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Optimization of parameters for the preparation of high yielded activated carbon from banana trunk

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Abstract
This experiment was conducted to optimize the operating conditions for the production of activated carbons from banana trunk. The dried banana trunk which contained 6.43% moisture, 8.8% ash content, 25% volatile matters, and around 59.77% fixed carbon was found suitable for the production of activated carbon. The chemical activation method was adopted in this experiment. The dried banana powderimpregnated with different concentrations of phosphoric acid was optimized for high yielding activated carbons using rotatable central composite design of response surface methodology (RSM). Three operating parameters, such as activation time (35.5, 50.0, 85.0, 120.0, and 134.5 min), activation temperature (367, 450, 650, 850, and 932 °C), and H_3PO_4concentration (0.36, 1.50, 4.25, 7.00, and 8.14 mol/L) played a significant role in the production of activated carbons. The results showed that the maximum yield of banana trunk activated carbon was achieved at the activation time of 60 minutes, activation temperature of 480 °C, and H_3PO_4 concentration of 3.94 mol/L. At optimum conditions of operating factors, the percent yield predicted through statistical model was 47%, whilst on experimental verification it was found 46.05%.

Keywords: Activated carbon, Banana Trunk, Chemical activation, Optimization, Yield

Introduction
With the growing pollution in water and air, we need some sort of low mass and large surface area materials thatcouldbe used against water and air borne pollutants. Activated carbons are fulfilling the requirement of large surface area with small mass and proven to be effective against wide range of pollutants in gaseous as well as in aqueous media. Activated carbon is a carbonaceous adsorbent that has been widely used for variety of industrial applications such as, in wastewater treatment plants, in chemical reactions industries as a catalyst support materials, in medicine as medical adsorbent and drug carrier, and in electronic industry as electrical double-layer capacitors due to its large surface area and pore volume [1, 2]. Environmental issues are becoming more serious day by day that leads to the increasing demand for activated carbon. According to survey agency (Roskill) the demand of activated carbon in world market is increasing every years, and the demand in 2017 is projected to be nearly 2.4 Million tones [3]. To fulfill this huge demand of world market, researchers need to explore alternate production source with economic viability. The production and regeneration of activated carbon are still considered to be expensive, and many researches are being conducted to produce activated carbon by using low-cost raw materials and methods. Hence, the necessity demands to explore the suitable inexpensive precursor materials that can have far better characteristics than the conventional raw materials have [4]. The adsorption properties of activated carbon strongly depend on nature of precursor materials as well as the methods and process conditions employed for activation.
In recent years, researchers have studied the production of activated carbon from cheap and renewable precursors, such as date stone [5], *Acacia mangium* wood [6], Pomegranate wood[7], coconut husk [8], rice

husk [9] and waste tea [10]. Banana is native to Southeast Asia, most of the bananas produced are consumed locally[11]. In Malaysia, banana is the second most widely cultivated fruit. It covers about 26,000 ha, with a total production of 530,000 metric tons [12], which mean a large amount of banana waste such as banana trunk are produced and damped without proper use. Enormous amounts of waste are disposed of, resulting in a severe environmental problem through the release of foul odors (H_2S and methane) when it is left to decompose in anaerobic conditions. Hence, the comprehensive utilization of this waste in production of value added product will be a promising means to increase the revenue generation for the banana grower farmers. Banana trunk is a renewable precursor for activated carbon production and could be used as potentially cheap alternative to existing commercial sources. The major challenge of converting fresh banana trunk into activated carbon is it high moisture content, which may cause lot of vapor generation during activation and significantly low yield of activated carbon. To the best of our knowledge, no report has been documented on the preparation of phosphoric acid activated banana trunk-activated carbon as a low-cost alternative adsorbent.
Therefore, the aim of this study was to find the optimum operating conditions for the higher yield production of activated carbon from the banana trunk by chemical activation and simultaneously considering the activating agent concentration, activation temperature and activation time. Desirable product output based on yields was evaluated as a response.

