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MODIFYING COCONUT SHELL BIOCARBON BY BASE ACTIVATION METHOD USING RESPONSE SURFACE MODELLING

Nor Asfaliza A[1], Palsan Sannasi A[1] and Mohamad Faiz M.A[2]
[1]Faculty of Agro Based Industry, Universiti Malaysia Kelantan, Jeli Campus, Jeli, Kelantan, Malaysia
[2]Faculty of Earth Science, Universiti Malaysia Kelantan, Jeli Campus, Jeli, Kelantan, Malaysia
E-Mail: asfalizaabdullah@gmail.com

ABSTRACT

In this study, activated biocarbon was prepared from coconut shell biocarbon by base activation using potassium hydroxide (KOH) as the dehydrating agent. The optimum preparation condition was determined by Response Surface Modelling (RSM) using Box Behnken Design (BBD). The relationship of independent factors i.e. activation temperature (T), holding time (t) and impregnation ratio (IR) was investigated towards maximum yield response, as measured through iodine value (mg/g). The optimum activation conditions were found to be temperature = 900 ºC, holding time = 15 min, and impregnation ratio = 1.75 which yielded higher iodine value (1169.19 mg/g). The correlation coefficient (R^2=0.9223) obtained showed that the model is able to predict the iodine number value efficiently.

Keywords: coconut shell, activation, box-behnken design, response surface modelling, iodine value.

INTRODUCTION

Environmental problem is a major concern all over the world. Development of various industrial operations like metal plating, leather tanning, electronic, paint, textile dyeing, paper and pulp are progressively increasing with economic growth. However, their effluents commonly generate sludge consisting of hazardous pollutants i.e. lead, chromium, nickel and many more which may deteriorate water quality. The excessive amount of this carcinogenic and mutagenic pollutants also will unfavorably increase chemical oxygen demand (COD) and disturb the growth of aquatic organisms and plants. This becomes a threat to food and drinking water availability and later may cause severe health risks to human (Bakheet *et al*., 2013). Therefore, treatment of industrial effluents containing these pollutants is vital before they flow into the water bodies (Naidoo & Olaniran, 2014).

Numerous treatments have been developed to remove pollutants from industrial wastewater. These include chemical precipitation, ion exchange, coagulation and oxidation, membrane separation, nano-filtration and flocculation. Unfortunately, these methods are mostly expensive, single-waste oriented, inconsistent performance and have many technical limitations. Biosorption is one of the wastewater treatment methods that has been discovered to be the most sought-after technique due to its low cost, accuracy, high efficiency, viability and simple design requirements (Baig *et al.*, 2014). It is described as a surface phenomenon where adsorbate in a solution come into contact with a highly porous surface structure solid and deposited onto/ into porous structure (Rashed, 2013).
Agricultural wastes are known for its great potential as precursors for adsorbent (Sulaiman *et al.*, 2017). They are much preferred due to its availability, renewability, low cost, and environmental friendly. In Malaysia, *Cocos nucifera* or coconut is the fourth most important plantation concerning acreage, after oil palm, rubber and paddy. As an industry, coconut may contribute very little to the overall Malaysia's economy but it has significant socio-economic implications as it provides a source of revenue and employment to the people residing in rural areas. Generally, the liquid in the coconut fruit and its flesh are commercialized by the food and beverage industry, meanwhile the virgin coconut oil (VCO) has many uses in cosmetics with health benefits. In contrast, waste contribution of coconut may come from their shell, husk, frond and empty bunches (Sulaiman *et al.* 2017). Their accumulation is expected to increase over the years due to the steady demand and increasing population. With utilization of this waste as adsorbents, the disposal at the landfills or surrounding area can be reduced effectively (Farah-Amni *et al*., 2016).

Activation process on biosorbents will create internal porosity, inhibits particle shrinkage and volume contraction (Guo *et al.*, 2005). The aim of activation process is also to enlarge the diameters of small pores and create new pores on the biocarbon (Anisuzzaman *et al.*, 2015). Activation can be produced by two ways; physical and chemical activation. Chemical activation requires low temperature and less time hence always being chosen when conducting activation process with biocarbon. Dehydrating agent can be strong acids and strong bases like zinc chloride, sodium hydroxide, acid sulphuric, and acid phosphoric.

