Open Journal of Applied Sciences, 2024, 14, 2133-2143
https://www.scirp.org/journal/ojapps
ISSN Online: 2165-3925
ISSN Print: 2165-3917

Chemical Analysis of Activated Carbon from Bull and Cow Horns Pyrolysis to Be Used as Antidotes

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How to cite this paper: Mwabi, A.N., Yassa, P.Y. and Ntakarutimana, V. (2024) Chemical Analysis of Activated Carbon from Bull and Cow Horns Pyrolysis to Be Used as Antidotes. *Open Journal of Applied Sciences*, **14**, 2133-2143.
https://doi.org/10.4236/ojapps.2024.148141

Received: December 11, 2023
Accepted: August 12, 2024
Published: August 15, 2024

Abstract

The purpose of this study is to compare the results of chemical analysis of two types of activated from the pyrolysis of bull horn and that of cow. Six samples were used to measure pH, carbon, calcium and to determine adsorbent power. The pH was measured at a temperature of 20˚C using an "ANION 7010 ionomer" pH meter, the carbon (C) content was analyzed using a "EURO EA 3000" analyzer. and the electronic balance: "Sartorius CP-2P", calcium (Ca) was analyzed using a DFS-8 spectrograph. For the adsorbency test, the 0.15% methylene blue R solution was used. At the end of this study, we found that the activated carbon from the bull horn demonstrated a carbon content that is higher than that of the cow horn (20.79% against 15.63%), activated carbon of cow horn is richer in calcium than that of bull horn (16.27% against 3.69%) and then the pH. The cow horn is higher than that of the bull horn (7.43 versus 6.5). For the adsorbent power, the sample (75% bull horn and 25% cow horn) was recorded with the greatest adsorbent power. Thus, from this study, it can be recommended as an activated carbon antidote to be used for poisonings treatment.

Keywords

Activated Carbon, Bull Horn, Cow Horn, Oil Palm Nut Shells, Absorbent Power

1. Introduction

Poisoning is one of the biggest causes of human death worldwide and can result from industrial activities, incessant bushfires, drug overdose, accidental poisoning or snake envenomation. In fact, 1100 to 1200 poisonings per 100,000 people per year are reported in the Montreal region [1] [2]. In addition, according to the report of the World Health Organization, more than 500,000 cases of acute poisoning due to pesticides each year [3].

Moreover, it has been demonstrated that in the Eastern of the Democratic Republic of Congo (DRC) in general and in the city of Bukavu, South Kivu province in particular, that modern medicine is often limited in the treatment of poisonings compared to traditional medicine, formerly known "alternative medicine" because for some cases of poisonings treatment, medicinal plants are better than modern medications [4].

To treat poisonings, traditional healers use substances called "antidotes" that neutralize toxins' action. Depending on their nature, antidotes can be mechanical (by counteracting the action of the poison) or chemical (by changing the chemical nature of the poison) or physiological (by developing opposite effects to that of poison) [5].

Activated carbon is the most preferred antidote that is used in the poisonings removal process and it is made from vegetable materials [4] [5]. The gap here is that former researches don't show the limitations of these materials in terms of adsorbent power. In most publications, it is considered like a universal antidote whereas it is not remmended for heavy metals removal [6]. The performance of antidotes depends on the nature of the adsorbent in one hand and the chemical composition of the adsorbed material. In fact, formers researches don't demonstrate the importance of these two aspects.

Normally, each poison has its own antidote in the city of Bukavu, most traditherapeutics use phytoantidotes, consisting essentially of aqueous extracts of medicinal plants that are prescribed to poisoned patients at a dose of approximately 5 liters each week. The effects are often vomiting and diarrhea, which demonstrate that poison is eliminated [7]. This action is not sustainable because after losing much water in the body, poisoned patients die from dehydration. In addition to that, the consumption of these aqueous solutions of medicinal plant extracts increases the risk of getting liver cirrhosis that can lead to death of persons.

