

Evaluation of the Adsorptive Capacity of some Activated Plant Materials on Cyanide: An In vitro Study

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ABSTRACT

Background and Purpose: Chemical intoxication of dietary origin is one of the major health problems confronting the global community. Cyanide is a very toxic chemical which reacts and forms a stable complex with iron in cytochrome oxidase thereby inhibiting oxidative phosphorylation. Adsorbents are carbon materials that attract poisons to their surfaces thus preventing the absorption of poisons into the body. The clinically available activated charcoal is expensive and often not readily available.

Methods: Four (4) different concentrations ranging from 0.5 g/dL to 2.0 g/dL of activated carbon from plantain peels, castor oil seed shells, coconut shells, and rice husks were used to prepare adsorbent samples. The same range of concentrations was used for activated charcoal (standard). Each concentration was introduced into a 1 L of pyrex beaker containing 250 mL aqueous solution of 1 mol/mL of potassium cyanide. The cyanide-ninhydrin adducts obtained were subjected to UV-spectrophotometry, and the degree of adsorption of cyanide by the various activated carbon samples was determined.

Results: Plantain peels showed the least amount of un-adsorbed cyanide (20.03±0.48 mg/dL), followed by coconut shells (24.34±0.43 mg/dL), next was castor oil seed shells (26.48±0.36 mg/dL). These values were all significantly ($P<0.0001$) lower than the value obtained for the commercial (standard) activated charcoal (36.87±0.02 mg/dL). At the sample amount of 2.0 g/dL, the lowest un-adsorbed cyanide concentration (15.28±0.83 mg/dL) was seen in the combination of plantain peels + castor oil seed shells + coconut shells.

Conclusion: Adsorbents prepared from some plant materials showed better in vitro adsorptive capacity for cyanide than the standard (commercially and clinically available) activated charcoal. The combination of the materials also showed better adsorption for cyanide than the single agents. They therefore seem more efficacious and may also be cheaper than the commercial product.

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INTRODUCTION

Exposure to cyanide can take place by a variety of routes, including oral, dermal, and inhalation. Acute cyanide intoxication has resulted in many emergency hospital cases. Cyanide interferes with the process of energy production by the body and causes rapid respiratory depression, coma and eventual death if treatment is not instituted urgently (Niknahada *et al.*, 2008; Marziaz *et al.*, 2013; Singh *et al.*, 2015).

Oral exposure to cyanide in the environment can take place through the consumption of food bearing residual cyanide from insecticides, drinking water contaminated by industrial effluents and pesticides (Ghods and Baghshani, 2013; Zuccarello *et al.*, 2022; Adams *et al.*, 2024). Other potential sources of cyanide exposure include pharmaceutical preparations such as laetrile (a cancer medication which can be degraded to cyanide), sodium nitroprusside (a pharmaceutical agent used to treat hypertension and to control bleeding during surgery), and succinonitrile (an antidepressant) (Eyer *et al.*, 2007). Activated charcoal adsorbs many noxious substances such as drugs, phytotoxins and poisonous chemicals onto its surface, preventing their absorption from the gastrointestinal tract. As a secondary decontamination mechanism, it interrupts potential entero-hepatic and/or entero-enteric circulation (Eyer *et al.*, 2007; Pfab *et al.*, 2016; Zellner *et al.*, 2019).

Carbon-based compounds used in the manufacturing of activated charcoal for various purposes include coconut shells, rice husks, plantain peels, peat, banana peels and fluted pumpkin (Olson, 2010; Prauchner *et al.*, 2012; Ezeokunkwo *et al.*, 2018; Zhang *et al.*, 2020; Alcaniz-Monge *et al.*, 2022). Some peculiar qualities enhance the capacity of activated carbons. These include pore structure, functional groups, ash content, carbon yield, bulk density, methylene blue number and iodine number (Neuvonen and Olkkola, 1984; Alaspaa *et al.*, 2000). The physical and chemical characteristics of the adsorbate which include functional groups, polarity, molecular size and molecular weight also affect their adsorptive capacity (Neuvonen and Olkkola, 1984; Alaspaa *et al.*, 2000; McGoodwin and Schaeffer 2000; Cooper *et al.*, 2005). There is need to explore alternative local and cheap sources of adsorbents for possible clinical use because the commercially available activated charcoal is relatively expensive and not readily available. This study investigated the adsorptive capacities of different agro-based materials, on the *in vitro* disposition of cyanide.

