PREPARATION AND CHARACTERIZATIONOF ACTIVATED CARBON FROM FLUTED PUMPKIN SEED WASTE

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ABSTRACT

This work investigated the optimum conditions for the preparation of activated carbon (AC) from fluted pumpkin seed wastes. Chemical activation using H_2SO_4 as activating reagent was employed. The influence of parameters (carbonization temperature, concentration of the activating reagent, particle size, impregnation ratio and activation time) affecting surface area of the prepared adsorbent was studied at two levels using full factorial design of experiment. The result showed that all the factors considered had effect on the surface area of the adsorbent at different levels. The optimum condition for preparing adsorbent from fluted pumpkin seed waste were carbonization temperature of 200 ^{o}C, activating reagent concentration of 30%, activation time of 24 hours, particle size of 10 μm and impregnation ratio was 1:1. These conditions resulted in the production of adsorbent with high surface area of 477.33 m^2/g. The experimental value obtained was in agreement with the value predicted by the model. The quality of the prepared adsorbent in terms of carbon yield, ash content and iodine sorption capacity as determined were 41.33%, 0.04% and 81.71% respectively. These data showed that quality adsorbent can be prepared from fluted pumpkin seed waste under optimized conditions.

KEYWORDS: Adsorbent, design expert, furnace, model, pore size, seed

INTRODUCTION

Activated carbons are group of porous material with highly developed internal surface area. They have the tendency of absorbing chemicals from gases and liquids. Activated carbons are made from a variety of precursor materials of organic origin such as wood, coal and lignite [1]. In recent times, agricultural by-products with high carbon content are being sourced as precursor materials for the production of activated carbon. This is as a result of the increasing demand for adsorbents which has led to the exploitation of many agricultural byproducts that are available at

little or no cost to meet these demands. Examples of such precursor materials include cassava waste, rice husk, fluted pumpkin seed shell, mango nuts, palm kernel shell, etc. [2-6,]. Activated carbons find use as adsorbents for the removal of pollutants (dye, metal ions, etc.) from aqueous systems [7-10], gas treatment and applications in medicine and pharmacy. The characteristics of an adsorbent can be related to the physical and chemical properties of the starting raw materials as well as the method of activation [11]. There are basically two methods for the production of activated carbon: physical activation and chemical activation. The physical activation involves two steps, carbonization, followed by activation using steam or carbon dioxide. The chemical activation involves the impregnation of the material with an activating reagent ($ZnCl_2$, H_2SO_4, H_3PO_4, KOH), followed by carbonization under an inert atmosphere. The chemical activation technique has more advantages over the physical activation technique since the chemical reagents enhance the yield and increases the surface area of the resulting product [12].

Fluted pumpkin is a vegetative shrub with large lobed leaves and twisting tendrils. It is grown majorly in East Africa for its oil and protein rich seeds and in West Africa for its nutritious leaves and seeds [13]. Due to the high demand on the oil from this plant, the seeds are being exploited on daily basis, which results in the release of massive wastes into the environment, thereby causing gradual fermentation and subsequent release of odour if not managed properly. Although attempts are being made to manage these wastes, but to no avail. In this regard, the conversion of fluted pumpkin seed wastes into a more value added product, like activated carbon, will assist, to a large extent, in solving the waste management challenges locally [14]. In the present study, parameters for the optimal production of activated carbon from fluted pumpkin with good qualities in terms of surface area, ash content, carbon content and iodine sorption capacity were studied. The chemical activation method, using H_2SO_4 as the activating reagent was adopted, as it has the potential of producing adsorbents with good qualities [6]. The effect of preparation conditions; activation temperature, impregnation ratio, activation time, particle size, and activating reagent concentration on the surface area of the prepared adsorbent were studied using Full factorial design of experiment, which permits easy study of interactions between two or more variables.

