Optimization of Process Parameters for the Carbonization of Flamboyant Pod Bark (*Delonix Regia*)

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Abstract

This study investigates the carbonization of flamboyant pod bark (FPB) for the purpose of production of effective activated carbon from the agricultural residue. Central Composite Design (CCD) under the Response Surface Methodology was employed to combine the selected process parameters [Temperature (300 - 600 ^{0}C) and Time (30 - 65 mins)] for the carbonization. FPB were collected within the fields of Ladoke Akintola University of Technology, Ogbomoso, mechanically cracked, crushed, washed with distilled water and sun-dried for seven days before eventually subjecting to carbonization, after which the resultant yields were determined and the statistical analysis was evaluated. The maximum (45.45%) and minimum (11.82%) yields were obtained at Run 1 (300^{0}C/30 mins) and Run 11 (600^{0}C/ 65 mins). The quadratic model equation is given as $Yield = 23.27 - 3.48A - 4.38B - 2.81A^2 + 0.19B^2 + 0.11AB$ and the R^2 value for the model equation is 0.9705 while the adjusted as well as predicted R^2 values are 0.9459 and 0.8578, respectively. The numerical optimization by the Design Expert (6.0.8) software suggested minimum yield of 12.89%, (600 ^{0}C/ 65 mins) at desirability of 0.941. This research has indicated the suitability of using CCD for the optimization of process parameters for the carbonization of Flamboyant Pod Bark.

Keywords: Carbonization, Central Composite Design, Flamboyant Pod Bark, Yields

Introduction

Activated carbon (AC) is a solid carbonaceous material with a porous structure (Sugumaran *et al.,* 2012). Activated carbon of high quality will have extended surface area, microporous structures, high adsorption capacity and high degree of surface reactivity (Hameed *et al.,* 2009). Activated carbon produced from high carbon content agricultural residues such as corn cob, coconut shell, grain sorghum, coir pith, walnut shell, rice bran, oil palm shell, flamboyant pod bark and sugarcane bagasses were found to have good adsorbent properties which makes it suitable for treatment of wastewater and adsorption of hazardous gases (Tsai *et al.,* 1997; Hu and Srinivasan, 1999; Diao *et al.,* 2002; Ash *et al.,* 2006; Martinez *et al.,* 2006; Suzuki *et al*., 2007; Tan *et al.,* 2007; Hu *et al.,* 2009; Sugumaran and Seshadri, 2009).

Several treatment methods such as adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, distillation, solvent extraction and bio-remediation are available for the removal of organic and inorganic pollutants from wastewater. Among the various methods, adsorption process has been found to be superior compared to other methods for the removal of colour, odour, organic and inorganic pollutants from wastewater (Krishnaiah *et al.,* 2013). Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or liquid which is known as adsorbent, forming a film of molecules or atoms which is called adsorbate. It differs from absorption in which a gas diffuses into a liquid or solid to form a solution. The term sorption capture both processes, while desorption is the reverse of adsorption (Goyal *et al*., 2004). Adsorption onto activated carbon produced from agricultural wastes has a fast adsorption kinetics which makes it applicable for treatment of high strength and low volume phenolic wastewater (Tan *et al.,* 2008). Activated carbon can be produced by carbonization and activation of the raw materials (Baseri *et al.,* 2012).

Tan *et al.* (2008) studied the preparation of activated carbon from coconut husk using physico-chemical activation method which consists of potassium hydroxide (KOH) treatment and carbon dioxide (CO_2) gasification which resulted in 191.73 mg/g for the uptake of 2,4,6-trichlorophenol and 20.16 % of activated carbon yield. Hameed *et al.* (2009) investigated the effects of three preparation variable: activation temperature, activation time and potassium hydroxide (KOH) - char impregnation ratio on the uptake of 2, 4, 6 – trichlorophenol and the activated carbon prepared from oil palm empty fruit butch which resulted in 17.96 % activated carbon yield, Brunauer-Emmett-Teller (BET) surface area of 1141 m^2/g and total pore volume of 0.6 cm^3/g. Wahi *et al.* (2009) investigated the ability of activated carbon prepared from oil palm empty fruit bunches by chemical and physical activation processes for the removal of mercury, copper and lead. It was noted that the produced adsorbents which was chemically activated with sodium hydroxide (NaOH) could effectively remove mercury (Hg (II)) and Lead (Pb (II)) ions from wastewater with percentage removal up to about 100 %. Bakhtiar *et al.* (2011) studied the used of oil palm shell for the preparation of activated carbon for the removal of 4-chloro-2-methoxylphenol from aqueous solution using potassium trioxocarbonate (lV) K_2CO_3 for chemical activation. The effects of solution pH, agitation time and initial concentration were evaluated. The Brunauer-Emmett-Teller (BET) surface area was 1571 m^2/g, the total pore volume was 0.8 cm^3/g and the average pore diameter was 2.15 nm. Adsorption data were fitted using a Langmuir isotherm, with a maximum monolayer adsorption capacity of 323.62 mg/g. The adsorption kinetics was found to follow a pseudo-second-order model.