2. Materials and methods

2.1. Banana trunk collection and sample preparation

The banana trunk was collected from banana plantation garden located in Durian Tunggal, Melaka, Malaysia. The collected trunk was cut into smaller pieces (shown in Fig. 1) for fast drying convenience. After sun drying for two days, the partially dried banana trunk pieces were again dried in the hot air oven at 105°C for 24 hours to make it uniformly dried at minimum possible moisture level (shown in Fig. 1). At this stage the moisture of the dried banana trunk were recorded by weighing 10 g of dried banana trunk pieces in each three petri dish (triplicate sampling). The initial weights were recorded using highly precise Sartorius electronic balance. After drying, the glass petri dish with samples were kept for some time in a desiccators to cool down, then final weights of the petri dish with banana trunk pieces were recorded. With these initial and final weights of the banana trunk the moisture content were calculated. Once we achieved the constant moisture for the whole dried banana trunk pieces, then these dried pieces were ground into powder and sieved to make a uniform particle size of 0.5 micro meter (as shown in Fig. 1). The proximate analysis (moisture, ash, and volatile matter content) of the banana trunk were calculated according to ASTM standard methods. The fixed carbon was calculated from the difference. The results of the proximate analyses of the banana trunk activated carbon are given in Table 1.

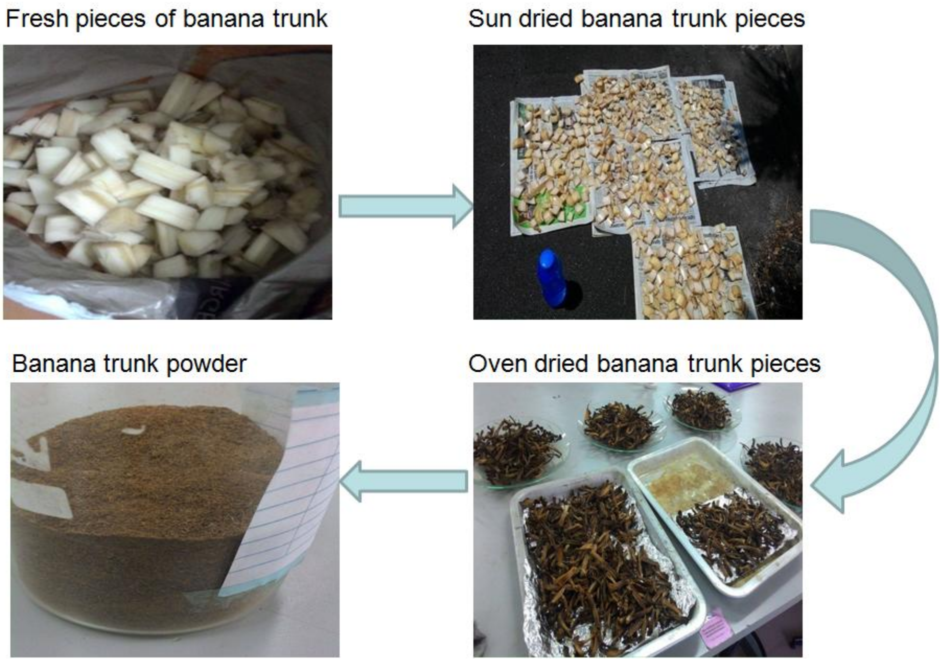

Figure 1: Banana trunk drying and conversion into powder form.

Table 1: Proximate analysis of dried banana trunk

Characteristics	Values
Moisture content	6.43 %
Ash content	8.80 %
Volatile matter	25.00 %
Fixed carbon	59.77 %
Total	100.00 %

2.2. Preparation of Activated Carbon from Banana Trunk Powder Using Response Surface Methodology (RSM)

The preparation of activated carbon was carried out based on three parameters such as, time of activation, temperature of activation, and concentration of phosphoric acid. Ten grams of powdered banana trunks were mixed well with 20 mL of desired concentration of H_3PO_4 solutions. The mixing was performed at room temperature. The soaked banana trunk powder was then transferred into crucibles with caps. The capped crucibles were placed inside a muffle furnace (CARBOLITE CWF 1200) at a set temperature for a fixed period of time. The combination of different activation time, temperature, and concentration of H_3PO_4 were planned according to Table 2. The crucibles were left inside the furnace (in off condition) for 24 hours to cool downat room temperature. After cooling the crucibles were removed from the furnace. The prepared activated carbon was washed with hot and cold water to remove the adhered water soluble byproducts and un-reacted chemical agents. Finally, the washed activated carbon was dried in hot air oven for 24 hours, weighed and packed in sealable plastic bags for further use.

