points, and 6 replicates at the center points and can be calculated by using the following Equation (4) where  $n$  denotes the number of independent variables and  $N$  is the total number of experiments.

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \quad (4)$$

The ranges and the levels of the three variables such as activation temperature ( $x_1$ ), activation time ( $x_2$ ), and impregnation ratio ( $x_3$ ) studied in this work are listed in Table 1.

**Table 1.** Independent Variables and their Actual and Coded Levels for the Central Composite Design (CCD)

Variables	Code	Units	Variable Levels				
			$-\alpha$	-1	0	+1	$+\alpha$
Activation Temperature	$x_1$	$^{\circ}\text{C}$	431.82	500	600	700	768.18
Activation Time	$x_2$	hour	0.32	1	2	3	3.68
Impregnation Ratio	$x_3$	-	0.32	1	2	3	3.68

The sequence of the experiments was randomized to minimize the effects of uncontrolled factors (Sumathi *et al.* 2009). Replicates at the central points are used to estimate residual error. The independent variables are coded to the (-1, +1) interval where the low and high levels are denoted by -1 and +1, respectively. The axial points are located at  $(0, 0, \pm\alpha)$ ,  $(0, \pm\alpha, 0)$ , and  $(\pm\alpha, 0, 0)$ . Here,  $\alpha$  represents the distance of the axial point from the center (Montgomery 2001).

An empirical model was developed in order to correlate the responses with three independent preparation variables by using a second degree polynomial Equation (5)

$$Y = b_0 + \sum_{i=1}^n b_i x_i + (\sum_{i=1}^n b_{ii} x_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (5)$$

Here,  $Y$  represents the predicted response,  $b_0$  is the constant coefficient,  $b_i$  denotes the linear coefficients,  $b_{ij}$  is the interaction coefficient,  $b_{ii}$  is the quadratic coefficient and  $x_i$ ,  $x_j$  are the coded values of the activated carbon production variables (Myers and Montgomery 2002; Zainudin *et al.* 2005).

The mathematical models and graphical analysis for each response with subsequent statistical significance were performed by using Design-Expert software (version 6, Stat-Ease, Inc., Minneapolis, USA). The complete design matrix containing the actual and coded levels of studied variables with their respective responses are given in Table 2.

**Table 2.** Experimental Design Matrix for Preparation of Kenaf Core (KCAC) Based Activated Carbon

Run	Type of Point	Level (coded Factors)			Activated Carbon Preparation Variables (Actual Factors)			Percentage Removal, Cu (II) $Y_1$ (mg/g)	Percentage Yield $Y_2$
					Temperature $x_1$ , (°C)	Time, $x_2$ (Hour)	Ratio IR, $x_3$		
1	Fact	-1	-1	-1	500	1	1	60.03	32.87
2	Fact	+1	-1	-1	700	1	1	77.09	21.87
3	Fact	-1	+1	-1	500	3	1	66.65	27.99
4	Fact	+1	+1	-1	700	3	1	83.59	16.54
5	Fact	-1	-1	+1	500	1	3	64.09	24.66
6	Fact	+1	-1	+1	700	1	3	84.33	16.89
7	Fact	-1	+1	+1	500	3	3	76.87	23.22
8	Fact	+1	+1	+1	700	3	3	95.09	15.98
9	Axial	-1.682	0	0	431.82	2	2	59.78	33.09
10	Axial	+1.682	0	0	768.18	2	2	97.97	13.33
11	Axial	0	-1.682	0	600	0.32	2	69.09	26.76
12	Axial	0	+1.682	0	600	3.68	2	95.54	18.99
13	Axial	0	0	-1.682	600	2	0.32	75.58	24.66
14	Axial	0	0	+1.682	600	2	3.68	92.33	17.02
15	Center	0	0	0	600	2	2	93.08	21.09
16	Center	0	0	0	600	2	2	94.77	22.54
17	Center	0	0	0	600	2	2	93.99	23.01
18	Center	0	0	0	600	2	2	93.78	21.87
19	Center	0	0	0	600	2	2	94.09	22.88
20	Center	0	0	0	600	2	2	94.02	22.99

### Batch Adsorption Studies

Copper, Cu(II) was taken here as an adsorbate due to its frequent presence in waste process effluents and strong adsorption affinity for the prepared activated carbon (KCAC). A precisely weighed amount (0.2 g) of activated carbon was mixed with 50 mL solution of adsorbate, Cu (II) solution having a concentration range of 50 mg/L, 60 mg/L, 70 mg/L, 80 mg/L, 90 mg/L, and 100 mg/L in 250 mL Erlenmeyer flasks at pH 5.5. The flasks were placed in a thermal water bath shaker equipped with a cover to prevent heat loss. The

mixture was agitated at 150 rpm for equilibrium contact time. Aqueous samples were withdrawn from the flasks at definite time intervals until equilibrium, and the remaining concentrations of Cu(II) ions in the solutions after adsorption were determined using an atomic absorption spectrophotometer (Perkin-Elmer Model 3100). However, for isotherm generation, the concentration range varied from 50 mg/L, 60 mg/L, 70 mg/L, 80 mg/L, 90 mg/L, and 100 mg/L, while for response calculation in Table 2, the removal percentage was calculated using the highest concentration of 100 mg/L. However, the optimum agitation speed (150 rpm) and equilibrium contact time (6 hours) were determined by our preliminary studies. Each experiment was carried out three times, and the average results were used for isotherm generation and response calculation. The amount of equilibrium uptake by prepared activated carbon was calculated using Equation (6),

$$q_e = \frac{(C_o - C_e)V}{W} \quad (6)$$

where,  $q_e$  (mg/g) is the amount of ion adsorbed at equilibrium.  $C_o$  and  $C_e$  (mg/L) are the liquid-phase concentrations of Cu (II) ions at initial and equilibrium conditions, respectively.  $V$  (L) is the volume of the solution, and  $W$  (g) is the weight of activated carbon used.

### Physio-Chemical Characterization

A scanning electron microscope (SEM, Model Leo Supra 50VP Field Emission, UK) was used to obtain the surface textural features of the precursor, semi-carbonized char and prepared carbon (KCAC).

The BET Surface area, pore volume, and pore size distribution of the prepared adsorbent was analyzed with an Autosorb 1, Quantachrome Autosorb automated gas sorption system supplied by Quantachrome. The activated carbon was outgassed under vacuum at 300 °C for 4 hours to remove moisture content before nitrogen gas adsorption. Surface area was calculated by Brunauer Emmett Teller (BET) method, and micropore volume was calculated by the Dubinin-Radushkevich (DR) method. The cumulative adsorption surface area was calculated by the well-known BJH method. All these procedures were automatically conducted by software (Micropore version 2.26) supplied with the instrument.

