

Utilization of Cassava Peel Waste as a Raw Material for Activated Carbon Production: Approach to Environmental Protection in Nigeria

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ABSTRACT

This work has been carried out to use cassava peel to develop activated carbon (an adsorbent) for use in effluent treatment. In the process development, cassava peel obtained from the wastes of cassava processing was carbonized at different temperatures between 250 and 400°C for 15, 30, 45 and 60 min in order to determine the optimal conditions for the pre-treatment of the cassava peels. The chemical activations of the resulting carbons were carried out using different concentrations of H₂SO₄, HCl and ZnCl₂ from 0.5 to 1.5M. According to the results obtained, it was discovered that the optimum carbonization temperature and time for the preparation of good cassava peel carbon with high fixed content were 350 °C and 45 min, respectively. In addition, the results of the characterizations revealed that good quality carbon from cassava peel was able to be prepared using zinc chloride with 1.0M concentration. It has, therefore, been discovered from this study that indigenous agricultural waste like cassava peel may profitably be exploited and used as potential raw materials for activated carbon development, which is nowadays assuming ever increasing importance due to its low level of environmental pollution.

Keywords: Cassava peels, activated carbon, environmental pollution.

1.0 INTRODUCTION

Cassava processing generates a lot of waste, which, if not properly disposed, can create sanitation and environmental problems. A survey conducted on cassava processing in Ghana revealed that about 28% of the cassava peel generated during garri production has no use. Hence, the peels are either heaped in refuse dump or abandoned in the living community. As a consequence, the vegetation and soil around the heaps of cassava peels are rendered unproductive and devastated due to biological and chemical reactions taking place amidst of the continuously fermenting peels, soil and the surrounding vegetation thereby constituting environmental nuisance (Ubalua, 2007). Subsequent negative impact could lead to foul odour that is sometimes poisonous and also air pollution, which when inhaled by man or animal may result in infection and diseases that may take a long time to manifest. Most of the studies have focused on the quantity and composition of the waste generated by this industry, but do not consider its environmental impacts (Irene et al, 2007).

In Nigeria, for example, cassava is one of the most important commercial crops. The explosive expansion of cassava farms for the production of biofuels (ethanol) and the recent Federal Government policy on cassava flour inclusion in wheat flour for bread baking has generated enormous amounts of vegetable waste. Nigeria is reported to rank the top producer of cassava worldwide, followed by Brazil, Thailand, Zaire and Indonesia (Olanbiwoninu et al, 2012), and it has been reported that 450,000 tons of cassava peel waste is generated annually with an increasing trend as statistics reveal (FAO, 2006). The waste generated at present poses a disposal problem and would even be more problematic in the future with increased industrial production of cassava products.

Most of the cassava peels produced in Nigeria each year are sold to animal feed formulation as a low value product, however, additional product outlets need to be identified to create high value products from cassava peel (Alinnor and Nwachukwu, 2012). Since these peels could make up to 10% of the wet weight of the roots, they constitute an important potential resource, if properly harnessed (Obadina et al., 2006).

In recent years, the development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity. The use of cassava peel with

surface modification to improve its metal removal performance would add its economic value, help reduce the cost of waste disposal, and most importantly, provide a potentially inexpensive alternative to existing commercial activated carbon (Cameron, 2006), which is an adsorbent.

This study, therefore, focused on investigating the optimal conditions required for the pre-treatment of cassava peel waste in order to make it suitable for the development of adsorbent for heavy metal removals from industrial effluents. The operating parameters considered were carbonization temperature and carbonization time. Furthermore, chemical modifications of the resulting adsorbents were subsequently carried out using different reagents (HCl, ZnCl₂ and H₂SO₄) at different concentrations in order to determine the best chemical for the modification of the developed adsorbent.

2.0 MATERIALS AND METHODS

2.1 Material Collection and Preparation

The major raw material used in this research work was cassava peel that was obtained from a garri processing plant in Minna, Niger State. Analytically graded reagents used as activating agent were zinc chloride (ZnCl₂ - 98.00%) and sulphuric acid (H₂SO₄ - 98.0%), hydrochloric acid (HCl - 36.0%). The cassava peel sample was sun dried for 5-7 days to drastically reduce its moisture content and then crushed with a mortar and pestle for size reduction.

