Production of Activated Carbon from Watermelon Peel

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Abstract— Watermelon peel is one of the several unwanted by-products generated by restaurants, fruit juice producers and food industries in Nigeria. A great quantity of this waste is got rid of indiscriminately into the environment thereby causing pollution one way or the other. In this study, instead of discharging them into the environment where they normally negatively affect the environment, watermelon peels have been carbonized at different temperatures between 200 to 350 ^{o}C for 15, 30, 45 and 60 min for the determination of optimum conditions for pre-treatment. The chemical treatment of the resulting carbon produced using the obtained optimum conditions was carried out using different concentrations of H_2SO_4, HCl and $ZnCl_2$ (from 0.5 to 1.5 M). The results obtained revealed that the optimum carbonization temperature was 300 ^{o}C while the time was 60 min. Moreover, the best watermelon peel activated carbon that produced the highest percentage reduction of the heavy metals considered was the one treated with 1.0 M sulphuric acid. Therefore, it has been discovered that local agricultural wastes like watermelon peels should always be considered worthwhile raw materials for the production of high quality materials one of which is activated carbon that is very useful industrially.

Index Terms— Watermelon peels, activated carbon, carbonization temperature, carbonization time.

1 INTRODUCTION

Diverse types of fruits are eaten in Nigeria daily. This is because they supply the body with the needed vitamins, minerals and fibres. However, for most fruits, only the fleshy pulps of these fruits are consumed leaving behind the seeds and the peels. This result to great amount of agricultural wastes (peels) generated and discarded. Getting rid of these peels can have serious environmental impact that has been very difficult to solve. Therefore, there is the need for an intensified research in the development of the possible nutritional and industrial potential of fruit wastes.

In Nigeria, watermelon peel is generated from restaurants, small scale fruit juice producers, fruit sellers, food beverages processing lines and these wastes are not much being reused. In fact, the value of watermelon peel is not recognized at present due to limited investigation into on how the waste can be converted into a more useful form, instead of being dumped as a solid waste to the environment.

Although most of the studies on watermelon fruits have focused on the anti-nutritional (Johnson *et al.*, 2012), phytochemical and anti-oxidant properties (Oseni *et al.*, 2013) of the fruit juice, little has been done on the nutritional/quality (proximate) contents (Fila *et al.*, 2013) of the peels which could encourage their consumptions or further use. For example, in Malaysia, watermelon peels have been analyzed and re-utilized as potential raw materials for production of jam (Mohamad *et al.*, 2012). Sensory evaluation of the jam prepared from watermelon peels with different flavors was found to possess acceptable physical, chemical and rheological properties.

Moreover, watermelon peels chemically contain large amount of water with promising levels of solid matters (Mohamad *et al.*, 2012), which further makes them worthwhile to be considered for industrial production of high quality activated carbon. This novel use of watermelon peels will not only minimize the wastes being discarded, but also create more income for farmers, food processors and more importantly reduce many negative environmental impacts.

The area of concern in this study is, therefore, on investigating the optimum conditions required for the pre-treatment of watermelon peel wastes in order to make them suitable as adsorbents for heavy metal removals from industrial effluents. This study looked at the influence of operating parameters such as carbonization temperature and carbonization time. Apart from that, chemical modifications of the resulting carbons were subsequently carried out using HCl, $ZnCl_2$ and H_2SO_4 at different concentrations. The developed and selected adsorbent was characterized for proximate and FT-IR analyses to know the functional groups present in it.

2 MATERIAL AND METHODS

2.1 Fruit Waste Collection and Preparation

The major raw material used in this research work was watermelon peels that were obtained from different fruit seller locations in Minna, Niger State.

Analytically graded reagents used were activating agents like zinc chloride ($ZnCl_2$ - 98.00%), sulphuric acid (H_2SO_4 - 98.0%) and hydrochloric acid (HCl - 36.0%).