Proximate analysis was carried out using Thermal Gravimetric analysis (TGA) equipment (Model Perkin Elmer TGA7, US) to determine moisture content, volatile matters, fixed carbon, and ash residues of the precursor, semi-carbonized char, and activated carbon (KCAC). Ultimate analysis was carried out using the Elemental Analyzer (PerkinElmer, Series II 2400) to evaluate the percentage of carbon, hydrogen, and nitrogen in the precursor, semi-carbonized char, and the activated carbon (KCAC).

The average bulk density was calculated by water displacement of a definite amount of activated carbon (Zahangir *et al.* 2008).

## RESULTS AND DISCUSSION

### Development of Regression Model

For both the responses of removal percentage and yield, models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased based on the sequential model sum of squares (Arami-Niya *et al.* 2012; Chowdhury *et al.* 2011b). Model parameters were estimated from the design matrix depicted in Table 2. For removal percentage of copper, a quadratic model and for carbon yield, a 2FI model were developed. The final empirical models in terms of coded factors after excluding the insignificant terms for the above mentioned responses are represented by following Equations (7) and (8), respectively.

$$\text{Percentage removal of Cu(II)} \quad Y_1 = 94.12 + 10.01x_1 + 5.94x_2 + 4.48x_3 - 6.39x_1^2 - 5.17x_2^2 - 4.59x_3^2 - 0.27x_1x_2 + 0.56x_1x_3 + 1.30x_2x_3 \quad (7)$$

$$\text{Yield \%} = 22.41 - 5.18x_1 - 1.88x_2 - 2.30x_3 + 0.0013x_1x_2 + 0.930x_1x_3 + 0.980x_2x_3 \quad (8)$$

The coefficients with one variable of temperature ( $x_1$ ), time ( $x_2$ ), and impregnation ratio ( $x_3$ ) represent the effect of that particular factor on the responses of removal percentage ( $Y_1$ ) and activated carbon yield ( $Y_2$ ). The coefficients multiplied between two variables and others with second order terms demonstrate the interaction between the two variables and quadratic effect, respectively. A positive sign in front of the terms indicates a synergetic effect, whereas a negative sign indicates an antagonistic effect. The quality of the model developed can be understood by the coefficient of determination,  $R^2$  and standard deviation values.  $R^2$  indicates the ratio between sum of the squares (SSR) with total sum of the square (SST), and it depicts how well the model approximates experimental data points (Myers and Montgomery 2002).

The performance of the models can also be visualized by observing the plots of predicted versus experimental percentage yield and removal by Figs. 1(a) and 1(b), respectively. As can be observed from Fig.1(a) and Fig.1(b), the predicted values for removal percentages of Cu(II) ions and activated carbon yield were closer to their experimental values reflecting suitability of the models represented by Equations 7 and 8. This might be due to their large  $R^2$  values. The  $R^2$  value for Equations (7) and (8) were 0.972 and 0.968 for removal percentage (Fig. 1a) and yield (Fig. 1b), respectively, which ensures excellent adjustment of the developed models with the experimental data.

Figures 2(a) and 2(b) show outlier  $t$  plot for removal percentage of Cu (II) ions and carbon yield. For successful resolution of designed experiments, the outliers should be carefully observed. Outlier  $t$  plots reflect a simple data recording error. Sometimes it shows the region of independent variables where the fitted model has showed poor approximation to the true response surface (Myers and Montgomery 2002). From Fig. 2(a) and 2(b), it was observed that most of the standard residuals fell within the interval of  $\pm 3.50$ . This showed that the data approximation for the fitted models (Equation 7 and 8) to the response surface was fairly good and reflected no data recording error. However, there was only one data point recorded over  $+3.50$  for removal percentage (Fig. 2a). This



might be due to the insignificant terms or nonlinear influence of the studied variables over the response. A similar observation has been reported for adsorption studies of Cu (II) ions onto a type of seaweed, *Enteromorpha prolifera* (Ozer *et al.* 2009).

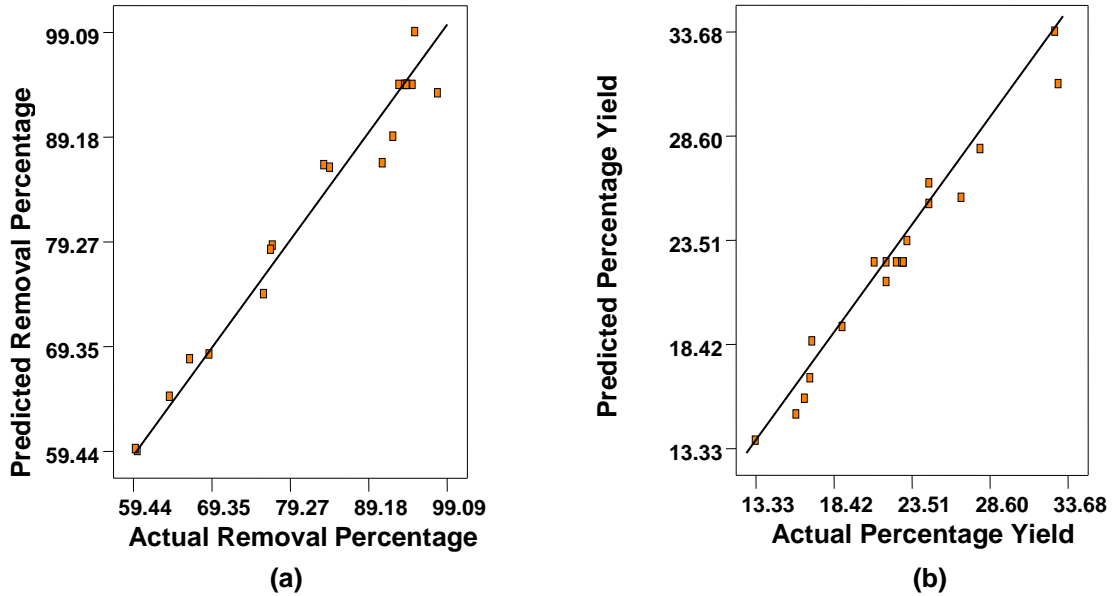


Fig. 1. Predicted vs. Actual values of (a) Removal % of Cu (II) (b) Production Yield % of Kenaf Core based Activated Carbon (KCAC)