Studies of the effect of process parameters for the carbonization of flamboyant pod bark using central composite design (CCD) under Response surface methodology (RSM) of the Design expert software are not well reported in the literature. Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables. This method is suitable for fitting a quadratic surface and it helps to optimize the effective process parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters. Generally, the CCD consists of a 2^n factorial runs with 2*n* axial runs and *nc* center runs (six replicates) where n is the number of variables in the experiment. Depending on the number of factors involved, the total number of experiment needed will be given by

$$N=2^n + 2(n) + 6 \quad (1)$$

The center points will be used to determine the experimental error and the reproducibility of the data. The axial points are at (±α, 0, 0), (0, ±α, 0), (0, 0, ±α) where α is the distance of the axial point from the center point and make the design rotatable. The experimental sequence will be randomized in order to minimize the effect of uncontrolled factors. The response (Carbon yield Y) will be used to develop an empirical model which correlates the response to the five parameters of the adsorption process variables (Bokhari *et al.,* 2012).

Methodology

Materials

Flamboyant (*Delonix regia*) pod bark was collected from the field of Ladoke Akintola University of Technology, Ogbomoso, Oyo State, Nigeria.

Methods

The barks was mechanically cracked and crushed to reduce its size and increase its surface area. It was later washed with distilled water and sun-dried for seven days according to Amuda and Ibrahim (2006).

Carbonization

Carbonization was carried out according to the method adopted by Verla *et al.,* (2012). Eleven (11 g) of flamboyant pod bark (FPB) was weighed into crucible and charged into the muffle furnace at selected temperature range between (300-600 °C) and selected time range between (30-65 min) as shown in Table 1. The process parameters (Temperature and time) were input into the central composite design (CCD) under the Response surface methodology (RSM) of Design Expert software to generate the number of experimental runs at random to determine the optimum yield.

Table 1: Factors Level Selected for Carbonization

Factors	Units	Level	
		Low	High
Temperature	°C	300	600
Time	Min	30	65

Yield

The percentage yield of carbonized carbon was determined according to the method adopted by Ekpete and Horsfall, (2011) as shown in equation 2:

$$\text{Yield (\%)} = W_c/W_o * 100 \qquad (2)$$

where W_c is the dry weight of final carbonized carbon and W_o is the dry weight of precursor.

Results and Discussion

Results of Response from Experimental Data

Table 2 showed the experimental runs generated by central composite design for carbonization of flamboyant pod bark. The results showed that process parameters (temperature and time) has a significant effect on the yield obtained. It was observed that carbon yield decreases with increase in temperature and time. This is because an increase in temperature with time would increase the release of volatile matters due to dehydration and elimination reactions which result in decrease in carbon yield (Adinata *et al.,* 2007). The maximum yield of 45.45 % was obtained at run 1 at temperature of 300 °C and time 30 min while the minimum yield of 11.82 % was obtained at run 11 at temperature of 600 °C and time of 65 min.

Table 2: Central Composite Design for Carbonization (Experimentation)

Run	Factor		Response
	Temperature (°C)	Time (min)	Yield (%)
1	300	30	45.45
2	600	30	20.91
3	450	22.75	30
4	450	47.50	21.82
5	450	72.25	18.36
6	450	47.50	22.72
7	662.13	47.50	13.64
8	237.87	47.50	22.72
9	300	65	19.09
10	450	47.50	23.64
11	600	65	11.82
12	450	47.50	24.55
13	450	47.50	23.64

The maximum percentage yield obtained for the flamboyant pod bark investigated in this study compares well with yields from other agricultural wastes like pistachio (20 %), almond (32 %), hazelnut (52 %), walnut (57 %) as well as others (Kazemipour *et al.*, 2008).
Table 3 shows the comparison of carbon yield obtained from various agricultural residues.