MATERIALS AND METHODS

Preparation of activated carbon

Fluted pumpkin seeds were collected from farm land areas in Agbaha-Otukpa, in Ogbadigbo Local Government Area of Benue state, Nigeria. The seed waste used in this research was generated after oil was extracted from the fluted pumpkin seeds. The seed waste was oven dried and crushed with laboratory mortar and pestle. The resulting particles were sieved to obtain particle sizes of 3.00 μm and 10.00 μm respectively. These were then kept for further analysis. The activation method adopted for this work is chemical activation using sulphuric acid (H_2SO_4) as the activating reagent. The procedure reported by Kwaghger and Adejoh [14] was used. Table 1 gives the summary of the selected factors (concentration, activation time, and impregnation ratio, temperature of carbonization and particle size) with their respective ranges, which were chosen based on preliminary results and literature.

Table 1: Factors and their levels for AC production

Factors	Symbol	Factor Levels	
		Low level (-1)	High level (+)
Concentration (%)	C	10.00	30.00
Impregnation Ratio (g/cm^3)	IR	1.00	3.00
Activation Time (hrs.)	AT	2.00	24.00
Carbonization Temp.(^{o}C)	C	200	400
Particle Size (μm)	PS	3	10

Product characterization

Determination of ash content: About 10.00g of prepared adsorbent was placed into a porcelain crucible and weighed (Wi). This was then transferred into a preheated furnace set at a temperature of 900 °C. The crucible was left on for one hour after which the crucible and its content was transferred into desiccators and allowed to cool. The crucible and content was then re-weighed (W_f) and the weight noted. The percentage ash content (on dry basis) is given by:

$(W_i - W_f)/W_i \times 100$

Where W_i is the initial weight of crucible with sample and W_f is the final weight of crucible with sample.

Determination of Surface Area: The diameter (assuming spherical shape) of the adsorbent was obtained by passing the crushed carbon through sieve size of 300μm and the external surface area was calculated by the relation [14];

Surface area, SA $=6(cm^2/g)/ B_d P_d$

Where, B_b = bulk density

P_d = particle size (particle diameter)

The particle bulk density was determined using Ahmedna *et al* [15] procedure as follows: An empty measuring cylinder was weighed and the weight noted. The cylinder was then filled with a sample of activated carbon from the seeds and gently tapped until no more change in the level of the sample in the measuring cylinder. The volume occupied by the packed sample was recorded and noted. W_c is the weight of empty cylinder and W is the weight of cylinder and sample then weight of sample; $W_s = W - W_c$.

Then, Bulk Density (B_d) = W_s/V_s

Where V_s is the volume occupied by the packed sample.

Activated carbon yield

Dried weight, W_{ca} of each carbon sample was determined and the carbon yield (CY) was calculated as follows [16];

$$Carbon\ yield\ (\%) = \frac{Wca}{Wf} \times 100\%$$

Where, W_{ca} is the oven dried weight of carbon sample,

W_f is the weight of carbon retrieved from the furnace.

Iodine sorption capacity

Iodine sorption capacity of prepared adsorbent was determined as follows: Exactly 1.00 g each of the AC samples was weighed into a 250 cm^3 flask and 10.00 cm^3 of 5% HCl was added. The flask was swirled until the carbon became wet. 100.00 cm^3 of iodine solution (2.70g of iodine and 4.10 g of potassium iodide in 1litre of de-ionized water) was added and the mixture was shaken for 5 minutes. All the samples were filtered using whatman No.1 filter paper. 50.00 cm^3 of filtrate was titrated with 0.1M sodium thiosulphate until the solution became pale yellow. Then 1.00 cm^3 of starch indicator solution (1%) was added and the titration was continued with sodium thiosulphate until the solution became colourless. A blank was prepared without adding AC and titrated similarly. The % iodine sorption by each AC sample was calculated by applying the following formular [17]:

$$Iodine\ sorption\ capacity\ (\%) = \frac{Vsb - Vss}{Vsb} \times 100$$

Where Vsb is the volume of sodium thiosulphate used for blank and Vss is the volume of thiosulphate used for sample.

Scanning Electron Microscopy Observation

The texture and pore structure of the activated carbon prepared was observed under a scanning electron Microscope (SEM) at different magnifications.

Fourier Transform Infrared (FTIR) Analysis

Surface organic functional group analysis of the AC was performed by mixing sample with potassium bromide (KBr), followed by subjection to spectral analysis by Fourier Transform Infrared spectroscopy.

