

## **AVALIAÇÃO PRELIMINAR DE CARVÃO TERMICAMENTE ATIVADO A PARTIR DE RESÍDUOS DE CASTANHA-DO-BRASIL PARA REMOÇÃO DE METAIS PESADOS**

*PRELIMINARY EVALUATION OF THERMALLY ACTIVATED CHARCOAL FROM BRAZIL NUT WASTE FOR HEAVY METAL REMOVAL*

*EVALUACIÓN PRELIMINAR DEL CARBÓN ACTIVADO TÉRMICAMENTE A PARTIR DE RESIDUOS DE CASTAÑA DEL BRASIL PARA LA REMOCIÓN DE METALES PESADOS*

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## RESUMO:

Este trabalho tem como objetivo preliminar utilizar a casca da castanha-do-brasil (*Bertholletia excelsa* L.) para produzir carvão ativado termicamente modificado e avaliar sua capacidade de adsorver metais pesados, como cromo hexavalente (VI) e cobre bivalente (II). As concentrações de metais pesados em efluentes industriais podem ser reduzidas através de diferentes métodos, tais como: adsorção, troca iônica, separação por membranas e eletroquímica. Uma técnica promissora para a captura de metais pesados é a adsorção por sólidos porosos. Neste processo, é essencial que o adsorvente tenha alta seletividade para com os metais, bem como grande capacidade de adsorção. O carvão a partir foi obtido através da carbonização do resíduo da casca de castanha-do-brasil por 1 hora a 600°C em forno mufla. Depois, ele foi submetido a ativação térmica por 3 hora a 800°C. O carvão ativado foi caracterizado quanto à área específica, tamanho dos poros, porosidade, pH, grupos funcionais de superfície pelo método de Boehm e espectroscopia de infravermelho com transformada de Fourier (FTIR). As experiências para determinar a eficiência de remoção de cromo e cobre foram realizadas para as concentrações iniciais das soluções: 5, 10, 20, 30, 50, 100, 150 e 200 mg L<sup>-1</sup>. A adsorção do cromo hexavalente (VI), sem alteração do pH natural da solução sintética, não foi satisfatória, pois a remoção ficou em torno de 10%. Por outro lado, os resultados apresentados para a remoção do cobre bivalente, nas mesmas condições de adsorção, atingiram valores acima de 90% para a maioria das concentrações iniciais. Os resultados mostraram maior afinidade do cobre em relação ao cromo pelo carvão ativado. Além disso, este estudo motiva futuras pesquisas, principalmente na avaliação da capacidade de adsorção de cobre em soluções com diferentes pH.

**PALAVRAS-CHAVE:** Castanha do Brasil, carvão ativado, adsorção, metais pesados.

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## ABSTRACT:

*This paper aims to use Brazil nut bark (*Bertholletia excelsa* L.) to produce thermally modified activated charcoal and evaluate its capacity to adsorb heavy metals such as hexavalent chromium (VI) and divalent copper (II). The concentrations of heavy metals in industrial effluents can be reduced through various methods, such as: adsorption, ion exchange, membrane separation, and electrochemical techniques. A promising technique for heavy metal capture is adsorption by porous solids. In this process, it is essential that the adsorbent has high selectivity for metals as well as high adsorption capacity. The charcoal was obtained through the carbonization of Brazil nutshell residue for 1 hours at 600°C in a muffle furnace. Then, it was subjected to thermal activation for 3 hours at 800°C. The activated charcoal was characterized in terms of specific surface area, pore size, porosity, pH, surface functional groups by the Boehm method, and Fourier-transform infrared spectroscopy (FTIR). Experiments to determine the*

removal efficiency of chromium and copper were carried out for the initial concentrations of the solutions: 5, 10, 20, 30, 50, 100, 150, and 200 mg·L<sup>-1</sup>. The adsorption of hexavalent chromium (VI), without adjusting the natural pH of the synthetic solution, was not satisfactory, as removal remained around 10%. On the other hand, the results for divalent copper removal under the same adsorption conditions reached values above 90% for most initial concentrations. The results showed a greater affinity of copper compared to chromium for the activated charcoal. Furthermore, this study encourages future research, especially in the evaluation of copper adsorption capacity in solutions with different pH levels.