Table 3: Results of maximum percentage yield (%) of char materials after carbonization.

Agricultural waste	Yield (%)	References
FPB300–FPB600	45.45	Present work
Apricot stones	18.2	Savova *et al.*, (2001)
Net shell	17.9	Savova *et al.*, (2001)
Cherry stones	11.2	Savova *et al.*, (2001)
Grape seeds	26.2	Savovaa *et al.*, (2001)

Model Summary statistics

Table 4 explained the model summary statistics of the yield obtained. The standard deviation showed the degree of deviation (errors) of the experimental values from the actual values while R^2 reflects the efficiency of the experiments, adjusted R^2 and Predicted R^2 are the adjusted values and the values predicted by the Design Expert Software respectively. Quadratic model was suggested and cubic model was aliased.

Table 4: Model Summary Statistics for Yield.

Response	Source	Standard deviation	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Comments
Yield	Linear	2.66	0.7572	0.7033	0.4502	44.68	
	2FI	2.80	0.7620	0.6723	0.2632	93.87	
	Quadratics	1.14	0.9705	0.9459	0.8578	7.43	Suggested
	Cubic	1.04	0.9836	0.9549			Aliased

Response for Analysis of Variance (ANOVA) of Yield

ANOVA test was used to evaluate the statistical significance of the model equation. Table 6 showed the results of the analysis of variance of yield. The model F-value of 39.48 implies the model is significant and there is only a 0.02 % chance that a "model F-value" this large could occur due to noise. Values of "Prob>F" less than 0.0500 indicate the model term are significant and values greater than 0.1000 indicate the model term are not significant. A, B, and A^2 are significant model terms. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The "lack of fit F-value" of 1.60 implies the lack of fit is not significant relative to the pure error. There is a 30.94 % chance that a "lack of fit F-value" this large could occur due to noise. Standard deviation of 1.14, mean of 21.08, C.V of 5.40, PRESS of 37.43, R-Squared of 0.9705, Adjusted R-Squared of 0.9459, Predicted R-squared of 0.8578, Adequate Precision of 21.284 were obtained. "Adeq Precision" measures the signal to noise ratio and a ratio greater than 4 is desirable. The ratio of 21.284 indicates an adequate signal and this model can be used to navigate the design space.

Table 5: Analysis of Variance (ANOVA) of Yield

Source	Sum of Squared	DF	Mean squared	F-value	Prob>F	Comments
Model	255.37	5	51.07	39.48	< 0.002	Significant
A	72.53	1	72.53	56.07	0.0003	Significant
B	115.34	1	115.34	89.16	< 0.0001	Significant
A^2	51.40	1	51.40	39.73	0.0007	Significant
B^2	0.22	1	0.22	0.17	0.6929	Not Significant

AB	0.028	1	0.028	0.022	0.8874	Not significant
Residual	7.76	6	1.29			
Lack of fit	3.44	2	1.72	1.60	0.3094	Not significant
Pure Error	4.32	4	1.08			
Cor Total	263.14	11				

The final empirical model in terms of coded factor for the yield is given by equation 2:

$$Yield = +23.27 - 3.48A - 4.38B - 2.81A^2 + 0.19B^2 + 0.11AB \qquad 3$$

From the coded factors, it can be seen that A and B has negative coefficients which implies that they affects the yield of flamboyant pod bark (FPB) negatively.

Diagnostic Case Studies

Diagnostic Case Studies for Yield

Table 6 showed the result of the diagnostic case studies of the Yield, the actual values on the Table represent the amount of yield from flamboyant pod bark and the predicted value represent the standard generated by the software (DOE). The residual showed the closeness of the actual to the predicted value. Negative value of the residual indicates that the actual value is greater than the predicted value while the positive value implies than predicted value is greater than the actual value. Predicted value of zero means that the actual is tantamount to the standard value on which it comparison is based.

