

## APPLICATION OF CASSAVA PEELS ACTIVATED CARBON IN THE TREATMENT OF OIL REFINERY WASTEWATER – A COMPARATIVE ANALYSIS

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### ABSTRACT

A comparative analysis of the efficiency of activated carbon produced from fermented cassava peels (CPB), unfermented cassava peels (CPA) and commercial grade activated carbon (CAC) in the treatment of refinery wastewater was carried out. CPB was found to be 8% and 18% more efficient when compared to CPA and CAC in the removal of COD, and 14% and 3% better than CAC and CPA respectively in the removal of BOD<sub>5</sub>. The removal efficiency of Pb<sup>2+</sup> by CPB was 100% compared to 95% and 57% by CPA and CAC while 96% of phenol was removed by CPB against 93% and 83% by CPA and CAC respectively. This better performance of CPB over CPA and CAC is not unconnected with its higher pH resulting from the removal of cyanide from the peels during the fermentation process. However, despite the high phenol removal efficiency by CPB, the concentration of phenol in the treated effluent does not meet the environmental guidelines for disposal. It is therefore, recommended that a two-stage CPB adsorption column arranged in series is necessary to treat refinery wastewater efficiently if it is desired to totally remove phenol from the effluent or reduce the concentration to 0.005 mg/l allowed by the Federal environmental protection agency (FEPA). The equilibrium adsorption test conducted showed that the Freundlich isotherm is a better fit for the adsorption of phenol by the three activated carbons with correlation coefficients (R<sup>2</sup>) of 0.9364, 0.9383 and 0.9541 for CAC, CPA and CPB respectively. CPB was found to be a better adsorbent as it has the highest adsorptive capacity as evidenced from its better Freundlich exponent.

**Keyword:** Cassava peels, activated carbon, adsorption, refinery wastewater, environment, pollutant.

### INTRODUCTION

Refinery wastewater most often contains hydrocarbons, spent catalyst and acid as well as soluble bases used as raw materials and treatment reagents. Most of these pollutants, which often include toxic, hazardous and priority pollutants, accounts for between 0.5–15% weight of the process wastewater [Bhatnaga and Minocha, 2009; Girish and Murty, 2013]. The need to comply with environmental regulations require that such pollutants be removed to an acceptable level

before being discharged into the environment or recycled back into the plant depending on water economics [Nekoo and Shoreh, 2013; Hariz and Monser, 2014]. Since refinery wastewater pollutants is made up of both organic and inorganic sources, the treatment of such wastewater will involve chemical, physical, biological or a combination of these processes [Adeyinka and Rimi-Rukeh, 1999; Fetter et al., 1982]. To measure the organic content of wastewater, the biological oxygen demand (BOD) and chemical oxygen demand (COD) as well as the total organic matter

(TOC) lumped parameters are usually employed [El-Naas et al., 2010]. Various physical, chemical and biological methods are traditionally employed for the treatment of refinery wastewater which is normally oily in nature [Pant and Adholeya, 2007]. Some of these methods include gravity separator pretreatment, preceded by flocculation and dissolved air flotation (DAF) aimed at reducing the suspended solids, oil and grease in the wastewater before being subjected to further biological and or chemical treatment as required [Nekoo and Shohreh, 2013; Hussani et al., 2011]. Because the steps required for the traditional physicochemical treatment of industrial wastewater including refinery effluent is highly cost effective, adsorption on activated carbon is now widely used for the removal of a variety of organics and other pollutants from wastewater [Tandale and Shide, 2008; Foo and Lee, 2010]. However, it was observed that the application of carbon in a form of commercial activated carbon or charcoal (ACC), which had proved to be very effective in treating most complex industrial wastewater, is exorbitantly expensive and about 10–15% of it is lost during regeneration [Tandale and Shide, 2008]. There is a need therefore, to source for cheap alternative form of effective carbon-based adsorbents.