Response Surface Methodology (RSM) is a statistical modelling technique used in this study for analyzing the effects of different operating parameters on activation process. Box-Behnken design is a method adopted in RSM technique relating to fewer number of experimental runs and higher outcome efficiency (Mourabet *et al.,* 2013). The process parameter like activation temperature, holding time and impregnation ratio were optimized, and were evaluated for the porous structure.

This study focused on the preparation of base treated bioproduct material in the form of activated biocarbon derived from agricultural waste (coconut shell), optimization of activation process via Response Surface Modelling (RSM) and characterization of the selected

bioproduct based on their optimal conditions to generate highest iodine number by base activation method.

The preparation of base treated bioproduct material from agricultural waste was derived from coconut shell biocarbon where potassium hydroxide (KOH) was used as the dehydrating agent.

MATERIALS AND METHODS

Preparation of Activated Biocarbon

Coconut shell biocarbon was produced through top-lit updraft (TLUD) drum carbonization method. The carbonized coconut shell pieces were crushed and sieved to attain particle sizes in the range of 63 to 150 µm and labelled as CSB. Coconut shell activated biocarbon (CSAB) was prepared through base activation; CSB was impregnated with potassium hydroxide (KOH) at different impregnation ratios (w/w) overnight. The mixture was then placed into a muffle furnace (Carbolite ELF 11/6B) at specific temperature (T) and holding time (t). After cooled down in the furnace, the product was extensively washed with distilled water until the filtrate pH was in the neutral range.

Selection of the Significant Parameters

The three level independent factors and experimental conditions were determined by means of BBD as listed in Tables 1 and 2, respectively. The BBD consists of 15 experimental runs together with the 3 factors, including activation temperature (X_1), activation holding time (X_2) and impregnation ratios (X_3), tested at two levels, high (+1) and low (-1). The range of each factors was decided based on pre-determined batch experimental values. Three center point's repetitions were run to measure process stability and inherent variability (Igder *et al*., 2012). Meanwhile, the value of iodine value (mg/g) were taken as the response, denoted as Y.

Table-1. Experimental ranges with three level independent factors.

Independent Factors	Level		
	-1	0	+1
Temperature (ºC), X_1	700	800	900
Holding time (min), X_2	15	30	45
Impregnation ratio (g/g), X_3	0.50	1.75	3.00

Table-2. Box Behnken experimental design matrix.

Experimental run number	Independent Factors (x)		
	x_1	x_2	x_3
1	0	0	0
2	0	+1	+1
3	0	+1	-1
4	+1	0	+1
5	0	-1	+1
6	+1	+1	0
7	-1	0	+1
8	+1	-1	0
9	0	0	0
10	0	0	0
11	0	-1	-1
12	-1	-1	0
13	-1	0	-1
14	+1	0	-1
15	-1	+1	0

Determination of iodine Value

A 40 mL standard iodine solution was treated with 0.2 g of biocarbon samples. The solution was shaken for 50 min and filtered after equilibrium. Ten mL of the filtrate was titrated with 0.05 N sodium thiosulphate solution, using starch as the indicator. Similarly, the quantity of thiosulphate to titrate 10 mL of the blank solution was determined. Each titration was carried out in triplicates and the average titre was used in calculating the iodine number (IV) using equation [Equation (1), (2), (3)] below:

$$IV = C \times Conversion\ factor\ (C_f) \quad (1)$$

$$C = B - A \quad (2)$$

$$C_f = \frac{atomic\ mass\ of\ iodine \times N \times 40}{w \times B} \quad (3)$$

where, atomic mass of iodine is 127, N is the normality of the iodine solution used, w is the mass of biocarbon used (g), 40 is the volume (mL) of thiosulphate for biocarbon free aliquot, and B is the volume (mL) of thiosulphate for blank solution. Iodine number or iodine value is calculated as the amount of iodine adsorbed by 1 g of the biocarbon material (mg/g).