MATERIALS AND METHODS

Preparation of Adsorbent Materials and Chemical Activation

The carbon materials (rice husks, coconut shells, castor oil seed shells and plantain peels) were collected from a local market in Enugu State, Nigeria. They were washed thoroughly with clean water and allowed to dry in the sun before grinding into fine powder with an electric blender. The materials were then dried in an oven at 110°C for 24 h and were each divided into three portions and stored in separate beakers. The chemical agents used for activation were zinc chloride, phosphoric acid and nitric acid. A solution of 100 mL of 10% w/v of zinc chloride was mixed with 50 g of powdered carbon sample, 500 mL of 0.5 mol/L of phosphoric acid was mixed with 50 g of powdered carbon sample and 500 mL of 0.5 mol/L nitric acid was mixed with 50 g of the carbon sample. The procedure described by Ekpote *et al.* (2017) was adopted with minor modifications. The different mixtures were left to stand for 24 h with regular stirring to allow for the chemical activating agents to penetrate the carbon materials thoroughly. Afterwards, the samples were carbonized in a muffle furnace for one hour at a temperature of 800°C. The samples were thereafter, soaked in 0.5 N HCl for one hour and then washed thoroughly in distilled water until neutral. Materials were finally dried in an oven at temperature of 110°C for 24 h and kept in air-tight containers.

Determination of the Adsorptive Capacities of the Various Materials

Specific known concentrations of 0.5 g/dL, 1.0 g/dL, 1.5 g/dL and 2 g/dL of each activated samples were used (Reffas *et al.*, 2010; Ekpote *et al.*, 2017). Each concentration of the activated carbon was introduced into a litre of pyrex beaker containing 200 mL aqueous solution of 1 mol. of KCN. Phosphoric acid (10 mL) was added to 100 mL of aqueous sample solution and left for 12 h. The samples were filtered with Whatman's filter paper #1, and 1 mL was pipetted into a spectrophotometer cuvette followed by the addition of 0.5 mL of ninhydrin solution.

To increase the sensitivity of the reaction, potassium hydroxide (KOH) solution was added and the deep-red or deep-blue colour obtained was measured at 485 nm and 590 nm respectively. A reagent blank with no cyanide was used for the experiment. The UV-Vis spectra were recorded from 200 nm to 700 nm. The recorded absorbance value for the un-adsorbed cyanide was converted to cyanide concentration (g/mL) using a standard cyanide concentration curve.

To compare the adsorbing capacity of each of the adsorbents with that of activated charcoal on the *in vitro* disposition of cyanide poison, the cyanide-containing aqueous samples were treated with equal concentrations of each adsorbent and activated charcoal. Four (4) concentrations ranging from 0.5 g/dL to 2.0 g/dL were used for each prepared adsorbent sample (Reffas *et al.*, 2010). The same concentrations of activated carbon was used. Each concentration was introduced into a 1 L of pyrex beaker containing 250 mL aqueous solution of 1 mol. of KCN.

The mixtures were stirred for 30 min at 0, 50, 100 and 300 rpm, using a mechanical stirrer, at room temperature. At the end of stirring, the mixtures were allowed to settle for a few minutes and 200 mL of the supernatant was collected and filtered with a Whatman's filter paper for KCN analysis using the ninhydrin method. The cyanide-ninhydrin adducts obtained were subjected to UV-spectrophotometry to read the absorbance (Reffas *et al.*, 2010).