For decades now, research has been intensified to source for an inexpensive replacement for ACC from locally available materials, especially agricultural waste and by-products such as coconut shell and husk, rice husk, corn cob, banana peels, palm oil empty bunch, fly ash, cassava peels and many others [Ahmed and Tan, 2008; Alinnor and Nwachukwu, 2012; Chukwuedo and Okieimen, 2008; Rangaraj et al., 2002; Sarka and Acharya, 2006]. Recently, one agricultural waste that attracted serious attention of researchers, especially in sub-Saharan Africa, is cassava peels. This is because cassava peels currently constitute a disposal menace in most cassava processing countries where it serves as a staple food [Oghenejoboh, 2015; Oghenejoboh, 2012]. Earlier studies on the effectiveness of activated carbon produced from cassava peels in the treatment of wastewater generated from different industries was very encouraging. For example, it was found to remove more than 85% phenol from water artificially contaminated with phenol [Alinnor and Nwachukwu, 2012]. In another study, cassava peels activated carbon was reported to adsorb 80% of  $Pb^{2+}$  and 77%  $Cu^{2+}$  from water collected from a stagnant pond

where various waste is indiscriminately dumped by villagers [Ilaboya et al., 2013].

However, in all these documented studies, little or no attention is paid to the cyanide content of the cassava peels. Cyanogen glycoside found in great quantity in cassava is concentrated majorly in the peels [Oghenejoboh, 2015]. Though, cyanogenic glycoside may not be toxic and harmful as a compound but it hydrolyses to form toxic and harmful hydrocyanic acid [Olayinka, 2013; Oti, 2002]. This may possibly happen when the cassava peels activated carbon is contacted with the wastewater during the adsorption process. Despite the unstable nature of cyanogenic glycoside, it can be converted to heat resistant salts that may persist in the effluent water if it is not subjected to further treatment stage such as alkaline chlorination which involves conversion of the cyanide to cyanogen chloride that can easily be hydrolyzed to harmless cyanate at alkaline pH [Eisler and Wiemeyer, 2004]

In the present study, the adsorption parameters, efficiency and adsorption isotherms for commercial grade activated carbon is compared with activated carbon produced from cyanide laden and cyanide free cassava peels in the treatment of refinery wastewater

## MATERIALS AND METHODS

Some of the materials used for the experiments were fresh peelings of bitter cassava (*utilissima*) variety obtained from a cassava farm in Ughelli, Delta State of Nigeria, wastewater collected from the downstream of the dry air flotation (DAF) unit of the wastewater treatment plant of the Warri refinery and petrochemical company (WRPC) in Warri, Delta state of Nigeria, commercial grade activated carbon (CAC) obtained from Pyrex chemical/laboratory equipment in Benin city, citric acid, distilled water, muffle furnace, crucibles, measuring cylinders, filter papers, beakers, weighing balance, mortar and pestle as well as Perkin Elmer HGA 900 spectrophotometer.

### Production of cassava peels activated carbon

The fresh cassava peels were divided into two parts labeled CPA and CPB. CPA was properly washed in distilled water without other pretreatment; sun-dried for 7 days under scorching sun and packaged in an air-tight polythene bag in preparation for the experiment. CPB was soaked

in an open container exposed to the atmosphere for 5 days with the water being replaced with fresh one every 24 hours to release cyanogen glycoside contained in the peels before carbonation. After the 5day fermentation process, the fermented cassava peels were properly washed three times with distilled water before drying it under scorching sun for 7 days.

The dried CPA and CPB were then subjected to size reduction by crushing using a mortar and pestle and then filtered with a 500µm sieve filter. The filtrates were then washed thoroughly with distilled water to remove any unwanted matter introduced during the crushing process. The washed CPA and CPB samples were then placed in an oven maintained at 105 °C for 12 hours for moisture removal. 500 g each of the dried CPA and CPB were measured and introduced into the hot zone of the muffle furnace for 120 minutes at 380 °C. The carbon formed was allowed to cool for 5 hour at room temperature. 100 g each of the carbonized and cooled CPA and CPB were then activated with 150 g 1.0 M Zinc chloride following the method employed by [Awoyale et al., 2012].

