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Activated Charcoal from Alternatives Wastes: Preparation and Application

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ABSTRACT
The main goal of this work was production of charcoal from wastes of dried coconut fiber, banana and orange peels, chemically activated with zinc chloride, aiming the correct usage of contributing to its correct disposal. The waste was collected, prepared and impregnated with $ZnCl_2$, chemically activated and had their efficacy tested using water from the Capibaribe River, in the city of Recife, state of Pernambuco, Brazil. The results obtained were an activated charcoal with a fix mass in all samples (coconut/banana = 25/75), (coconut/banana = 75/25), (coconut/orange = 75/25), presenting efficacy in the reduction of pH, EC values and water turbidity.

Keywords
Turbidity. Adsorption. Porosity. Chemical activation.

1. INTRODUCTION
In the recent years, it has been increasingly used for the preventation of environmental pollution and antipollution laws have increased the sales of activated carbon (AC) for control of air and water pollution. Brazil is the third largest world producer of fruits, standing behind only of India and China. Production of orange and banana accounts for nearly 60% the total amount of produced fruits in this country (Agrianual, 2014), with a harvest that exceeds 40mi tons in a year. Being products highly consumed by the internal market, especially due to the increase in average Brazilian net income, the country has also detached itself in increasing exportation (Brazilian year report on fruit cultive, 2013).

According to Fao (2013), banana is the world's largest cultivated fruit, being responsible in many countries for employing a large part of the local population. The fruit is rich in carbohydrates, vitamins and minerals, and is considered by many nutritionists an important part of the diet of all age groups. In Brazil, banana holds a strong acceptance and its production is destined almost entirely to the internal market.

The Northeastern region is the largest Brazilian producer of banana, particulary the states of Bahia, Ceará, Pernambuco and Rio Grande do Norte. In Pernambuco, the banana is cultivated in all the micro regions, occupying nearly 80 thousand permanent work vacations in its plantation fields (Almeida, 2011; Brazilian Institute of Geography and Statistics, 2011).

Orange is a largely cultivated in Brazil. Cultivated nationwide, the fruit has suffered mutations resulting in new varieties of it. The fruit is consumed in natura, in the form of ingredient for several dishes of the Brazilian cuisine or as juices. Besides being a savory fruit, the orange has several other properties, such as a tranquilizer and antidepressant. The essential oils found in orange peels are used in cosmetics, perfumes and cleaning products (Fiorentin et al., 2010; Fao, 2011; Franco Jr., 2012; Passos et al., 2013). According to Neves (2000), Brazil has become the largest world producer of orange since the decade of 1980.

Studies were carried out evaluating the potential of rock melon shell waste as alternative adsorbent for cadmium, nickel and copper ions in aqueous solution. The rock melon shells were dried, ground and separated based on the sizes through sieve shaker. Then, the rock melon shell powder was activated at temperature range of 400˚C - 650˚C. The results showed highest removal of Cd(II), Ni(II) and Cu(II) ions equilibrated within 120 min., at pH of 8 and adsorbent dosage was 0.3 g which was exceed 99% (Nurdin et al., 2015).

The Brazilian production of citrus is concentrated in the Southeastern and Northeastern regions of the country. According to Almeida (2011) the production of citrus has an important role in specific areas of the Northeastern region, particularly those of the states of Alagoas, Ceará and Pernambuco.

The activated carbon (AC) is a well known adsorbent that can be used efficiently for removal of a broad spectrum of pollutants from air, soil and liquids. The adsorbents are usually porous solids, and adsorption occurs mainly on the pore walls inside particles. Among them, AC is more efficient adsorbent for elimination of many pollutants (organic, inorganic, and biological) of concern in water and wastewater treatment (Mohammad-Khah, Ansari, 2009).

According to Alves (2015) and Calgon (2015), activated charcoal (AC) has the ability of selectively collect gases, liquids and impurities inside its pores, being such the reason of its large usage in the filtering systems. However, it is important to point out that the potential of activated charcoal is limited. A carbon filter can become ineffective once all its pores are filled. The compromised adherence surface impedes the impurities to be fixed to carbon.