Statistical Analysis

The results are presented as mean $\pm$ SD (standard deviation) of four replicates. Analysis was done using one-way

analysis of variance (ANOVA) followed by Bonferroni post hoc test (SPSS software version 24). P-values less than 0.05 were considered to be statistically significant.

RESULTS

Effect of Zinc Chloride-activated Samples on Cyanide Adsorption

Table 1 shows the effect of changes in concentrations (g/dL) of zinc chloride-activated materials on the *in vitro* cyanide adsorption compared with the standard activated charcoal. Generally, there were significant differences ($P < 0.0001$) in the adsorptive capacities of each carbon sample for cyanide with increased amount of the sample. The lowest un-adsorbed cyanide concentrations were at the sample concentration of 2.0 g/dL.

Plantain peels showed the least concentration of un-adsorbed cyanide (20.03 ± 0.48 mg/dL), followed by coconut shell (24.34 ± 0.43 mg/dL), next was castor oil seed shell (26.48 ± 0.36 mg/dL). These values were all significantly ($P < 0.0001$) lower than the value obtained for standard activated charcoal (36.87 ± 0.02 mg/dL).

Table 1: Effect of changes in amount of zinc chloride-activated charcoal samples on *in vitro* cyanide adsorption.

Sample	Un-adsorbed cyanide (mg/dL)			
	0.5 g/dL	1.0 g/dL	1.5 g/dL	2.0 g/dL
Standard	50.11 ± 0.002	45.25 ± 0.02	40.33 ± 0.01	36.87 ± 0.02
Rice Husk	$56.20 \pm 0.22^{***}$	$50.90 \pm 0.22^{***}$	$40.42 \pm 0.33^{***}$	38.46 ± 0.11
Plantain Peels	$46.91 \pm 0.25^{***}$	$38.75 \pm 0.14^{***}$	$28.96 \pm 0.40^{***}$	$20.03 \pm 0.48^{***}$
Castor oil seed shell	$47.01 \pm 0.14^{***}$	$41.31 \pm 0.20^{***}$	$33.65 \pm 0.27^{***}$	$26.48 \pm 0.36^{***}$
Coconut shell	$46.04 \pm 0.81^{***}$	$40.49 \pm 0.37^{***}$	$30.05 \pm 0.78^{***}$	$24.34 \pm 0.43^{***}$

$^{**}P < 0.0001$ compared with same weight of standard activated charcoal. n-value = 4

Effect of Nitric Acid-activated Samples on Cyanide Adsorption

Table 2 shows the effect of different concentrations of nitric acid (HNO_3) activated carbon samples on *in vitro* cyanide adsorption compared with standard activated charcoal. The cyanide adsorptive capacities for the different samples increased significantly ($P < 0.0001$) with increasing concentrations of the samples. The lowest un-adsorbed

cyanide concentrations was at the sample concentration of 2 g/dL.

The lowest concentration of un-adsorbed cyanide at 2 g/dL was by castor oil seed shell (18.99 ± 0.22 mg/dL), followed by coconut shell (21.63 ± 1.19 mg/dL), next was plantain peels (32.72 ± 0.17 mg/dL). These values were all significantly ($P < 0.0001$) lower than the value obtained for standard activated charcoal (36.87 ± 0.02 mg/dL).

Table 2: Effect of changes in amount of nitric acid-activated charcoal samples on the *in vitro* cyanide adsorption.

Sample	Un-adsorbed Cyanide (mg/dL)			
	0.5 g/dL	1.0 g/dL	1.5 g/dL	2.0 g/dL
Standard	50.11 ± 0.002	45.25 ± 0.02	40.33 ± 0.01	36.87 ± 0.02
Rice Husk	$58.15 \pm 0.14^{***}$	$52.34 \pm 0.34^{***}$	$40.56 \pm 0.36^{***}$	$38.50 \pm 0.05^{***}$
Plantain Peels	$50.57 \pm 0.08^{***}$	$44.66 \pm 0.66^{***}$	$36.55 \pm 0.09^{***}$	$32.72 \pm 0.17^{***}$
Castor oil seed shell	$42.16 \pm 0.84^{***}$	$30.45 \pm 0.01^{***}$	$22.84 \pm 0.02^{***}$	$18.99 \pm 0.22^{***}$
Coconut shell	$45.50 \pm 0.38^{***}$	$34.16 \pm 0.17^{***}$	$28.59 \pm 0.41^{***}$	$21.63 \pm 1.19^{***}$

$^{***}P < 0.0001$ compared with same weight of standard activated charcoal. n-value = 4.

