Production of Activated Carbon from Agroindustrial Residues and Application in the Treatment of Desalinator Reject

ABSTRACT

Residues of agroindustrial origin can be used for various purposes, including the production of activated carbon. In order to conduct the experiment, residual biomass of *Cocos nucifera*-C and grape marc-B were used at the doses corresponding to 100C/0B, 75C/25B, 50C/50B, 25C/75B and 0C/100B. The appropriate operating ranges for the production of activated carbon were identified and an experiment was carried out with a full factorial design, type 3^2, with three replicates and a control. The activated carbon produced was in contact with the desalinator reject for 30, 60, 120 and 180 minutes, after which the extracts were physico-chemically analyzed. The data were submitted to statistical analysis, using Statistic software, with a percentage reduction in the characteristics evaluated: pH (13.2), electrical conductivity (1), sodium (4.7), potassium (35.6), calcium (3.2), magnesium (zero) and chloride (18.2), indicating the mixture of coconut fiber and grape marc in 50C/50B ratio as being the most promising in the adsorption of the chemical elements of the reject, when in contact for up to an hour.

Keywords: Desalination; saline effluent; alternative residues; carbon; biosorbent.

1. INTRODUCTION

The production of carbon from agroindustrial residues is a very promising process in market terms, since activated carbon is a product of economic value used as a source of renewable energy or in more noble applications such as in the treatment of water and effluents [1].

As a country with a continental dimension, Brazil stands out in the agroindustrial context for its vast extension of arable land and for the consequent and high production of biomass. However, a significant part of this biomass is lost as residue and requires more attention in order to be reused [2, 3].

According to [4] data, Brazil, together with Indonesia, the Philippines, India and Sri Lanka, are the largest producers of *Cocos nucifera* L. in the world. The fibrous material that constitutes the mesocarp of the fruit, also called coir, bonote or fiber, is a traditional

product in countries like India and Sri Lanka, accustomed to process the mature coconut. The growing demand for coconut fibers is due to the interest in ecologically correct products, because it is from a renewable source, biodegradable and low cost, and because of their characteristics, they offer various possibilities of use [5].

Grape is a very nutritious fruit and consumed all over the world, both *in natura* and its derivatives (juices, wines). The marc coming from the production has been the object of numerous studies, due to the large number of compounds present in it, besides its importance in the biological functions of the human being. The use of these components has a significant impact on residues reduction and the possibility of creating products with high added value [6].

The objectives of this research were: to produce activated carbon from agroindustrial residues (coconut fiber and grape marc) and analyze its efficiency in order to use the residues so that they are not discarded incorrectly and do not pollute the environment.

2. MATERIAL AND METHODS

The activated carbon production experiment was conducted at the Analytical Chemistry Laboratory, on the 8th floor of Block D, at the Center of Science and Technology of Catholic University of Pernambuco, Recife, Pernambuco, Brazil.

2.1. Preparation of materials

The dry residues of the coconut shell (*Cocos nucifera L.*) were collected at the coconut water sale sites, discarding the mesocarp (fibre beam) of brown color, because they present greater difficulty to be processed.

The grape marc, Isabel variety, was supplied by the owner of Engenho Açude Novo, municipality of São Vicente Ferrer - Boqueirão, state of Paraíba, Brazil.

The coconut and grape samples were air dried and ground in a forage-type crusher, at Agronomic Institute of Pernambuco - IPA, Recife, Pernambuco, being sifted in 14 mesh sieves to obtain a uniform granulometry, according to [7, 8].

2.2.Statistical treatment

The experimental design was a randomized block design, with five replications, with coconut / marc (treatment) ratio equal to 100C/0B; 75C/25B; 50C/50B; 25C/75B; 0C/100B. Once the appropriate operating ranges were identified, for the production of activated carbon, experiments were conducted guided by a complete factorial design,

type 32, with three replicates and a control. Statistical models were used to determine optimized working conditions.

2.3. Determination of granulometry and chemical composition

For the immediate analysis of the carbon, the treatments were sifted in sieves of 40 mesh, determining the contents of fixed carbon, volatile materials and ashes according to the norms [8, 9] and the calorific value according to the norm [10].

The immediate analysis of the coconut fiber was: moisture (%) = 5.94; ashes (%) = 8.12; volatile materials (%) = 3.55; fixed carbon (%) = 82.39; and calorific power (kJ/kg) = 0.45. The immediate analysis of grape bagasse was: moisture (%) = 7.07; ashes (%) = 6.98; volatile materials (%) = 1.89; fixed carbon (%) = 84.06; and calorific power (kJ/kg) = 0.83.