**KEYWORDS:** Brazil nut, activated charcoal, adsorption, heavy metals.

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## RESUMEN:

Este trabajo tiene como objetivo preliminar utilizar la cáscara de la castaña de Brasil (*Bertholletia excelsa* L.) para producir carbón activado térmicamente modificado y evaluar su capacidad de adsorber metales pesados, como cromo hexavalente (VI) y cobre divalente (II). Las concentraciones de metales pesados en los efluentes industriales pueden reducirse mediante diferentes métodos, tales como: adsorción, intercambio iónico, separación por membranas y técnicas electroquímicas. Una técnica prometedora para la captura de metales pesados es la adsorción por sólidos porosos. En este proceso, es esencial que el adsorbente tenga alta selectividad hacia los metales, así como una gran capacidad de adsorción. El carbón se obtuvo mediante la carbonización del residuo de cáscara de castaña de Brasil durante 1 hora a 600°C en un horno mufla. Luego, fue sometido a activación térmica durante 3 horas a 800°C. El carbón activado fue caracterizado en cuanto a área superficial específica, tamaño de poro, porosidad, pH, grupos funcionales superficiales mediante el método de Boehm y espectroscopía infrarroja por transformada de Fourier (FTIR). Los experimentos para determinar la eficiencia de remoción de cromo y cobre se realizaron para concentraciones iniciales de las soluciones: 5, 10, 20, 30, 50, 100, 150 y 200 mg·L<sup>-1</sup>. La adsorción de cromo hexavalente (VI), sin alterar el pH natural de la solución sintética, no fue satisfactoria, ya que la remoción fue de aproximadamente un 10%. Por otro lado, los resultados para la remoción de cobre divalente, en las mismas condiciones de adsorción, alcanzaron valores superiores al 90% para la mayoría de las concentraciones iniciales. Los resultados mostraron una mayor afinidad del cobre en comparación con el cromo por el carbón activado. Además, este estudio motiva futuras investigaciones, especialmente en la evaluación de la capacidad de adsorción de cobre en soluciones con diferentes niveles de pH.

**Palabras clave:** Nuez de Brasil, carbón activado, adsorción, metales pesados.

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## INTRODUÇÃO

Many economic activities give rise to a large volume of waste from different sources, which, regardless of its intensity and physical-chemical properties, causes major changes in the environment and the disposal requires previous treatment. Among this waste is the residual biomass from Amazonian fruits (Brazil nuts, açai and cupuaçu), consumed by the population and whose shells and stones are mostly piled up in unsuitable places such as gutters and sidewalks where these products are sold, without any kind of intended use, and are usually considered "garbage", as Figure 1 depicts. An alternative to reuse this waste is to produce activated charcoal from, added value to it, as suggested by: Cruz Júnior (2010), Melo (2012), Silva et al. (2012), Thue et al. (2022), Thomaz et al. (2023).



Figure 1 - Nut residue after kernel removal

Several raw materials from residual biomass have been used to produce activated charcoal, including wood, vegetables, bones, coconut shells, Bahia coconut endocarp, sugar cane bagasse, fruit seeds and others (Soleimani and Kaghazchi, 2008; Dermibas et al., 2008; Guo and Rockstraw, 2007; Guo and Rockstraw, 2006). The process of producing activated charcoal involves two main stages: the carbonization or pyrolysis of the raw material and the activation of the carbonized material (Aworn, 2008; El-hendawy et al., 2008; Ong et al., 2009). Carbonization is carried out at a high temperature (above 400°C), under an inert atmosphere and involves the thermal decomposition of organic matter with the release of volatile products (CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>). The second stage is activation, which can be physical, chemical or chemical and physical. Physical activation uses the oxidizing properties of gases such as water vapor, CO<sub>2</sub> or a mixture of these at temperatures above 800°C (Girgis and El-Hendawi, 2002; Guo and Rockstraw, 2006). In general, physical activation produces a very fine slit-like pore structure, making the coals obtained suitable for use in gas phase adsorption processes, while chemical activation generates coals with larger pores, more suitable for liquid phase applications (Sai and Krishnaiah, 2005).