While preparing for the carbonization experiments, the watermelon peel samples gathered were sun-dried for 5-7days to drastically reduce their moisture contents before they were then crushed with a mortar and pestle to reduce their

sizes.

2.2 Carbonization of Watermelon Peel

In the course of the carbonization experiments, the dried watermelon peels were crushed into powder form and 15 g of the powdered samples was weighed into six different clean and pre-weighed crucibles, which were then introduced into the hot zone of a muffle furnace. The peels were carbonized at different temperatures (250, 300, 350 and 400 ^{o}C). The samples were held at each of the temperatures for various times (15, 30, 45 and 60 min) in order to establish the optimum conditions for the process. The content was then removed from the muffle furnace after the set period and cooled in an open air for one hour. This process was repeated until a substantial amount of carbonized sample was obtained. The carbonaceous materials produced at different temperatures and time were then characterized.

2.3 Chemical Modification of Carbonized Materials

The activations of the carbonaceous materials produced using zinc chloride and hydrochloric acid were carried out in accordance with the description reported in the work of Yalc *et al*. (2000) while the chemical activations using sulphuric acid of various concentrations were accomplished by employing the method adopted by Kobya *et al*. (2005).

2.4 Proximate Analysis of Carbon Produced

The activated material produced was subjected to characterization in order to test it for properties like fixed carbon, bulk density, ash content, volatile content and moisture content. The fixed carbon content was determined in accordance using the procedure of ASTM (2001) while the volatile content, ash content, fixed carbon were conducted with the procedure laid down by the Association of Analytical Chemistry (AOAC) (1994).

The FTIR spectra of the developed sample was recorded with an FTIR spectrophotometer Leo Supra 50vp model using potassium bromide (KBr) pellet method before and after adsorption of heavy metals using the activated carbon. The standard values of the physicochemical properties of the adsorbent were used as references to judge the characteristics of the carbon for use for industrial effluent treatments.

3 RESULTS AND DISCUSSIONS

3.1 Effect of Carbonization Temperature and Time on Carbon

The influences of carbonization temperature and time on fixed carbon content, charcoal yield, moisture content, volatile content and ash content were studied for watermelon peels, in the course of preparing the activated carbon from the peels, and the results obtained are as presented in Tables 1 and 2.

From Table 1 that is showing the variations of the parameters (fixed carbon content, charcoal yield, moisture content, volatile content and ash content) with changes in the carbonization temperature, it can be seen that, using constant carbonization time of 15 min and constant sample mass of 5 g, all the parameters investigated were found to actually vary as the carbonization temperature was also varied. This has revealed the dependence of the parameters considered on the carbonization temperature of the process.

Table 1: Measured parameters of peel of watermelon material carbonized at different temperatures

S/N	Temperature	Time (min)	Mass (g)	Ash Content (%)	Volatile content (%)	Moisture Content (%)	Fixed Carbon (%)	Charcoal Yield (%)
1	200	15	5	18.6	34.0	2.0	47.4	50.0
2	250	15	5	21.4	28.6	1.0	50.0	43.3
3	300	15	5	26.2	22.9	1.9	50.9	33.3
4	350	15	5	28.6	20.4	2.0	50.8	33.0

Shown in Table 2 are the responses from the parameters investigated as the carbonization time was varied, but, this time around, keeping the carbonization temperature constant at 300 ^{o}C and the mass of the sample used for all the runs was also constant at 5 g. The effects of the carbonization time on the characteristics of the developed watermelon peel activated carbon are as given in Table 2. Similar to the observations noticed in the case of varying the carbonization temperature, it has been discovered in this case also that the considered parameters were found to respond to changes in the carbonization time of the process. This was an indication that the carbonization time of the process was also among the important factors affecting this process.