2.2 Carbonization of Cassava Peel

The dried cassava peels were crushed into powder form and 15 g of the samples were weighed into six different clean and pre-weighed crucibles, which were then introduced into the hot zone of a muffle furnace. The furnace temperature was increased at a rate of 10 °C/min from room temperature. The peels were carbonized at different temperatures of 250, 300, 350, and 400 °C. The samples were then held at this temperature for various times (15, 30, 45, and 60 min) in order to establish optimum conditions. The content was later removed from the muffle furnace after the set period and cooled in open air for one hour. This process was repeated until a substantial amount of carbonized sample was obtained. Carbonaceous materials produced at different temperatures and time were then characterized.

2.3 Chemical Modification of Carbonized Materials

Activation of the carbonaceous materials produced using zinc chloride and hydrochloric acid was carried out in accordance with the description reported by Yalcet *et al.*, (2000). Chemical activation using sulphuric acid was carried out using the method adopted by Kobya, *et al.*, 2005.

2.4 Proximate Analysis of Carbon Produced

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

The FTIR spectra of the selected sample was recorded with an FTIR spectrophotometer Leo Supra 50vp model, using potassium bromide (KBr) pellet method. The standard values of the physicochemical properties of the adsorbents were used as references in order to judge the characteristics of the carbon for use for industrial effluent treatments.

3.0 RESULTS AND DISCUSSIONS

3.1 Effect of Carbonization Temperature and Time on Carbon

The influence of carbonization temperature and time on each of fixed carbon content, charcoal yield, moisture content, volatile and ash content was studied for carbonized cassava peel and the results obtained are as presented in Tables 1 and 2. Table 1 shows the variations of the parameters with changes in temperature while the carbonization time was kept constant and using 5 g of the sample. In Table 2, keeping the carbonization temperature constant and also using 5 g of the sample, the variations of the investigated parameters with changes in the carbonization time are shown.

Looking at Table 1, it can be seen that all the parameters tested for except charcoal yield and volatile content increased with increase in carbonization temperature. For instance, fixed carbon increased from 59.0 at 250°C to 66.4 % at 350°C, while charcoal yield decreased from 83.3 to 46.7% over the same temperature range. This observation was found to be in agreement with the reported work of Guo and Lua (1998) in which high fixed carbon content was obtained at a high temperature range of 400-600 °C for cassava peel carbonization. The observed decrease in charcoal yield while the temperature was increasing was found similar to the observation reported by Sugumaran and Seshadri (2008) and Yusuf *et al.*, (2012). In fact, Sugumaran and Seshadri (2008) reported that carbonization of lignocellulosic materials at high temperature involves depolymerisation, cracking and dehydration of lignin and cellulose in biomass resulting to low charcoal yield.

Table 1: Measured parameters of carbonized cassava peel (CCP) materials

S/N	Temperature	Time (min)	Mass (g)	Ash content (%)	Volatile content (%)	Moisture content (%)	Fixed carbon (%)	Charcoal yield (%)
1	250	15	5	7.0	34	1.0	59.0	83.3
2	300	15	5	10.1	28.6	2.0	60.9	66.7
3	350	15	5	11.6	22.0	3.0	66.4	46.7
4	400	15	5	12.8	11.0	3.0	66.7	46.1

As mentioned earlier, the effect of carbonization time on CCP is presented in Table 2. The carbonization (treatment) of this agricultural peel was carried out so that after the removal of a certain amount of volatile matter, the maximum amount of fixed carbon might be available for chemical activation process.

Table 2: Measured parameters of carbonized cassava peel (CCP) materials

S/N	Temperature	Time (min)	Mass (g)	Ash content (%)	Volatile content (%)	Moisture content (%)	Fixed carbon (%)	Charcoal yield (%)
1	350	15	5	11.6	22.0	3.0	76.4	46.7
2	350	30	5	13.2	19.5	3.0	79.3	36.0
3	350	45	5	19.9	12.4	3.0	83.5	35.8
4	350	60	5	20.8	12.2	3.0	83.9	35.1

As can be seen from the table (Table 2), increase in carbonization time was discovered to reduce the quantity of the carbonized product (charcoal yield). This may probably be due to excessive burning/oxidation and collapse of pore structures which predominate at longer residence (carbonization) time and high temperature. This observation was actually found to be in conformity with that of Gimba and Turoti (2008) who observed in the production of carbon from coconut peel that when carbonization time was increased, charcoal yield decreased.

