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Temperature Controlled Microwave-Induced CO_2 Activated Carbon: Optimization Using Box-Behnken Design

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ABSTRACT
Over the years, microwave power has been used as a control parameter for the preparation of activated carbon (AC) via microwave heating due to the volatile nature of temperature inside the microwave. This paper investigates the use of bed temperature as a control parameter for the preparation of activated carbon using microwave heating. Activated carbon has been prepared from an oil palm shell (OPS) in a two-step microwave-induced CO2 activation. The response surface methodology (RSM) and Box-Behnken design (BBD) were utilized to optimize the operating parameters of the preparation process. The influences of the three preparation parameters namely, bed temperature, activation time and CO2 flow rate on the porosity of the AC and the AC yield were investigated to identify the significant parameter(s) using the analysis of variance (ANOVA). The optimum preparation conditions as identified from ANOVA are bed temperature of 900 oC, the ctivation time of 40 min and CO2 flow rate of 400 cm3 min-1. The AC prepared at optimum conditions had a BET surface area (S_{BET}) of 574.37 m2 g-1, total pore volume (V_t) of 0.244 cm3 g-1, micropore volume (V_μ) of 0.198 cm3 g-1 and yield of 74.06%.

Keywords: *Bed temperature, optimization, Box-Behnken design, activated carbon*

1. INTRODUCTION

In the last decade, activated carbon (AC) which is carbonaceous material in its crude state blessed with highly porous surface area and controllable pore structure have found application in various fields such as electrodes for energy storage devices [1], industrial wastewater [2] and gas treatment [3] and purification purposes [4]. In the same vein, the usage of agricultural and forestry waste products as a forerunner for the preparation of activated carbons have also been on the increase during this period. The choice of agricultural by-products as precursor materials over and above fossil fuel-based forerunners such as coal, lignite, and peat is due to the abundant availability, renewability, sustainability, environmentally friendly and low cost of the agricultural biomass [5]. The application of activated carbon is a function of its properties, that is, surface area, internal porosity, pore volume and pore size distribution, which in turn, are influenced by the preparation method, activation conditions and the physicochemical properties of the raw material.

An essential property of AC is its surface area that is exceedingly affected by the preparation parameters and conditions. Thus, to assess the influence of treatments on the development of the surface area of activated carbon, appropriate experimental design becomes imperative. Response surface methodology (RSM) is an efficient experimentation and multivariate technique used in optimization analysis and assessment of the consequence of parameters on treatment responses [6]. By the use of RSM maximum amount of complex information could be extracted with minimum experimental time, material and personal costs because of the drastic fall in the number of the tests to be carried out. Also, RSM provides a better appraisal of the interactions among the studied factors optimized through numerical and graphical analysis and analysis of variance (ANOVA) [2,7]. RSM contains various second-order symmetrical designs, and each of these

designs is differentiated by the number of levels for factors, choice of the experimental points and the number of runs and blocks [8].

Among the second-order symmetrical designs, Box-Behnken design (BBD) was chosen to examine the influence of the three activated carbon preparation parameters, i.e. bed temperature, activation time and CO2 flow rate simultaneously. For a three-factor-three-level design, BBD has fewer runs, permits estimations of the response function at middle levels and more effective than other RSM designs [6]. The RSM techniques have been applied to various processes including the production of AC. So far, only central composite design (CCD) has been used by researchers for the fabrication of AC. Apparently, there is no reported study on the use of Box-Behnken design with microwave radiation for the fabrication of activated carbon.

Therefore, this study aimed at founding out the effect of using bed temperature as against microwave power in the microwave-induced CO2 activation of oil palm shell and use BBD to determine the optimum conditions for the preparation of activated carbon for high carbon yield and surface area. The bed temperature of the sample is the temperature of the sample measured at middle of the sample, that is, the internal temperature of the sample.

2. EXPERIMENTAL

2.1. Preparation of Activated Carbon

Oil palm shell (OPS) waste was collected at a palm oil mill site in Johor, Malaysia. Proper cleansing of the OPS was carried out to remove grime and any contaminant. Then, the OPS were sun-dried for two days followed by oven-drying at 105 ºC for 48 h. The dried OPS was crushed to fine particles with average size of 2.0 mm. OPS is a poor microwave absorber, thus required a microwave absorber to initiate the carbonization process. Commercial activated carbon (CAC) supplied by Laju Group of Company, Malaysia has average particle size of less than 1 mm, and was used as microwave absorber. A modified domestic microwave (1 kW, 2.45 GHz) with a maximum power of 800 W was used for both the carbonization and activation process. PID controller with a K-type thermocouple is connected to the microwave for the monitoring and control of the bed temperature of the char and activated carbon (Figure 1).