### Adsorption test and analysis

Three fixed, equal size adsorption columns packed with commercial grade activated carbon (CAC), unfermented cassava peels activated carbon (CPA) and fermented cassava peels activated carbon (CPB) were arranged in parallel as shown in Figure 1. Oil and suspended particle-free wastewater obtained from the outlet of the DAF unit of the WRPC wastewater treatment plant was placed in a 20 litres plastic container with its outlet connected to the three columns by

means of valves that were opened to allow equal volume of wastewater through the three adsorption columns by gravity. In order to provide a high interfacial area for adsorption, distilled water was passed through the columns to wet the activated carbon bed before the experiment. Effluents collected from flasks 1–3 were analysed at three hour’s interval for 9 hours to obtain triplicate reading of the adsorption parameters for comparative purpose.

The refinery wastewater as well as the treated effluent obtained from flasks 1–3 were analysed for COD, BOD<sub>5</sub>, TDS, turbidity, pH, DO and heavy metals. The COD, BOD<sub>5</sub>, TDS, pH, DO, conductivity and turbidity were analysed by means of the respective meters while heavy metal analysis was done using UV absorption spectrophotometer.

### Batch adsorption model study

Batch adsorption experiments were carried out to compare the efficiency of adsorption of phenol, a prominent pollutant in oil refinery wastewater by the three activated carbon used in this work. Completely mixed batch reactors (CMBR) consisting of 20 ml glass centrifuge tubes containing 5 gm each of the activated carbon to be tested and 15 ml of the refinery wastewater, closed with open closure and sealed with Teflon-lined silicone septa were used for the experiment. Three replicates CMBR were used for each phenol concentrations of 20, 40, 60, 80 and 100 mg/l prepared from the initial stock of 120 mg/l of phenol in the analysed refinery wastewater. The tube’s contents were agitated with vortex mixer and allowed to attain to equilibrium at room temperature for 12

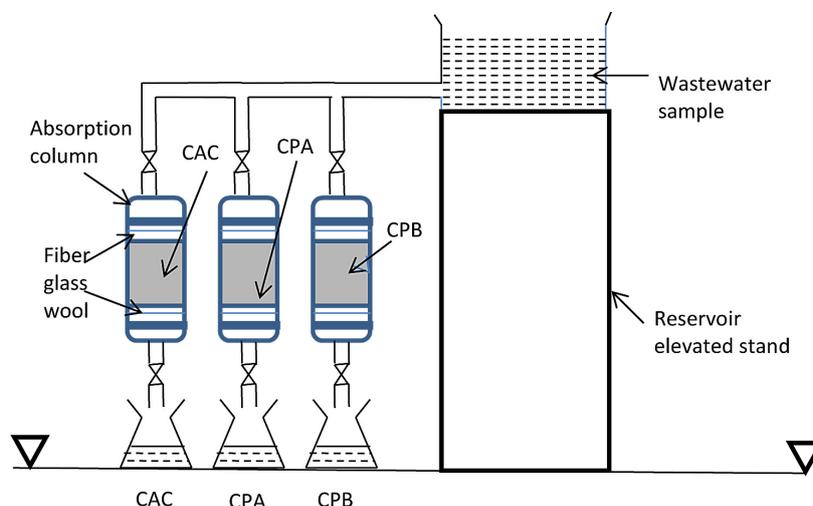


Figure 1. Experimental set-up for fixed-bed activated carbon treatment of refinery wastewater

hours. After the 12 hours equilibration period, the tubes were then centrifuged at 2500 rpm for 30 minutes to separate the solid and liquid phase. A 100  $\mu\text{L}$  aliquot was removed from each tube and transferred to 5ml vial and analysed by means of a UV spectrophotometer to measure the absorbance from where the equilibrium concentration was obtained by means of a calibration chart. The concentration of phenol ( $C_s$ ) adsorbed by each of the tested activated carbon was then calculated as follows [Oghenejobh et al., 2008]:

$$C_s = \frac{V}{M}(C_o - C_e) \quad (1)$$

where:  $C_s$  – is the concentration of phenol adsorbed by the activated carbon (mg/g),

$C_o$  – is the initial concentration of phenol in the wastewater (mg/l),

$V$  – is the volume of wastewater used ( $\text{cm}^3$ ),

$M$  – is the mass of activated carbon used (g).