In accordance to Kunz et al. (2002), the fundamental techniques of water treatment in processes of coagulation, followed by separation by flotation or sedimentation present high efficacy in the removal of particulate material in water. However, removal of color and organic components dissolved is ineffective with such techniques and the processes of adsorption with activated charcoal being more efficient than the former.

The processes of adsorption, which involves the transference of a solid mass in a fluid phase to the surface of a solid component, are being largely studied due to their high efficacy and for being economically viable in the treatment of textile effluents. The utilization of low cost material in the production of activated charcoal is an alternative pathway to food industry waste, which is usually disposed and end up losing its value (Juchen et al., 2013).

The challenge is to produce activated charcoal with all the characteristics of the ones already available in the marked that come from industrial processing, with high surface area, diversity of pores and aggregated value that could justify the research and the need of a better understanding and environmentally correct practice. In the present date the material that has the highest capacity of adsorption, being largely utilized to treat water effluents is the activated charcoal (Muller, 2008). However due to material loss during the recovery of the adsorbent its use becomes, in many circumstances, onerous. Being such, there is a rising interest in the search of alternate, low cost materials that can be employed in the production of activated charcoal (Gonçalves et al., 2007; Auta, Hameed, 2011).

Therefore, the goal of this research was to produce activated charcoal (AC) from coconut, banana and orange wastes in order to contribute to preservation of environment with the reduction of possible polluting agents.

2. DATA AND METHODOLOGY

The present work was performed in the Analytic Chemistry lab in the 8th floor, block D, of the Catholic University of Pernambuco, in the city of Recife, Pernambuco, Brazil. The dry coconut shells were collected in regular coconut sale points, disposing of the ones which were brown because their processing is harder. Orange and banana waste was collected in industrial units of juice processing.

After collecting and selecting, the waste (coconut, orange and banana) was submitted to sun exposure for a few days, the enough to dry them out, and milling at a knife mill was performed in Pernambuco's Agronomic Institute – IPA. The next step was sieving at 14 mesh to obtain particles of homogenous sizes. Right after that the doses (mixtures) of the wastes were used as proposed by Macedo (2012): coconut/banana (60-65 cal/g; 50-55 cal/g) = 25/75 and 75/25, coconut/orange (40-45 cal/g) = 75/25.

The samples (with five repetitions) were put into a porcelain melting pot and submitted to the carbonizing process in a muffle oven (model LF00613) at an inert atmosphere for 1 hour at 550ºC, in a heating rate of 15ºC.min^{-1} and a nitrogen flow rate of 100mL.min^{-1}. After carbonization was concluded samples were washed with a solution of hydrochloric acid at 50% until a pH close to 7 was obtained.

After the washing each 10g of the sample was added of 10g of zinc chloride to impregnation in a 1:1 rate ($ZnCl_2$: waste) and put in the stove at 100ºC for 24 hours (Ramos et al., 2009). In this process the reactions between the prime matter and the agent occur, modifying the material's structure. Waste washing, chemical activation and carbonization procedures were established based on Hayashi et al., (2010), Rocha et al., (2012), Gonçalves et al., (2007) and Deng et al., (2011), who produced charcoal from vegetable waste.

The material thus prepared was named banana-derived activated charcoal (BAC) and orange-derived activated charcoal (OAC).

1. Coconut (25) /Banana (75) – 5 samples (C25B75);
2. Coconut (75) /Banana (25) – 5 samples (C75B25);
3. Coconut (75) /Orange (25) – 5 samples (C75O25)

To assess the activated charcoal's efficacy a Jar Test was developed with five repetitions, using 300mg of activated charcoal water, which was collected from the Capibaribe River, in the city of Recife, Pernambuco, Brazil, with the following characteristics: pH = 7.14, turbidity = 10.64 UNT, electric conductivity – EC = 8032 mS.cm^{-2}. The mixture occurred in consecutive time intervals, T_1 and T_2. In T_1 the employed rotation was 150 rpm, during 15 seconds, and in T_2 the rotation was of 25 rpm during 15 minutes. After a 15 hours rest, 500mL of the supernatant water was withdrawn to chemical characterization. In order to compare the efficacy of the activated charcoal 3mL of aluminum sulfate per water liter was used (the one used in Water Treatment Stations – ETA's) in the same waste experimental conditions.