The adsorption capacity of activated charcoal is determined by its specific surface area, its internal porous structure and the presence of functional groups on the surface, cation exchange capacity, density, phenol and methylene blue (Diao et al., 2002; Haimor and Emeish, 2006; Soleimani and Kaghazchi, 2008). The adsorptive properties of activated charcoal depend on the natural

precursors, the type of activation: physical or chemical and the processing conditions (Chen and Wang, 2000; Stavropoulos and Zabaniotou, 2005). An effective activated charcoal must have a large surface area, appropriate pore sizes to trap the desired species and surface charges opposite to those of the adsorbates. Thus, the adsorption behavior of activated charcoal cannot be interpreted by taking surface area alone into account. Activated charcoal that have the same surface area but are prepared using different methods or different activation treatments show different adsorption capacities. The ash content also interferes in the adsorptive behavior of activated charcoal (Kikuchi et al., 2006). Ash is mainly inorganic oxides, and to a lesser extent phosphates, sulphates, chlorides, carbonates and silicates of K, Na, Ca, Mg, Fe and Al, soluble in water and dilute inorganic acids (Jankowska, 1991). The ash content can be low (0.1 - 1%) or reach over 20% (Smísek and Cerný, 1970) and depends on the raw material and activation. Simple pre-treatments such as washing with deionized water or inorganic acid solutions can be used to eliminate the interference of ash. The elimination of ash increases the hydrophobic character of activated charcoal and its adsorption capacity (Moreno-Castilla, 2004; Toledo et al., 2005). Several recent studies have demonstrated the efficiency of biomass as a sustainable alternative for the removal of heavy metals from contaminated environments. The study by Similarly, Silva (2020) evaluated the use of sugarcane bagasse as an adsorbent for  $Pb^{2+}$  and  $Zn^{2+}$ , reporting good results, particularly for zinc. Silva (2020) also demonstrated high performance in removing heavy metals using banana peel flour combined with chitosan-functionalized magnetic nanoparticles in treated sewage. These studies confirm the strong potential of residual biomass as a viable and environmentally friendly solution for the treatment of water contaminated with heavy metals. Abiodun et al. (2023) investigated the remediation of heavy metals using biomass-based adsorbents, focusing on adsorption kinetics and isotherm models. The research highlighted the effectiveness of various biomass-derived materials in adsorbing heavy metals from aqueous solutions, analyzing factors such as contact time, pH, and initial metal concentration. The study concluded that biomass-based adsorbents are promising for heavy metal remediation due to their availability, cost-effectiveness, and environmental friendliness. Hackbarth (2023) used biomass from the marine macroalga *Pelvetia canaliculata* to remove metal ions from petrochemical effluents, emphasizing the importance of ion exchange interactions in the biosorption process. Finally, Manna et al. (2025) highlighted the use of biosorbents and biochars derived from organic waste for the removal of metals such as zinc, copper, and lead, achieving removal efficiencies of up to 99.99%, reinforcing the potential of these materials as effective and low-cost alternatives.

The surface properties of activated charcoal vary depending on the precursor and the pyrolysis and activation conditions, it is essential to characterize it with regard to the number and type of chemical groups on the surface, the polarity of the surface, the distribution of pore sizes and the total surface area. The method proposed by Brunauer, Emmet and Teller, BET, (Brunauer et al., 1938) and titration with bases of different strengths (Boehm's method) are the most widely used techniques for quantifying the surface area and surface oxides of coals, respectively.

