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Effect of Zinc Chloride Activation on Physicochemical Characteristics of Cassava Peel and Waste Bamboo Activated Carbon

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***Abstract*—**Cassava peels and bamboo waste materials discarded from construction are two sources of waste that could constitute serious menace where they exist in large quantities and inadequately handled. The study examined the physicochemical characteristics of activated carbon materials derived from cassava peels and bamboo waste materials discarded from construction site. Both materials were subjected to carbonization and chemical activation using zinc chloride. Results show that the chemical activation of the materials had a more effect on pore formation in cassava peels than in bamboo materials. Bamboo material exhibited a reverse trend for zinc and sulphate ion decontamination efficiencies as the value of zinc chloride impregnation varied unlike cassava peel carbon biomass which exhibited a more consistent result of decontamination efficiency for the seven contaminants tested. Although waste bamboo biomass exhibited higher adsorption intensity as indicated by values of decontamination for most of the contaminants tested, the cassava peel carbon biomass showed a more balanced adsorption level.

***Keywords*—**Zinc chloride, cassava peels, activated carbon, bamboo waste, SEM

I. Introduction

THE quest for more efficient heavy metal removal methods from water, soil and plant has been a major challenge among various researchers over the years. The attempt to solve this problem has led to the discovery of various removal and recovery mechanisms, recently occupying a prominent position in operative heavy metal handling process is the employment of adsorption in the treatment process for waste water in moderately low doses using activated carbon.

Activated carbon (AC) materials are carbonaceous adsorbents which possess extremely porous media with a very large surface area available for adsorption or chemical reaction. It is one of the most popular adsorbents used in numerous industries for the removal and recovery of organic and inorganic compounds from gaseous and liquid streams [1]. According to [2], AC is a non-graphitic and microcrystalline form of carbon having a porous surface with high internal porosity. Activation of carbon materials can be achieved through physical or chemical methods. Physical activation involves carbonization of materials at high temperatures (between 600 and 1200 ºC) under an inert condition using gases like argon, nitrogen etc. This is followed by activation using mild oxidizing agent such as carbon dioxide (CO_2), oxygen (O_2) or steam at high pressure ranging between 68.9 and 172 kPa [3], [4]. On the other hand, chemical activation is achieved by chemical impregnation of the carbon material under heat. During chemical activation process the carbonized biomass is impregnated with a specified ratio of acid, strong base or salt such as phosphoric acid, potassium hydroxide, sodium hydroxide and zinc chloride [5]. Phosphoric acid and zinc chloride are the most commonly used salt for activating lignocellulosic materials [6]-[8]. Zinc chloride (also referred to as Lew $ZnCl_2$ is acid) is a strong dehydrating agent which alters the structure of carbon materials producing porous surface with higher reaction sites for chemical reactions. However chemical activation is preferred over physical activation since it requires lower temperature (200-750 ºC) and shorter time. The adsorptive characteristic of any adsorbent material is dependent on the configuration of its surface area, thus the process of activation leads to improvement in adsorptive characteristics of the biomass.

Cassava (*Manihot esculenta* Crantz) and Bamboo (*Bambusa vulgaris*) are biomass materials that exist in abundance in Nigeria. Cassava is a major staple food in most African and some tropical countries and its processing often leads to generation of a large volume of waste which could pose environmental nuisance when poorly managed. Annual cassava production in Africa is about 84 million tons [9]. According to [10], cassava peels account for up to 10% of the wet weight of cassava tubers. On the other hand, bamboo although sometimes used in ornamental designs is mainly used as support material in construction site most of which are left as construction waste after project is completed. It is therefore clear that these two materials have a common denominator of constituting environmental menace where not adequately managed. The objective of this study is to compare the physico-chemical properties of ACs produced from these waste materials with the aim of suggesting its suitability for specific uses in treatment of wastewater.