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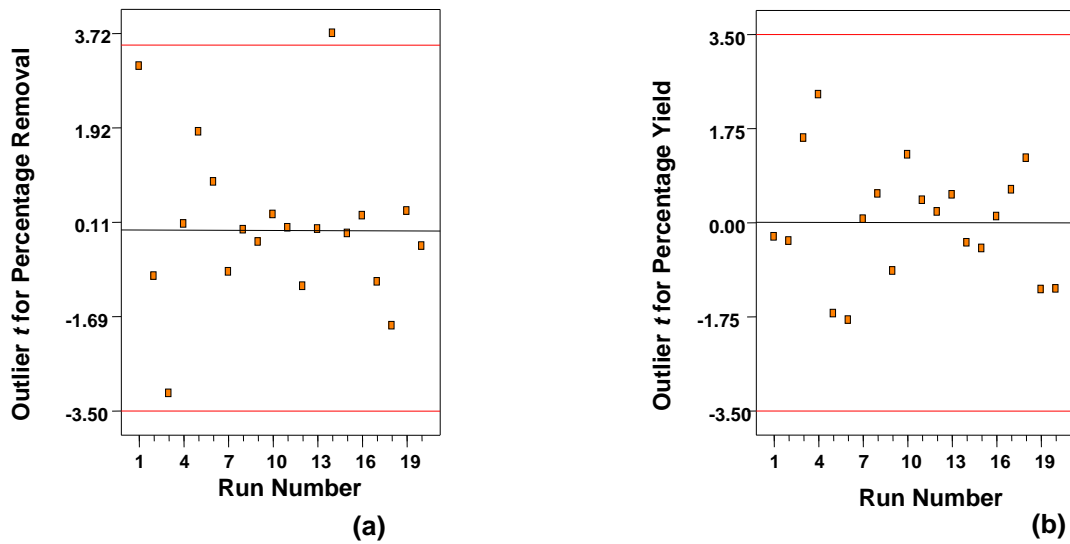
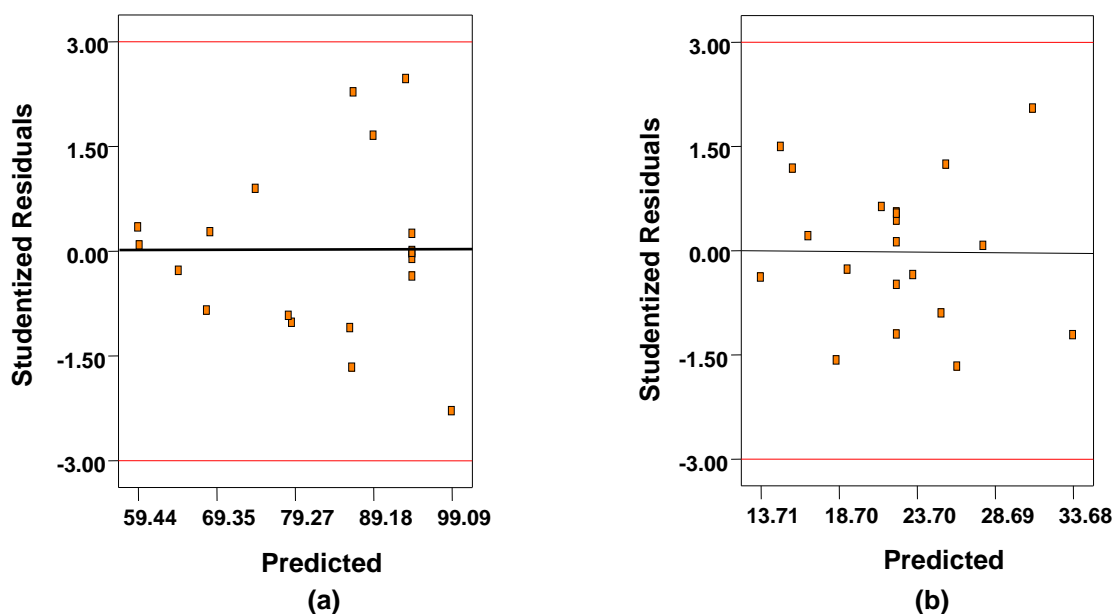


Fig. 2. Outlier *t* plots for (a) Removal % of Cu (II) (b) Production Yield % of Kenaf Core based Activated Carbon (KCAC)

Figures 3(a) and 3(b) show studentized residuals and predicted plots for removal percentage of Cu(II) ions and carbon yield, respectively. The data points in these plots should be randomly scattered, demonstrating that the variance of experimental observations were constant for all the values of response depicted by Table 2. The data points obtained were between  $\pm 3.00$ , which implied that no response transformation was needed for the experimental design of this study (Myers and Montgomery 2002).



**Fig. 3.** The studentized residuals and predicted response plots for: (a) Removal % of Cu (II); (b) Production yield % of Kenaf Core Based Activated Carbon (KCAC)

### ANOVA Analysis and Lack of Fit

The competence of the developed models was further justified through analysis of variance (ANOVA), and the results obtained are depicted in Tables 3 and 4. The significance of the empirical models were investigated by the F-test value, which is a statistical measure of how well the empirical model describes the variation in the data about the mean. The greater the F-value from the unity, the more certain it is that the model explains adequately the variation in the data, and the estimated significant terms of the adsorbent preparation variables are closer to the actual value (Myers and Montgomery 2002). Based on a 95% confidence level, the model F-value for removal percentage of copper and yield were 25.97 and 66.24, respectively which implied that these models were significant. Nevertheless, the values of Prob > F for uptake of copper and yield were less than 0.05, which indicated that the model terms were significant. For Cu (II), activation temperature ( $x_1$ ), activation time ( $x_2$ ), and activation ratio ( $x_3$ ), as well as their quadratic terms of ( $x_1^2$ ), ( $x_2^2$ ), and ( $x_3^2$ ) were significant whereas the interaction terms of  $x_1x_2$ ,  $x_1x_3$ , and  $x_2x_3$  were all insignificant to the response.