This paper aims to use Brazil nut bark (*Bertholletia excelsa* L.) to produce thermally modified activated charcoal and evaluate its ability to absorb heavy metals, such as: hexavalent chromium (VI) and bivalent copper (II). Although some authors have used Brazil nuts to produce activated carbon, to the authors' knowledge there is a gap in the literature for a comparative study of their absorption capacity involving heavy metals, such as: chromium and copper. According to Mohan and Pittman (2006), the industrial processes that produce liquid effluents rich in heavy metals are: the automobile industry, pulp and paper, oil refining, textiles, organic and inorganic chemical products, fertilizers, plastics, acid mine drainage, mines, glass. The processes that mainly produce hexavalent chromium, Cr (VI), as a pollutant are the manufacture of stainless steel and other metal alloys, the refractory and electroplating industries, the manufacture of pigments, tanneries and wood treatment (Nova et al., 2018). Heavy metals are biocumulative and toxic to humans and animals, and their presence in rivers and lakes is responsible for various health problems for animals, plants and humans. Therefore, controlling the bioavailability of metals in aquatic environments through adsorption by mineral surfaces is a recognized process.

The paper is organized as follows. First, methodology to produce the activated charcoal from Brazil nut waste and the analyses methods are presented in Section 2. Section 3 discusses the characterization of the activated charcoal as well the hexavalent chromium (VI) and bivalent copper (II) adsorption capacity. Finally, this paper is concluded.

## METODOLOGIA

### PRODUCTION OF ACTIVATED CHARCOAL FROM BRAZIL NUT WASTE

The Brazil nut shells (*Bertholletia excelsa* L.) were collected from a local market in Brazil. The raw biomass was manually crushed to reduce particle size and then thoroughly washed with deionized water to remove dust, oils, and other impurities. The washed material was subsequently dried in a convection oven at 105 °C for 12 hours to eliminate moisture content. For the production of activated carbon, a two-step thermal method was employed, following the procedures adapted from Ello et al. (2013) and Thomaz et al. (2023). Initially, the dried biomass was sieved to a particle size of 1–2 mm to ensure uniform thermal treatment. Approximately 50 g of the dried material was placed in ceramic crucibles and introduced into a muffle furnace for carbonization. During the carbonization step, the furnace was purged with nitrogen gas (N<sub>2</sub>) at a constant flow rate of 150 mL min<sup>-1</sup> to create an inert atmosphere and prevent oxidation. The temperature was raised from room temperature to 600 °C at a heating rate of 10 °C min<sup>-1</sup> and maintained for 1 hour. After carbonization, the samples were cooled to room temperature under the same inert atmosphere. In the second stage, thermal activation was performed. The carbonized samples were subjected to a further thermal treatment at 800 °C for 3 hours in the same muffle furnace. After activation, the samples were allowed to cool down naturally to room temperature.

## CHARACTERIZATION OF ACTIVATED CHARCOAL

- *Specific surface area:* The analysis of the specific surface area was carried in a BET (Brunauer, Emmet and Teller) method by a porosimeter. Approximately 60 adsorption-desorption cycles of N<sub>2</sub> at 77 K was applied. The samples of activated charcoal were treated at the temperature of 250°C for 2 h before each test.
- *Medium Diameter and Total Pore Volume:* The mean diameter and total pore volume were obtained from the method of Barrett, Joyner and Halenda (BJH) by a porosimeter.
- *Surface functional groups:* The surface chemical properties of charcoal were determined by the acidity or basicity. which when treated with solutions such as nitric acid, sodium hypochlorite or hydrogen peroxide modify the nature and the amount of oxygen in the complex surface of charcoal.

## HEXAVALENT CHROMIUM (VI) AND BIVALENT COPPER (II) SOLUTIONS PREPARATIONS

The solution of 1000 ppm (mg L<sup>-1</sup>) of hexavalent chromium was prepared from 100% potassium dichromate salt (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) P.A. The pH and solution temperature are 5.48 and 26.2 °C, respectively. They were measured using a potentiometer pH<sub>21</sub> from HANNA company. The bivalent copper was prepared from copper sulphate salt (CuSO<sub>4</sub>.5H<sub>2</sub>O) P.A. The pH and solution temperature equal to 5.7 and 26.5 °C. Aliquots were taken from these solutions to prepare aqueous solutions of both Cr(VI) and Cu(II) at the concentrations of 5, 10, 20, 30, 50, 100, 150 and 200 mg L<sup>-1</sup>. The reagents were provided from Reagem company.