RESULTS AND DISCUSSIONS

The Regression Model and Statistical Analysis

A well-fitted regression model of obtained the iodine value was determined by statistical analysis. Both BBD matrices with experimental (IVexp) and predicted

response values (IVpre) are summarized in Table-3. The predicted response for the given level of each coded factors was obtained according to Equation (4):

$$Y = 785.31 + 241.85x_1 + 8.32x_2 - 8.52x_3 - 133.83x_1x_2 - 17.28x_1x_3 - 11.37x_2x_3 + 88.38x_1^2 - 191.80x_2^2 - 94.68x_3^2 \quad (4)$$

where Y is iodine value (response), x_1, x_2, x_3 are codified values for temperature, holding time and impregnation ratio. As can be seen in Table-3, experimental iodine value obtained in this study was in the range of 324.76-1169.19 mg/g.

Table-3. Experimental and predicted values for the response of quadratic model.

Experimental run number	Response, Y (IV, mg/g)	
	IV_{exp}	IV_{pre}
1	792.9	785.31
2	577.88	487.26
3	583.25	527.04
4	931.32	995.05
5	437.13	493.35
6	771.33	798.22
7	575.23	545.91
8	1169.19	1049.24
9	779.46	785.31
10	783.56	785.31
11	397.03	487.65
12	324.76	297.86
13	592.12	528.39
14	1017.33	1046.65
15	462.24	582.19

Meanwhile, analysis of variance (ANOVA) was used to test significance and adequacy of the model (Table-4). F-value is the ratio of the model mean squares (MS) to the appropriate error mean square. If F-value of the model is equal to one, it means that the ratio of model mean squares is equal to the appropriate error mean squares. From Table-4, it is observed that the F-value of the model is 6.59 (larger than 1) which indicate that the model is significantly larger than random error. As general rule, the conclusion was confirmed by the p-value. P-value (0.0257) is less than 0.05 ($p < 0.05$), indicating model parameter (in Table-4) is significant.

Table-4. Analysis of variance (ANOVA) for response surface modelling.

Source	Sum of squares	df	Mean Squares (MS)	F-value	p-value
Model	7.462E +005	9	82913.40	**6.59**	**0.0257**
A-Temp	4.679E +005	1	4.679E+005	37.20	0.0017
B-Time	554.28	1	554.28	0.044	0.8420
C-IR	580.89	1	580.89	0.046	0.8384
AB	71647.23	1	71647.23	5.70	0.0627
AC	1194.39	1	1194.39	0.095	0.7704
BC	516.88	1	516.88	0.041	0.8474
A^2	28837.71	1	28837.71	2.29	0.1904
B^2	1.358E +005	1	1.358E+005	10.80	0.0218
C^2	33100.42	1	33100.42	2.63	0.1657
Source	Sum of	df	Mean	F-value	p-value
Residual	62903.61	5	12580.72		
Lack of fit	62808.72	3	20936.24	441.25	0.002261967 0930571
Pure error	94.89	2	47.44		
Core total	809124.25	14			

R^2;0.9223, Adj R^2;0.7823, Pred R^2; -0.2423; Adeq precision;8.204

The accuracy of a response value for the model was affirmed by the correlation coefficient (R^2 = 0.9223) value which imply almost perfect match between the predicted value to the experimental value. 'Adeq Precision' measures the signal to noise ratio. A ratio greater than 4 is desirable for the model to be used precisely (Mourabet *et al.*, 2014). Ratio of 8.204 indicates an adequate signal. Obtained ratios indicate that this model can be used to navigate the design space further.

Effect of Process Variables on iodine Value

Better understanding regarding the relationship between independent factors and response was evaluated by response surface plots. The combined effect of temperature and holding time on iodine value is presented in Figure-1. The maximum iodine value (1169.19 mg/g) was obtained at higher temperature (900 ºC) and lower residence time (15 min). Higher activation temperature may lead to the release of more CO_2 and CO gases hence creating micropores inside the mesopores structure. In contrast, further increase in activation or holding time at constant temperature (900 ºC), lowered the iodine value due to the rupturing of the pore walls.