Although the results of cassava peel carbonization presented in Tables 1 and 2 showed that the maximum results in terms of percentage fixed carbon were obtained at temperature of 400°C and 60 min., however, 350°C was selected as the optimum carbonization temperature because the energy required to raise the temperature from 350 to 400°C did not justify the resulting increase in the amount (%) of fixed carbon content from 66.4 to 66.7%, as seen in Table 1. Similarly, 45 min was chosen as the optimum carbonization time, instead of 60 min (see Table 2).

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

CCP obtained at the chosen optimum percentage fixed carbon content whose physicochemical properties are presented in Table 6 was activated with different concentrations of H₂SO₄, HCl and ZnCl₂ (0.5, 1.0 and 1.5 M). The resulting cassava peel activated carbons (CPACs) were used to remove heavy metals from effluent of an electroplating processing industry. The summary of the results obtained from the overall percentage reduction of heavy metals using CPAC are as presented in Tables 3, 4 and 5 below.

Table 3: Overall percentage reduction of heavy metals using HCl treated CPAC (adsorbent dosage=1.0 g/20 mL, pH =2, agitation time = 75 min)

S/N	Heavy metals	CPAC	CPAC	CPAC
		(0.5 M HCL)	(1.0 M HCL)	(1.5 M HCL)
		% Reduction	% Reduction	% Reduction
1	Zinc	7.8	2.1	1.1
2	Copper	29.8	17.2	18.4
3	Iron	55.4	43.4	61.4
4	Lead	80.0	20.0	100.0

Table 4: Overall percentage reduction of heavy metals using H₂SO₄ treated CPAC (adsorbent dosage = 1.0 g/20 mL, pH =2, agitation time = 75 min)

S/N	Heavy metals	CPAC	CPAC	CPAC
		(0.5 M H ₂ SO ₄)	(1.0 M H ₂ SO ₄)	(1.5 M H ₂ SO ₄)
		% Reduction	% Reduction	% Reduction
1	Zinc	0.6	1.5	0.6
2	Copper	50.7	60.2	57.4
3	Iron	30.1	48.2	30.1
4	Lead	40.0	43.5	40.0

Table 5: Overall percentage reduction of heavy metals using ZnCl₂ treated CPAC (adsorbent dosage =1.0 g/20 mL, pH = 2, agitation time = 75 min)

S/N	Heavy metals	CPAC	CPAC	CPAC
		(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	60.5	35.6
3	Iron	88.0	89.1	67.5
4	Lead	100.0	100.0	20.0

From the results obtained, it was clear that activated carbon prepared using 1.0 M zinc chloride showed a better performance in terms of heavy metal removals from the industrial effluent used as against those of sulphuric acid and hydrochloric acid at the different concentrations investigated. For instance the percentage heavy metal reductions obtained were 2.6%, 60.5%, 89.1% and 100% for Zn, Cu, Fe and Pb, respectively using 1.0 M zinc chloride. This, therefore, indicated that the pore surface and structure of 1.0 M ZnCl₂ activated carbonized cassava peel was the best developed compared to the concentrations of the other two chemicals.

3.3 Characterizations of Produced Activated Carbon Materials

It can be seen from this study that a carbonization temperature and time of 350°C and 45 min, respectively have been selected to be appropriate for preparing improved cassava peel carbon in high fixed content. Carbonaceous material so obtained was used for the subsequent chemical activation. It was also seen that better results were obtained with improved activated carbon from cassava peel

prepared using zinc chloride at 1.0 M concentration. This resulting activated carbon was consequently subjected to detail characterization. Presented in Table 6 are the results obtained from the characterization of the activated carbon developed from cassava peel.

Table 6: Measured parameters of cassava peel activated carbon at optimum percentage fixed carbon

S/N	Property	Unit	Experimental value	
			CPAC at 350 °C, 45 min with 1.0 M ZnCl ₂	Literature value
1.	Moisture content	%	1.20	2-8
2.	Ash content	%	5.90	≤ 8
3.	Volatile content	%	13.5	< 20
4.	Fixed carbon	%	87.40	>75
5.	Pore volume	cm ³	1.15	1.109
6.	Porosity	mL/g	0.198	0.214
7.	Bulk density	g/cm ³	0.38	0.4-0.5
8.	Charcoal yield	%	34.0	39.99- 55.44