## ADSORPTIONS EXPERIMENTS

The adsorption experiments were carried out in batches using a 250 mL Erlenmeyer. 100 mL of Cr (VI) and Cu (II) solutions were tested, separately, at initial concentrations of 5, 10, 20, 30, 50, 100, 150 and 200 mg L<sup>-1</sup>. Duplicate experiments were carried out for each concentration using 1 g of the activated charcoal. The Erlenmeyer were closed and submitted to agitation, for 60 min at a frequency of 150 rpm. After, the samples were filtered using qualitative filter paper.

The samples were added to tubes for subsequent analysis of the final concentration of chromium and copper. They are conducted in an AA 904

atomic absorption spectrophotometer from CG Scientific instruments LTDA. From the equilibrium concentration data and Equation 1 it is possible to calculate the percentage metal removal,  $R(\%)$  of each heavy metal.

$$R(\%) = \left[ \frac{(C_i - C_e)}{C_i} \right] 100 \quad (1)$$

where  $C_i$  is initial concentration of Cr (VI) and Cu (II) ( $\text{mg L}^{-1}$ ) and  $C_e$  is the final or equilibrium concentration of Cr (VI) and Cu (II) ( $\text{mg L}^{-1}$ ). The equilibrium study of the amount of metal adsorbed per mass of coal was calculated by:

$$Q_e = \frac{(C_i - C_e)V}{M} \quad (2)$$

where  $Q_e$  is amount of Cr (VI) and Cu (II) adsorbed by the adsorbent ( $\text{mg}$  of adsorbate/ $\text{g}$  of adsorbent),  $C_i$  is initial concentration of Cr (VI) and Cu (II) ( $\text{mg L}^{-1}$ ),  $C_e$  is equilibrium concentration of Cr (VI) and Cu (II) ( $\text{mg L}^{-1}$ ),  $V$  is volume of solution ( $\text{L}$ ) and  $M$  is mass of activated charcoal ( $\text{g}$ ).

## RESULTADOS E DISCUSSÃO

The textural analyses of the activated charcoal produced from Brazil nuts waste are shown in Table 1. They reveal that the specific area of activated charcoal is approximately:  $443 \text{ m}^2\text{g}^{-1}$  by BET analyses,  $455 \text{ m}^2\text{g}^{-1}$  from relative pressure ( $P/P_0$ ) and  $613 \text{ m}^2\text{g}^{-1}$  from Langmuir methods. The pore volume is  $0.0531 \text{ cm}^3 \text{ g}^{-1}$  and the diameter is  $5.01642 \text{ nm}$ . They were obtained by the BJH method (Barret, Joyner and Halenda). According to Figueroa et al. (2008), the adsorption capacity can be influenced by the characteristics of the adsorbate and the nature of its surface, which in turn is associated with the activation process and the characteristics of the raw material. As shown in Table 1, the values for specific surface areas, considering the BET and BJH methods, are relatively high. They indicate good porosity of the sample and, consequently, an interesting adsorption capacity.

Tabela 1- Áreas Superficiais Específicas, Volume e Raio de Poros

BET Area ( $\text{m}^2/\text{g}$ )	BJH Area ( $\text{m}^2/\text{g}$ )	Porus Volume ( $\text{cm}^3/\text{g}$ )	Porus diameter ( $\text{nm}$ )
443	455	0.0531	5.01642

According to the recommendations of the IUPAC (International Union of Pure and Applied Chemistry), porous materials are classified into groups based on pore size: micropores ( $< 2 \text{ nm}$ ), mesopores (between  $2$  and  $50 \text{ nm}$ ), macropores ( $> 50 \text{ nm}$ ), ultramicropores ( $< 0.7 \text{ nm}$ ), and supermicropores (between  $0.7$  and  $2 \text{ nm}$ ) (Thommes et al., 2015). Therefore, based on the presented data, the pores of the sample in question are classified as mesopores. They are pores with sizes between  $2$  and  $50 \text{ nm}$ , offering a balance between surface area and



accessibility. They are crucial for applications like catalysis, gas storage, and filtration, as they allow efficient adsorption and faster diffusion of molecules compared to micropores.