II. Methods

A. Preparation of Carbon Samples

Samples of the cassava peels and bamboo waste were collected from a cassava processing industry and a construction site in Ibadan, Oyo state. The materials were inspected to ensure that no impurities were present. The

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bamboo material was then reduced to sizes of 30 cm each, both materials were then washed to remove impurities (Figs. 1 and 2). The waste bamboo was soaked for 24hrs to remove any form of mud, stones, cement and leaves that may have adhered onto its surface during its utilization on the construction site. Both materials were then subjected to sun drying until a moisture content of 8-10% wet basis was attained.

Fig. 1 Prepared Cassava Peel sample

Fig. 2 Prepared Waste Bamboo sample

The dried biomass was then carbonized using a muffle furnace (Carbolite, England model AAF 11/18). Samples of the cassava peels were carbonized at a temperature of 420 °C for a period of 90 min as recommended by [11] while that of bamboo material was done at a temperature of 350 °C for 2 hrs as recommended by [12] after which samples were cooled under inert condition overnight. Both biomasses were then wrapped in aluminium foil during carbonization process. This acted as an antioxidant and also reduced the rate at which the heat from the oven reached the samples in order to ensure equal reaction.

Carbonized samples (Figs. 3 and 4) were then weighed and the yield percentages were calculated as:

$$Yield\ (\%) = \frac{w_1\ x\ 100}{w_2} \quad (1)$$

where W_1 = Weight of AC sample. W_2 = Initial weight of sample.

Fig. 3 Carbonised Cassava Peels

Fig. 4 Carbonized Bamboo Material

B. Preparation of AC samples and analysis

The charred samples were further reduced with the aid of mortar and pestle and sieved to 500 µm particle size. Three samples of cassava peel carbon of mass 100 g each were measured and required $ZnCl_2$ weighed to give an impregnation ratio of 0, 33.3 and 66.6% respectively while three samples of 200 g each of waste bamboo carbon was also weighed and $ZnCl_2$ also measured to give the impregnation ratio of 0, 10 and 20%. The $ZnCl_2$ solution used in the impregnation process was obtained by dissolving the measured weight of $ZnCl_2$ for each of the samples in 100 ml of deionized water. After mixing the solution of $ZnCl_2$ with carbon (impregnation), complete dissolution of each weight percentage was done separately for each biomass by adding 150 ml of distilled water into the mixture to form slurry. The impregnated carbon samples were then left to stand for about 45 minutes to allow the $ZnCl_2$ get enough contact time with the carbon. The samples were put in aluminium containers, covered with aluminium foil to prevent loss of $ZnCl_2$ and later placed in a hot air oven. Impregnated carbonized cassava peels (ICCP) were placed for oven (JPW SKU0002, USA) for 50 min at 150 °C while impregnated carbonized waste bamboos (ICWB) were also placed in the oven for 2 hours at 200 °C as recommended by [13]. The oven temperature for ICCP and ICWB were increased to 200 °C for 60 minutes and 450 °C for 4 hours respectively as recommended by [14] to ensure complete impregnation of $ZnCl_2$. The obtained AC materials were then left to cool down in a desiccator. After cooling, each sample was washed with slightly boiled deionized water to remove residual $ZnCl_2$. This was then followed by washing with distilled water to pH of 6.8±0.2 The obtained CPAC and WBAC were then dried by placing in the oven at 90 °C for 6 hours and 110 °C for period of 8 hrs respectively. The final products were allowed to cool at ambient temperature and stored in airtight containers for subsequent experiments.

Physiological and morphological changes in the carbon biomasses were monitored by subjecting 1.5 g of each of the samples of CPAC and WBAC to micrograph analysis with the aid of a Scanning Electron Microscope (ZEISS EVO® MA 15), equipped with variety of signals used to focus the surface of the carbon materials at the Sheda Science Technology complex located (SHETCO), Abuja, Nigeria.