Phytoantidotes are exposed to fermentation which could modify the therapeutic properties of the antidote if patients do not have a refrigerator to properly preserve the liquid solution [8]. Some traditherapeutics working in the city of Bukavu, being aware of this situation, have tried to make other types of antidotes that are easy to store. For this purpose, many of these traditional healers use activated carbon from bull horn that is non-fermentable and therefore easy to store before or after its administration to poisoned people. This charcoal is mixed with other ingredients such as black pepper and Mwenga salt (local term given to potash crystals produced from aquatic plants including papyrus) that poisoned people lick for recovering.

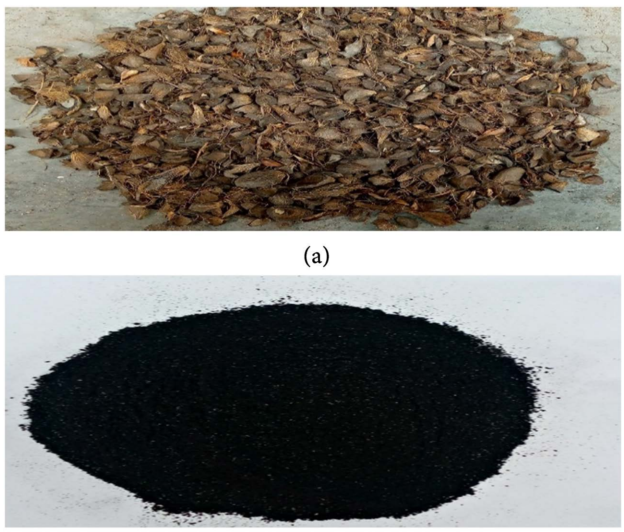
People usually ask themselves why therapeutics utilize only bull horn as the main raw material in antidote making and not cow horn? Between these two resources which one contains high content of carbon and calcium? Which one among them has a high pH value? In terms of adsorbent power, between the activated carbon from bull horn and that of cow horn, which one decolorizes better the 0.15% methylene blue R solution? The aim of this study is to analyze a certain number of chemical parameters, to test the adsorbent power of bull and cow activated carbon, and to make comparison of results before concluding which one is so relevant in antidote making to fight against poisonings.

2. Materials and Methods

This paragraph concerns oil palm nuts which were obtained from oil palm tree from sange after oil palm extraction using local extraction method. Oil palm nuts shells were taken from oil palm factory after separation of liquid and solid materials. The sample size was 3.5 cm of diameter and 4.5 cm of length. Concerning bull and cow horns resources, they were collected from the abattoir of Bukavu town after slaughtering process with a mean size of 12 cm of dameter and 25 cm of length. It has been proved that the blue methylene adsorption method has proved to be a fast and reliable method to indicate the presence of swelling clay minerals in agroindustrial solid wastes [9]. This test consists of mixing coal samples from these wastes and blue methylene solution which changes the color after mixing that indicates the adsorbent power of charcoal tested.

2.1. Biomaterials

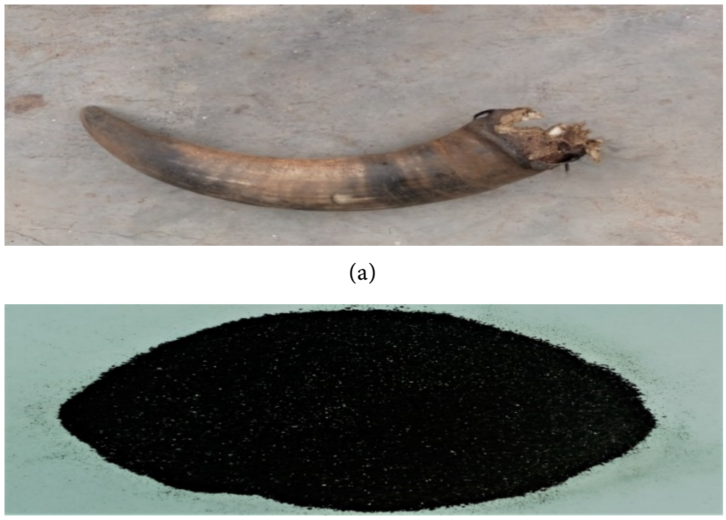
Figures 1-3 below show the picture of each biomaterial and its charcoal.