RESULTS AND DISCUSSION

Table 2 shows the complete design matrix for 32 experimental runs, including the actual factor combinations and the responses obtained (surface area) for the prepared adsorbent. The highest surface area of 477.33 m^2/g was obtained at 200 ^{o}C activation temperature (TEMP), reagent concentration (CONC) of 30%, particle size (PS) of 10μm, activation time (AT) of 24 hours and impregnation ratio of 1:1. The competence and significance of the model adopted by the software for each response was justified by the analysis of variance (ANOVA). Tables 3 shows the test for significance for the regression analysis of the adsorbent produced. The model F-value observed was 631.48, indicating that the model was significant. Values of prob>F less than 0.05 reflects the significance of the model terms. The statistical results calculated show that the model was well defined to predict the surface area of the adsorbent produced within the range of variables applied in this work for the preparation of the adsorbent. The "Adeq. Precision" obtained was 91.490; it measures the signal to noise ratio. The ratio determined is greater than 4, indicating that the model can be used to navigate the design space.The quality of the model was also evaluated based on the coefficient of determination (R^2) value. The closer the R^2 value to unity, the better the model as this gives predicted values which are closer to the actual values for the response [18]. The R^2 values obtained was 0.9998. This value indicates that 99.98%, of the total variation in the Surface area of the adsorbent is attributed to the experimental variables studied. The R^2 value obtained is considered very high, indicating that there is a good agreement between the experimental and the predicted values for obtained surface area of the adsorbent, as suggested by the model. Determination of coefficient of variance (CV) value is essential, as it

indicates the ratio between standard error of estimate and the mean value of the observed response as percentage. It measures the probability of the model. If the value is less than 10% then the model can be considered reasonably reproducible [19]. It was found that the CV value obtained for surface area of the prepared adsorbent was 0.76, thus indicating the reproducibility of the model.

Table 2: Experimental design matrix and response for THAC production

| Run	CONC	IR	AT	TEMP.	PS	SA
%	-	hrs.	^{O}C	mm	m^2/g	
1	30.00	3.00	2.00	200.00	3.00	422.54
2	10.00	1.00	24.00	200.00	3.00	353.77
3	30.00	3.00	24.00	400.00	3.00	250.00
4	10.00	1.00	2.00	400.00	3.00	298.21
5	10.00	3.00	2.00	200.00	10.00	418.70
6	30.00	1.00	2.00	400.00	10.00	333.33
7	10.00	1.00	2.00	400.00	10.00	298.51
8	10.00	3.00	2.00	200.00	3.00	438.92
9	10.00	1.00	2.00	200.00	3.00	394.74
10	30.00	1.00	24.00	200.00	3.00	441.18
11	30.00	3.00	2.00	200.00	10.00	385.85
12	10.00	3.00	2.00	400.00	10.00	318.13
13	10.00	3.00	24.00	200.00	10.00	456.62
14	10.00	1.00	2.00	200.00	10.00	375.00
15	10.00	3.00	24.00	200.00	3.00	360.58
16	30.00	3.00	24.00	200.00	3.00	387.10
17	30.00	3.00	24.00	400.00	10.00	256.62
18	10.00	3.00	24.00	400.00	3.00	295.57
19	10.00	1.00	24.00	400.00	10.00	320.68
20	**30.00**	**1.00**	**24.00**	**200.00**	**10.00**	**477.33**
21	30.00	3.00	24.00	200.00	10.00	355.87
22	10.00	1.00	24.00	200.00	10.00	305.03
23	30.00	1.00	2.00	200.00	10.00	425.53
24	30.00	1.00	2.00	200.00	3.00	370.37
25	10.00	3.00	2.00	400.00	3.00	295.13
26	10.00	1.00	24.00	400.00	3.00	309.12
27	30.00	1.00	24.00	400.00	3.00	308.80
28	30.00	1.00	2.00	400.00	3.00	306.44
29	30.00	3.00	2.00	400.00	10.00	274.98
30	30.00	1.00	24.00	400.00	10.00	318.13
31	10.00	3.00	24.00	400.00	10.00	326.44
32	30.00	3.00	2.00	400.00	3.00	260.87