The adsorption process is studied using experimental techniques that evaluate the equilibrium state through pressure variation in the free fluid (volumetric or manometric method) or through the weight gain of the adsorbent (gravimetric method). By varying the gas pressure and measuring the amount adsorbed, either volumetrically or gravimetrically, it is possible to construct the adsorption isotherm, as shown in Figure 2.

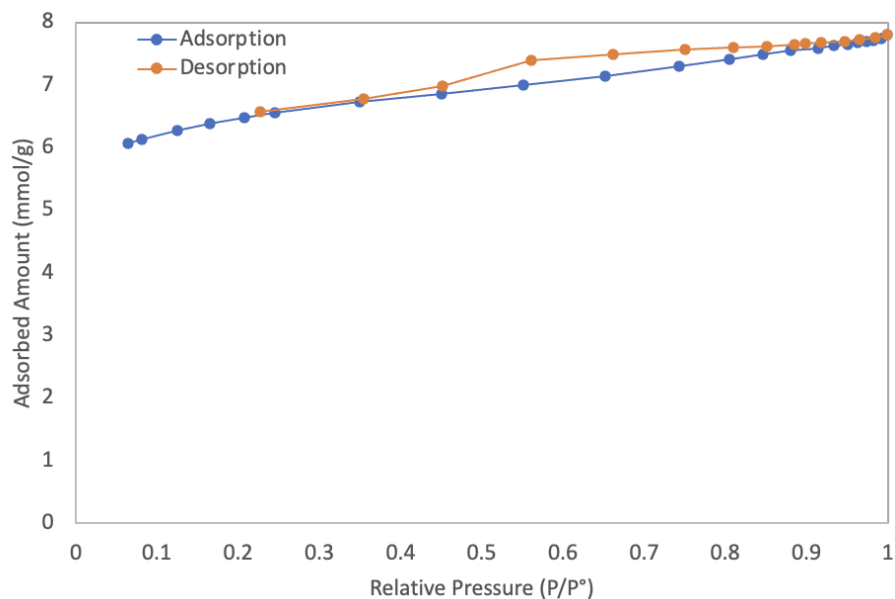


Figure 2 - Adsorption and desorption isotherms

Figure 2 indicates that the isotherms are type 2, as classified by IUPAC, are characteristic of materials with a wide distribution of pore sizes, typically mesoporous materials. These isotherms exhibit a sigmoidal shape, where adsorption occurs rapidly at low pressures, filling smaller pores first. As pressure increases, adsorption slows, and larger pores start to contribute, with the plateau representing the maximum adsorption capacity. Type 2 isotherms indicate multilayer adsorption, driven by intermolecular forces like van der Waals forces, and are common in materials with high surface areas and significant porosity, useful in applications such as gas storage and purification. Agro-industrial residues like coconut shell (Saka et al., 2012), with a BET surface area of 894 m<sup>2</sup>/g, sugarcane bagasse (Dotto et al., 2013), with a BET surface area of 612 m<sup>2</sup>/g, olive pit (Ioannidou & Zabaniotou, 2007), with a BET surface area of 687 m<sup>2</sup>/g, and tamarind seeds (Naiya et al., 2009), with a BET surface area of 1137 m<sup>2</sup>/g, have shown high adsorption efficiency after physical or chemical activation.

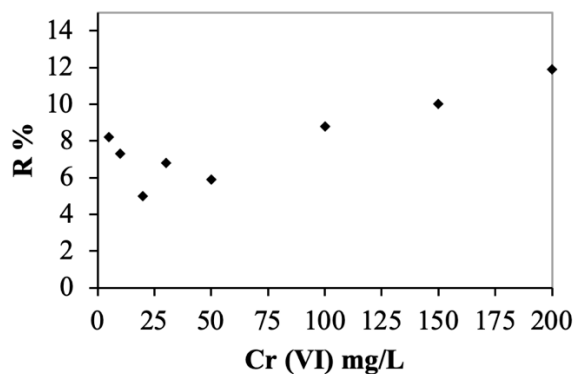
Besides, the activated charcoal has a basic character. Basic coals develop basic oxides on their surface and in their ashes. These are responsible for raising the pH when in solution, thus adsorbing acidic compounds. Boehm's titration

identified a greater quantity of phenolic hydroxyl groups (-OH, 79.56%) than carboxylic groups (-COOH, 16.98%) and lactones (-COOR, 3.46%).