(a)

(b)

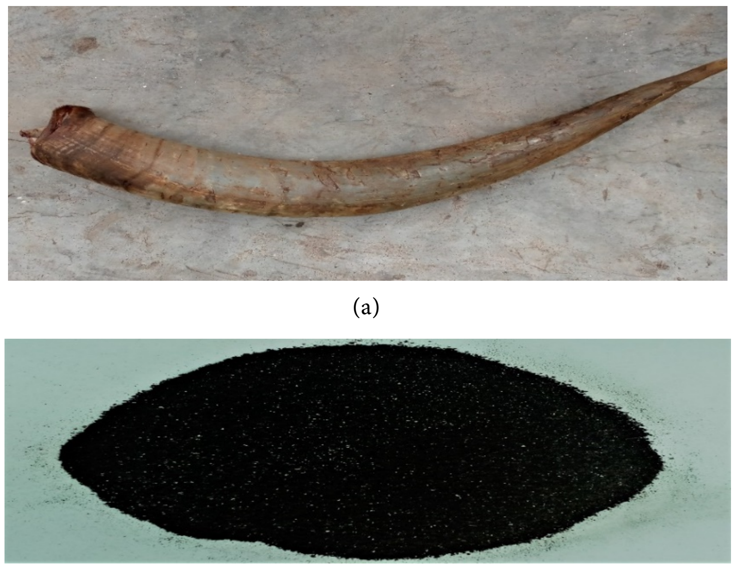
Figure 1. Photos of samples of oil palm nut shells (size n: 3.5 cm - 4.5 cm) and the activated carbon prepared by the treatment of this biomaterial (b).



(a)

(b)

Figure 2. Photos of samples of bull horns ((a) ø 12 cm - L: 25 cm) and activated carbon prepared by the treatment of animal resource (b).



(a)

(b)

Figure 3. Photos of samples of cow horn ((a) spécimen: ø 10 cm & L: 46 cm) and activated carbon prepared by the treatment of this biomass (b).

2.2. Laboratory Materials and Reagents

2.2.1. Materials

To carry out chemical activation of each type of horn and adsorbent power test of activated carbon for each biomaterial, following materials and reagents were used.

- WTZ binder brand oven;
- 100 ml plastic bottle;
- Ten 250 ml Erlenmeyer flasks;
- 500 ml beaker;

- Shimadzu brand electronic scale model AWW 220D;
- Desiccator;
- Filter paper;
- A thermolysis type 1400 Fumace oven;
- A porcelain mortar and pestle;
- A roll of paraffin.

2.2.2. Reagents

- Phosphoric acid (55% H_3PO_4);
- Hydrochloric acid (HCl 0.1 M);
- Methylene blue R at 0.15%;
- Distilled water.

3. Methods

3.1. Preparation of Activated Carbon Samples

Bull and cow horns as well as oil palm nut shells were washed using tap water then rinsed three times with distilled water and then dried in an oven under the temperature of 105˚C for 24 hours. After that. they pass into a desiccator to cool for at least 4 hours [10].

3.1.1. Chemical Activation of Local Resources to Be Carbonized

We haved prepared 200 ml of 80% aqueous solution of phosphoric acid. Contained in a 250 ml erlenmeyer flask then placed in an oven at a temperature of 1200˚C for 11 h. We removed the particles impregnated with the oven then we put them in beakers then we closed hermetically then keep for 24 hours. We preheated the oven to a temperature of 250˚C for 5 hours before starting the carbonization in order to obtain an equilibrium state temperature. After that, we introduced the impregnated horn samples into the Fumace type 1400 thermolysis oven for their pyrolysis at a temperature of 400˚C for 4 h. The carbons obtained had become active and then we cooled them to room temperature in a desiccator [11]. To eliminate possible carbonization residues, the activated carbons were washed in 250 ml of a 0.1 M hydrochloric acid solution, rinsed it several times with distilled water until a constant pH. Obtained carbons were washed, rinsed and dried in an oven at 105˚C for 8 hours then cooled in a desiccator and stored away from air in bottles then we closed them hermetically until the characterization tests [11].

3.1.2. Transformation of Activated Carbon Grains into Powder

To carry out this process, we grounded separately each type of activated carbon grains in a mortar with a porcelain pestle then sifted using a sieve with a mesh size of 0.1 mm. The powder that we obtained for each material was kept in a 500 ml beaker then covered with parafilm [12].

