Calcium and Magnesium Adsorption by Activated Carbon Produced with Alternative Materials

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Authors' contributions

This work was carried out in collaboration among all authors. Author SSAL performed the experiment as a master's thesis, performed the statistical analysis and wrote the first draft of the manuscript. Authors SCP and HJBLF together with author GMCT managed the analysis of the study. Author ASM designed the study and wrote the protocol. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Residues originated from agro-industry can be used for various purposes, including in the production of activated carbon. Thus, for the conduction of this research, an Activated Carbon (AC) was prepared with mixtures of grape bagasse (B) and coconut fiber (C), with the mass relations of coconut/bagasse of 100/0; 75/25; 50/50; 25/75 and 0/100. The 50C/50B considered statistically the most suitable for the production of CA was activated with $ZnCl_2$, under N_2 flow of 100 ml/min, at 550°C, for 1 hour. To evaluate its efficiency, 200.00 mg of AC were used in 200,0 ml of the desalinator tailing from the municipality of Riacho das Almas, Pernambuco, Brazil, with contact time of 30, 60, 120 and 180 minutes, in a statistical design entirely randomized. Data were subjected to statistical analysis, generating Box Plot type charts. The result of calcium and magnesium adsorption revealed the efficiency of activated carbon with a dose of 50C/50B when in contact for up to 60 minutes with desalinator tailing.

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1. INTRODUCTION

Planet Earth is made up of ¾ water and ¼ earth. Of this total, approximately 97.5% consists of salt water. Of the remaining 2.5% of freshwater, however, about 68.7% is in the form of glaciers, ice caps or mountainous regions [1]. Brazil is a privileged country in relation to water availability. Its territory has 13.7% of the world's fresh water. However, all this water is not evenly distributed among the regions. Thus, many regions of Brazil suffer from the scarcity of potable water for the simplest purposes of daily life, such as the northeast region of Brazil that, in addition to lack of availability, are high in levels of salinity in the waters [2].

In the Brazilian Northeast, among the serious problems that permeate the region, water scarcity is the main limiting factor for food production. In arid and semi-arid climates, agriculture is highly vulnerable, mainly due to the occurrence of small volume rainfall with very irregular distribution [3].

Society lives in search of alternatives to minimize the effects of drought, using technologies where one of the alternatives is the desalination process. Desalination is a rapidly expanding form of saltwater treatment with a promising future. Part of the estimated increase is mainly due to the great advance in increasingly effective desalination technologies, which allow a marked reduction in the cost of cubic meter of treated water. Another reason for the expansion of this technique is the constant need to find alternative sources of water due to the increasingly worrying pollution or scarcity of fresh water [4].

The salinization of waters in the Brazilian Northeast has been proving as a worrying phenomenon as the low precipitation. After desalination of water, some of the solutes that were obtained in the process produce a byproduct, a wastewater called tailings, of much higher saline concentration than the original brackish water and of polluting power to the soil, fauna and flora. In some places, the waste is up to 60% of the original volume and one of the environmental problems encountered in this process is the disposal site, as it can cause damage to the environment [5].

All sectors of the economy (primary, secondary, tertiary) have high solid waste production. In Brazil, agricultural activity (primary sector) results in approximately 23% of gross domestic product (GDP), according to [6]. The country is considered one of the largest agricultural producers in the world and the second largest agricultural exporter in the world. On the other hand, coupled with this huge high levels of food waste and consequently large generation of solid waste accompany production. Estimates indicate that approximately 35 to 64% of all annual agricultural production is wasted [7]. Therefore, waste and solid waste generation occur at all stages of the production chain processes.

The wine industry generates substantial volumes of solid organic waste, which is either underused or discarded. It is estimated that 73 million tons of grapes, mainly grown as Vitis vinifera, are produced worldwide [8]. It is one of the most important cultivated plants in the world where it is the main source of food and income for the population, and partly due to the large number of products obtained from the industrialization of its fruits [9].