Table 2: Measured parameters of peel of watermelon material carbonized for various times

S/N	Temperature	Time (min)	Mass (g)	Ash Content (%)	Volatile Content (%)	Moisture Content (%)	Fixed Carbon (%)	Charcoal Yield (%)
1	300	15	5	26.2	22.9	1.9	50.9	33.3
2	300	30	5	27.5	19.5	2.5	53.0	33.0
3	300	45	5	27.8	12.4	2.9	59.8	32.4
4	300	60	5	26.2	12.2	3.5	61.6	32.1

As can be seen in Table 2, increasing the carbonization time was found to reduce the quantity of the carbonized product (charcoal yield) obtained from the watermelon peels. This was found to be due to the excessive burning/oxidation and collapse of the pore structures of the peels which was found to predominate at long carbonization time.

From the results of the watermelon peel carbonization presented in Tables 1 and 2, it was discovered that maximum percentage fixed carbons were obtained when the carbonization temperature and the carbonization time were 300 ^{o}C and 60 min, respectively. As such, these temperature (300 ^{o}C) and time (60 min) were selected as the optimum conditions for the process.

3.2 Effect of Concentration of Activating Agents on Adsorption of Heavy Metals

Watermelon peel carbon obtained at optimum percentage fixed carbon content was activated with different concentrations of H_2SO_4, HCl and $ZnCl_2$ (0.5, 1.0 and 1.5 M). The resulting watermelon peel activated carbons (WPACs) were then used to remove heavy metals from the effluent acquired from an electroplating processing industry. The results of the overall percentage reduction of heavy metals using the watermelon peel activated carbon are as given in Tables 3, 4 and 5 for HCl, H_2SO_4 and $ZnCl_2$ treated carbons, respectively.

Table 3: Overall percentage reduction of heavy metals using HCl treated WPAC

S/N	Heavy metals	WPAC (0.5M HCL)	WPAC (1.0M HCL)	WPAC (1.5M HCL)
		% Reduction	% Reduction	% Reduction
1	Zinc	7.9	2.8	2.6
2	Copper	91.5	94.3	31.0
3	Iron	95.1	95.1	81.9
4	Lead	100.0	100.0	100

Table 4: Overall percentage reduction of heavy metals using H_2SO_4 treated WPAC

S/N	Heavy metals	WPAC (0.5 M H_2SO_4)	WPAC (1.0 M H_2SO_4)	WPAC (1.5 M H_2SO_4)
		% Reduction	% Reduction	% Reduction
1	Zinc	12.9	1.4	2.0
2	Copper	96.8	99.1	16.1
3	Iron	60.8	90.6	78.8
4	Lead	40.0	100.0	100.0

Table 5: Overall percentage reduction of heavy metals using $ZnCl_2$ treated WPAC

S/N	Heavy Metals	WPAC	WPAC	WPAC

		(0.5 M $ZnCl_2$)	(1.0 M $ZnCl_2$)	(1.5 M $ZnCl_2$)
		% Reduction	% Reduction	% Reduction
1	Zinc	2.3	2.6	2.6
2	Copper	50.6	10.3	35.6
3	Iron	88.0	25.3	67.5
4	Lead	100.0	0.0	20.0

From the results obtained, it was discovered that that the activated carbon treated with 1.0 M sulphuric acid showed the best performance in terms of heavy metal removal from the industrial effluent used compared to those treated with zinc chloride and hydrochloric acid. This was an indication that the pore surface and the structure of the 1.0 M H_2SO_4 treated watermelon activated carbon were the best among all the treated watermelon activated carbons.

3.3 Characterizations of Produced Activated Carbon Material

It can be seen from this study that a carbonization temperature and time of 300 ^oC and 60 min respectively have been found to be appropriate for preparing high quality watermelon peel carbon (WPC) with high fixed content. Further, the carbonaceous material obtained using the chosen optimum conditions was used for subsequent chemical activation. Treating the watermelon peel carbon prepared with the optimum conditions with different chemicals of different concentrations, it was also discovered that the best heavy metal reductions were obtained with the watermelon peel activated carbon (WPAC) treated with 1.0 M sulphuric acid. This activated carbon was then later subjected to other characterizations. Given in Table 6 are the results obtained from the characterizations of the developed activated carbon from the watermelon peel used.