In order to evaluate the Cr (IV) adsorption behavior by activated charcoal, Table 2 and Figure 3 show the percentage removal of Cr (VI) for several CR(VI) solutions concentrations. The experiments were conduct in duplicate, A and B tests, as shown in Table 3.

**Table 2** - Influence of initial Cr (VI) concentration on adsorption

Ci (mg/L)	A Ce(mg/L)	B Ce(mg/L)	Ce (mg/L) Média	(R%)
5	4,87	4,31	4,59	8,2
10	9,61	8,93	9,27	7,2
20	19,1	18,88	18,99	5,0
30	27,2	28,73	27,97	6,8
50	47,96	46,13	47,05	5,9
100	89,74	92,59	91,17	8,8
150	137,79	132,26	135,03	10,3
200	172,54	179,7	176,12	11,3

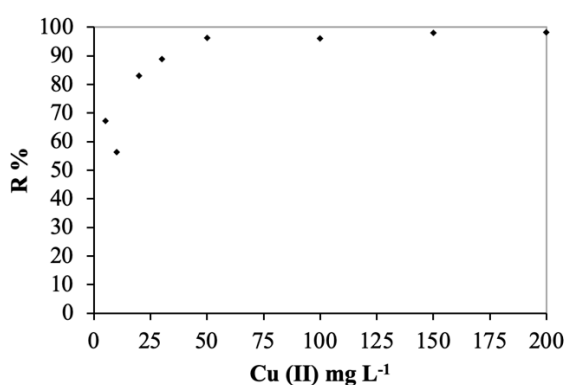


**Figure 3** – Cr (VI) removal for several initial concentration of the solution

The adsorbent's ability to remove Cr (VI) depends on the surface area and chemical composition of the chestnut shell charcoal where the active functional groups are responsible for removing the chromium. The results from Table 2 and Figure 3 showed that the removal of the metal Cr (VI) was not significant (less than 10%, in average), indicating that the surface of the charcoal is not favorable for the adsorption of hexavalent chromium. In order to compare the results, the experiments from the bivalent copper Cu (II) adsorption were carried out using the same methodology as mentioned above. The results of the adsorption efficiency of Cu (II) by activated charcoal, for several initial concentration (Ci) of Cu (II), from a solution of copper sulphate (CuSO4), are shown in Table 3 and Figure 4.

**Table 3** – Influence of initial Cu (II) concentration on adsorption

Ci (mg/L)	A Ce(mg/L)	B Ce(mg/L)	Ce(mg/L) Média	(R%)
5	1,70	1,58	1,64	67,2
10	4,18	4,57	4,38	56,2
20	3,71	3,12	3,42	82,9
30	3,24	3,46	3,35	88,8
50	1,04	2,80	1,92	96,1
100	3,87	4,10	3,99	96,0
150	2,29	3,81	3,05	97,9
200	4,63	2,90	3,77	98,1

**Figure 4** – Cu (II) removal for several initial concentration of the solution

The graphs in Figure 3 and Figure 4 show the removal curves for Cr (VI) and Cu (II), respectively, as a function of initial metal concentrations and activated carbon performance. In Figure 3, the removal curve for Cr (VI) shows a sharp increase in adsorption efficiency with rising initial concentrations, reaching a peak before leveling off, indicating that the activated carbon has a limited capacity and becomes saturated. In contrast, Figure 4 for Cu (II) demonstrates a more gradual and stable removal efficiency across different concentrations, suggesting a stronger affinity of the activated carbon for Cu (II) ions. This reflects both the chemical properties of the metals and the carbon's pore structure, which may be more effective for larger ions. Overall, both curves show that removal efficiency decreases as metal concentration approaches the adsorption capacity of the carbon.