Table 2: Levels and ranges of independent variables used during the experiments

Parameters	Factors	Variable level				
		-1.414	-1	0	1	1.414
Time of Activation (min.)	X_1	35.5	50	85.0	120	134.5
Temperature (°C)	X_2	367	450	650	850	932
Activating Agent Concentration (mol/L)	X_3	0.36	1.5	4.25	7.00	8.14

2.3. Design of experiments

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to develop a regression model relating the experimental response to the process variables [13]. A rotatable short central composite design (CCD) of response surface methodology was utilized to plan the number of experiments with different combination of operating parameters to optimize the process conditions. This method is suitable for fitting a quadratic surface design, and it helps to optimize the useful parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [14].The independent variables selected in the present study were activation time (X_1), activation temperature (X_2) and H_3PO_4 concentration (X_3). A short factorial CCD for the three variables, consisting of six factorial points, four axial points, and five replicates at the center points are employed, with a total of fifteen experiments calculated from the equation below [14]:

$$N = 2^{n-1} + 2n + n_c = 2^2 + (2\times 3) + 5 = 15 \tag{1}$$

In this experiment, the levels and ranges of the studied process parameters that affect the yield during the activation process of the banana trunk based activated carbons are given in Table 2. The experiments were planned to run between the selected range of each parameters. The star values (±1.414) were considered for each parameters to test the effect of each parameters on yield when their values extrapolated below the lowest values and above the highest value. This method will give the freedom to find the optimum outside the selected range, if it lies above or below the range. For the simplest case of short factorial design p=1, and rs=rc=1 , the star values can be calculated by the following equations:

$$\alpha = (2^{n-p} \times \frac{r_c}{r_s})^{1/4} = (2^{3-1} \times 1)^{1/4} = 1.414 \quad (2)$$

2.4. Model fitting and statistical analysis

For model fitting and statistical analysis such as regression analysis of experimental data to fit the empirical mathematical equation and three-dimensional (3D) plots of the response surface, the statistical software package Design-Expert 6.0.6, Stat-Ease, Inc., Minneapolis, USA, was used. The analysis of variance (ANOVA) for data was also estimated using the same software.

3. Results and discussion

3.1. Central composite design regression model analysis

The second-order model was used to develop the correlation between the activated carbon preparation variables, such as activating agent concentration, activation temperature and activation time, and the percentage yield of the obtained activated carbon. The layout of this proposed design is shown in the (Table 3), along with the response experimental results. Run number 1, 3, 5, 8, 12 and 15 were used to determine the experimental error. According to the sequential model sum of squares, the models were considered based on highest order polynomials. Regression analysis was conducted to fit the response function percentage yield. The final empirical models in terms of actual factors and coded factor after excluding the insignificant terms for percentage yield (Y_1) are given in below eq. (3) and eq. (4), respectively.

$$Yield(\%) = 37.06 - 0.23 \times x_1 + 0.02 \times x_2 + 8.85 \times x_3 - 1.22 \times 10^{-4} \times x_2{}^2 - 0.77 \times x_3{}^2 + 6.44 \times 10^{-2} \times x_1 \times x_2 - 0.06 \times x_1 \times x_3 + 7.18 \times 10^{-3} \times x_2 \times x_3 \quad (3)$$

$$Yield(\%) = 40.56 + 3.06 \times x_1 - 11.22 \times x_2 + 4.39 \times x_3 - 4.89 \times x_2^2 - 5.84 \times x_3^2 + 4.51 \times x_1 \times x_2 - 6.05 \times x_1 \times x_3 + 3.95 \times x_2 \times x_3 \quad (4)$$

Table 3:Different operating parameters in coded as well as in actual values (in brackets)