**Table 3.** ANOVA Analysis and Lack of Fit Test for Response Surface Model for Removal Percentage of Cu (II) from Synthetic Waste Water by Using Kenaf Core Based Activated Carbon (KCAC)

Source	Sum of the Squares	Degree of Freedom	Mean Square	F Value	Prob> F	Comments
Model	3213.34	9	357.04	25.97	<0.0001	<i>Significant</i>
$x_1$	1368.07	1	1368.07	99.50	<0.0001	<i>Significant</i>
$x_2$	482.12	1	395.48	35.06	<0.0001	<i>Significant</i>
$x_3$	274.16	1	268.17	19.94	0.0012	
$x_1^2$	588.03	1	559.87	42.77	<0.0001	<i>Significant</i>
$x_2^2$	385.43	1	488.32	28.03	<0.0004	
$x_3^2$	303.85	1	274.73	22.10	0.0008	
$x_1x_2$	0.570	1	0.570	0.042	0.8424	
$x_1x_3$	2.490	1	2.490	0.18	0.6797	
$x_2x_3$	13.57	1	13.57	0.99	0.3439	
Residuals	137.50	10	13.75			
Lack of Fit	136.01	5	27.20	91.64	<0.0001	
Pure Error	1.48	5	0.30			

**Table 4.** ANOVA Analysis and Lack of Fit Test for Response Surface Model for Activated Carbon Yield by Using Kenaf Core Based Activated Carbon (KCAC)

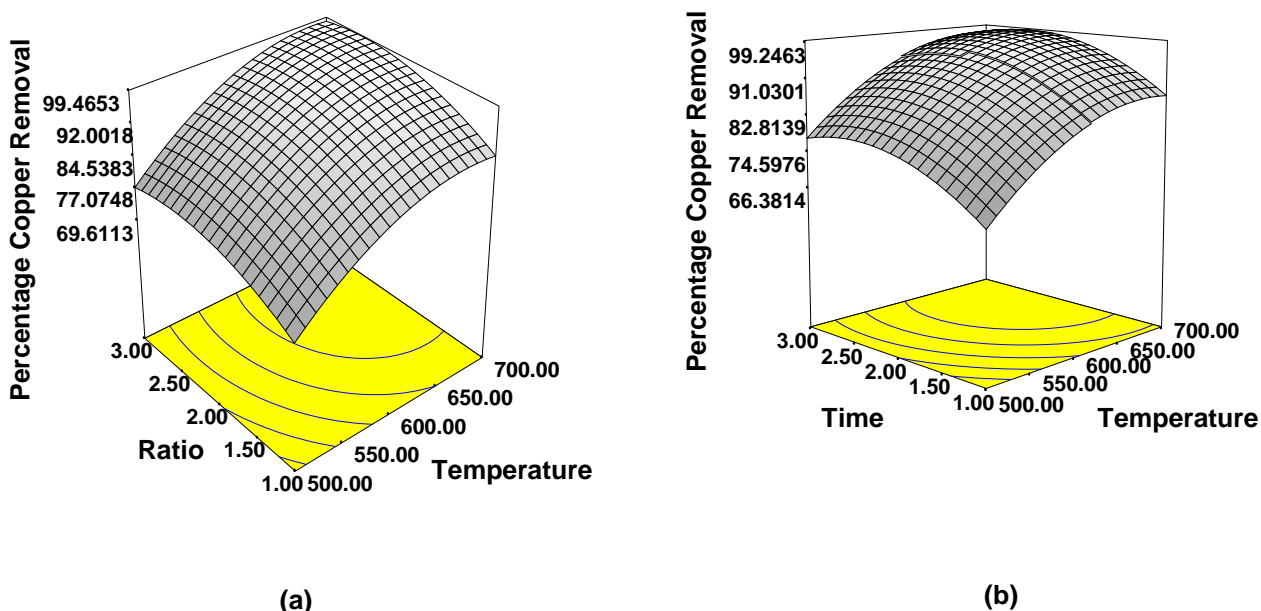
Source	Sum of the Squares	Degree of Freedom	Mean Square	F Value	Prob> F	Comments
Model	500.71	9	83.45	66.44	<0.0001	<i>Significant</i>
$x_1$	365.93	1	365.93	291.31	<0.0001	<i>Significant</i>
$x_2$	48.09	1	48.09	38.29	<0.0001	<i>Significant</i>
$x_3$	72.05	1	72.05	57.36	<0.0001	<i>Significant</i>
$x_1x_2$	0.001	1	0.001	0.001	0.9802	
$x_1x_3$	6.92	1	6.92	5.51	0.0354	<i>Significant</i>
$x_2x_3$	7.72	1	7.72	6.15	0.0276	<i>Significant</i>
Residuals	16.33	10	1.26			
Lack of Fit	13.36	5	1.67	2.81	0.1347	
Pure Error	2.97	5	0.59			

Referring to Table 4 for 2FI model for yield (Equation 8),  $x_1$ ,  $x_2$ ,  $x_3$ , and interaction terms of  $x_2x_3$  and  $x_1x_3$  were significant model terms, whereas other interaction terms of  $x_1x_2$  were negligible relative to the response.

### Effect of Preparation Variables on Adsorption Capacity

Based on the F values shown in Table 3, the activation temperature was found to have greatest effects on the adsorption capacity of Cu (II) ions onto the activated carbons prepared from KC, whereas activation time and impregnation ratio showed almost similar

impact on this response. Figure 4(a) depicts the three-dimensional response surfaces with a contour plot that showed the effects of the combined effects of two significant variables, activation temperature and impregnation ratio, on the adsorption capacity, where the activation time was fixed at zero level, which was 2 h. Figure 4(b) was constructed to show the effects of activation temperature and time on the removal percentage of copper where activation ratio was kept constant at 2.



**Fig. 4.** The three dimensional response surfaces: (a) Effect of temperature and ratio on removal % of Cu (II); (b) Effect of temperature and time on removal % of Cu (II)