C. Adsorption Study of the AC

An experimental set up consisting of a reservoir, connected to three specially constructed transparent perspex adsorption columns of 0.003 m thickness, 0.18 m length, 0.18 m breath and 0.65 m height was used to contain 200 g of each of the biomass to be tested the treatment process. The wastewater was then released from a reservoir into the three constructed transparent perspex adsorption columns containing the carbon materials simultaneously at a rate of 0.378 l/hr. Water samples were strained from the adsorption columns after a period of 4hrs from the three adsorption columns and analyzed for BOD_5, SO_4^{2-}, NO^{3-}, PO_4^{3-}, Cl^-, Ni^- and Zn^{2+} ions pollution in the water samples.

The efficiency of the carbon biomasses was determined by the percentage decontamination method. This percentage is a measure of the total contaminant in the water sample removed by the AC through adsorption, as expressed in (2):

$$\text{Percentage Decontamination} = \left[\frac{C_1 - C_2}{C_1}\right] x100 \quad (2)$$

where, C_1= Wastewater concentration before treatment (mgl^{-1}); C_2= Wastewater concentration after treatment (mgl^{-1}).

III. Results and Discussion

A. Physicochemical Properties of CPC and WBC

The physicochemical properties of AC from cassava peels and bamboo waste are shown in Table I. The effect of $ZnCl_2$ impregnation on adsorption capacity of the AC materials was also shown. It can be seen that the bulk density of CPC slightly increased with activation ratio. The RBC also showed an increase in bulk density with corresponding increase in activation ratio while bulk density exhibited a reverse trend.

TABLE I
Comparison of Physicochemical Characteristics of Carbon Materials

Biomass	Impregnation (%)	pH	Bulk Density	Ash Content	Moisture Content	Average Pore Area (um)*	Average Pore Width (um)*	Average Pore Length (um)*	Carbon Yield (%)**
CPC	0	5.3	0.407	2.65	2.31	166.60	10.39	13.78	34.63
	33	5.3	0.410	2.38	2.21	674.00	61.73	25.20	
	66	5.4	0.413	2.44	2.33	863.30	18.91	27.70	
WBC	0	6.8	0.167	2.83	2.42	50.45	172.30	15.00	34.10
	10	6.9	0.177	2.67	2.41	69.11	200.20	17.00	
	20	7.2	0.191	2.40	2.43	104.83	354.26	18.76	

* Results obtained from subjecting 1.5g of Cassava Peel Carbon and Waste Bamboo Carbon to SEM analysis
** Results obtained from carbonization process

The morphological features of carbon biomasses also revealed that the values of average pore area, average pore width and average pore length increased with level of $ZnCl_2$ impregnation. This implies that the $ZnCl_2$ impregnation process was able to open up the pores on the carbon materials as expected in a chemical activation process. However, a comparison of average pore width value for the two biomasses at the different impregnation levels reveals that the bamboo biomass had much higher value than those of the cassava biomass, this trend is reversed in the average pore area measurements for the carbon material. Table I also reveals that the percentage carbon yield of both biomasses was very close; this shows that the base materials used for the activation process had a relatively close transformation effect.

B. Morphology of CPC and WBC

The micrograph images of the carbon materials obtained from SEM as shown in Plate 5-10 shows a marked difference in structural presentation of the biomasses at different $ZnCl_2$ impregnation ratios.

The waste bamboo biomass at 0% $ZnCl_2$ impregnation (Fig. 5) can be observed to exhibit pore spaces which are not as well defined as the hexagonal shaped outline at 5 and 10% impregnation level (Figs. 6 & 7). It can be observed that the WBAC materials both had a similar appearance which was different from that of the WBC. The well-defined structure of the impregnated bamboo biomass is synonymous to improvement in adsorption intensity as it shows that the carbon material had developed more surface area.

Micrograph image of the CPC (Fig. 8) reveals that the surface was rough with no clearly defined pore space formation, however the CPAC at 33% impregnation (Fig. 9) shows a surface configuration which has a partly developed pore formation. This is indicative of an improvement in adsorptive characteristics as a result of increased surface area. CPAC at 66% impregnation ratio was observed to have developed a clearer outline of pore formation with the surface exhibiting a honeycomb structure (Fig. 10), this is also indicative of an increased surface area configuration.