Run	Variables			Response
	X_1	X_2	X_3	Yield
	Min.	^oC	mol/L	%
1	1.414(35.5)	0.00(650)	0.00(4.25)	46.9
2	-1.00(50.0)	1.00(850)	1.00(7.00)	27.1
3	0.00(85.0)	0.00(650)	0.00(4.25)	41.2
4	0.00(85.0)	0.00(650)	0.00(4.25)	40.6
5	0.00(85.0)	0.00(650)	-1.414(0.36)	22.2
6	-1.414(134.5)	0.00(650)	0.00(4.25)	38.2
7	0.00(85.0)	0.00(650)	1.414(8.14)	34.7
8	0.00(85.0)	0.00(650)	0.00(4.25)	38.3
9	0.00(85.0)	0.00(650)	0.00(4.25)	45.3
10	-1.00(50.0)	-1.00(450)	-1.00(1.50)	37.6
11	0.00(85.0)	0.00(650)	0.00(4.25)	38.1
12	1.00(120)	-1.00(450)	1.00(7.00)	35.7
13	0.00(85.0)	-1.414(367)	0.00(4.25)	46.2
14	0.00(85.0)	1.414(932)	0.00(4.25)	14.5
15	1.00(120)	1.000(850)	-1.00(1.50)	25.5

The effect of experimental variable factors on the production of activated carbon from banana trunk with considerably good yield has been visualized through the above equations. For variables in coded terms(1.414, 0, 0) and (0, -1.414, 0), the yield was around 46 %; whereas, for variables (0, 0, -1.414) and (1, 1, -1), the yield was around 22 % (Table 3). These results indicated that the optimized value of the determining factors viz. activating agent concentration, activation temperature and activation time for maximum yield of activated carbon lies within these coded experiments.

3.2. Analysis of Variance (ANOVA)

Table 4 shows the ANOVA values for the model and the process factors. According to statistical calculation, the models F-value of 18.38 implies that the model is statistical significant (Prob. >F value 0.0026), there is only a chance of 0.26% for this large *F* value to occur due to noise. The variables X_1, X_2, X_3, X_2^2, X_3^2, X_1X_2, X_1X_3 and X_2X_3 were found significant model terms (as given in Eq. 2). The "Prob.>F" values for variables greater than 0.100 implied that model variables are not significant, and these variable can be removed from the model to improve the mathematical model.

The “lack of fit” *F* value for the percentage yield was calculated as 0.24, this implies that the “lack of fit” was non-significant statistically relative to the pure error. The lack of fit data were non-significant (Prob. >F value 0.6495);the model and 'lack of fits' having “Prob>*F*” values < 0.05 are considered to be as potentially significant. The non-significant lack of fit is desired to be statistically valid model. Hence, the proposed model is valid. The “Adeq Precision” measures the signal to noise ratio. A ratio greater than four is desirable. For the designed model, it was calculated as 14.9 for yield. This showed that the current model had an adequate signal and can be used to navigate the design space above and below the selected range of operating factors. Moreover, the “Pre R^2 ” was in reasonable agreement with the “AdjR^2” value.

The values of R^2 and *adj* $R^2$for yield were found to be 0.9707 and 0.9178, respectively. These values verified the linearity between the results calculated by model and experimental data for yield. For percentage yield, the model *F* value was found to be 18.38, which implies that the model is significant.

Table 4: Analysis of variance (ANOVA) for the fitted models

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	Prob>F
For Yield (R^2=0.9707, adj. R^2=0.9178, Pre R^2= 0.0.7784, Adeq. Precision=14.9, Std.dev.=2.67, C.V.=7.53, Mean=35.49)					
Model	$1.18x10^3$	9	131.2	18.38	0.0026*
X_1	37.54	1	37.54	5.26	0.0704
X_2	507.69	1	503.69	70.55	0.0004*
X_3	77.23	1	77.23	10.82	0.0217*
X_1^2	11.57	1	11.57	1.62	0.2591
X_2^2	184.67	1	184.67	25.87	0.0038*
X_3^2	263.26	1	263.26	36.88	0.0017*
X_1X_2	40.61	1	40.61	5.69	0.0628
X_1X_3	73.33	1	73.33	10.27	0.0239*
X_2X_3	31.16	1	31.16	4.37	0.0910
Residual	35.69	5	7.14		
Lack of fit	2.02	1	2.02	0.24	0.6495
Pure error	33.67	4	8.42		
Correlation Total	$1.216x10^3$	14			