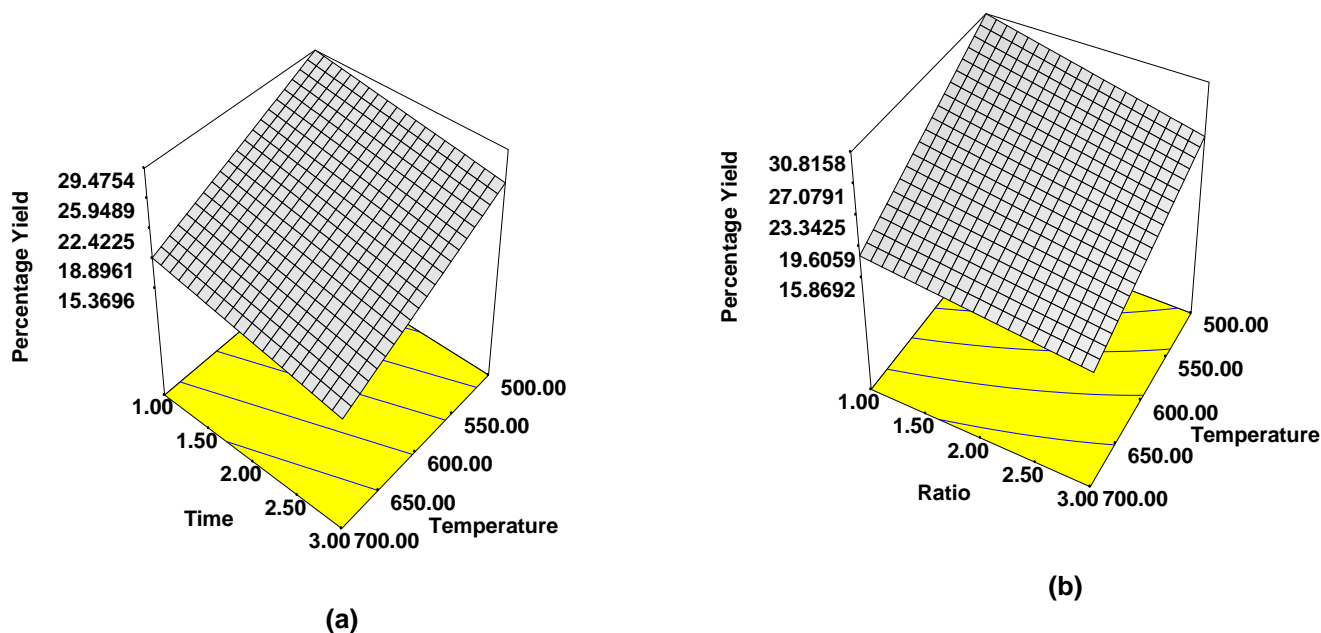
It was observed from Fig. 4(a) and 4(b) that, after a certain limit of temperature and KOH ratio, as well as temperature and time, the adsorption capacity was reduced slightly. The plausible explanation for this may be the disruption or lessening of the intensity of some surface functional groups at higher temperature. It was reported in the literature that an activation time that was too long or too short and an activation temperature that was too high or too low could reduce the surface area and the adsorption capacity of activated carbon. This was because longer activation time and/or higher activation temperature might destroy the pore structure formed previously, whereas a shorter activation time and/or lower activation temperature could not enhance the formation of porosity (Cao *et al.* 2006). At very high temperature, thermal annealing causes the walls of the micropore to collapse and form more mesopores, which are helpful for carrying the adsorbate towards the interior of micropores for liquid phase adsorption. But in some cases, even with high surface area, if the pore distribution is not suitable or pore diameter of those mesopores are larger, then it fails to capture and retain the smaller cations, resulting in a low removal efficiency. However, the same observation was reported for preparing activated carbon from oil palm frond for removal of zinc from aqueous solution by RSM technique. It was observed that at high temperature and longer

contact time, more ash residues were formed, which blocked the pores and resulted in a low removal efficiency of zinc from waste water (Zahangir *et al.* 2008).

In this work, all three variables studied were found to have synergistic effects on the adsorption capacity of the preselected cations of copper. This was expected because the progressive increase of temperature and activation time would increase the reaction between the char and KOH and char with CO<sub>2</sub>. The increase in activation temperature and time would ensure sufficient contact time between the carbon matrix and physical and chemical activating agent of CO<sub>2</sub> and KOH for the dissolution of cellulosic structure (Baçaoui *et al.* 2001; Stavropoulos and Zabaniotou, 2005; Lua and Yang, 2004). Nevertheless, the impregnation ratio played a crucial role in the formation of pores (Adinata *et al.* 2007). The increase in KOH accelerated the reaction rate, and the quantity of the pores increased correspondingly. However, there was a maximum range for the impregnation ratio and time beyond which the uptake capacity of Cu (II) ions would reduce onto KC activated carbon. Excessive quantity of KOH caused additional reaction between KOH and carbon, which might obliterated the pore structure formed at an earlier stage (Cao *et al.* 2006).

### Effect of Preparation Variables on Activated Carbon Yield

For activated carbon yield, activation temperature was found to have the greatest effect on this response by showing the highest F value of 365.93, as shown in Table 4, whereas activation time was not significant to the response, which was not as noteworthy compared to activation temperature and impregnation ratio. The interaction effect of activation time and ratio was more pronounced than the other two interaction terms relative to the yield of KC activated carbon.



**Fig. 5.** The three dimensional response surfaces: (a) Effect of temperature and time on yield percentage; (b) Effect of temperature and ratio on yield % of Kenaf Core based activated carbon (KCAC)

Figures 5(a) and (b) show the three-dimensional response surfaces that were constructed to reveal the effects of the activated carbon preparation variables on the activated carbon yield. Figure 5(a) represents the combined effect of activation temperature and activation time on the response, where impregnation ratio was fixed at zero level (Ratio = 2). Figure 5(b) illustrates the effect of activation temperature and impregnation ratio on the same response, where activation time was fixed at zero level ( $t = 2$  h). In general, the KC activated carbon yield was found to decrease with activation temperature, activation time, and impregnation ratio. As can be seen from both the plots (Figs. 5a and 5b), activation temperature was more dominant relative to the activated carbon yield as compared to the other two variables. The lowest carbon yield was obtained when temperature was at the maximum point within the studied range. This outcome was also in agreement with the previous work carried out by Sudaryanto *et al.* (2006), where activation temperature was found to play a vital role on the yield of cassava peel based activated carbon, whereas activation time did not show much effect on the carbon yield. However, for KC based activated carbon, the effect of activation time was moderate. The increase in temperature would release more a volatile component as a result of intensified dehydration and elimination reactions during the preparation of activated carbon. This would increase the C-KOH and C-CO<sub>2</sub> reaction rate, thereby resulting in decreasing carbon yield (Bacaoui *et al.* 2001, Lua and Yang, 2004; Adinata *et al.* 2007).

### Process Variables Optimization

In the production of commercial activated carbons, high adsorption efficiency with adequate product yields are expected. Therefore, in the practical manufacturing process, a compromise should be made between the activated carbon yield and the adsorption performance of the prepared activated carbon. However, optimizing both these responses under the same condition is complicated because the interest region of the factors are completely different (Ahmad *et al.* 2010). As observed from the basic design matrix from Table 2, as adsorption performance increased, carbon yield decreased and vice versa. Therefore, in order to compromise between these two responses, the numerical optimization menu was selected using Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, LTS). In order to optimize the preparation conditions, the targeted criteria was set as maximum values for removal percentage along with yield, while the values of the three variables (CO<sub>2</sub> activation temperature, CO<sub>2</sub> activation time, and impregnation ratio) were set in the ranges being studied. However, after model simulation, the operating conditions were suggested by the software. The optimum activating temperature ( $568 \pm 1$ )°C, activating time 2.02 hour, and impregnation ratio of 1.75 were suggested by the software to obtain maximum output of the process. Activated carbon was prepared at these optimum conditions and its sorption capacity and yield were determined. The experimental results obtained for activated carbon prepared under optimum conditions along with other statistical parameters to validate the developed models are listed in Table 5.