Key: CONC – Concentration; IR- Impregnation Ratio; AT- Activation Time; PS- Particle Size; SA- Surface Area; TEMP- Temperature

Table 3: Analysis of variance for prepared adsorbent

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	1.198E+005	27	4437.87	631.48	< 0.0001 signf.
B	546.56	1	546.56	77.77	0.0009
C	278.54	1	278.54	39.63	0.0033
D	79817.10	1	79817.10	11357.39	< 0.0001
E	735.46	1	735.46	104.65	0.0005
AB	12892.57	1	12892.57	1834.52	< 0.0001
AC	485.55	1	485.55	69.09	0.0011
AD	3101.37	1	3101.37	441.30	< 0.0001
BC	782.40	1	782.40	111.33	0.0005
BD	2788.36	1	2788.36	396.76	< 0.0001
CD	275.71	1	275.71	39.23	0.0033
CE	143.61	1	143.61	20.43	0.0107
DE	264.21	1	264.21	37.60	0.0036
ABC	1962.67	1	1962.67	279.27	< 0.0001
ABD	971.85	1	971.85	138.29	0.0003
ABE	4073.21	1	4073.21	579.59	< 0.0001
ACD	2672.72	1	2672.72	380.31	< 0.0001
ACE	656.94	1	656.94	93.48	0.0006
BCD	184.27	1	184.27	26.22	0.0069
BCE	972.52	1	972.52	138.38	0.0003
BDE	53.69	1	53.69	7.64	0.0506
CDE	198.15	1	198.15	28.20	0.0060
ABCD	2219.28	1	2219.28	315.79	< 0.0001
ABCE	359.99	1	359.99	51.22	0.0020
ABDE	1891.59	1	1891.59	269.16	< 0.0001
ACDE	100.22	1	100.22	14.26	0.0195
BCDE	830.79	1	830.79	118.22	0.0004
ABCDE	563.22	1	563.22	80.14	0.0009
Residual	28.11	4	7.03		
Cor Total	1.199E+005	31			

Std. Dev.	2.65	R-Squared	0.9998	
Mean	348.13	Adj R-Squared	0.9982	
C.V.	0.76	Pred R-Squared	0.9850	
PRESS	1799.11	Adeq Precision	91.490	