* Indicates significant values

3.3. Response surface plots

Three-dimensional (3D) response surface plots can be highly informative about the behavior of system variables within the experimental design. It can facilitate an examination of experimental factors in selected responses like yield [15]. Therefore, 3D response surface curves were plotted for a statistically significant model to understand the interaction of applied operating factors. The 3D plots helps in interpreting the interaction of two operating

factors simultaneously. The graphical representation of the obtained mathematical models as in Eq. (2) facilitates an examination of the effects of the experimental factors on the yield.
The plots of yield (Fig. 2 [a] [b] and [c]) have curvature in the surface plot as well as in the contour plot because the model was defined by the quadratic mathematical equation. It is clear from the response surface 3D figure that yield has more interactive variables among the selected factors.
The preparation of activated carbons from the raw banana trunk was mainly based on three process variables such as time of activation, activation temperature, and H_3PO_4 concentration. These independent variables have their own effects on the physical, textural characteristics and yield of the prepared activated carbons. The following sections explain the combined effects of variables on the production of activated carbons.

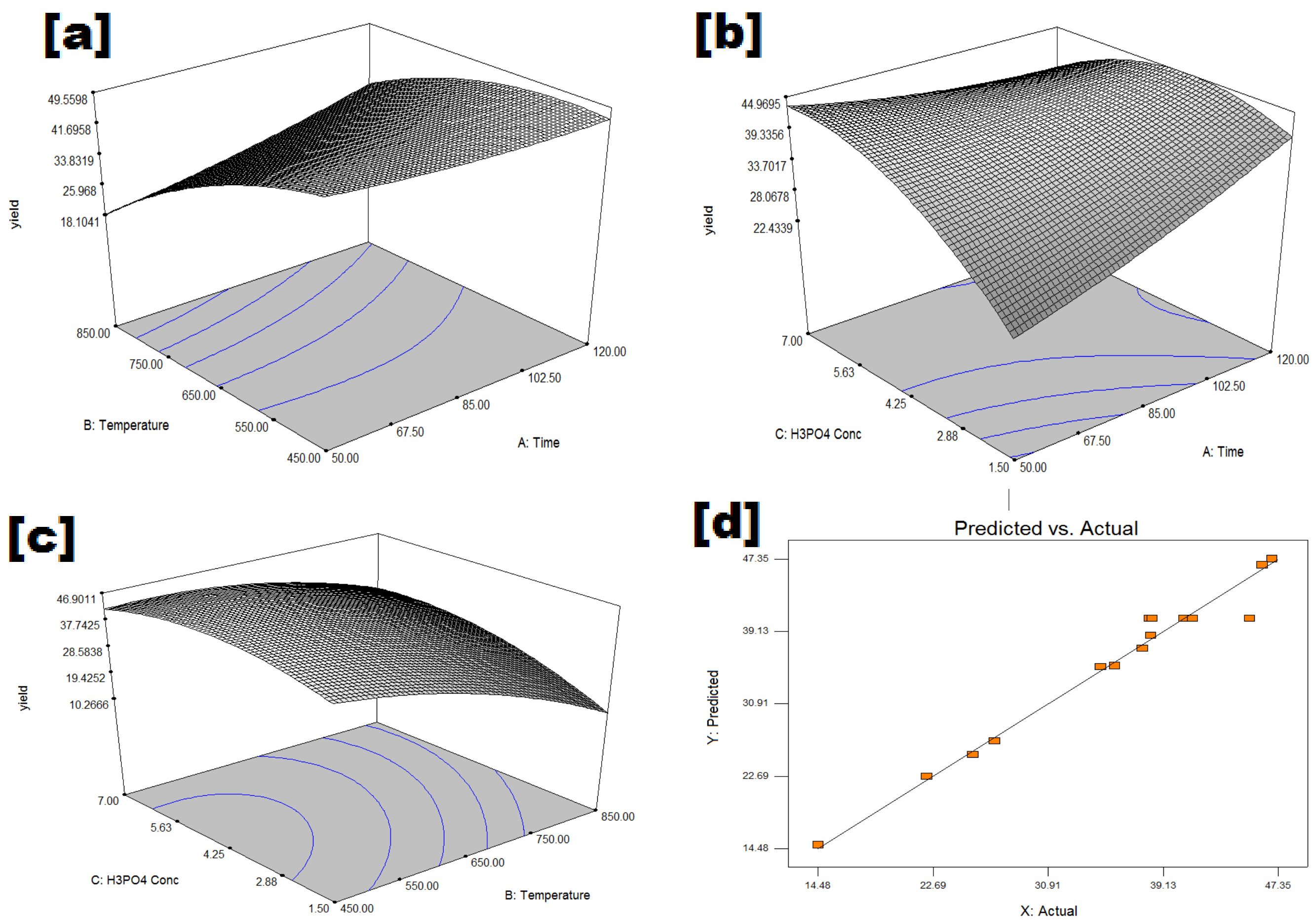

Figure 2: Response surface 3D plots [a] Yield against variable time and temperature, [b] Yield against variable time and H_3PO_4 concentration, [c] Yield against variable temperature and H_3PO_4 concentration, [d] Predicted vs actual yield plot.

3.3.1. Combined effect of activation time and temperature

The plots for yield as shown in Figure 2 [a] have a curvature in response surface plot. It can be observed that the yield of banana trunk activated carbon marginally changed when move on the activation time axis from low (50 min) to high (120 min), from model also this phenomenon was supported by the insignificant term (x_1^2). This implied that activation time have limited effect on the yield. The yield of activated carbon decreases gradually as the activation temperature increases. At high activation time and high activation temperature, the yield was below the average condition. The maximum yield of activated carbon was obtained at low activation temperature and minimum or maximum time has not much effect on it.

3.3.2. Combined effect of activation time and activating agent concentration

From Figure 2 [b], it was evident that the yield of activated carbon was raised as the H_3PO_4 concentration increased. When we analyzed the plot by considering the combined effect of concentration and time, it was observed that at low time and concentration low yield was formed. This is due to interaction of phosphoric acid with the chemical constituents of banana trunk required some time to form stable complex at certain temperature. With the increase of activation time and H_3PO_4 concentration the yield increased till mid concentration value of H_3PO_4, after that yield decreased due to excess of chemical agent. The yield of activated carbon was observed to be minimum at low activation time and low H_3PO_4 concentration.