Variation of iodine value of samples with different temperature and impregnation ratio is shown in Figure-2. It can be seen that within the investigated temperature, the iodine value increased and then decreased after their optimum value point. A slight downward trend was observed from ratio 1.75 to 3.00 in the surface plot because more volatile matter are released with increasing impregnation ratio leading to more mesopores or macropores.

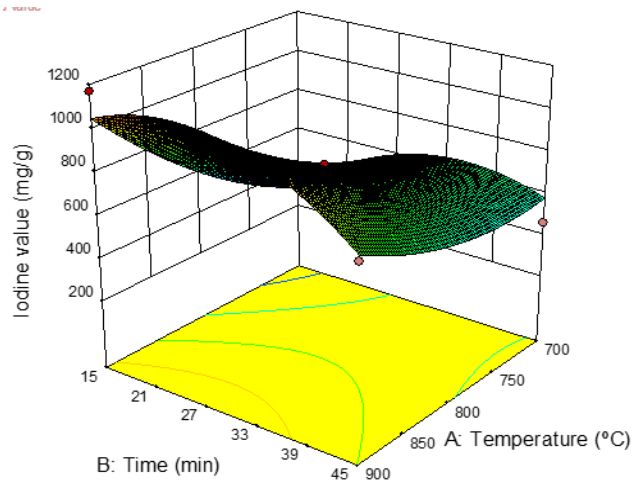

Figure-1. 3D response surface plot on effect of temperature and time towards iodine value of AC.

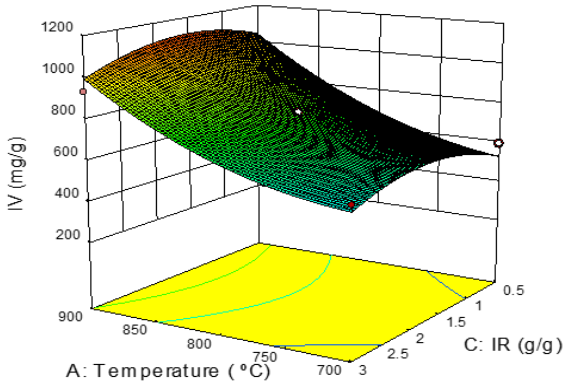

Figure-2. 3D response surface plot on effect of temperature and impregnation ratio towards iodine value of AC.

As shown in Figure-3, larger amount of dehydrating agent (KOH) may also reduce iodine value due to excessiveness of the potassium compound covering the surface of AC hence inhibiting iodine adsorption. Mopoung *et al*. (2015) have previously reported that the decrease in iodine value with increasing impregnation ratio might also be caused by strong basic KOH used during impregnation which destroys the pore structure of the carbon samples. Meanwhile, longer activation time of more than 30 min causes carbon burn off, even at various impregnation ratios. Thus, more surface functional groups will decompose that will adversely affect adsorption properties.

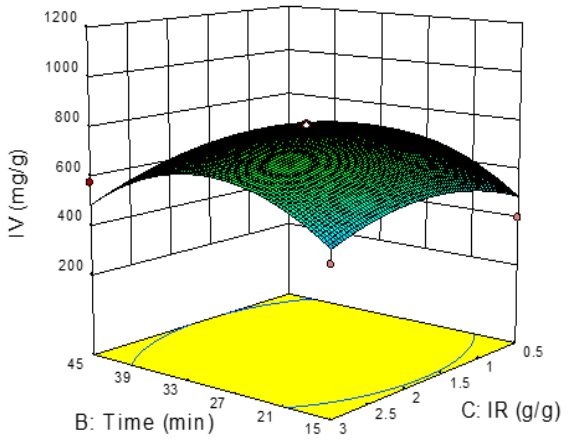

Figure-3. 3D response surface plot on effect of time and impregnation ratio towards iodine value of AC.

CONCLUSIONS

The data obtained from this study revealed that activated biocarbon can be prepared from coconut shell by base activation producing larger pore distribution. The 3D response surface plots demonstrated that all the investigated independent factors (temperature, holding time and impregnation ratio) strongly influenced the response (iodine value; mg/g). Optimum iodine value (1169.19 mg/g) was obtained at 900 ºC and 15 min activation condition with a KOH impregnation ratio of 1.75.

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