3.1.3. Methods for Chemical Analysis of Samples and pH Measurement

The carbon content was analyzed using a "EURO EA 3000" analyzer and the electronic balance: "Sartorius CP-2P", calcium (Ca) was analyzed using a DFS-8 spectrograph. The pH was determined by suspending a mass of 5.0 g of sample in 95 ml of distilled water, stirring vigorously for 3 min then sedimenting for 10 min and filtrate. After that, the pH was measured at a temperature of 20˚C with an "ANION 7010 ionomer" pH meter [13].

3.1.4. Test of Adsorbent Power of Prepared Activated Carbons

In a 50 ml erlenmeyer flask, we placed 0.20 g of adsorbent carbon of each type, recently dried at 110˚C in an oven. After that, we added 35 ml of 0.15% methylene blue R solution and closed with a ground cap then shook vigorously for 5 minutes before filtering. The test is compliant if the filtrate is less colored than the 0.05% methylene blue R control solution. After 4 tests, we classified the adsorbent powers from the most adsorbent to the least adsorbent. The charcoal produced from the carbonization of oil palm nut shells has constituted the control during this comparison because it has a great adsorbent power compared to the others [14]. Materials related to isothem adsorption are required for further research to confirmed our results.

4. Results

The results of chemical analyzes as well as those of the comparison of the adsorbent power test are given below:

4.1. Results of Chemical Analyzes of Certain Parameters in the Selected Samples (Table 1)

Table 1. Results of total carbon and calcium content and pH for each analyzed sample.

N˚	Sample	(%) C	(%) Ca^{2+}	pH
Control	C.N.P	27.47	0.093	8.67
1	C.D.T	20.72	3.69	6.5
2	C.D.V	15.63	16.27	7.43
3	T_1	16.80	20.13	8.57
4	T_2	18.12	19.15	8.01
5	T_3	17.03	22.79	8.72

(Laboratory of "International Institute of Tropical Agriculture" (IITA), Bukavu, Kalambo, February 2022). **Note: CNP**: oil palm nut shells, **CDT**: bull horn, **CDV**: Cow horn, $\mathbf{T_1}$: 50% bull horn and 50% cow horn, $\mathbf{T_2}$: 75% bull horn and 25% cow horn, $\mathbf{T_3}$: 75% cow horn and 25% bull horn.

4.2. Results of the Test of the Adsorbent Power of Activated Carbons

Figure 4 below shows the results of the qualitative test of the adsorbent power of each sample of activated carbon.

According to different colors of this figure, we realize that the activated carbon T_2 demonstrated higher adsorbent power compared to others because of its performance in the decolonization of the 0.15% methylene blue R solution (picture 2) in the same manner like the oil palm nut activated carbon used as control. The high value of carbon content of bull horn activated charcoal contained in T_2 activated carbon (20.72 %) compared to that of cow horn activated charcoal contained in T_3 (15.63%) should be the root cause of this behavior of T_2 compared to T_2. This sub section is more discussed in the sub section 5.3 of section 5 of this paper.