Effect of Phosphoric Acid-activated Samples on Cyanide Adsorption

The effect of changes in the concentrations of phosphoric acid (H_3PO_4) activated carbon samples on *in vitro* cyanide adsorption compared with standard activated charcoal is shown in Table 3. There were significant ($P<0.0001$) increases in the cyanide adsorptive capacities of the carbon samples as the concentrations of the samples increased. The lowest un-adsorbed cyanide concentrations were shown at the sample concentration of 2.0 g/dL.

The lowest concentration of un-adsorbed cyanide at 2.0 g/dL of sample was seen in coconut shell (18.92 ± 0.58 mg/dL) followed by castor oil seed shell (24.47 ± 0.35 mg/dL), next was plantain peels (26.34 ± 0.15 mg/dL). These values were all significantly ($P<0.0001$) lower than 36.87 ± 0.02 mg/dL shown by the standard activated charcoal. The highest un-adsorbed cyanide concentration (41.66 ± 0.24 mg/dL) was seen in rice husks.

Effect of Combination of Activated Samples on Cyanide Adsorption

Table 4 shows the effect of different concentrations of various combinations of the different activated samples on

the *in vitro* adsorption of cyanide. There were significant increases in the cyanide adsorption by the activated samples as the concentrations of the samples increased ($P<0.0001$ for AB, $P=0.003$ for AC, $P<0.003$ for BC, $P<0.0001$ for ABC). The lowest un-adsorbed cyanide concentrations were shown at the sample concentration of 2.0 g/dL.

At the sample concentration of 2.0 g/dL, the lowest un-adsorbed cyanide concentration (15.28 ± 0.83 mg/dL) was seen in the combination of plantain peels + castor oil seed shells + coconut shells (ABC), followed by the castor oil seed shells + coconut shells combination (BC) (20.55 ± 1.09 mg/dL), and next was the plantain peels + coconut shell combination (AC) (22.64 ± 0.63 mg/dL). These un-adsorbed cyanide values were significantly lower than the value for the standard activated charcoal (36.87 ± 0.02 mg/dL): $P<0.01$ for AB and AC, $P<0.05$ for BC, $P<0.001$ for ABC. The highest un-adsorbed cyanide concentration (23.25 ± 0.40 mg/dL) was seen in the plantain peels + castor oil seed shells combination (AB).

Table 3: Effect of changes in amount of phosphoric acid-activated samples on *in vitro* cyanide adsorption.

Sample	Un-adsorbed Cyanide (mg/dL)			
	0.5 g/dL	1.0 g/dL	1.5 g/dL	2.0 g/dL
Standard	50.11 ± 0.003	45.25 ± 0.02	40.33 ± 0.01	36.87 ± 0.02
Rice Husk	$53.61\pm0.28^{***}$	$50.62\pm0.22^{***}$	$44.35\pm0.30^{***}$	$41.66\pm0.24^{***}$
Plantain Peels	$50.13\pm0.22^{***}$	$43.74\pm0.17^{***}$	$36.74\pm0.54^{***}$	$26.34\pm0.15^{***}$
Castor oil seed shell	$47.54\pm0.18^{***}$	$42.36\pm0.65^{***}$	$34.11\pm0.47^{***}$	$24.47\pm0.35^{***}$
Coconut shell	$40.36\pm0.42^{***}$	$32.80\pm0.02^{***}$	$24.73\pm0.78^{***}$	$18.92\pm0.58^{***}$

*** $P<0.0001$ compared with same weight standard activated charcoal. n-value = 4.

Table 4: Effect of various weights of the combinations of the different samples on the *in vitro* cyanide adsorption.