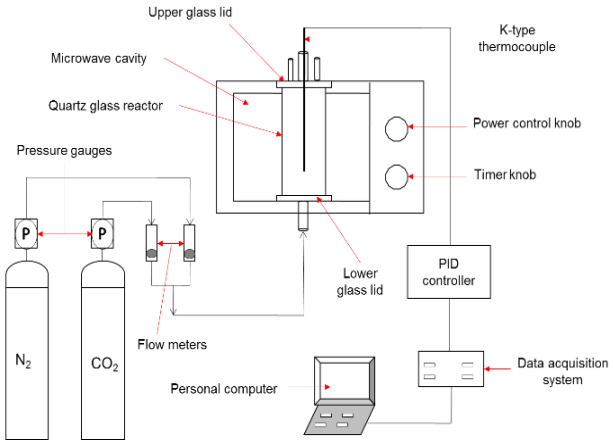

Figure 1 Experimental set up

The activated carbons were fabricated via a two-step microwave-induced CO_2 activation involving carbonization and activation. For the carbonization, OPS and CAC were arranged in a layer form in the ratio of 2:1 inside the quartz glass reactor and then placed in the microwave. 60 g of OPS was put into the quartz reactor and was heated at a controlled heating rate of 50 $^oC\ min^{-1}$ to 800 ºC and this temperature was maintained for 20 min. For the activation process, 20 g of biochar was kept constant throughout the experiments. The microwave power was set at 800 W and was kept constant throughout the experiments. The biochar was heated under inert environment with a N_2 flow rate of 200 $cm^3\ min^{-1}$ at a heating rate of 50 $^oC\ min^{-1}$up to the desired activation temperature. Comprehensive details of the adopted preparation method is available in our previous study [9].

2.2. Experimental Design

RSM is a well-known mathematical and statistical technique for the modeling, analysis of problems and optimization of imparts of various process factors on the properties of the prepared products [10,11]. Standard RSM and three-factor-three-level BBD were utilized for the determination of the best process factor combination for the activation process as well as for analysis of the interactions between the factors. Since activation temperature (X_1), activation time (X_2) and CO_2 flow rate (X_3) would significantly influence the pore formation of the AC, they were chosen as the critical factors to be optimized to achieve the highest BET surface area (S_{BET}), total pore volume (V_t), micropore volume (V_μ) and AC yield. Three factors BBD requires only 15 experiments which are made of 12 runs and three replicates at the center. In the BBD, the correlation between the coded variable x_i and the independent variable X_i is given as follows:

$$x_i = (X_i - X_0)/\Delta X_i \quad (1)$$

where X_0 represents the independent variable in the center point and ΔX_i is the value of the step change. Table 1 depicts the independent factors and their coded levels for BBD.

The responses were fitted to the following second-order polynomial equation:

$$Y_i = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{1 \le i \le j}^{n} \beta_{ij} x_i x_j \qquad (2)$$

where Y_i stands for predicted response, β_0 stands for constant term, n stands for number of factors, β_i stands for coefficient of the linear parameters, x_i stands for coded values of the factors, β_{ii} stand for coefficient of the quadratic parameters and β_{ij} stands for coefficients of the interaction parameters.

Table 1. BBD coded levels for independent factors

Factors	Code	Coded level		
		-1	0	1
Bed temperature (°C)	X_1	800	850	900
Activation time (min)	X_2	20	30	40
CO2 flow rate (cm_3 min^{-1})	X_3	200	300	400

3. RESULTS AND DISCUSSION

3.1. Design Evaluation

Design evaluation was performed to ensure that the effects being seek can be estimated. Although design evaluation ought to be done before collecting response data, however, it can be done after the fact. The standard error curve (3D) for the fabrication of AC was generated using a base standard deviation of 1.0, and is depicted in Figure 2. Although the standard deviation determines the real magnitude of the plot, however, it also depends on the response data. As can be seen in Figure 2, the shape of the standard error fitted well on the design points. Also, the fitted polynomial displayed low and flat error with circular contours that are symmetrical around the centroid, thus conform to the optimal condition. A standard error value of 0.6667 was obtained around the centroid, which is the best value. Usually, there is an increase in standard error both at the centroid and away from optimization point.