It can be observed from Table 2 that all the factors under consideration had effect on the surface area of the adsorbent prepared. Figures 1a to 1d show three the three dimensional response
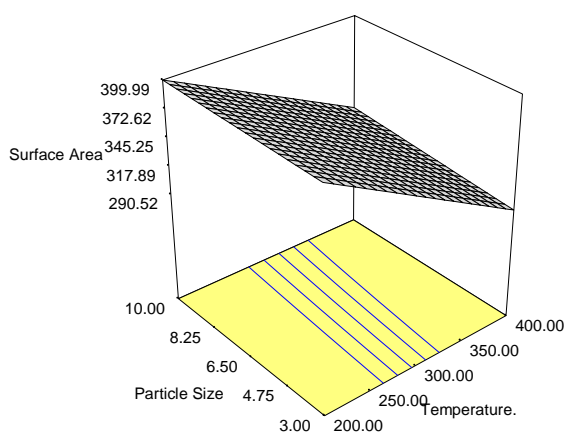
surfaces of significant variables on the surface area of the prepared adsorbent. The factors under consideration had effect on the surface area of the adsorbent prepared with temperature imposing the greatest effect. Higher values of these factors result in higher surface area except for the carbonization temperature. The result shows that the preparation of adsorbent with high surface area was favoured at low temperature of carbonization and longer duration of activation. This observation is in line with the work carried out by Gratuito et al [20], who reported that the duration of activation has significance on the development of the carbon porous networks, which relates directly to the surface area of the adsorbent. [14] also reported that the interaction of concentration and impregnation ratio also have significant effect on the surface area of prepared adsorbent. In this present work, the optimal conditions for the preparation of the adsorbent are ;carbonization temperature 200°C, duration of activation 24 hours, particle size 10μm, impregnation ratio 1:1 and activating reagent concentration 30%. The combination of these conditions culminated in the production of activated carbon with surface area 477.33m^2/g. This experimental value is in agreement with the value predicted   by the software with minimal error (Table 4), indicating that the process optimization exercise was successful.
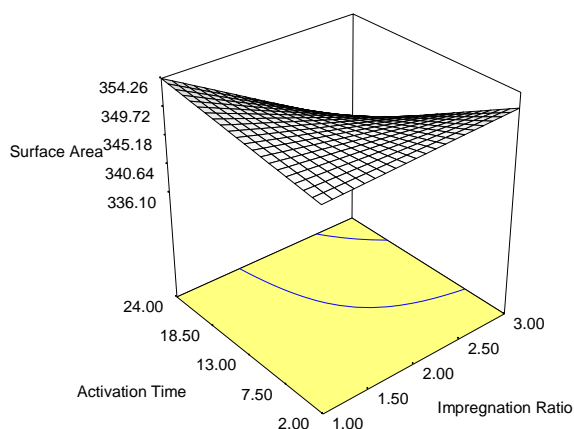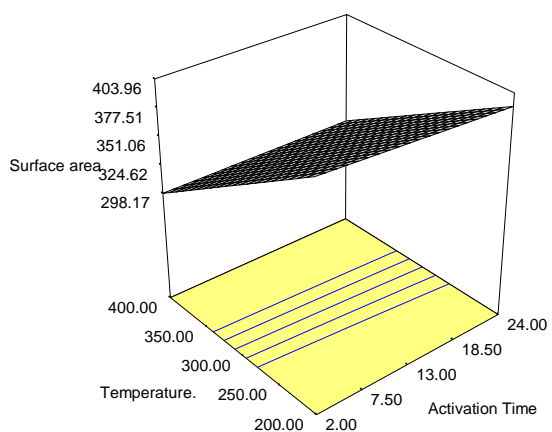

(1a)
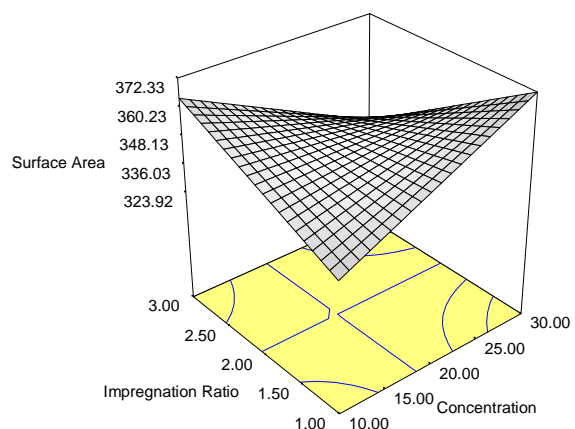
(1b)

(1C)

(1d)

Figure 1a-d: three dimensional response surfaces of significant variables on the surface area of the prepared adsorbent.

Table 4: Model validation.

Temperature (°C)	Activation Time (hr)	Impregnation Ratio	Particle Size (μm)	Concentration (%)	Surface area (m^2/g)		
					Actual	Predicted	Error (%)
200	24	1	10	30	477.33	476.38	0.20

Characterization of adsorbent

From the results obtained in characterizing the adsorbent, the carbon yield was 41.33% which is good, as a high yield is desirable for every precursor used for adsorbent preparation. The ash content of the prepared adsorbent was found to be 0.04%. High ash content is undesirable for adsorbents, as it has the potential of reducing the mechanical strength of carbon, thereby affecting its adsorptive capacity. Ash is the non-carbon or mineral additives that do not combine chemically with the carbon surface. The lower the ash value, therefore, the better the activated carbon is when used as an adsorbent. The low ash content value obtained for the prepared adsorbent is an indication that it will serve as a good adsorbent. Iodine adsorption capacity, also known as iodine number, is a quick and simple procedure to determine the adsorptive capacity of activated carbon; it is related to the degree of micro and meso porosity of adsorbents [17]. The iodine adsorption capacity of the adsorbent prepared was 81.71%. The implication of this high value is that the surface area of the adsorbent is also high.