The Cu (II) removal efficiency was above 80% for concentrations above 20 mg L<sup>-1</sup>. The lower mass transfer flow in the first stages of the adsorption mechanism explains the reduction in removal efficiency for concentrations of 5 and 10 mg L<sup>-1</sup> as explained by Pinto (2011). A comparative analysis of the adsorption between the two metals reveals that potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) showed high solubility in water forming hydrogenated chromate ion or acid chromate (HCrO<sub>4</sub><sup>-</sup>). This ion, at a pH of around 5.20, showed low electrostatic interaction with the charcoal surface. So, acid chromate requires high electrostatic energy with the charcoal surface in order to be adsorbed. On the other hand, the hydrolysis of CuSO<sub>4</sub>, which has low solubility in water and

excellent interaction with the surface of the adsorbent, obtaining good efficiency in the removal of Cu (II), above 90% for most of the analyses, using the same activated charcoal.

Some characteristics of the charcoal, such as: the predominance of basic groups (OH- represents more than 78%), the low concentration of carboxylic groups (COOH - less than 18%) and the presence of an H4-type hysteresis, can be associated to very narrow slit-shaped pores, indicating microporosity and reducing, significantly, the efficiency of chromium removal. Therefore, according to Silva (2012), the low removal of metal can be attributed to the chemical characteristics of the adsorbent surface. These include a predominance of basic groups, low concentrations of ionizable groups (carboxylic groups) and high hydrophobicity. The mechanism of electrostatic interactions between the ions formed during hydrolysis and the active surface of the activated charcoal determines the efficiency of the metal removal process. Finally, this findings are in agreement with literature Babel and Kurniawan, (2004), who studied the adsorption of Cr (VI) by activated charcoal, without pH control, showing low efficiency in removing the metal.

Although electrostatic interaction is a key factor in the adsorption of heavy metals, it is important to detail how this interaction occurs between metal ions and the functional groups on the surface of activated carbon. The surface of activated carbon is rich in functional groups, such as carbonyls ( $-\text{C}=\text{O}$ ), hydroxyls ( $-\text{OH}$ ), carboxyls ( $-\text{COOH}$ ), and phenols ( $-\text{C}_6\text{H}_5\text{OH}$ ), which have negative charges or can form hydrogen bonds with metal cations. Metal ions like  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$ , with positive charges, are attracted to these negatively charged surfaces, establishing electrostatic interactions. Additionally, metal ion adsorption can occur through ion exchange, where metal ions replace hydrogen or other cations on the surface of activated carbon. This mechanism is particularly relevant for metals like  $\text{Cu}^{2+}$ , which have a strong tendency to interact with carboxylic and phenolic groups, forming coordination complexes with the oxygen atoms of these groups. This type of interaction increases the affinity between the metal and the surface, optimizing the adsorption process.

## CONCLUSIONS

This paper investigates the use of Brazil nut bark (*Bertholletia excelsa* L.) to produce thermally modified activated charcoal and evaluates its ability to adsorb hexavalent chromium (Cr (VI)) and bivalent copper (Cu (II)). The results indicate that activated charcoal, with a surface area of  $443 \text{ cm}^2/\text{g}$ , without any surface treatment, is not very effective in removing Cr (VI) from aqueous solutions. The low adsorption of chromium may primarily be attributed to hydrophobic interactions between the activated charcoal and the metal ions, along with the potential influence of other factors such as pH and the chemical properties of the charcoal. For Cr (VI) concentrations of 150 and  $200 \text{ mg L}^{-1}$ , the highest adsorption (around 12%) is observed in the initial stages of the process, likely due to the high mass transfer rate. In contrast, for copper (Cu (II)), the activated charcoal showed excellent adsorption capacity,

as indicated by the higher removal percentages, demonstrating a stronger affinity for copper compared to chromium. These findings suggest that surface characteristics, including the presence of functional groups and the pH of the solution, play crucial roles in the adsorption process. Future studies should explore not only the impact of pH but also other variables such as contact time, activation temperature, and pre-treatment methods to further optimize the adsorption capacity of activated charcoal.

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