Table 6: Characterization of WPAC obtained at optimum percentage fixed carbon

S/N	Properties	Unit	WPAC at 300 ^oC, 60 min with 1.0 M H_2SO_4	Literature value
1.	Moisture Content	%	1.4	2-8
2.	Ash Content	%	18.6	≤ 8
3.	Volatile Content	%	10.3	< 20
4.	Fixed Carbon	%	66.0	>75
5.	Pore Volume	cm^3	0.93	1.109
6	Porosity	mL/g	0.204	0.214
7.	Bulk Density	g/cm^3	0.25	0.4-0.5
8.	Charcoal Yield	%	34.0	39.99- 55.44

It was indicated in the results presented in Table 6 that the moisture content of the activated carbon form watermelon peel obtained was 1.4%, which was not within the range 2-8% recommended by Tchobanoglous *et al.* (2002). However, according to Jabit (2007), for many purposes, moisture content does not really affect the adsorptive power of activated carbon. For the volatile content of the WPAC as shown in Table 6, the value obtained was 10.3%, and it was found to be within the range specified by the British Standard as reported by Paddon (1987). Also shown in Table 6 is the fixed carbon content (the non-volatile fraction of the sample) of WPAC that was found in this work to be 66.0% for the developed activated carbon, as against the recommended range (>75) required by the British Standard as reported also by Paddon (1987). The carbon yield of the developed activated carbon was also obtained to be 34.0%. This value of the carbon yield of the activated carbon was discovered to be close to the finding of Savova (2001) who reported carbon yield of 39.99 to 55.44 % for most activated carbons.

3.4 FT-IR Analysis of Produced Activated Carbon

The FT-IR spectra of the developed watermelon peel activated carbon before and after adsorption of metal ions were carried out as a qualitative analysis to gain better insights into the surface functional groups available on the surface of the investigated adsorbent because the chemical structure of an adsorbent is of vital importance in understanding its adsorption nature. The FT-IR spectra of the watermelon peel activated carbon (WPAC) measured within the range of 500 – 4500 cm^{-1} recorded before and after adsorption are as shown in Figures 1 and 2, respectively.

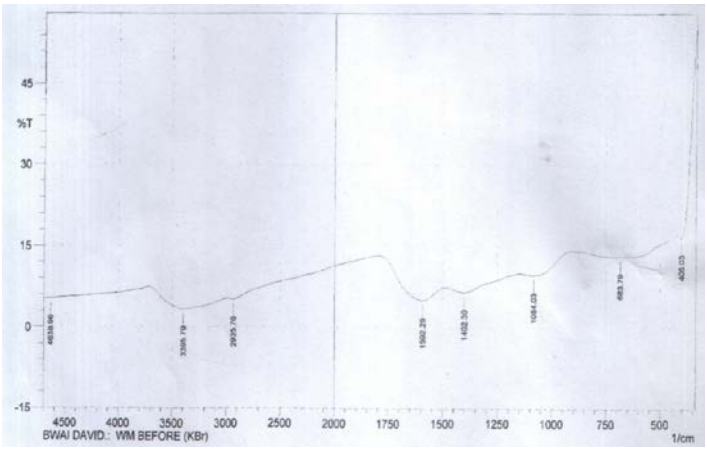

Figure 1: FT-IR spectrum for activated carbon from watermelon peel before adsorption

The FT-IR spectra of unloaded WPAC shown in Figure 1 was discovered to show a band at 3395.79 cm^{-1}, which was due to $O-H$ stretching of water. The band observed at 2935.76 cm^{-1} was found to correspond to methylene asymmetric, $C-H$ stretching. The band given at 1592.29 cm^{-1} was an indication of the presence of pyridine, $C=N$ stretching while the band at 1402.3 cm^{-1} was ascribed to azo compound, $N=N$ stretching. Finally the band at 1084.03 cm^{-1} was found to be due to aliphatic $C-N$ stretching while the band at 683.79 cm^{-1} was due to $P=S$ stretching.