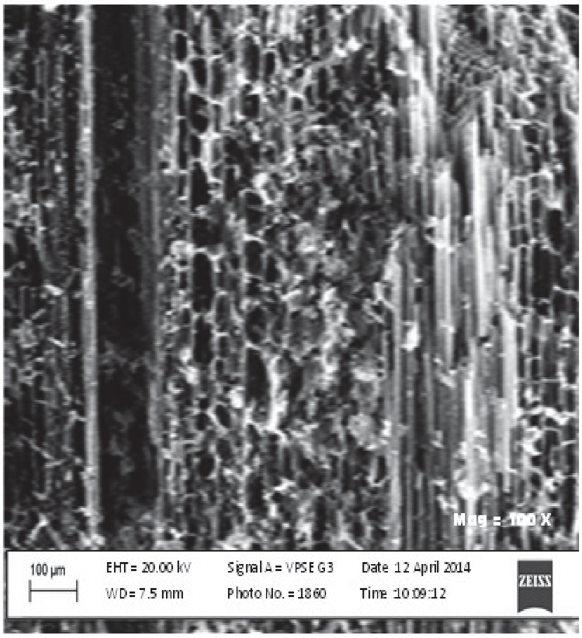

Fig. 5 Pore space of WBC at 0% $ZnCl_2$ Impregnation as viewed under SEM

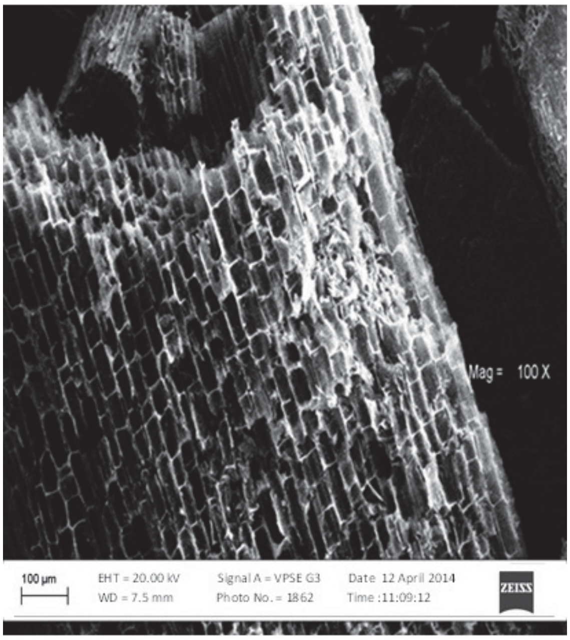

Fig. 6 Pore space of WBC at 10% $ZnCl_2$ Impregnation as viewed under SEM

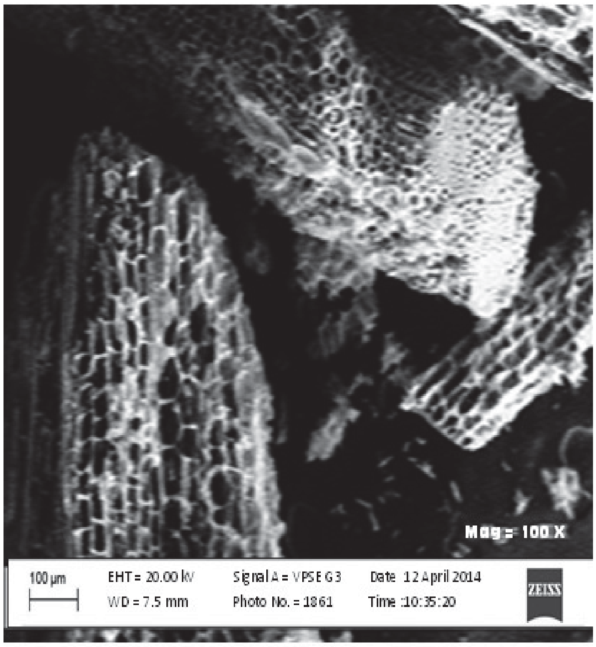

Fig. 7 Pore space of WBC at 20% $ZnCl_2$ Impregnation as viewed under SEM

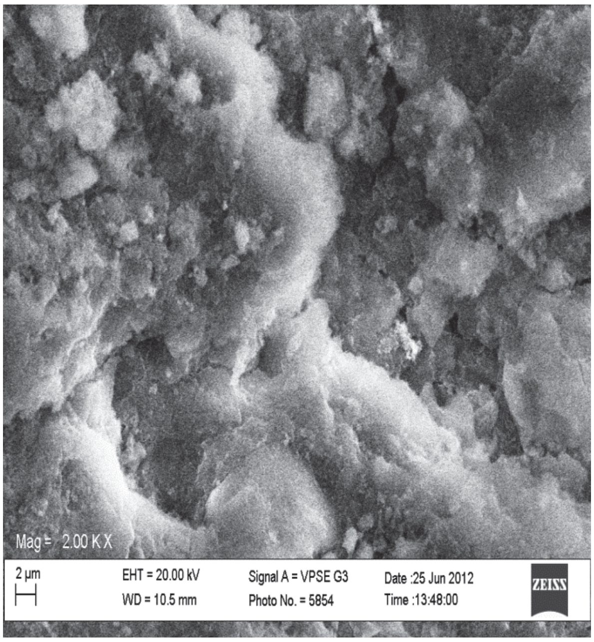

Fig. 8 Pore space of CPC at 0% $ZnCl_2$ Impregnation as viewed under SEM

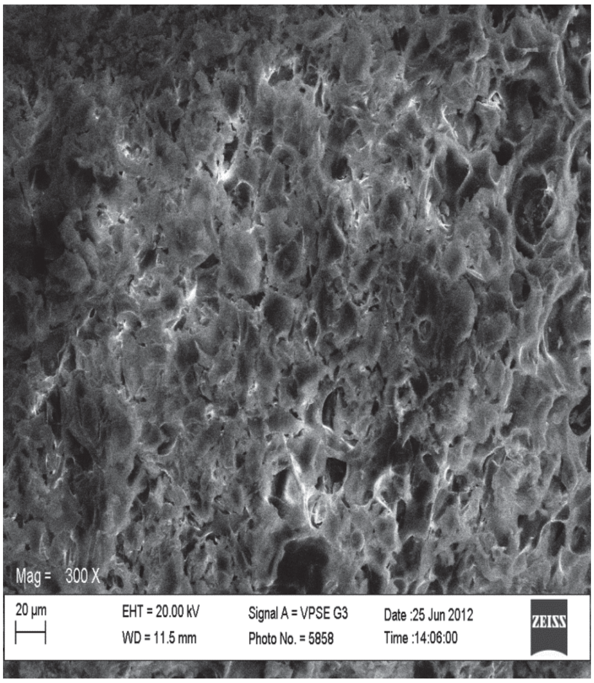

Fig. 9 Pore space of CPAC at 33% $ZnCl_2$ Impregnation as viewed under SEM

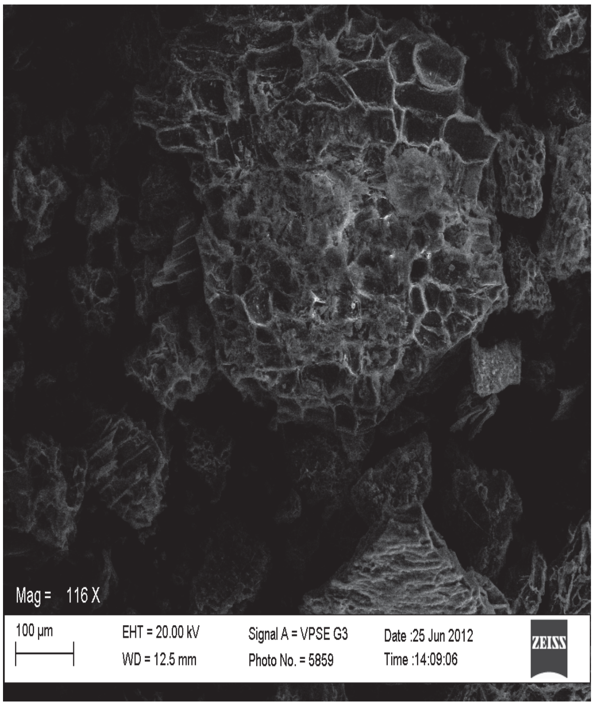

Fig. 10 Pore space of CPAC at 66% $ZnCl_2$ Impregnation as viewed under SEM

The result for decontamination efficiencies of CPC, cassava peel activated carbon (CPAC), WBC and waste bamboo activated carbon (WBAC) are shown in Table II. The decontamination efficiency for sulphate ion by the WBC and WBAC at 10% activation ratio showed a negative value; this implies that the concentration of sulphate increased in the treated water after contact with WBC. It was also observed that Zinc ion presence was also increased instead of reducing for the WBAC (10 and 20% impregnation) this may have been due to the presence of residual activation salt in the AC. The WBC however showed no effect on Zinc content of the water. The