2.4. Production of activated carbon

The values of ashes (%) and calorific power (kJ/kg) in the treatments used were respectively: 0C/100B = 6.98 and 0.83; 25C/75B = 6.94 and 0.72; 50/50 = 6.11 and 0.72; 75C/25B = 6.26 and 0.51; 100C/0B = 8.12 and 0.45.

Thus, the 50C/50B treatment was chosen because of its higher calorific value and low ash concentration, which favors the chemical quality of the carbon, according to [11].

For the production of the carbon, 10 grams of each sample received impregnation treatment with 1:1 $ZnCl_2$ (mixture of the residue / $ZnCl_2$), using porcelain capsule with reinforced wall to mix material, and placed in oven at 105 °C for 24 hours [12].

The process of production of activated carbon involved two main steps, according to [13]: the carbonization of the raw material and the activation, where the free valence binding of the adsorbent molecules occurs in the adsorbate.

Then, the samples placed in porcelain crucible were activated using a muffle furnace, LF00613 model, raising the temperature to 550 °C at a rate of 15 °C min^{-1}, maintaining the temperature for one hour under gas inert (nitrogen) with a flow of 100 mL / min N_2. After being removed from the muffle and cooled in a desiccator, samples of the activated carbon produced with 50% HCl solution were filtered, successively, until the pH stabilization was close to 7. All these procedures were performed with five repetitions of the sample worked.

2.5. Application of Activated Carbon

For the evaluation of the efficiency of the activated carbon, an experiment was set up, with five replicates, with a control and a dose equivalent to 200.0 mg of the activated carbon for 200.0 mL of the desalinator reject located in the municipality of Riacho das Almas, State of Pernambuco, Brazil, with a contact time of 30, 60, 120 and 180 minutes, and a completely randomized design, in laboratory conditions, for a total of 25 experimental units.

The determinations were: pH and electrical conductivity, using the methods [14, 15] respectively; sodium and potassium by flame emission spectrophotometry; calcium and magnesium and chloride by complexation titrimetry and precipitation respectively.

The data were submitted to statistical analysis, generating Box Plot type graphs using Statistica 10.0 software.

3. RESULTS AND DISCUSSION

Analyzing the data shown in Figure 1, it was identified that, in the predefined times for the contact of the activated carbon with the desalinator reject (30, 60, 120 and 180 minutes), there was a reduction of the contents of all the determined elements in the extract obtained, mainly up to 120 minutes of contact.

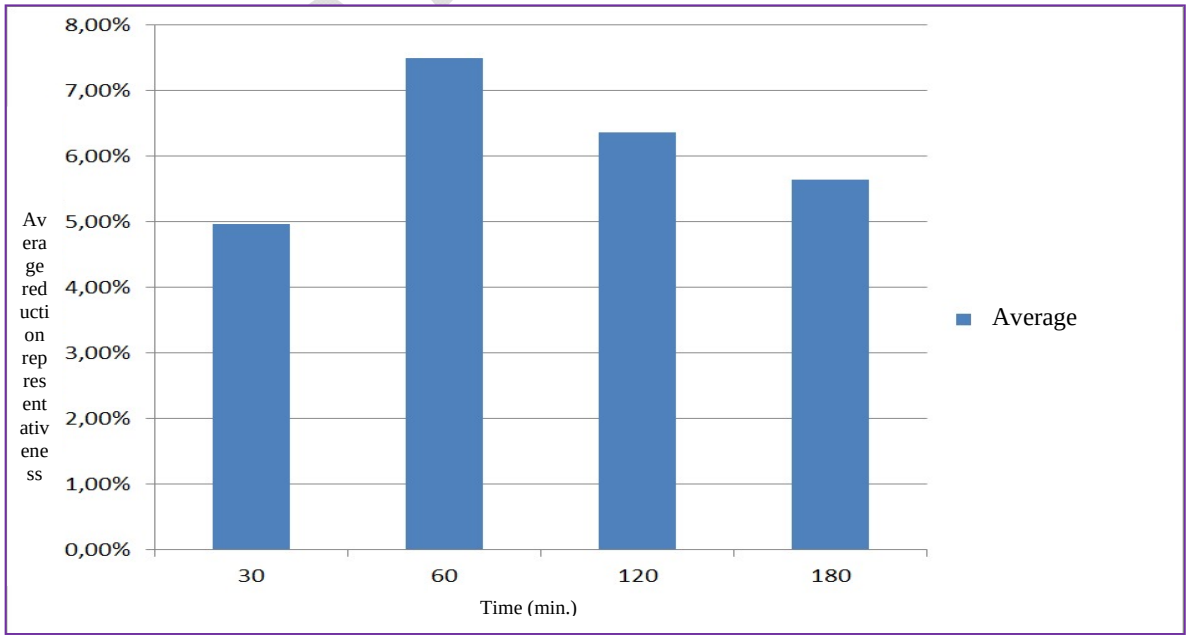
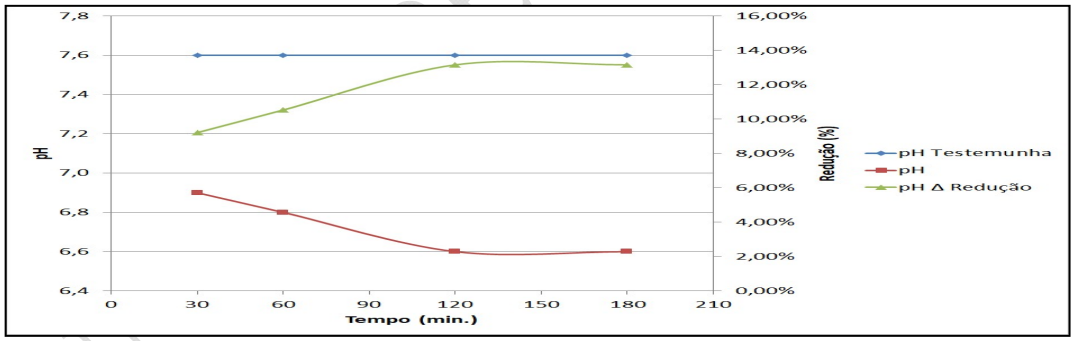