The results presented in Table 6 showed that the moisture content of the activated carbon from cassava peel obtained was 1.2%, which was found to be within the literature value range of 2-8% recommended by Tchobanoglou *et al.* (2002). The ash content of CPAC obtained (5.90%) was also found to fall within the recommended range (<8) also specified by Tchobanoglou *et al.* (2002). The result revealed that the volatile content of cassava peel activated carbon obtained was 13.5% as against less than 20% recommended by British Standard reported by Paddon (1987). Also shown in Table 6 was the fixed carbon content of the developed cassava peel activated carbon. The fixed carbon content of the developed cassava peel activated carbon obtained was found to be 87.40%, which was in agreement with the range (>75) recommended by British Standard and reported by Paddon (1987). The pore volume of the cassava peel activated carbon obtained was also 1.15 cm³/g and found to be close to the standard value of 1.109 cm³/g specified by Hameed *et al.*, (2006). Finally, the bulk density of 0.38 g/cm³ obtained for the cassava peel activated carbon produced was discovered to be very close to the range of 0.4 to 0.5 g/cm³ specified by Tchobanoglou *et al.* (2002).

It has been discovered that most of the results obtained from the characterization carried out on the developed cassava peel activated carbon were found to be in good agreements with the literature values.

3.4 FT-IR Analysis of Produced Activated Carbon

The chemical structure of an adsorbent is of vital importance in understanding its adsorption process. The FT-IR spectra of cassava peel activated carbon before and after adsorption of metal ions were carried out as a qualitative analysis to gain better insight into the functional groups available on the surface of the investigated adsorbent. Their FT-IR spectra measured within the range of 500 – 4500 cm⁻¹ before and after adsorption were recorded as shown in Figures 1 and 2, respectively

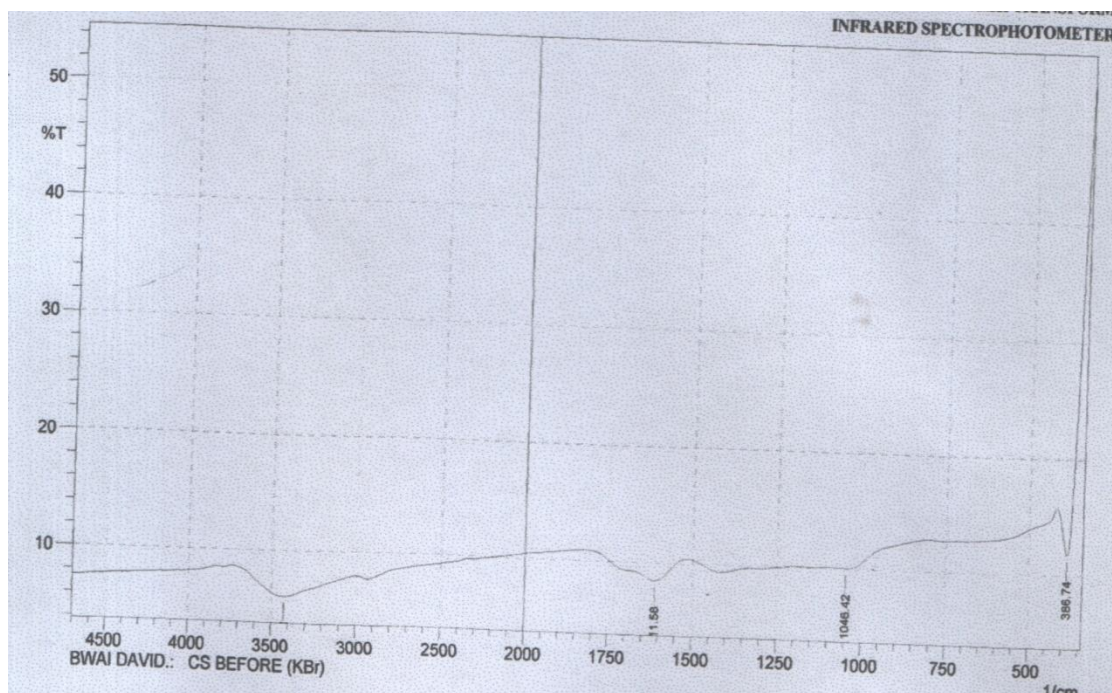


Figure 1: FT-IR spectrum for activated carbon from cassava peel before adsorption

From Figure 1, before adsorption, it was discovered that the FT-IR spectra of CPAC showed bands at 3427.62 cm^{-1} , which was due to $O-H$ stretching of water while the band observed at 1611.58 cm^{-1} indicated the presence of $C=C$ stretch of alkenes. Finally the band observed at 1046.42 cm^{-1} was an indication of $C-O$ stretching while the band at 386.74 cm^{-1} was found to be attributed to $P-S$ stretching. All these played extremely important roles in binding metal ions.