3.3.3. Combined effect of activation temperature and activating agent concentration

Based on Figure 2[c], the plot for yield shows a curvature in response surface plot where it can be observed that the yield of activated carbon is increasing at low activation temperature and high H_3PO_4 concentration. At high activation temperature and high H_3PO_4 concentration, the yield was lower than the average condition. The maximum yield of banana trunk activated carbon was found at high H_3PO_4 concentration and low activation temperature. At maximum temperature (840 °C or 932 °C) the decrease of yield is obvious due to removal of some high temperature sensitive molecules.

3.3.4. Comparison between actual and predicted values for yield

Figure 2[d] represents the comparison between the actual and model-predicted values of the yield. It can be seen that for banana trunk activated carbons prepared with different combinations of operating variables, the experimentally calculated yield and the theoretically predicted yield through statistically developed model have minor differences except for few runs. For runs 2, 3 and 9, the actual values for yield were slightly higher than the predicted model values for yield.

3.4. Response surface methodology optimization and propagation of error

It is recommended to use the desirability function to optimize the process with two or more output responses. Since, in this experiment we set only one output response, so desirability must be 1 as shown in table 5. It is the widely used method for optimizing multiple responses in the process of optimization. The range of desirability function is between 0 and 1. A desirability value of 0 indicates that one or more characteristics of the desired responses are an unacceptable; whilst the maximum desirability value of 1 indicates that all process characteristics responses are possible [15]. The goal of optimization was to achieve activated carbon from the banana trunk with higher yield within the range. To achieve maximum desirability (1.000) shown in Table 5, all the three parameters were fixed within the range. With the maximum desirability, it was found that the model predicted yield, 47.09% and on experimental verification under similar conditions yield was found to be 46.05% as shown in Table 5. Figure 3 (a-c), represents the desirability in 3D graphics for optimization of operating parameters, and figure 3 (d-e) represents propagation of error (POE) due to deviation in input variables. During the experiment the deviation was recorded for activation time, activation temperature, and activating agent concentration were ±2 min, ±3 °C, and ±0.01 mol/L, respectively. The propagation of error calculated in percent yield was within 2.67-2.71%.