Figure 1. Results of reduction of all the parameters determined in the extracts (pH, EC, Na, K, Ca, Mg and Cl) in the contact periods between the activated carbon produced and the desalinator reject (30, 60, 120 and 180 minutes) .

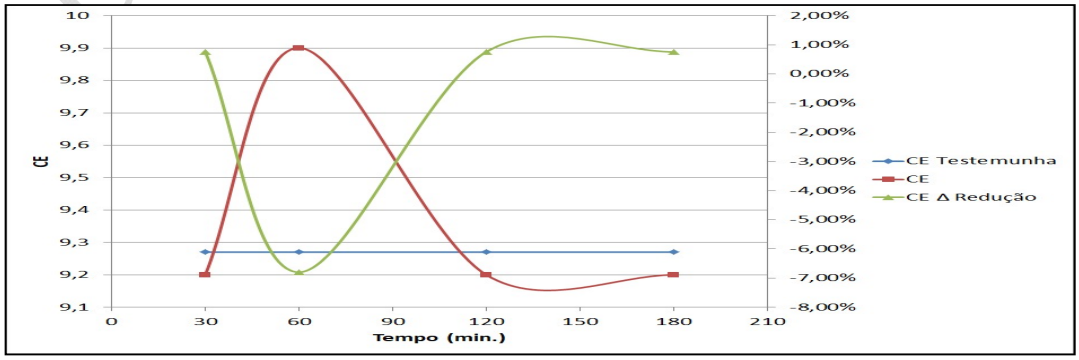
The results found in this study for the adsorption capacity of activated carbon elements as a function of the contact time can be compared with the studies carried out by [16] that produced activated carbon with coconut and bamboo fiber, determining the levels of drugs in river water.

In relation to the hydrogen ionic potential, it is observed (Figure 2A) a reduction of its values in the different times of contact. The largest reduction occurred up to 120 minutes (-13.16%), from 7.9 dS / m to 6.6 dS / m. After this period there was pH stabilization. In one of his experiments, [17] found pH between 6 and 7 in treated water treatments using commercial activated carbon and, after the adsorption process, concluded that there was no significant variation in pH in relation to the initial water. Also, [18] report similar behavior in their experiments with commercial granular activated carbon, where the pH does not usually vary significantly between adsorbate and adsorbent.