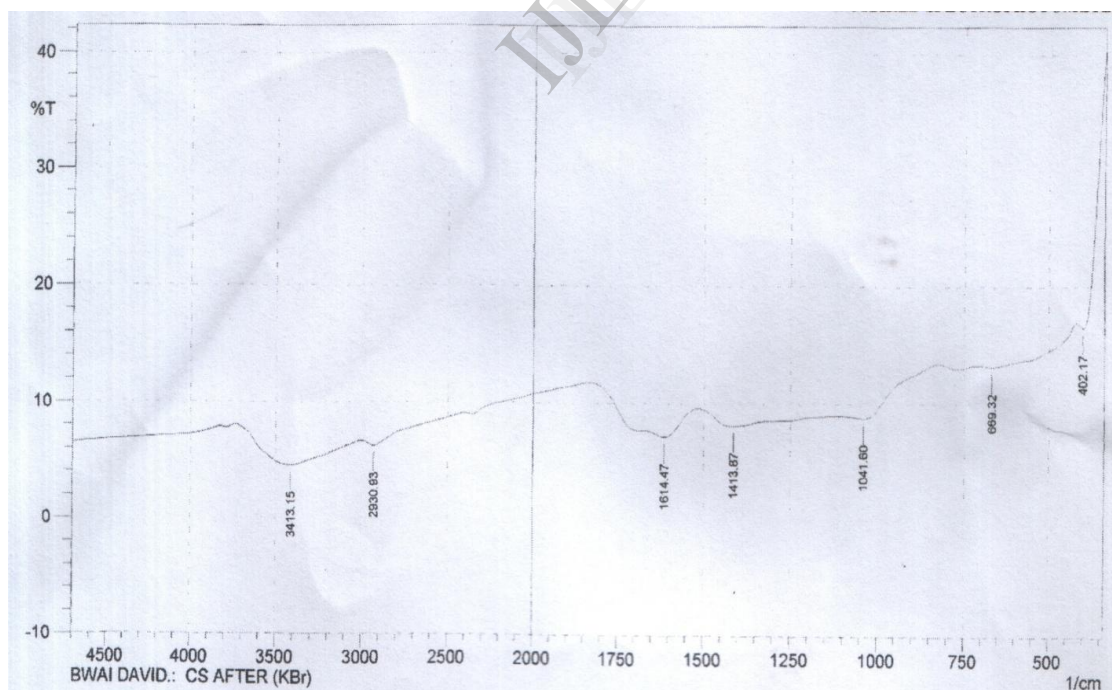


Figure 2: FT-IR spectrum for cassava peel activated carbon after adsorption

After the adsorption of the metal ions, as shown in Figure 2, the FT-IR spectrum showed visible shifts of some of the bands and appearance of some of the bands as shown. Bands at 386.74 , 1046.42 , 1611.58 and 3427.62 cm^{-1} (shown in Figure 1) were shifted to 402.17 , 1041.6 , 1614.47 and 3413.15 cm^{-1} , respectively, as shown in Figure 2. The shifts in the bands confirmed the participation

of the functional groups in the adsorption of metal ions on CPAC. The new bands which appeared at 669.32, 1413.87 and 2930.93 cm^{-1} were assigned to $P=S$, $N=O$ and $C-H$ stretching, respectively. The appearances of the new bands were due to the changes in the nature of binding after the interaction with metal ions occurred as a result of the adsorption.

4.0 CONCLUSIONS

Based on the results obtained from the experiments carried out in this work, it has been discovered that carbonization temperature of 350 °C and time of 45 min have been found to be the optimum conditions for the preparation of good cassava peel carbon with high fixed content. Also discovered was that good quality activated carbon from cassava peel could be obtained by treating the activated carbon using 1.0 M zinc chloride as the activating agent. Finally, the characterization of the activated carbon produced from cassava peel revealed that it had exciting properties that meet all the criteria required for heavy metal removal.

NOMENCLATURES

CCP Carbonized cassava peel
 CPAC Cassava peel activated carbons
 FAO Food and Agriculture Organization
 FT-IR Fourier transform infrared spectroscopy

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