The Langmuir and Freundlich isotherm models were used to test the adsorption efficiency of the three activated carbon studied in treating phenol-laden refinery wastewater. The model equations are:

- Freundlich:

$$\log C_s = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

- Langmuir:

$$\frac{C_s}{C_e} = \frac{1}{\alpha\beta} + \frac{C_e}{\beta} \quad (3)$$

Where  $K_f$ ,  $n$ ,  $\alpha$  and  $\beta$  are the partition coefficient, Freundlich exponent, Langmuir constant and adsorption capacity respectively.

## RESULTS AND DISCUSSION

The results of the wastewater analysis, before and after treatment with the three tested activated carbons, is presented in Table 1, while Figure 1 and Table 2 show the phenol adsorption capacity of the three activated carbons and their respective Freundlich and Langmuir model parameters

It will be observed from Table 1 that the pH of the refinery effluent water increased slightly from 6.07 to 6.62, 6.69 and 7.52 after treatment with commercial grade activated carbon (CAC) and unfermented cassava peels activated carbon (CPA) and fermented cassava peels activated carbon (CPB) respectively. The gradual transition of the treated effluent from acidic to basic may be as a result of the  $\text{H}^+$  concentration of the adsorbent. CPB with very low concentration of cyanide, resulting from the fermentation process exhibits the highest pH of 7.52, which is highly favorable for adsorption of organic and trace metal pollutants from wastewater [Alinnor and Nwachukwu, 2012; Awoyale et al., 2012]. The results of this study as can be seen from Table 1, agrees with the observation that the higher the pH of an adsorbent, the higher the removal efficiency of heavy metals and organic materials by the adsorbent from wastewater. As noted by Low et al. [Low et al., 1995], the surface of the adsorbent functional group is usually repulsively associated with hydroxonium ions ( $\text{H}_3\text{O}^+$ ) at low pH which invariably reduce the removal efficiency of heavy metals and organics during adsorption. From the analysis results presented in Table 1, it could be observed that the heavy metals removal efficiency from the wastewater increased as the pH

**Table 1.** Analyses result of untreated and treated Refinery wastewater

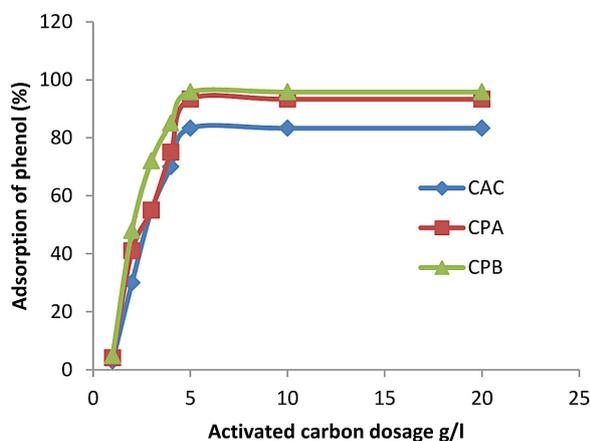
Parameters	Before treatment	After treatment		
		CAC	CPA	CPB
pH	6.07	6.62	6.69	7.52
COD (mg/l)	384	172	136	102
BOD <sub>5</sub> (mg/l)	52.5	14.8	8.9	7.5
DO (mg/l)	4.2	12.8	20.2	22.1
Electrical conductivity ( $\mu\text{S}/\text{cm}$ )	1520	1522	1520	1520
TDS (mg/l)	220	218	217	217
Turbidity (NTU)	52	2	0	0
Pb <sup>2+</sup>	2.05	0.89	0.10	<0.001
Cu <sup>2+</sup>	4.40	1.05	0.88	0.26
Fe <sup>3+</sup>	8.49	3.72	2.58	2.19
Phenol (mg/l)	120	20	8	5

**Comments:** CAC – commercial grade activated carbon; CPA – unfermented cassava peels activated carbon; CPB – fermented cassava peels activated carbon.