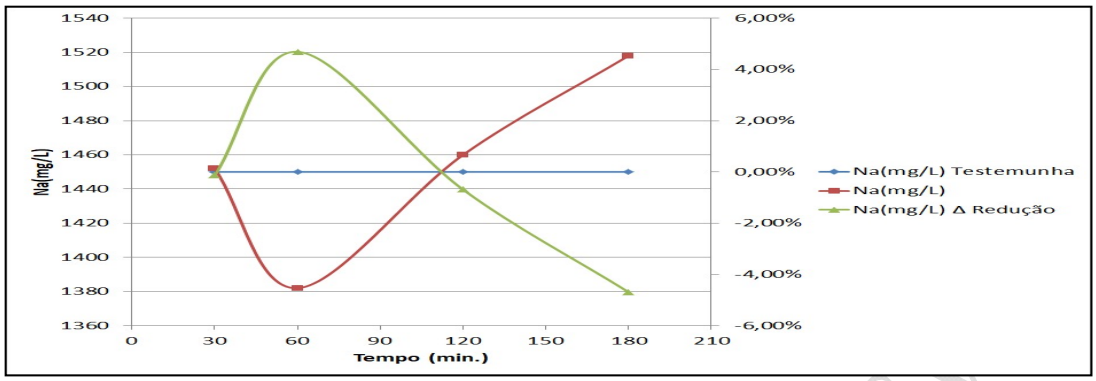
2A- pH



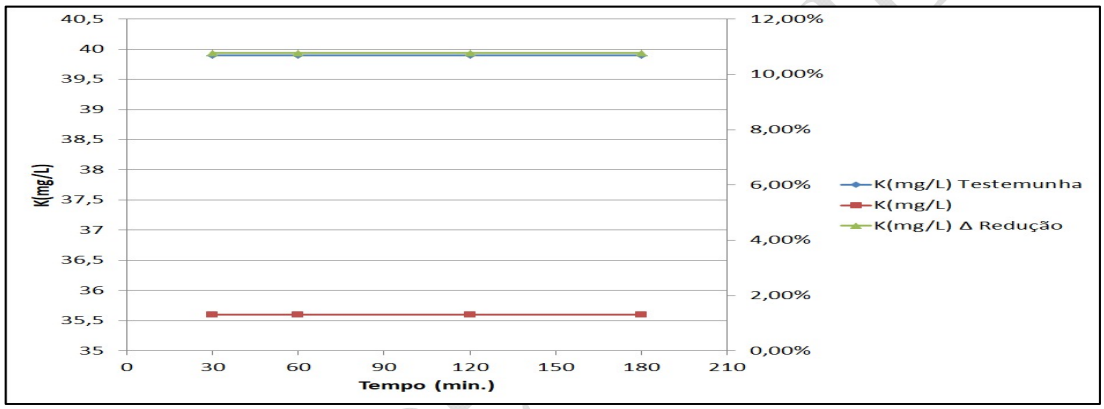
2B-EC



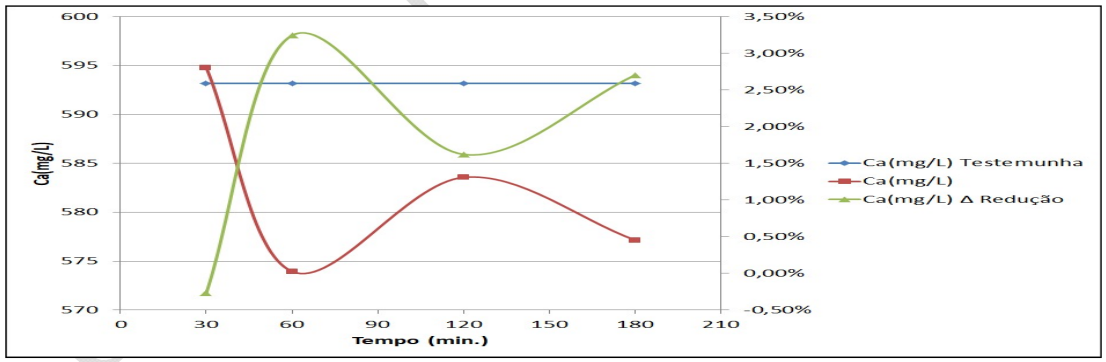
2C- Sodium



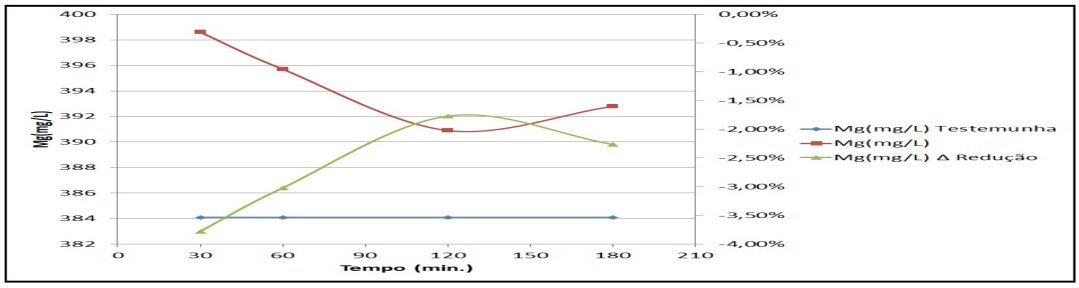
2D- Potassium



2E- Calcium



2F-Magnesium



2G- Chloride

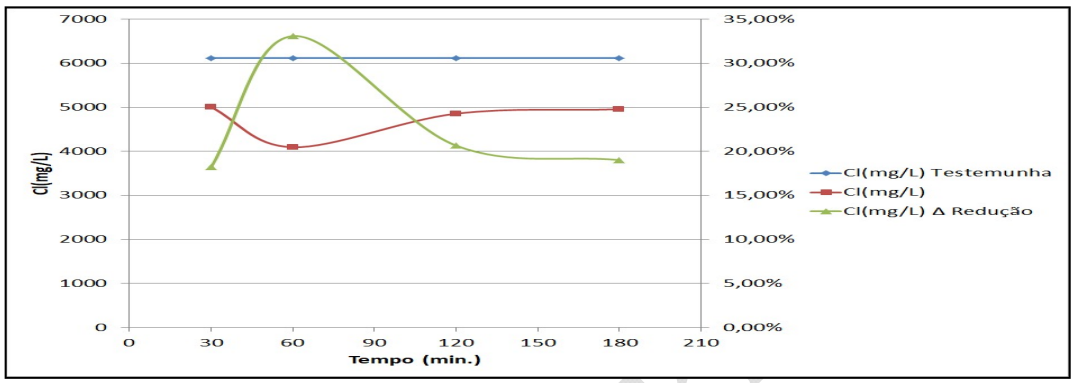


Figure 2. Results of all the parameters determined (A = pH, B = EC, C = Na, D = K, E = Ca, F = Mg and G = Cl), in the contact periods between the activated carbon produced and the desalinator reject (30, 60, 120 and 180 minutes).

Figure 2B shows that the electrical conductivity (EC) presented lower values (-0.99%) than the control (9.3 dS / m), with the exception of the contact time of 60 minutes (9.9 dS/m). Although EC is not a parameter controlled by legislation, its characterization is important because it is related to the concentration of total dissolved solids. According to [19], after the use of activated carbon, they found efficiency of 5.6% for the EC.

For the adsorption of sodium (Figure 2C), the greatest reduction in the mean concentration of the chemical element occurred with 60 minutes (-4.69%) of contact between activated carbon and reject, from 1450 mg/L in the control to 1382 mg/L in the extract. For the other periods of contact, there was no reduction with significant difference, possibly occurring with a certain ease the desorption of sodium due to the attractive forces between the adsorbate and the adsorbent become weaker. Similar reduction parameters were found by [20] in their experiments with saline water, where sodium reduction occurred immediately after filter installation, remaining stable in the other periods, distributed at different times of the lifespan of these filters.

It can be seen from Figure 2D that for the potassium content, there was a reduction in all contact times in relation to the control (39.9 mg / L), with a minimum contact value of 30 minutes (-35.6 mg / L). There were also similar results in the research by [20], where the increase in contact time did not mean an increase in the adsorption of potassium.