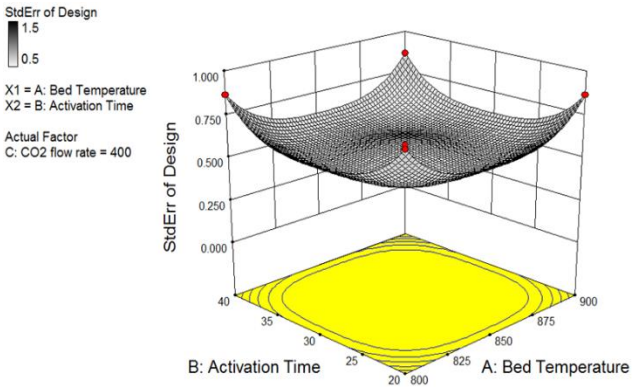

Figure 2 3D plot of standard error for the preparation of AC

3.2. Model Fitting and Statistical Analysis

The correlation between AC process factors and responses along with the identification of the variables' significant contribution to the regression model were carried out using BBD. Three-factor-three-level BBD matrix with the experimental results is depicted in Table 2.The experiment was randomly performed to avoid bias errors, and each of the experiment was replicated, and then the average value was used.

Highest order polynomials with insignificant additional terms, and the models were not aliased in accordance with the sequential model sum of squares formed the basis for the selection of the models. For all the responses, the model recommended by the software was selected since only one model was suggested for each response. Quadratic model was suggested for S_{BET}, V_t and V_μ,while linear model was suggested for yield. After eliminating the insignificant terms, except those terms that support hierarchy, the final empirical models for the responses in terms of coded factors are shown in following equations:

$$S_{BET} = 308.30 + 30.97x_1 + 73.08x_2 + 21.36x_3 - 47.16x_1x_3 - 39.87x_2x_3 + 97.15x_1^2 + 31.26x_2^2 + 99.47x_3^2 \qquad (3)$$

$$V_t = 0.12 + 0.014x_1 + 0.035x_2 + 0.009x_3 - 0.018x_1x_3 - 0.017x_2x_3 + 0.045x_1^2 + 0.041x_3^2 \qquad (4)$$

$$V_\mu = 0.11 + 0.010x_1 + 0.025x_2 + 0.007x_3 - 0.016x_1x_3 - 0.016x_2x_3 + 0.034x_1^2 + 0.009x_2^2 + 0.032x_3^2 \qquad (5)$$

$$yield = 73.41 + 0.61x_1 - 0.54x_2 + 6.78x_3 \qquad (6)$$

The sign in front of each term indicates the type of effect that the term has on the model; synergistic effects are indicated by positive sign while antagonistic effects are indicated. Based on the coefficients in Eqs. 3 - 5, it can be said that an increase in any or all of the preparation variables caused an increase in the value of the responses. However, activation time has more profound effect on S_{BET}, V_t and V_μ than activation temperature and CO_2 flow rate. Whereas, in the case of the activated carbon yield (Eq. 6), an increase in the activation time leads to a decrease in the yield of the activated carbon. Also, the interaction effects of the three planning variables with regard to S_{BET}, V_t and V_μ present negative values, indicating that the increase in these terms decreases the BET surface area, total pore volume and micropore volume.

The value of the correlation coefficient formed the basis of evaluation of the quality of the developed models. Eqs. 3, 4, 5 and 6 were used for the predicted S_{BET}, V_t, V_μ, and yield respectively. The R values for Eqs. 3, 4, 5 and 6 are 0.992, 0.9891, 0.9946 and 0.9938 respectively. All the R values were close to unity, thus signifying a good agreement between the predicted and experimental values. Also, the R^2 value for Eqs. 3, 4, 5 and 6 are 0.984, 0.9783, 0.9893 and 0.9876 respectively. Thus, indicating that 98.4%, 97.83%, 98.93% and 98.76% of the total variation in S_{BET}, V_t, V_μ, and yield, respectively were ascribed to the experimental factors studied.

The stability and appropriateness of the models were further corroborated through analysis of variance (ANOVA) as presented in Table 3 for S_{BET}, V_t and V_μ and Table 4 for yield. The regression coefficients, standard error, and significance of each coefficient were determined using the F-value and p-value. The F-values of 34.12, 25.08, 51.13 and 291.45 for S_{BET}, V_t, V_μ, and yield, respectively showed significance of the models. A lower value of p-value less than 0.05 is desirable for the model terms to be significant. That is the lower the p-value, the more significant the model term. Conversely, a p-value above 0.1 shows the insignificance of the model terms.