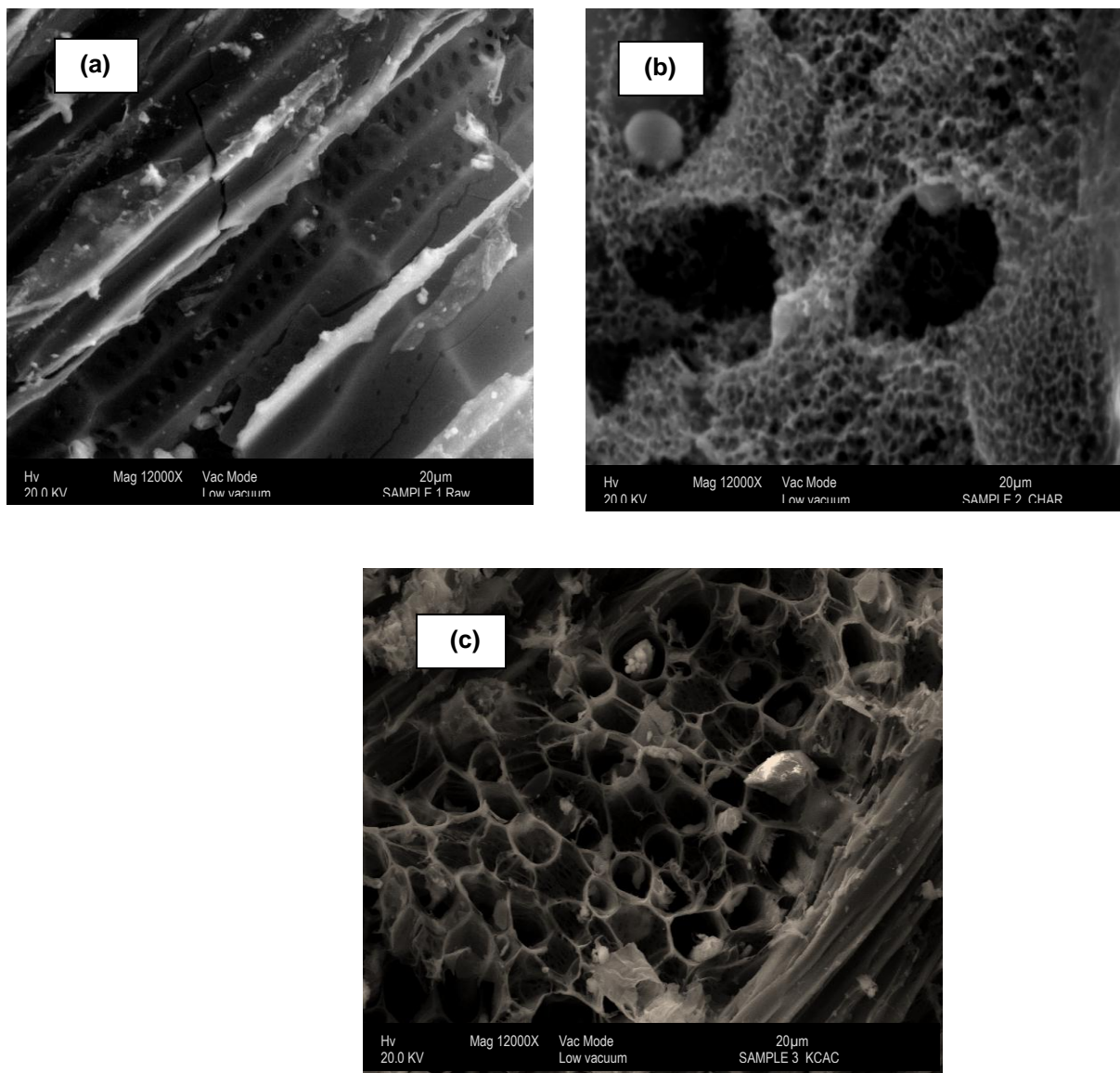
**Table 5.** Statistical Parameters for ANOVA Analysis for Model Regression of Removal Percentage of Cu (II) and Yield for Kenaf Core Based Activated Carbon (KCAC)

Statistical Parameters	Responses	
	Percentage Removal of Cu (II)	Yield
	$Y_1$	$Y_2$
Standard Deviation, SD%	3.71	1.12
Correlation Coefficient, $R^2$	0.960	0.968
Adjusted $R^2$	0.922	0.954
Mean	83.09	22.41
Coefficient of Variation, CV	4.46	5.00
Adequate Precision	15.58	30.13
Predicted Result at Optimum Condition	89.02	24.66
Experimental Observation at Optimum Condition	97.24	27.55
Error Percentage	8.45	0.10
Comments	Acceptable	Acceptable

From the statistical results shown in Table 5, it can be concluded that the models (Equations 6 and 7) were adequate to predict the removal percentage and the carbon yield within the experimental range of variables selected. The adjusted  $R^2$  is in reasonable agreement with the coefficient of determination,  $R^2$  for linear regression analysis of the two developed models. Estimation of CV values provides the ratio between standard error of estimate with the mean value of the observed response as percentage. This shows the reproducibility of the model. If the value is less than 10%, then the model can be considered practically reproducible (Myers and Montgomery 2002). It was found that the CV values obtained for percentage removal of Cu (II) ions and yield were 3.66 and 5.00, showing reproducibility of the models. “Adequate Precision” values determined were 15.58 and 30.13, which measures the signal to noise ratio. The ratio obtained were greater than 4, reflecting that the developed models can be used to navigate the design space. The results obtained for predicted and experimental observations for the responses revealed that both the deviation errors were less than 10%, which is within the acceptable limit. Similar range of error percentage of 7.15 and 8.71, respectively, were observed under optimum conditions for sorption studies of disperse dye and yield of activated carbon derived from rattan saw dust (Ahmad *et al.* 2009). Thus it can be concluded that the models developed were suitable and sufficient to determine the responses from the operating variables fixed for this study.