According to the calcium values presented in Figure 2E, adsorption and desorption processes are observed in relation to the contact time, showing instability in the sorption reactions. Thus, the contact time of 60 minutes may be considered as the most adequate (-3.24%), from 593.18 mg/L to 573.94 mg/L. The same instability was also found by [20] in the treatment of saline water with activated carbon produced with bone.

In relation to magnesium, it can be seen in Figure 2F that there was no reduction in its concentration at any of the contact times of the activated carbon with the desalting agent, compared to the control (384.18 mg / L). Activated carbons studied by [21] demonstrated that there was no significant reduction of magnesium, corroborating that this chemical element is difficult to adsorb, even at different times of contact.

For the chloride, Figure 2G demonstrates a greater adsorption in one hour of contact with the activated carbon, promoting reduction of 18.2% from 6164.4 mg / L to 4094.5 mg / L. As the contact time increased (120 and 180 minutes), there is an indication of the chloride desorption process. Similar results were found by [22].

Therefore, the experiment indicates that very long contact times can end up harming the efficiency of the removal by the activated carbon to favor the desorption process [23].

4. CONCLUSION

The results of this study enabled an evaluation of activated charcoal produced, thus providing the use of coconut fiber and grape bagasse. The values obtained for pH and CE did not present significant variations during contact times (30, 60, 120 and 180 minutes). The contact time of 60 minutes between activated charcoal and the reject favored the adsorption of sodium, calcium and chloride. Potassium showed a greater reduction in its values at 30 minutes of contact. There was no significant difference in the reduction of magnesium content in any contact time.

Therefore, the activated charcoal produced is efficient in removing chemical elements present in the desalinizer's reject.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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