Table 5: Optimal processing conditions for optimization

	Parameters			Response		
	X_1	X_2	X_3	%Yield		
	min	°C	mol/L	Exp.	Predicted	Desirability
Optimized value	59.9	479	3.94	46.05	47.09	1.00

Conclusion

The optimization of the preparation of activated carbons from banana trunk has been done in terms of percentage yield. The optimized variables are activation time, activation temperature, and activating agent (H_3PO_4) concentration. The central composite design of response surface methodology (RSM) approach was used, and the % yield of activated carbon was calculated as response. The optimum points for activation time, activation temperature, and H_3PO_4concentration were 3.94 mol/L, 479 °C and 59.9 min, respectively, for maximum yield of 47.09%. The experimentally found yield was 46.05%, which is quite close to the model predicted yield (47.09%).

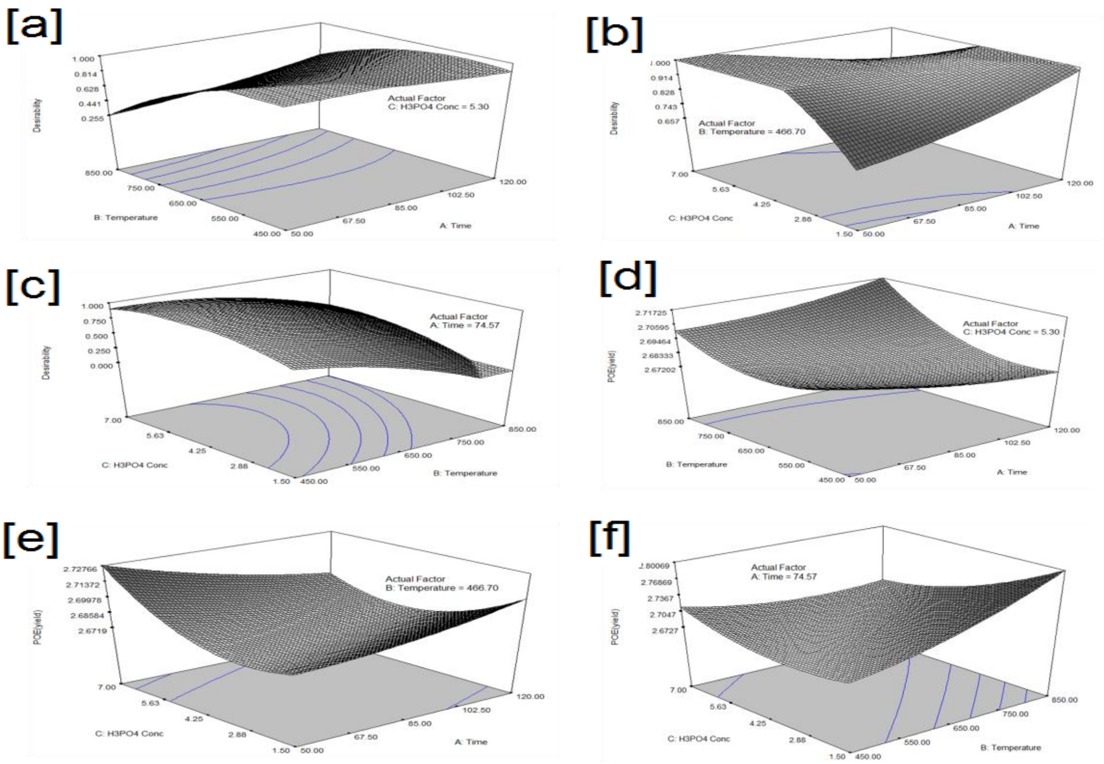

Figure 3: 3D desirability plots [a] against variable time and temperature, [b] against variable time and H_3PO_4 concentration, [c] against variable temperature and H_3PO_4 concentration; and propagation of error (POE) due to deviation in input variables [d] time and temperature, [e] time and H_3PO_4 concentration, [f] temperature and H_3PO_4 concentration.

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