The characteristics analyzed were water pH, turbidity and electric conductivity using the ASTM D1293 – 12, ASTM D6698 – 14, ASTM D1125 – 14 methods, respectively. The obtained data of pH, turbidity and electric conductivity were submitted to statistical analysis generating Box Plot graphics using the Statistic software version 7.0 (Oligari, Pacheco, 2004)

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3. RESULTS AND DISCUSSION

Table 1 and Figures 1 to 3 present graphics obtained for pH, turbidity and electric conductivity – EC, respectively, to coconut/banana in the doses of 25/75 and 75/25 and of coconut/orange in the corresponding dose of 75/25, in comparison with the standard aluminum sulfate to the collected water sample from the Capibaribe River, in the city of Recife, Pernambuco, Brazil.

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Table 1 - Data obtained from water samples treated with activated charcoal (five samples) to determine its characterization.

Sample	pH	Turbidity (UNT)	EC (µS)
C25B75	A – 7.28	A – 0.78	A – 7370
	B – 7.26	B – 0.78	B – 7180
	C – 7.27	C – 0.78	C – 7190
	D – 7.30	D – 0.78	D – 7890
	E – 7.34	E – 0.78	E – 7110
C75B25	A – 6.93	A – 0.78	A – 7010
	B – 7.07	B – 0.47	B – 7879
	C – 7.91	C – 0.78	C – 7096
	D – 8.05	D – 0.94	D – 7932
	E – 7.21	E – 0.47	E – 7091
C75O25	A – 7.03	A – 0.17	A – 7059
	B – 7.19	B – 0.17	B – 7059
	C – 7.21	C – 0.17	C – 7042
	D – 7.12	D – 0.17	D – 7000
	E – 7.20	E – 0.17	E – 7099
$Al_2(SO_4)_3$	A –6.99	A - 0.63	A – 7310
	B –6.95	B - 0.63	B - 7310
	C – 7.09	C - 0.47	C - 7420
	D - 7.01	D - 0.47	D - 7390
	E - 6.96	E - 0.47	E – 7380
Crude H_2O	A – 7.17	A – 11.15	A – 8091
	B – 7.14	B – 11.01	B – 8101
	C – 7.10	C – 10.08	C – 7984
	D – 7.12	D – 10.74	D – 7995
	E – 7.16	E – 10.22	E – 7991

Through Figure 1 it can be observed that activated charcoal produced with the mixture 75C25O (treatment 5) presented the most acceptable average value among the treatments employed in the experiment. With such results it could even replace aluminum sulfate in water treatment stations. The values of pH close to neutrality fit the recommendation of the 375/2005 resolution by CONAMA (6.0 to 9.5). In the pH range between 6.5 and 7.5 it is important to point out the presence of functional groups in the surface of activated charcoal that might interact with the effluent elements causing a pH elevation according to Oliveira (2014). However, according to Ferreira Filho and Marchetto (2006) in case optimal turbidity removal is being sought, values of pH below 5.8 could interfere in the turbidity removal efficacy.