Activated carbon is a chemically inactive product usually obtained from high carbon substances (precursor material). Used for removing dissolved impurities in the products to be treated. The impurities removal mechanism consists of the adsorption and retention process, in which the impurities are attracted by the porosity existing in the activated carbon, being an adsorbent most used in the water treatment process, because it has a high surface area [10,11]. Activated carbon production from low-cost alternative waste has been an attempt to mitigate environmental impacts and the cost of obtaining potable water [12].

The main objective of this work was to produce activated carbon from alternative solid residues such as coconut fiber and grape bagasse, to be used as adsorbent in the removal of calcium and magnesium present in the Pernambuco semi-arid desalination waste.

2. MATERIALS AND METHODS

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

2.1 Materials Preparation

The dried coconut shell (*Cocos nucifera* L.) residues were collected at the coconut water sales premises, discarding those of brown color, because they present greater difficulty to be processed.

Grape bagasse, variety Isabel, 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 crusher at the Pernambuco Agronomic Institute - IPA, Bongi, Recife, Pernambuco, and sieved in mesh 14 sieves to obtain a uniform grain size according to Brazilian Association of Technical Standards [13,14].

2.2 Statistical Treatment

The experimental design was a randomized block design with five replications, with the ratio coconut - C / bagasse - B (treatments) equal to 100C / 0B; 75C / 25B; 50C / 50B; 25C / 75B; 0C / 100B. Identifying the appropriate operating ranges for activated carbon production, experiments were conducted guided by a complete type 3^2 factorial design, with three replicates and one central point. In the obtained results, statistical models were applied to determine the optimal working conditions.

2.3 Determination of Granulometry and Chemical Composition

For the immediate analysis of the coal, the treatments were passed in 40 mesh sieves, determining the fixed carbon, volatile materials and ash contents according to the standards [14,15], and the calorific value according to the norm [16].

2.4 Activated Carbon Production

Thus, the 50C / 50B treatment was chosen because it has higher calorific power and low ash concentration, which favors the chemical quality of the coal, according to [17].

For carbon production, 10 grams of each sample received a 1: 1 $ZnCl_2$ impregnation treatment (residue / $ZnCl_2$ mixture), using the mortar and pistil to grind the material, and placed in a 105°C oven for 24 hours [18].

The activated carbon production process involved two main stages, according to [19]: carbonization of the raw material and activation, where the free valence bonding of the adsorbent molecules to the adsorbate occurs.

The porcelain crucible samples were then activated using a muffle furnace, model LF00613, raising the temperature to 550°C at a rate of 15°C. min^{-1}, maintaining the temperature for 1 hour under inert gas with a flow rate of 100 ml / min^{-1} N_2. After removing the muffle and cooled in desiccator, the activated charcoal samples with HCl solution at 50% were washed, successively filtered, until pH stabilization near 7. All these procedures were performed with five repetitions of the worked sample.

2.5 Activated Carbon Application

To evaluate the efficiency of activated carbon, an experiment was carried out with five replicates, with a control and a dose equivalent to 200.0 mg of activated charcoal for 200.0 ml of desalinator tailing implanted in the municipality of Riacho das Almas, Pernambuco, Brazil, with a contact time of 30, 60, 120 and 180 minutes and a completely randomized statistical design, under laboratory conditions, in a total of 25 experimental units. The physicochemical analysis of the desalinator's tailing was performed at the IPA Plant, Ration and Water Analysis Laboratory - LAPRA with the following characteristics: electrical conductivity = 11.541 dS/cm at 25°C, Ca^{+2} = 403 mg/L, Mg^{+2} = 384.18 mg/L, Na^+ = 200 mg/L and K^+ = 40 mg/L, RAS = 23.67, pH = 7.9, classification for irrigation = C4S4 (very high salinity water and high sodium concentration).

The determinations performed were calcium and magnesium, by complexation titrimetrics. The obtained data were submitted to statistical analysis, generating Box Plot graphs using Statistica 10.0 software.

3. RESULTS AND DISCUSSION

Comparing the data shown in Fig. 1, it was observed that there was a reduction in the content of the determined elements (calcium and magnesium).