**Table 2.** Freundlich and Langmuir parameters for CAC, CPA and CPB

Activated carbon	Freundlich Isotherm			Langmuir Isotherm		
	n	k	r <sup>2</sup>	$\alpha$	$\beta$	r <sup>2</sup>
CAC	0.9842	0.5915	0.9364	0.0078	243.91	0.1097
CPA	1.0549	0.4053	0.9383	0.0501	95.24	0.7231
CPB	1.0893	0.4146	0.9541	0.0033	909.09	0.0142

increases. Performance efficiencies of CPB, CPA and CAC were: 100%, 95% and 57% for lead and 96%, 93% and 83% for phenol respectively. Figure 2 shows the phenol removal efficiency by the three activated carbons. Though, CPB recorded 96% efficiency in the removal of phenol from the wastewater, the final concentration of phenol in the treated effluent is still above 0.005 mg/l allowed for the industry [FEPA, 1991]. The initial concentration of phenol in the treated wastewater stock is highly responsible for this trend, since it determines the equilibrium contact time for the adsorption process. The lower the initial phenol concentration in the wastewater stock, the shorter the equilibrium time, hence the better the adsorption efficiency [Alinnor and Nwachukwu, 2012]. Research showed that coconut shell activated carbon has the capacity to adsorb 205.8 mg/g of phenol from wastewater, which makes it a better adsorbent if phenol is the only targeted pollutant [Girish and Murty, 2013], however, coconut shells are not readily abundant like cassava peels. If it is desired, therefore, to properly treat refinery wastewater with cassava peels activated carbon, a two-stage fermented cassava peels activated carbon adsorption column arranged in series will be necessary. Thus, any trace metals and other pollutants, including phenol, which were not removed during the first stage adsorption column

**Figure 2.** Comparative adsorption capacity of phenol present in refinery wastewater by CAC, CPA and CPB

will be totally removed in the second stage adsorption column

In addition to the high removal efficiency of heavy metals and some organics by cassava peels activated carbon, especially CPB, other lumped organic parameters such as COD and BOD<sub>5</sub> as well as turbidity were also drastically reduced. The COD level reduced by 55%, 65% and 73% respectively with CAC, CPA and CPB, while the BOD<sub>5</sub> reduced by 72%, 83% and 86% respectively. The turbidity, on other hand, was reduced from 52 NTU to zero within the 5 hours treatment period. TDS and electrical conductivity of the analysed wastewater remained relatively constant after treatment with the three activated carbons. This is in order and agrees with the findings of Ilaboya et al. [2013] who noted that adsorption does not remove TDS from wastewater. The electrical conductivity which is a measure of the ability of the discharged water to carry electrical current, is a function of the concentration and mobility of ionic species in the water. This is determined by the concentration of total dissolved solids (TDS) in the water. The higher the TDS contained in a water sample the higher the conductivity of the water. The relative stability of the conductivity of the treated wastewater is unrelated with the stability observed for the TDS as contained in Table 1.

The equilibrium adsorption data were modeled using a two-parameter isotherm models-the Freundlich and Langmuir isotherms. As can be seen from Figure 2, the Freundlich model correlates well with the three activated carbons used in the study, as evidenced by the high correlation coefficient (R<sup>2</sup>). The Langmuir model does not fit the equilibrium data at all. The magnitude of the Freundlich exponent (n) which describes the adsorptive capacity of an adsorbent as seen from Table 2 is higher for CPB followed by CPA and least for CAC. This is an indication that CPB is a better adsorbent than the remaining two activated carbons. It was noted that an adsorbent having a Freundlich exponent greater than 1 is highly favored for adsorption [Saed et al., 2005].

## CONCLUSIONS

It was established from the results of this study that activated carbon produced from agricultural waste such as cassava peels hold a great promise in the treatment of wastewater containing organic materials and trace heavy metals. Fermented cassava peels activated carbon had the highest removal efficiency for all the refinery wastewater pollutants followed by un-fermented cassava peels activated carbon. This shows that the presence of free cyanide contained in the cassava peels lowers its pH which invariably impedes the efficiency. The adsorption of pollutants to cassava peels activated carbon is best described by the Freundlich isotherm with fermented cassava peels activated carbon exhibiting the highest adsorptive capacity. Therefore, for the efficient treatment of industrial wastewater containing organic and metallic pollutants fermented cassava peels activated carbon is preferred to unfermented cassava peels activated carbons.

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