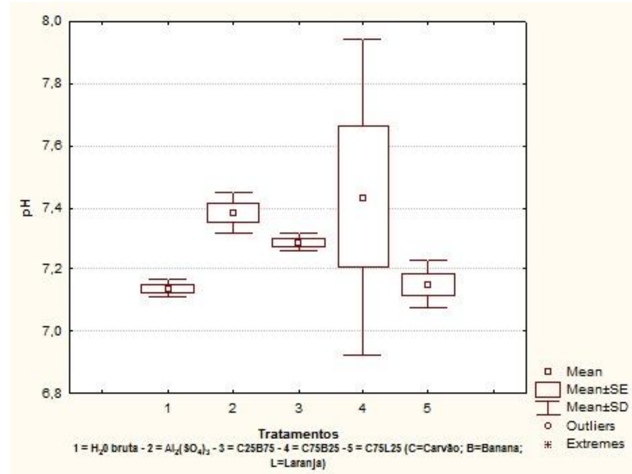

Figure 1 – pH values of the employed treatments

The turbidity value found in the Capibaribe river water was 10.64 UNT (Figure 2). According to Guimarães, et al., (2007), water whose turbidity value is below to 20 UNT can be directly moved to slow filtration, dismissing the chemical coagulation (with aluminum sulfate). As it can be observed in Figure 2 the low turbidity of treatments 3, 4 and 5 displays the good performance of the produced charcoal. Still looking at Figure 2 a possible economic solution is observed when comparing the results with aluminum sulfate turbidity values, proving water treated with AC produced mainly from orange waste lowers the content of particles in suspension on water (Valério, 2014) up to 97%. According to Selhorst Filho et al., (2011) research, an 85% efficacy was achieved in removing crude water turbidity.

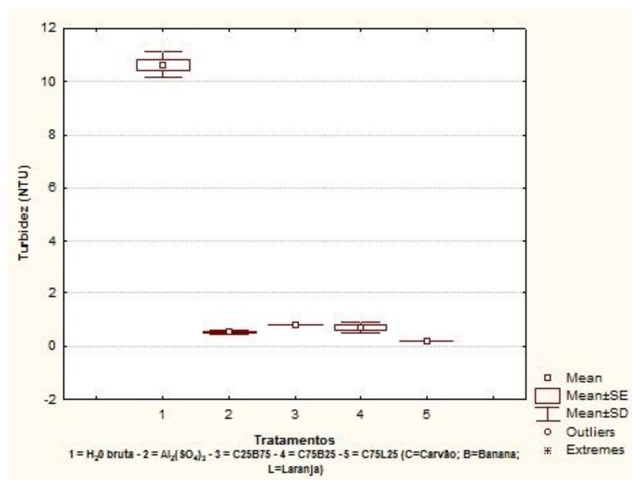

Figure 2 – Turbidity values of the employed treatments.

Even though EC is not a legislation-controlled parameter, it is of the greatest importance to the characterization of a waterbody. Electric conductivity measures the ability of water to transmit an electric current and is directly associated to the concentrations of ionic species dissolved, mainly the inorganic ones (Libanio, 2010).

This measure could be related to the concentrations of total dissolved solids, what facilitates the assessment of the waterbody for it is a direct measure. Values above a 1,000 µS.cm-2 threshold could indicate pollution issues. According to Figure 3, it can be perceived that the values of EC in the used treatments are above this value even after use of activated charcoal from banana and orange waste. However, we can infer that the use of the C75O25 dose (coconut:orange) as the most significant among the treatments that are able to replace aluminum sulfate.

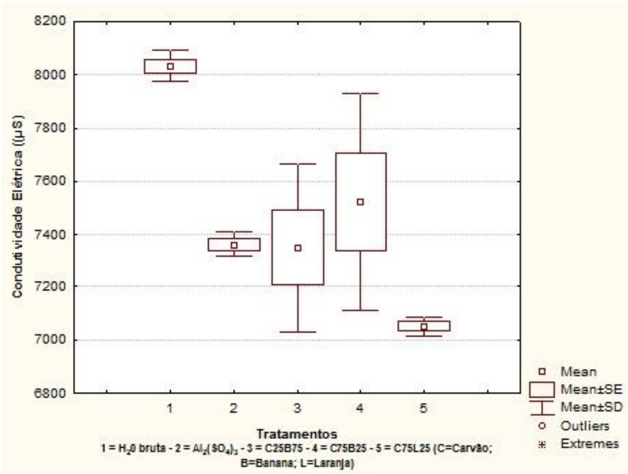

Figure 3 – EC values of the employed treatments

4. CONCLUSION

According to the data obtained in this experiment, we can conclude that:

1. The AC produced from orange was efficient in the removal of turbidity by 97%;

2. The activated charcoal from banana and orange waste caused reduction of pH and EC;

3. All the employed waste are potential substitutes to aluminum sulfate in water treatment stations.

5. ACKNOWLEDGMENTS

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