The actual values are date gotten from the experimental runs while the predicted values are estimated from the models. From Table, the predicted values were observed to be very close to the actual values, indicating the ability of the developed models to capture the correlation between the AC preparation variables and the responses successfully.

Table 2 Box-Behnken design matrix of three-factor-three-level with the experimental results

Run	X_1 (°C)	X_2 (min)	X_3 ($cm^3\ g^{-1}$)	S_{BET} ($m^2\ g^{-1}$)	V_t ($cm^3\ g^{-1}$)	V_μ ($cm^3\ g^{-1}$)	yield (%)
14	800	20	400	326.68	0.124	0.116	74.34
7	900	20	400	379.81	0.147	0.131	74.60
6	800	40	400	465.99	0.183	0.161	71.86
9	900	40	400	574.37	0.244	0.198	74.06
12	800	30	200	410.89	0.168	0.143	65.80
5	900	30	200	548.35	0.218	0.190	66.21
3	800	30	600	555.81	0.221	0.192	79.13
1	900	30	600	504.64	0.200	0.175	81.13
4	850	20	200	319.06	0.110	0.104	67.57
10	850	40	200	524.18	0.208	0.181	66.56
15	850	20	600	433.62	0.167	0.151	80.20
2	850	40	600	479.27	0.195	0.162	79.93
13	850	30	400	324.87	0.123	0.113	73.52
8	850	30	400	291.90	0.108	0.105	73.73
11	850	30	400	308.12	0.116	0.107	72.45

Table 3. ANOVA for response surface quadratic models for S_{BET}, V_t and V_μ

Source	S_{BET}					V_t					V_μ				
	Sum of Squares	**df***	**Mean square**	**F-value**	**p-value Prob > F**	**Sum of Squares**	**df***	**Mean square**	**F-value**	**p-value Prob > F**	**Sum of Squares**	**df***	**Mean square**	**F-value**	**p-value Prob > F**
Model	137500	9	15273.46	34.12	0.0006	0.028	9	3.102E-3	25.08	0.0012	0.016	9	1.810E-3	51.13	0.0002
X_1	7675.61	1	7675.61	17.14	0.009	1.536E-3	1	1.536E-3	12.41	0.0169	8.245E-4	1	8.245E-4	23.28	0.0048
X_2	42725.49	1	42725.49	95.43	0.0002	9.891E-3	1	9.891E-3	79.96	0.0003	4.999E-3	1	4.999E-3	141.16	< 0.0001
X_3	3649.14	1	3649.14	8.15	0.0356	7.575E-3	1	7.575E-3	6.12	0.0562	4.768E-4	1	4.768E-4	13.46	0.0145
X_1X_2	763.14	1	763.14	1.70	0.2485	3.620E-4	1	3.620E-4	2.93	0.1478	1.186E-4	1	1.186E-4	3.35	0.1267
X_1X_3	8895.32	1	8895.32	19.87	0.0067	1.275E-3	1	1.275E-3	10.31	0.0237	1.031E-3	1	1.031E-3	29.12	0.0030
X_2X_3	6357.67	1	6357.67	14.20	0.0130	1.218E-3	1	1.218E-3	9.85	0.0257	1.088E-3	1	1.088E-3	30.73	0.0026
X_1^2	34850.54	1	34850.54	77.84	0.0003	7.535E-3	1	7.535E-3	60.92	0.0006	4.387E-3	1	4.387E-3	123.90	0.0001
X_2^2	3608.75	1	3608.75	8.06	0.0363	6.527E-4	1	6.527E-4	5.28	0.0700	3.201E-4	1	3.201E-4	9.04	0.0299
X_3^2	36534.87	1	36534.87	81.61	0.0003	6.125E-3	1	6.125E-3	49.52	0.0009	3.882E-3	1	3.882E-3	109.62	0.0001
Residual	2238.52	5	447.70	-	-	6.185E-4	5	1.237E-4	-	-	1.771E-4	5	1.237E-4	-	-
Lack of fit	1694.96	3	564.99	2.08	0.3411	5.039E-4	3	1.680E-4	2.93	0.2646	1.446E-4	3	1.680E-4	2.97	0.2618

*Degree of freedom

Table 4. Analysis of variance (ANOVA) for response surface linear model for yield

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	p-value Prob > F
Model	373.16	3	124.39	291.45	< 0.0001
X_1	2.96	1	2.96	6.95	0.0232
X_2	2.31	1	2.31	5.42	0.0401
X_3	367.88	1	367.88	861.98	< 0.0001
Residual	4.69	11	0.43	-	-
Lack of fit	3.75	9	0.42	0.88	0.6352

The results of the statistical analysis showed that the models were sufficient to predict the porosity development in AC, and the AC yield within the range of the variables studied.