### Physio-chemical Characterizations of the Activated Carbon

The micrographs of the raw kenaf core (KC), semi-carbonized char, and powdered activated carbon (KCAC) were obtained by Scanning Electron Microscope (SEM) and shown by Figs. 6(a), 6(b), and 6(c), respectively.



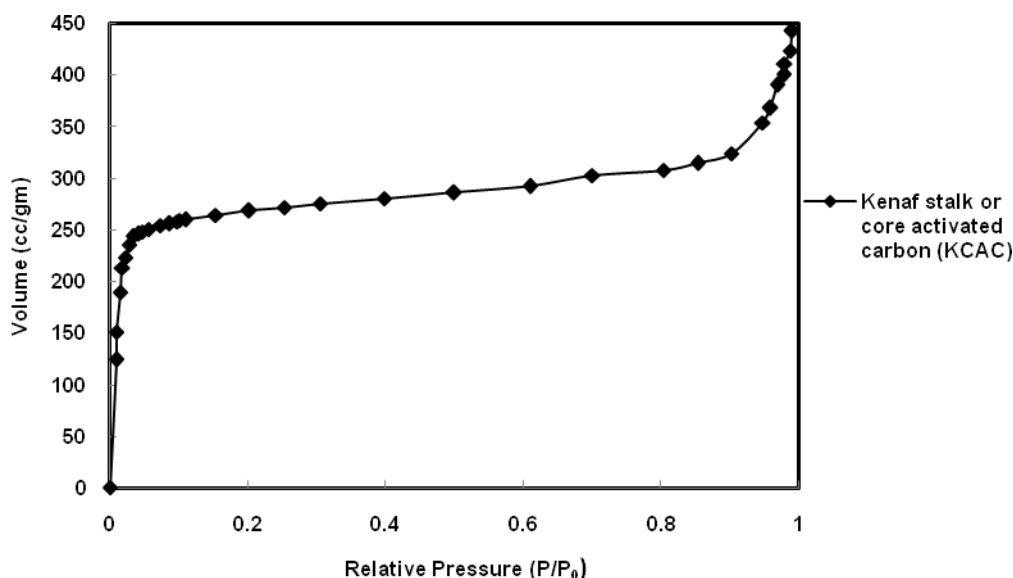
**Fig. 6.** SEM (12000x) Micrographs of: (a) Raw Kenaf Core; (b) Semi-carbonized Kenaf Core; (c) Kenaf Core Based Activated Carbon (KCAC)

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From the SEM micrographs obtained, the change in surface texture and pore development were visible. The surface of raw kenaf core was smooth with few pores. After semi-carbonization, the surface became rough and uneven with some irregular shaped pores. Some anonymous fragments were observed on the surface of char, which might be the residues of tarry substances formed during the semi-carbonization stage. The activated carbons produced from KC demonstrated homogeneous pore size distributions with uniform pore arrangements. As shown by Fig. 5(c), the pores available on the



surfaces of the activated carbons were well pronounced with distinct pore walls and were arranged in a group of honey-combed structures. The chars were gasified by the activation process. Thus, the tarry substances were eliminated by the exhaust gas, leaving most of the pores clear and easily absorbable by Cu (II) ions. The N<sub>2</sub> adsorption isotherm of the prepared activated carbon is illustrated by Fig. 7.



**Fig. 7.** N<sub>2</sub> adsorption isotherms kenaf core based activated carbon under optimum condition

It was observed that the adsorption isotherm contains three characteristic regions: (a) the initial part of the curve with a sharp knee resulted from nitrogen uptake at  $P/P_0 < 0.2$ ; (b) the second part that is the plateau of the curve between  $P/P_0 > 0.2$  but  $P/P_0 < 0.8$ ; and (c) the small upward bend of the curve at the last region when equilibrium was reached ( $P/P_0 \approx 0.9$ ).

The characteristics of the curve indicated a Type I isotherm. The shape of the isotherm indicated the presence of a high proportion of micropores with some contribution of meso and macropores (Khalili *et al.* 2000). The aforementioned surface analysis was carried out and it was found that the average pore diameter of the prepared activated carbon was 22.70 Å which was in the mesopore region based on IUPAC classification (IUPAC 1982).

Results obtained from surface area analysis, ultimate and proximate analyses of the raw precursor, as well as the activated carbon prepared under optimum conditions are summarized in Table 6.

**Table 6.** Physio-Chemical Characteristics of Raw Kenaf Core (KC) and Activated Carbon (KCAC)

Physio- Chemical Characteristics	Raw Kenaf Core (KC)	Activated Carbon (KCAC)
BET surface area	1.034 m <sup>2</sup> /g	1020.03 m <sup>2</sup> /g
Micropore Surface area (DR Method)	0.312 m <sup>2</sup> /g	815.04 m <sup>2</sup> /g
Total pore volume	0.201 cm <sup>3</sup> /g	0.5789 cm <sup>3</sup> /g
Average pore diameter	1.010 °A	22.70 °A
Cumulative adsorption surface area (BJH Method)	1.660 m <sup>2</sup> /g	545.45m <sup>2</sup> /g
Bulk density	-	0.312 g/mL
Ultimate Analysis		
% C	51.22	66.32
% H	15.79	7.790
% N	5.560	1.560
Others	27.43	24.33
Proximate Analysis		
Moisture Content	5.90	4.33
Volatile Matter	76.87	23.76
Fixed Carbon	12.33	65.28
Ash	4.90	6.63

From Table 6, it was observed that raw kenaf core was rich in volatile matters. The fixed carbon content was also reasonable. Thus this biomass can be considered suitable starting materials to produce activated carbon (Arami-Niya *et al.* 2012). The volatile matter decreased significantly, whereas the fixed carbon content increased after the activation process. This was because at high temperature, the organic substances inside the carbon matrix became unstable and formed liquid and gaseous substances. A similar phenomenon has been reported for preparing activated carbon from palm shell (Arami-Niya *et al.* 2010).

### Application of the Prepared Activated Carbon

From the view of industrial use, the production yield and quality of the product in terms of surface area, porosity, density, and sorption performance are important. In this regard, sorption performance of the prepared sorbent was measured at 30 °C, 50 °C, and 70 °C. The experimental data were analyzed by the Langmuir, Freundlich, and Temkin isotherm models.

The Langmuir isotherm is based on the following hypothesis (Langmuir 1916):

- Metal adsorbate cations or anions are adsorbed chemically at a fixed number of well-defined sites.
- These active sites occupied by metal ions are energetically equivalent.
- Each active site is capable of holding one ion.
- No interaction is present between the ions.