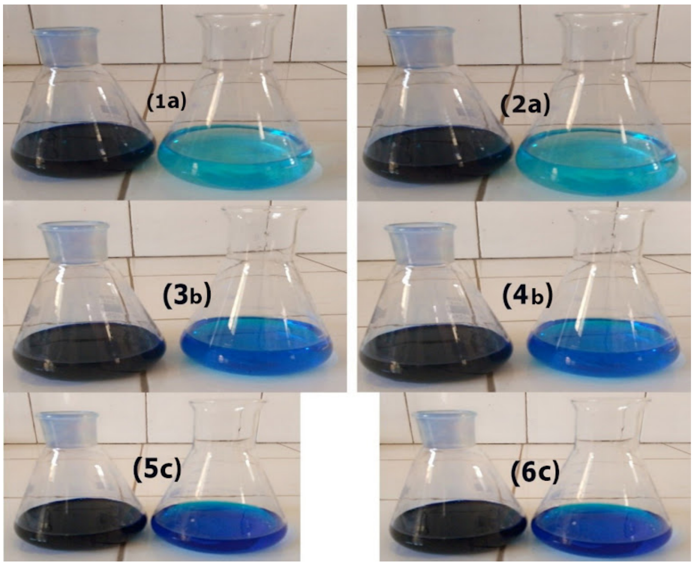


Figure 4. Results of the comparison between the color of the 0.15% methylene blue R solution, on the left in each photo, control solution with the color obtained after filtration of the mixture of 0.2 g of each carbonisate with 35 ml of the control solution previously shaken vigorously for five minutes in the right side on each photo. Legend: (1a) Result of the decolorization of the methylene blue solution by the activated carbon of the oil palm nut; (2a) Result of decolorization of the methylene blue solution by charcoal active from sample T_2; (3b): Result of the decolorization of the methylene blue solution by the activated carbon of sample T_3; (4b) Result of the discoloration of the methylene blue solution by the activated carbon of the bull's horn sample; (5c) Result of the decolorization of the methylene blue solution by the activated carbon of sample T_1; (6c) Result of the discoloration of the methylene blue solution by the activated carbon of the cow's horn sample.

5. Discussion

5.1. Discussion of the Results on the Carbon and Calcium Content

Results from Table 1 show that for carbon and calcium content mixed samples *i.e.* T_1, T_2 and T_3 have recorded higher values compared to those of simple biomasses. Furthermore, when we consider only the results obtained for carbon and calcium content for bull horn charcoal sample and that obtained from cow horn, the answer to the first question is that results analysis demonstrated that bull horn is richer in carbon than cow horn (20.72% & 15.72%). Concerning calcium content, we found contrary results; cow horn recorded a high content compared to bull horn (16.27% & 3.69%). The high carbon content recorded for bull horn would justify its use by traditional practitioners instead of cow horn during antidotes making process. We can just confirm this result by using for example a cyanide ion adsorption test in comparison with sodium thiosulfate known as its antagonist [13]. Furthermore, if we consider the decreasing order of carbon content of the charcoal obtained from each sample tested, the results in Table 1 show the following decreasing order: CDT > T_2 > T_3 > T_1 > CDV. If we closely analyze the decreasing order of carbon content recorded for samples T_1, T_2 and T_3, it is such that T_2: 18.02% > T_3: 17.03% > T_1: 16.80%. The useful order taken T_2 sample during this classification can be explained by its proportion of 75% bull horn compared to 25% cow horn. The low proportion of carbon in sample T_3 compared to T_2 could be explained by the 75% in cow horn with 15.72% in C, compared to 25% in bull horn with 20.72% in C. The last rank occupied by sample T_1 could be justified by the fact that during the mixing, the quantity of charcoal from the bull horn alone and that of cow' horn alone was reduced to half; situation that would affect the carbon content of the mixture. The high carbon content in bull horn (C: 20.72%) compared to that of cow horn (C: 15.72%) explains why traditional practitioners use bull horn and not cow horn. during antidotes making. The results on the calcium content show the following decreasing order: T_3: 22.79% > T_1: 20.13% > T_2: 19.15% > CDV: 16.27% > CDT: 3.29%. This order is reasonable because calcium content in cow horn: 16.27% is approximately 5.5 times more than 3.29 % found in bull horn. It is therefore normal that T_3 sample comes to the first position in terms of calcium content because the proportion of 75% cow horn compared to 25% of bull horn used during this mixture could influence this result. The calcium content of 20.13% for T_1 sample compared to 19.15% for T_2 sample could be explained by the proportion of 50% of cow horn used by making T_1 sample. The high calcium content in cow horn compared to that in bull horn could be explained by the mineral composition of the cow ration which is more favorable to this element compared to that of the bull because similar results on the zinc were recorded during a study carried out in Canada on the presence of certain heavy metals in the ration of cattle where cow horns were richer in zinc compared to those in bull horns [15].