Sample combinations	Un-adsorbed Cyanide (mg/dL)			
	0.5 g/dL	1.0 g/dL	1.5 g/dL	2.0 g/dL
Std.	51.11 ± 0.002	45.25 ± 0.02	40.33 ± 0.01	36.87 ± 0.02
AB	48.36 ± 0.00	$32.14\pm0.00^*$	$28.32\pm0.04^{***}$	$23.25\pm0.40^{**}$
AC	46.98 ± 0.27	$34.64\pm0.11^*$	$26.61\pm1.14^{**}$	$22.64\pm0.63^{**}$
BC	40.32 ± 1.29	34.66 ± 0.09	$24.14\pm1.39^*$	$20.55\pm1.09^*$
ABC	38.36 ± 0.00	$30.14\pm0.00^{***}$	$20.29\pm0.05^{***}$	$15.28\pm0.83^{***}$

A = Plantain peels, B = Castor oil seed shells. C = Coconut shells, ABC = Combination of the three preparations. * $P<0.05$, ** $P<0.01$, *** $P<0.0001$. n-value = 4.

DISCUSSION

Over all, coconut shells, castor oil seed shells and plantain peels showed the best adsorptive capacities among the various adsorbents, and their adsorptive capacity increased with the increasing amount of the adsorbents. High cyanide absorbance reading in the filtrate showed that the activated charcoal adsorbed only a little of the cyanide. On the other hand, low absorbance reading indicated that the filtrate had low cyanide concentration, thereby demonstrating a high cyanide adsorption capacity.

The concentration-dependent increase in the adsorption capacity of the prepared activated charcoal samples in this study is probably due to the increase in their surface area. This finding is similar to the results of Ekpete *et al.* (2011) in which different amounts of activated charcoal were used to evaluate adsorption capacities of various activated charcoal samples.

This study also showed that activated charcoal prepared from local sources had better adsorptive capacities than the standard commercial activated charcoal. Some previous studies made similar findings (Odebunmi and Okeola, 2001; Liou *et al.*, 2010; Dada *et al.*, 2012;). However, a study by Ekpete *et al.* (Ekpete *et al.*, 2011) found that activated charcoal from fluted pumpkin had a similar adsorptive capacity with standard commercial activated charcoal.

We also looked at the effect of different concentrations of the various combinations of the different prepared activated charcoal samples on the *in vitro* adsorption of cyanide. There were significant increases in the cyanide adsorption by the activated materials as the amount of the samples increased. The *in vitro* cyanide adsorption by these combinations were better than that of single standard activated charcoal. The adsorbent capacities of the combination of the different activated charcoal samples were therefore additive in their actions and can be exploited in treatment of cases of drug intoxication and poisoning. This finding is in agreement with the findings in a previous study in which combinations of activated charcoal from different sources were used to assess adsorption capacities (Maharani *et al.*, 2019), and another study (Saputro *et al.*, 2019) in which the combination of activated charcoal from coconut shell and corn cob showed a better adsorption for lead than the individual activated charcoal from each source.

CONCLUSION

In this study, adsorbents from various sources had a better *in vitro* adsorptive capacity for cyanide than the standard (commercially and clinically available) activated charcoal. The combination of the activated charcoal samples in this

study also showed better adsorption of cyanide than the single agents.

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AUTHORS' CONTRIBUTION

CCO and GCA conceptualized and designed the study. KIN, KAN and ESN helped in data collection and analysis. CCO, JII, DHN and GCA drafted the manuscript. All the authors read and approved the final manuscript for publication.

CONFLICT OF INTEREST

The authors hereby declare no conflict of interest in this study

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AUTHORS' DECLARATION

The authors declare that this work is original and that any liability for claims relating to the content of this article will be borne by them.

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