The type of functional groups present in the prepared adsorbent was determined using Infrared spectroscopy. The FTIR spectra obtained for the prepared adsorbent is displayed in Figure 2. Peaks detected on the spectra at 2877.89cm^{-1} may be assigned to C-H stretching in alkane groups. Peaks observed at1697 cm^{-1}correspond to C=O stretching vibration in carbonyls, such as ketones, aldehydes, lactones and carboxylic groups [21]. Peaks located at 2306.94cm^{-1}may be assigned to C≡C stretching vibrations in alkyne groups [22]. Peaks observed in the region of 1200-1000 cm^{-1} represent C-O stretching vibration of functional groups such as alcohols, esters, carboxylic and esters groups. SEM was applied in order to observe the morphology and pore size of the prepared adsorbent. Figure 3 shows the observed morphological structure of the adsorbent including traceable cavities.
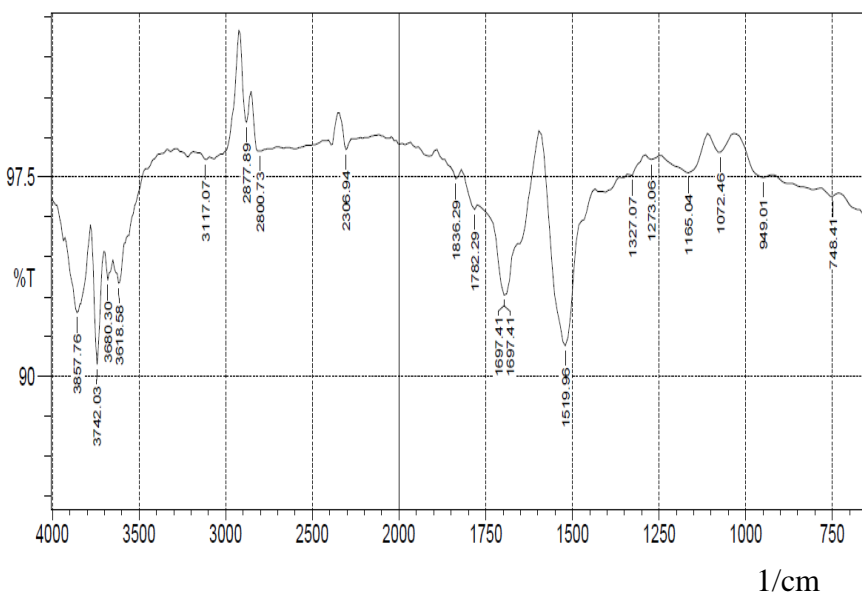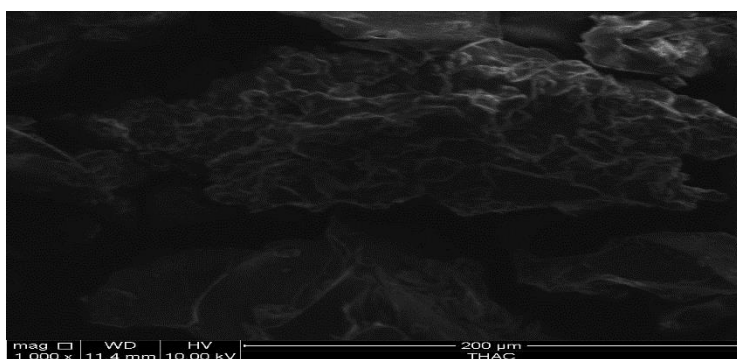
Figure 2: FTIR Spectra of prepared adsorbent.

Figure 3: SEM of prepared adsorbent.

CONCLUSION

The present study shows that fluted pumpkin seed waste can be converted into a value added product like activated carbon with good qualities, thereby ridding the environment of the nuisance associated with dumping of these waste. Full factorial design of experiment was applied to optimize the adsorbent preparation process in order to yield adsorbent with high surface area. The experimental factors considered were concentration of activating reagent, carbonization temperature, activation time, impregnation ratio and particle size. The optimal value obtained for the surface area was 477.33 m^2/g.

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