5.2. Discussion of the Results on the pH Value of Each Sample Analyzed

Concerning the answer to the second question relating to the measurements of pH in each sample, the pH value for cow horn is higher than that found for bull horn (7.43 versus 6.5). This situation is normal, especially since the high calcium content obtained after analysis of the activated carbon sample from cow horn (16.27%) shall increase the pH value compared to that of calcium obtained in the bull horn sample (3.69%). Taking into consideration the pH results of all samples, the decreasing order is similar to that recorded for calcium content as follows: T_2: pH: 8.72 > T_1: pH: 8.57 > T_3: pH: 8 .01 > CDV: pH: 7.43 > CDT: pH: 6.5. From these results, we realize that pH value of the mixed samples is higher than that of the unmixed samples. In fact, literature review indicates that elimination of acidic biological toxins such as salicylates and phenobarbital could be done, either by the hemoperfusion technique, or by increasing urinary alkalinity. using intravenous sodium bicarbonate therapy (pH > 7.5) [15] [16]. From this reason, the fact that for each activated carbon made from cow or bull horn alone, pH value is less than 7.5 (CDV: pH: 7.43 and for CDT: pH: 6.5), these kinds of antidotes are not favorable for biological toxins removal. However, for mixture antidotes *i.e.* T_1, T_2 and T_3, all pH recorded results were greater than 7.5: T_3: pH: 8.72, T_1: pH: 8.57 and T_2: pH: 8.01. These results are favorables for T_1, T_2 and T_3 antidotes to act better in biological acid toxins elimination. According to the aforementioned authors, this elimination is facilitated by the increase in the ionization of the toxin which consequently limits its tubular resorption.

5.3. Discussion of the Results on the Adsorbent Power Test

Considering the question of which one between bull horn activated carbon and cow horn activated carbon discolors better the methylene blue solution R 0.15%, we found that the sample: T_2 (75% CDT - 25% CDV) demonstrated a great adsorbent power compared to the other samples tested by decolorizing this solution in the same way as the oil palm nuts shells activated carbon. The carbon content of 20.72% obtained in the bull horn sample in one hand and the 75% of the activated carbon from this horn used during the preparation of T_2 sample would influence this result because in terms of adsorption, the richer a material is in carbon, the wider its surface area will be after activation; that will positively influence its adsorbent power and also the high pH value of an adsorbent positively influences its adsorbent power [16] [17]. Similar results were found by Saoud & Rabâché, in 2018 who, after working respectively on a comparative study of the adsorption of Bromothymol Blue on granulated activated carbon and activated carbon from date stones and on a parametric study of the elimination of an emerging pollutant "Methyl Blue" by coupling of heterogeneous adsorption-photocatalysis processes, all concluded that the increase in the initial concentration of the adsorbent solution as well as that pH makes improves the adsorption process [18].

6. Conclusions

The objective of this study was the chemical characterization of activated carbons from two types of materials including bull horn and cow horn, then compare their performance in terms of decolorization power of the 0.15% methylene blue R solution as a forecast for their use in the manufacture of antidotes to treat cases of poisoning. According to the obtained results, we can conclude that:

- Activated carbon from bull horn was characterized by a high value in carbon content compared to activated carbon from cow horn;
- High calcium content, as well as high pH value, were obtained in the cow horn sample;
- From the all activated carbon samples tested, T_2, *i.e.* 75% CDT and 25% CDV, demonstrated great adsorbent power by decolorizing the 0.15% meth-

ylene blue R solution in the same way as the oil palm nut shells used as control;

- The mixture composed of 75% activated carbon from bull horn and 25% activated carbon from cow horn is the activated carbon antidote that can be recommended for poisonings treatment using activated carbon.

Recommendations

After this study, we recommend that when treating poisoning with activated carbon from cattle horns, the activated carbon from bull horn can be mixed with that of cow horn. Using only activated carbon from bull horn and neglect that from cow horn is not sustainable. This has the advantage of providing the mixture with a high calcium content as well as boosting the pH of the charcoal towards alkalinity values which are favorable for the treatment of acidic biological poisons (pH > 7.5). Since bulls most often do not have developed horns, it would be more advantageous to supplement their quantity by using activated carbon from cow horns which are easily found.

Acknowledgements

The authors thank the Bukavu town slaughterhouse steering committee and the staff of chemistry laboratory of Pharmakina factory to avail cow and bull horns and the 0.15% methylene blue R solution respectively.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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