The linear form of Langmuir isotherm is,

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \quad (9)$$

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), and  $q_m$ , (mg/g) and  $K_L$  (L/mg) are Langmuir constants related to maximum monolayer adsorption capacity and rate of adsorption, respectively (Srivastava and Hasan 2011). When  $C_e/q_e$  is plotted against  $C_e$ , a straight line with slope of  $1/q_m$  and intercept of  $1/q_m K_L$  is obtained (Figure not shown). The essential characteristic of the Langmuir isotherm or separation factor,  $R_L$  is represented by,

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

where,  $C_0$  is the adsorbate highest initial concentration (100 mg/L).

The Freundlich expression is an exponential equation widely applied for describing a heterogeneous system (Freundlich 1906). It is based on the assumptions that the concentration of the adsorbate on the surface of adsorbent increases with the increase of initial concentration of the adsorbate. The linear form of Freundlich equation is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (11)$$

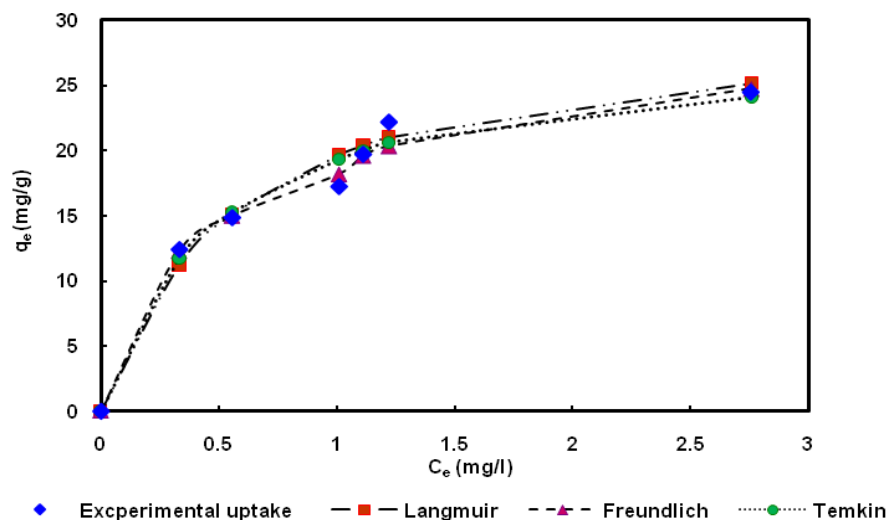
where,  $K_F$  (mg/g (L/mg)) represents the distribution coefficient, and  $n$  represents the intensity factor (Srivastava and Hasan 2011).

According to the Temkin model, (Temkin and Pyzhev 1940) adsorption occurs by a regular distribution of binding energies, up to a certain maximum binding energy. The linear form of Temkin Isotherm is:

$$q_e = B \ln K_T + B \ln C_e \quad (12)$$

$$B = \frac{RT}{b} \quad (13)$$

Here,  $R$  is the gas constant (8.314 J/mol K),  $T$  is the absolute temperature ( $^{\circ}$ K), and  $RT/b = B$ . The linear plot of  $q_e$  versus  $\ln C_e$  yields a linear line with  $B$  as the slope and  $B (\ln K_T)$  as the intercept (Figure not shown).  $K_T$  (L/g) represents the equilibrium binding constant, and  $B$  is the heat related constant (Srivastava and Hasan 2011). However, the isotherm model parameters were evaluated at 30  $^{\circ}$ C, 50  $^{\circ}$ C, and 70  $^{\circ}$ C to study the effect of temperature on the sorption process. Figure 8 shows experimental uptake capacity with uptake capacity determined from different models, and the model parameters are provided in Table 7.



**Fig. 8.** Equilibrium uptake of Cu (II) ions on activated carbon (KCAC) at 30°C temperature

On the basis of  $R^2$  value, it can be concluded that the Langmuir model was most suitable to explain the experimental data. It was observed that the Langmuir curve was almost superimposed by experimental data. This shows homogeneous texture of the adsorbent surface. Maximum monolayer sorption capacity,  $q_m$  (mg/g) increased with an increase in temperature. Thus, the sorption that occurred is endothermic. The Langmuir separation factor,  $R_L$  and Freundlich exponent,  $1/n$  values ranged from 0 to 1 for the studied temperature range, indicating that the adsorption process of Cu (II) was favorable. A similar phenomenon has been observed for Cu (II) sorption onto activated oil palm ash and kenaf bast fiber activated carbon in our previous work (Chowdhury *et al.* 2011c, d).

**Table 7.** Isotherm Model Parameters and Correlation Coefficient at Different Temperature

Temp. (°C)	Langmuir Isotherm				Freundlich Isotherm			Temkin Isotherm		
	$q_{max}$ (mg/g)	$K_L$ (L/mg)	$R_L$	$R^2$	$K_F$ (mg/g) (L/mg) <sup>1/n</sup>	1/n	$R^2$	B	$K_T$ (L/mg)	$R^2$
30	29.42	2.000	0.004	0.985	18.357	0.335	0.922	5.922	23.957	0.920
50	32.26	2.067	0.005	0.985	20.491	0.399	0.976	7.140	18.441	0.977
70	33.34	2.500	0.004	0.977	23.266	0.426	0.970	7.523	20.739	0.967

## CONCLUSIONS

The present study investigated the potential of utilizing kenaf core or dried stalk as an agricultural waste of the kenaf crop plantation process, with the determination of the adsorption capacity of copper (II) ions and activated carbon yield. Production parameters for preparing activated carbons were optimized to achieve maximum possible yield with highest sorption capacity for economic feasibility of the process. Based on the research findings, the following conclusions were made:

1. Process variables were optimized by applying a central composite design based on response surface methodology. Activation temperature, time, and impregnation ratio had significant impact on each response of adsorption uptake and production yield.
2. After validation of the optimum conditions, it was observed that the developed models were able to predict the values of the responses quite well. The deviation errors obtained between predicted and experimental results for adsorption capacity and yield were 0.972% and 0.968%, respectively which were near to unity.
3. The activated carbon exhibited high surface area of 1020.03 m<sup>2</sup>/g with increased proportion of fixed carbon of 68.28 % compared to the raw precursors.
4. The equilibrium data were well represented by linear regression of the Langmuir isotherm, showing maximum monolayer sorption capacity about 29.42 mg/g at 30°C which was increased up to 33.34 mg/g at 70°C.

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