The actual values are the data gotten from the experimental runs while the predicted values are estimated from the models. As illustrated in Figure 3 (a - d), the predicted values are very close to the actual values, demonstrating the capability of the developed models to capture the correlation between the AC preparation factors and the responses successfully.

3.3. Process Optimization using Desirability Functions

High carbon yield and excellent porosity are the factors usually use to determine the commercial viability of activated carbons' preparation process. Consequently, the activated carbon produced should have a high carbon yield and high surface area with well-distributed pore structure. However, the application of the same conditions for the optimization of these responses is challenging due to the difference in the region of interest of the variables. Thus, compromising between these responses required the use of numerical optimization tool of the Design-Expert software to determine the precise point where the desirability function is maximizes. After which a confirmatory experiment was carried out to corroborate the responses gotten from the software. The optimization criteria were set to maximize in the values within the experiment domain for $S_{BET}(291.90 - 574.37\ \mathrm{m^2 g^{-1}})$, $V_t(0.108 - 0.244\ \mathrm{cm^3 g^{-1}})$ and $V_\mu(0.104 - 0.198\ \mathrm{cm^3 g^{-1}})$, while the yield (66.21 – 81.13%) was maintained in the value range. Figure 3 presents the desirability bar graph of the individual desirability functions (d_i) for each of the responses and the calculated geometric mean as the maximum overall desirability (D = 0.947). The optimum process conditions for the preparation of AC were obtained as bed temperature: 900 °C, activation time: 40 min, and CO_2 flow rate: $400\ \mathrm{cm^3\ min^{-1}}$. The predicted values for S_{BET}, V_t,V_μ and yield and the experimental values obtained under the optimum process conditions are dicpted in Table 5. The differences between the predicted values of the model and the experimental values obtained for S_{BET}, V_t,V_μ and yield were $\pm 3.51, \pm 4.62, \pm 3.08$ and $\pm 0.79\%$ respectively. The yield having the least difference can be ascribed to errors associated with the yield being less than the errors associated with the porosity development.

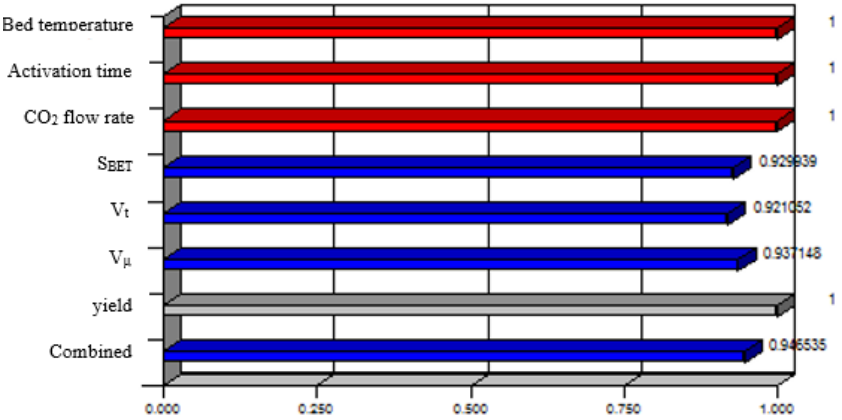

Figure 3 Desirability bar graph

Table 5. Predicted and experimental values for S_{BET}, V_t,V_μ and yield at optimum conditions

X_1 (°C)	X_2 (min)	X_3 (cm^3 g^{-1})	S_{BET}		V_t		V_μ		yield	
			Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.
900	40	400	554.58	574.37	0.233	0.244	0.192	0.198	73.48	74.06

4. CONCLUSION

In this study, the investigation of the effects of the three activated carbon preparation factors, namely, activation time, bed temperature and CO_2 flow rate was done using Box-Behnken design (BBD). Through the analysis of variance, it was established that the activation time has more profound effects on S_{BET}, V_t and V_μ. Also, CO_2 flow rate was found to have insignificant effect on the total pore volume. Additionally, all the three preparation parameters have been found to have significant effects on the AC yield with CO_2 having more profound effect. The optimum process conditions were obtained as bed temperature: 900 °C, activation time: 40 min, and CO_2 flow rate: 400 $cm^3 min^{-1}$.

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