Nickel content was totally removed by both levels of WBAC while WBC was only able to achieve 50% reduction in the treated water. Table II also shows that CPC and CPAC exhibited a general increase in level of decontamination of ions considered with the increase in activation/impregnation ratio with the exception of Nickel ion which maintained a constant value of 33.3%. This implies that Nickel adsorption was not dependent on activation level. It was also observed that the WBAC at both activation levels had a total decontamination of Nickel ion in the waste water was similar to results obtained by [15] who obtained an efficiency of 97.8% using AC derived from almond husk.

The CPC and CPAC did not exhibit such disparity in adsorption characteristics of any of the elements tested rather it exhibited an increasing trend with increasing $ZnCl_2$ impregnation ratio this is in consonance with findings of [16], [17] who opined that Nickel adsorption by granular carbon produced from agricultural waste can be improved through activation and surface enhancement. CPAC exhibited the highest decontamination level of 70.63% for BOD_5 while the lowest value for decontamination by CPAC was observed for Nickel.

TABLE II
PERCENTAGE DECONTAMINATION OF CPC AND WBC AFTER 4 HOURS CONTACT TIME WITH WASTEWATER

	Cassava Peels Carbon			**Waste Bamboo Carbon**		
	0	**33**	**66**	**0**	**10**	**20**
SO_4^{2-}	61.01	61.02	67.8	-42.86	-19.05	4.76
NO_3^-	53.60	59.20	59.20	60.87	65.22	73.91
PO_4^{3-}	40.02	48.04	51.4	33.33	50.00	66.67
Cl^-	38.78	42.86	47.45	30.00	36.00	50.00
Ni^-	33.33	33.33	33.33	50.00	100.00	1000.00
Zn^{2+}	28.57	64.29	64.29	0.00	-20.00	-30.00
BOD	61.11	70.24	70.63	96.79	97.44	97.86

NB: Units are in percentage

IV. CONCLUSION

The study shows that carbon materials derived from cassava peels and bamboo waste exhibited a marked difference in surface and pore space configuration with the impregnation using $ZnCl_2$ thus leading to an increase in adsorptive surface area. However, it was noticed that the cassava peel carbon material showed a visibly progressive pore space development in contrast to the bamboo biomass. The result of adsorption intensity shows that bamboo biomass had very high affinity for nickel ion leading to a total removal. The study also showed that the impregnating salt had a marked effect of increasing the concentration of sulphate and zinc ion concentration in the treated water treated with waste bamboo carbon materials, this trend was not noticed in the cassava peel carbon material as it exhibited a more consistent adsorption intensity although at a lower level when compared with some of the values on the bamboo biomass range.