Table 6: Diagnostic Case Studies for Yield

Standard Order	Actual value	Predicted value	Residual
1	23.64	22.95	0.69
2	21.82	22.95	-1.13
3	24.55	22.95	1.60
4	11.82	15.20	-3.38
5	18.36	13.77	4.59
6	22.72	22.95	-0.23
7	13.64	15.06	-1.42
8	45.45	39.34	6.11
9	30	32.13	-2.13
10	19.09	17.73	1.36
11	23.64	22.95	0.69
12	22.72	30.84	-8.12
13	20.91	19.54	1.37

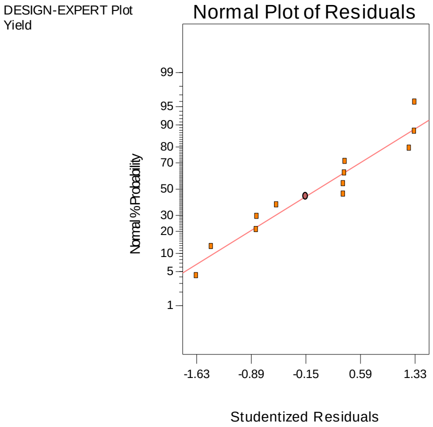

Figure 1: Yield Normal plot of Residual

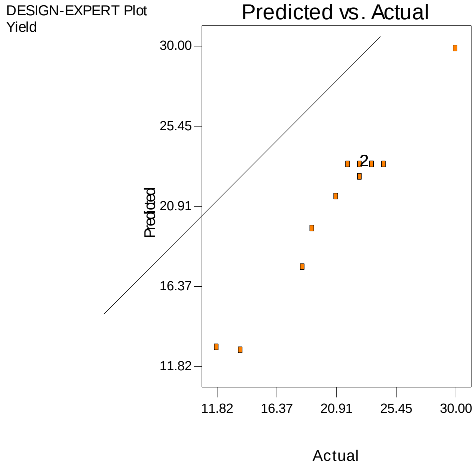

Figure 2: Yield plot of Predicted versus Actual

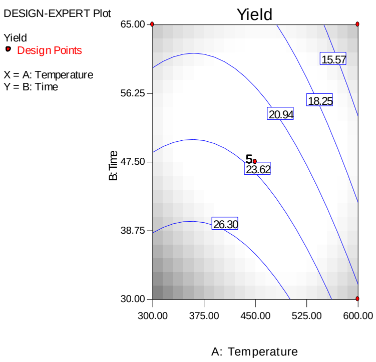

Figure 3: Yield plot of Temperature against Time

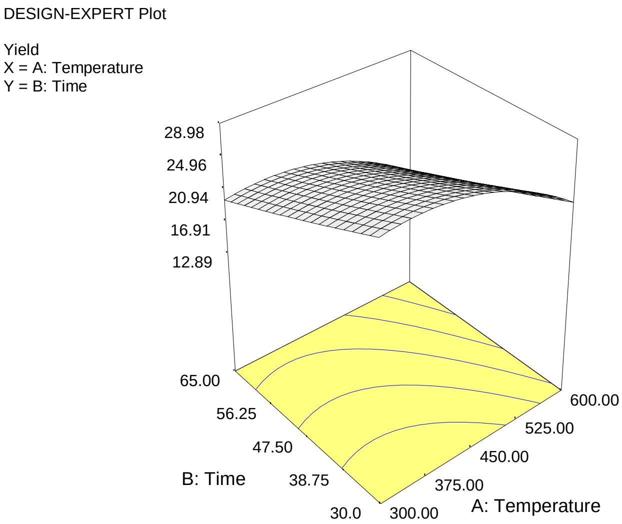

Figure 4: 3-D plot of Yield with respect to temperature and time

Conclusion

Central composite design under the Response Surface Methodology of Design Expert Software was successfully used to study the effects of process parameters (Temperature and time) for carbonization of flamboyant pod bark for the production of activated carbon for adsorption processes. An empirical model equation was developed for carbon yield as a function of parameters investigated. Quadratics model was developed to correlate the process parameter to the response. From the analysis of the response derived from the model, temperature and time were found to have the most significant effects on carbon yield.

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