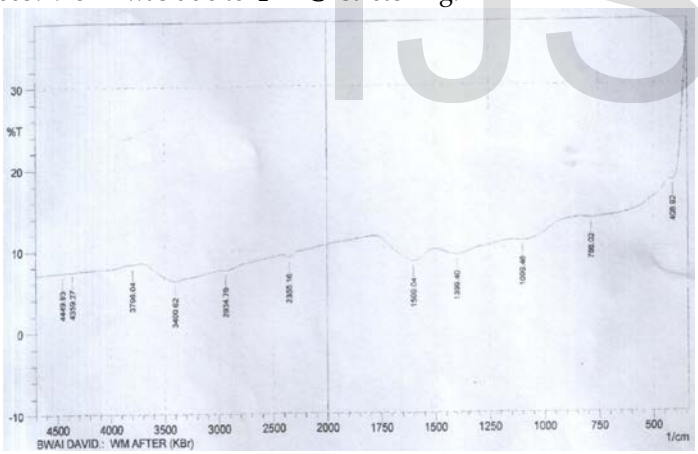

Figure 2: FT-IR spectrum for watermelon peel activated carbon after adsorption

As observed from Figure 2, after the adsorption of the metal ions present in the effluent by the developed activated carbon, the FT-IR spectra was found to show shifts in some of the bands, and there were also appearances of new bands. For instance, the bands at 406.03, 683.79, 1084.03, 1403, 1592.29, 2935.76, and 3395.79 cm^{-1} were shifted to 408.92, 786.02, 1099.46, 1399.4, 1599.04, 2934.79 and 3400.62 cm^{-1}, respectively. The shifts in the bands confirmed the participations of the functional groups in the adsorption of the metal ions of the effluent onto the developed activated watermelon peel carbon.

In addition, new bands were discovered to emerge at 3796.04, 4359.27 and 4449.93 cm^{-1} in the spectrum which were due to the changes in the nature of the binding after the interaction of the activated carbon with the metal ions of the effluent. The new band at 3796.04 cm^{-1} was found to be associated with hydroxylated compounds while the bands observed at 4359.27 and 4449.93 cm^{-1} were overtones or combinations of the fundamental stretching bands which were found to occur in the 3000-1700 cm^{-1} region, according to Weyer and Lo, 2002. The bands above 4000 cm^{-1} were found to be overlapped, which made them less useful for qualitative analysis. However, based on the information obtained from the work of Stuart (2004), the bands involved were usually $C-H$, $N-H$ or $O-H$ stretching.

The FT-IR spectra obtained for the developed watermelon peel activated carbon were found to be similar to the ones reported for the studies carried out on commercial granular activated carbons by Park and Jang (2002) and activated carbon made from cherry stones by Olivares (2006). The band in the region of approximately 1600 cm^{-1} has been noticed by many previous researchers but has not been definitely interpreted. However, for most carbonaceous materials, C=C stretching adsorption was found to frequently occurs at this region.

4 CONCLUSIONS

The results obtained from this work that was carried out to develop an adsorbent from watermelon peel for use in wastewater treatment, specifically for the adsorption of heavy metals, have revealed that the optimum carbonization temperature and time for the preparation of watermelon peel activated carbon with high fixed content were 300 ^{o}C and 60 min, respectively. In addition, the watermelon peel activated carbon treated with 1.0 M sulphuric acid was found to be the best among the treated ones because it has relatively the highest percentage reduction of the heavy metals investigated in this work.

NOMENCLATURES

AOAC Association of Analytical Chemistry
ASTM American Society for Testing and Materials
WPAC Watermelon peel activated carbon
WPC Watermelon peel carbon

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