REFERENCES

[1] P. L. Y. Foo and L.Y. Lee "Preparation of Activated Carbon from *Parkia Speciosa* Pod by Chemical Activation". *Proc. World Congress on Engineering and Computer Science (WCEC 2010),* Sept. 2010: 98-104, 2010.

[2] W. Hassler "Purification with Activated Carbon", Chemical Publishing Co, Inc., New York, 1974.

[3] P.T. Williams and A. R. Reed, A.R. "High grade of activation and pyrolysis of natural fiber textile waste". *Journal of Analysis, Application and Pyrolsis* vol. 7 no 1, pp. 971-986, 2004.

[4] T.H. Usmani, M. Tahir, I. SiddiQui and F. A. Perveen "Preparation of Activated Carbon from Date Pits by Physical Activation in Fluidized Bed Reactor", *Jour. Chem.Soc.Pak,* vol. 25, no 3, pp 183-187, 2003

[5] D. Adinata, W. M. A. W. Daud, and M. K. Aroua "Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3" *Journal of Bioresource Technology.* vol. 98, pp 145–149, 2007.

[6] A. Ahmadpour, B. King and D. Do "Comparison of equilibria and kinetics of high surface area activated carbon produced from different precursors and by different chemical treatments" *Ind. Eng. Chem. Res.,* vol 37, no 4, pp 133-136, 1998.

[7] A. M. Puziy, O. I. Poddubnaya, A. Matinez-Alonso, F. J. Suarez-Garcia and M. D. Tascon "Characterization of synthetic carbon activated with phosphoric acid" *Journal of Applied surface* vol 200 no 2002, pp 99-202, 2002.

[8] P. Subhashree, "Production and characterization of Activated Carbon produced from a suitable Industrial sludge" *National Institute of Technology Rourkela*. Pp. 1-69, 2011.

[9] L. A. Nwaogwu, N. C. Agha, C. S. Alisi and C. E. Ihejirika "Investigation on the effect of cassava effluent-polluted soil on germination, emergence and oxidative stress parameters of *Telferia occidentalis,*" *Journal of Biodiversity and Environmental Sciences* (JBES) vol. 1, no. 6, pp 104-111, 2011.

[10] A. O. Obadina, O. B. Oyewole, L. O. Sanni, and S. S. Abiola "Fungal enrichment of cassava peels proteins", *African Journal of Biotechnology*. 5(3): 302-304, 2006.

[11] O. A. Omotosho, "Production and Utilization of Cassava Peel Activated Carbon in Treatment of Effluent from Cassava Processing Industry", *M.Sc. thesis, Dept. of Agricultural and Environmental Engineering University of Ibadan, Nigeria,* pp. 50-72, 2012.

[12] O. O. Ijaola, "Production and utilization of activated carbon from waste bamboo as adsorbent in water treatment". *M.Sc. Thesis submitted to Faculty of Technology University of Ibadan.* pp.59-70, 2011.

[13] O. O. Ijaola, "Production and utilization of activated carbon from waste bamboo as adsorbent in water treatment". *M.Sc. Thesis submitted to Faculty of Technology University of Ibadan.* pp.59-70, 2011.

[14] O. A. Omotosho, "Production and Utilization of Cassava Peel Activated Carbon in Treatment of Effluent from Cassava Processing Industry", *M.Sc. thesis, Dept. of Agricultural and Environmental Engineering University of Ibadan, Nigeria,* pp. 50-72, 2012.

[15] H. Hasar, "Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk". *Journal of Hazardous Materials* B97 (2003) 49–57, 2003.

[16] V. R. Kinhikar "Removal of Nickel (II) from Aqueous Solutions by Adsorption with Granular Activated Carbon (GAC)". *Research Journal of Chemical Sciences,* vol 2 no 6, pp 6-11, 2012.

[17] M. E.l-Batouti and A. M. Ahmed "Adsorption Kinetics Of Nickel (II) Onto Activated Carbon Prepared From Natural Adsorbent Rice Husk", *International Journal of Technology Enhancements and Emerging Engineering Research,* vol 2 no 15 pp 145-148, 2014.