Adsorption started within 60 minutes. After this period, a decrease in the reduction is noticed. As the surface of the solid reaches saturation, the adsorption rate begins to be controlled by the

rate of adsorbate transfer to the active sites located within the adsorbent [20].

According to the calcium values presented in Fig. 2, it is noticed that in relation to the contact time, the adsorptive and desorptive processes show instability. Thus, the 60 minute contact time may be considered as the most appropriate (-3.24%), from 593.18 mg / l to 573.94 mg / l. The same instability was also found by [21] in treating saline water with bone-activated activated carbon.
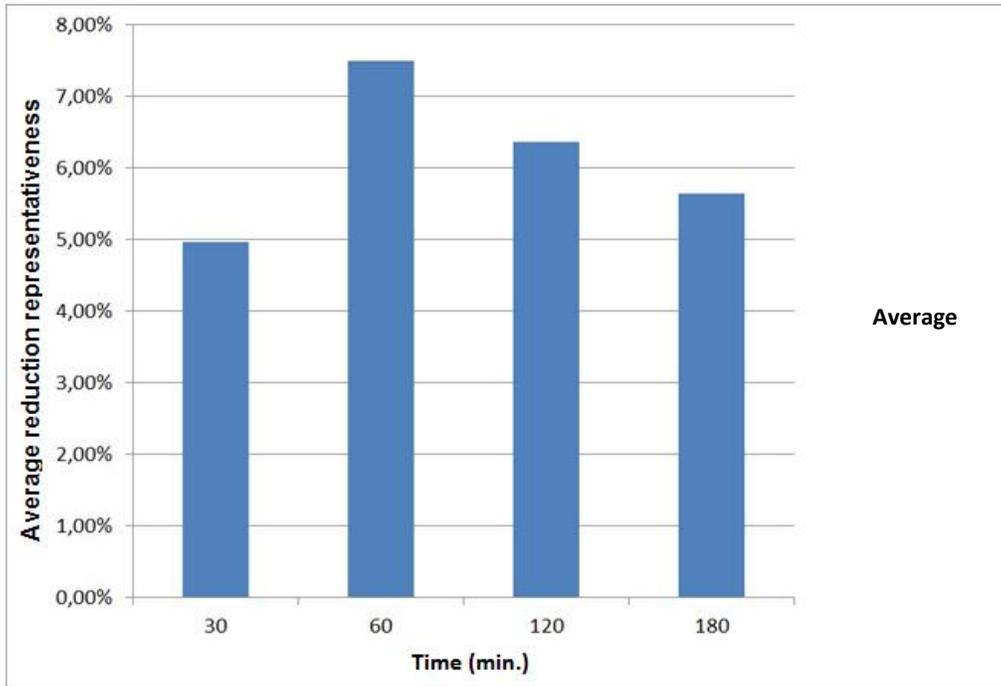
Fig. 1. Average reduction for calcium and magnesium at different times of contact between activated carbon produced and desalinator tailing
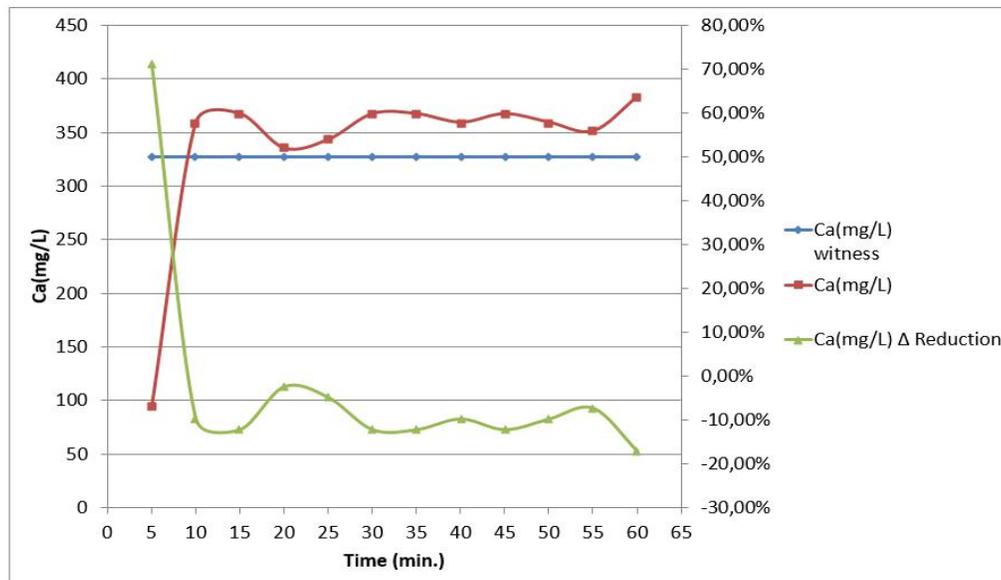
Fig. 2. Results obtained for the different contact times of the activated carbon with desalinator tailing in calcium adsorption
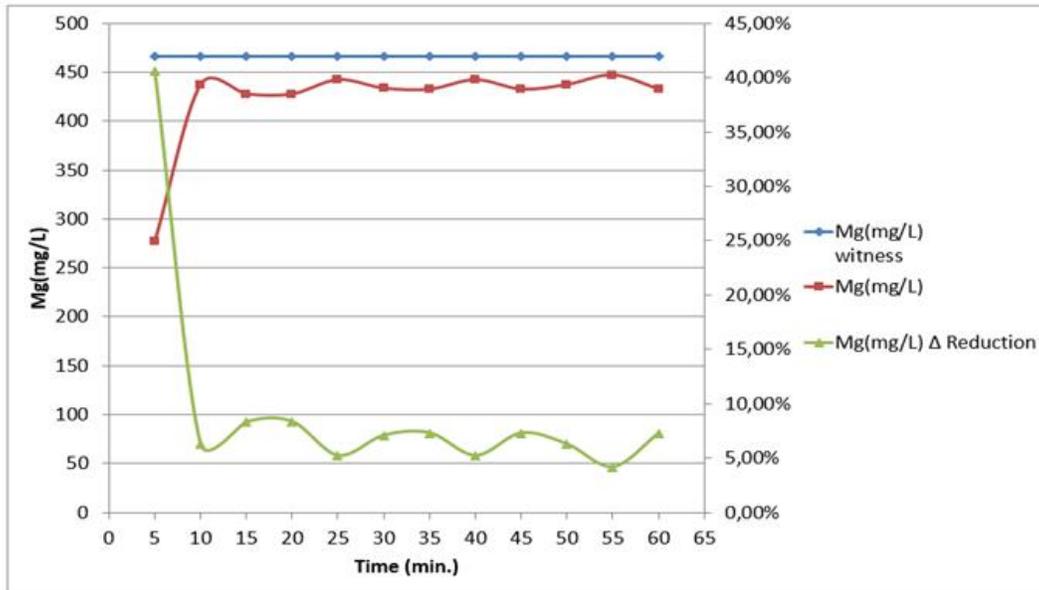
Fig. 3. Results obtained for the different contact times of the activated carbon with desalinator tailing in magnesium adsorption

In relation to magnesium, it can be seen in Fig. 3 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 [22] demonstrated that there was no significant reduction of magnesium, corroborating that this chemical element is difficult to adsorb, even at different times of contact.

4. CONCLUSION

According to the studies done, it can be noted that the 50C / 50B treatment (50% coconut fiber mixed with 50% grape bagasse) presented satisfactory results in the adsorption of the chemical elements, with a contact time of 60 minutes, favoring calcium adsorption. There was no significant difference in magnesium content reduction at any contact time. Therefore, activated carbon produced from coconut fiber and grape bagasse becomes yet another alternative for reuse for waste of agroindustrial origin, with added value that was, for the most part, incorrectly disposed of in the environment. Thus, the results obtained with the production of activated carbon are promising to minimize the level of chemical elements present in saline groundwater, and may even make it more suitable for human and agricultural consumption.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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