Cashew nut shell (*Anarcadium accidentale L*) charcoal as bioadsorbent to remove Cu\(^{2+}\) and Cr\(^{3+}\)

Carvão da casca da castanha de caju (*Anarcadium accidentale L*) como bioadsorvente para remover Cu\(^{2+}\) e Cr\(^{3+}\)

Carbón de la cáscara del anacardo (*Anarcadium accidentale L*) como bioadsorbedor para eliminar Cu\(^{2+}\) y Cr\(^{3+}\)

Received: 01/21/2021 | Reviewed: 01/23/2021 | Accept: 01/25/2021 | Published: 01/02/2021

Karine Fonseca Soares de Oliveira
ORCID: https://orcid.org/0000-0002-4895-0887
Universidade Federal do Rio Grande do Norte, Brasil
E-mail: karine_953@hotmail.com

Joemil Oliveira de Deus Junior
ORCID: https://orcid.org/0000-0002-5633-1808
Universidade Federal do Rio Grande do Norte, Brasil
E-mail: joemiljunior@gmail.com

Talita Lorena da Silva do Nascimento
ORCID: https://orcid.org/0000-0002-8103-4047
Universidade Federal do Rio Grande do Norte, Brasil
E-mail: talitalorenasn@gmail.com

Raoni Batista dos Anjos
ORCID: https://orcid.org/0000-0002-4612-0855
Universidade Federal do Rio Grande do Norte, Brasil
E-mail: raonianjos@gmail.com

Dulce Maria de Araújo Melo
ORCID: https://orcid.org/0000-0001-9845-2360
Universidade Federal do Rio Grande do Norte, Brasil
E-mail: daraujomelo@gmail.com

Renata Martins Braga
ORCID: https://orcid.org/0000-0002-6232-0945
Universidade Federal do Rio Grande do Norte, Brasil
E-mail: renatabraga.r@gmail.com

Marcus Antonio de Freitas Melo
ORCID: https://orcid.org/0000-0003-3697-2859
Universidade Federal do Rio Grande do Norte, Brasil
E-mail: mafm.ufrn@gmail.com

**Abstract**

Lignocellulosic materials have been used as bioadsorbents for contaminants removal from industrial effluents due to their physical-chemical properties, renewable source, low-cost and efficiency that make them competitive to commercial activated carbon. The objective of this work is to develop an efficient and low cost bioadsorbent reusing the cashew nut shell (*Anarcadium accidentale L*), CNS, for the removal of metal ions (Cu\(^{2+}\) and Cr\(^{3+}\)). The CNS was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), the point of zero charge (pHpzc) and the Boehm titration. The kinetics and adsorption equilibrium experiments were carried out in a monoelementary system, in batch runs at room temperature. The adsorption kinetics was evaluated by the mathematical models of pseudo first-order, pseudo second-order and intraparticle diffusion, while the adsorption isotherm was adjusted according to the Langmuir, Freundlich and Redlich-Peterson models. The removal percentage was 91% (Cu\(^{2+}\)) and 96% (Cr\(^{3+}\)) and adsorption kinetics was better adjusted to the pseudo second-order model, suggesting the predominance of chemisorption. The fit of the Langmuir isotherm was better for the experimental data of Cu\(^{2+}\) and Cr\(^{3+}\) ions, indicating adsorption in monolayers. It is concluded that the bioabsorbent produced from the cashew nut shell has a high potential for the removal of metals, in addition to being an abundant product in nature, is renewable and biodegradable and its reuse contributes to the reduction of environmental pollution, the production of waste and improves the local circular economy through the valorization of the byproduct.

**Keywords:** Adsorption; Metals; Biomass; Agro-industrial waste; Sustainability.
Introduction

In recent decades, the industrial growth has contributed significantly to the water and soil pollution. Currently, serious problems caused by contamination by organic and inorganic chemical pollutants through the inappropriate disposal of industrial wastewater, mining and agricultural activities has gained prominence in society. Water pollution is a major concern as it causes a change in the physicochemical and biological characteristics of water, which affects the environment and the ecosystem of the affected regions (Santos et al., 2019).

Water pollution by toxic metal ions has attracted attention due to its high toxicity, non-biodegradability, bioaccumulation in the food chain, as well as its carcinogenic and mutagenic potentials (Santos et al., 2019). The most common heavy metals found in the environment are chromium (Cr), nickel (Ni), zinc (Zn), manganese (Mn), copper (Cu), cobalt (Co) and lead (Pb) (Soliman e Moustafa, 2020). Among these toxic metals, Cu²⁺ and Cr⁶⁺ ions are easily found in industrial effluents and may cause different problems to human health and the environment. Exposure to high concentrations of chromium, for a short period of contact, causes skin ulcers and irritation to the nasal mucosa (Ma et al., 2019). Copper traces are essential for plant and animal growth; however, excess may cause brain and heart disease in humans (Badsha et al., 2020).

The liquid effluent generated by industries has high toxicity and complexity in its composition and this has led to the development of new technologies that request adequate treatment so that the limits of the contaminants are within the...
requirements established by the environmental laws in force in the country, state or municipality (Tavares, Souza e Santos, 2020). In recent years, several methods such as reverse osmosis, oxidation/precipitation, bioremediation, nanofiltration, photodegradation and adsorption have been developed to improve the removal of metals and other contaminants in polluted media (Zhang, Zeng e Cheng, 2016). However, most of these methods have disadvantages such as high operating costs, disposal of final waste, in addition to an enormous energy expenditure (Bhatnagar e Sillanpää, 2011).

Adsorption is the most widely used process, as it is easy to handle, has a low operating cost, high removal efficiency, is versatile and environmentally friendly. The main adsorbent is the activated carbon (AC), because it has a high specific area, microporosity and a high adsorption capacity, but it has a high cost and is hardly regenerated or reactivated after each adsorption cycle (SenthilKumar et al., 2011). One of the alternatives for replacing AC is the use of lignocellulosic materials as a bioadsorbent, and its use has been promising due to the excellent physical and chemical properties, as well as its availability in nature and its renewable and biodegradable properties (Velazquez-Jimenez, Pavlick e Rangel-Mendez, 2013).

Lignocellulose is a polymer formed by cellulose, lignin and hemicellulose and contains many hydroxyl groups on the surface, which can be easily modified to improve the performance of the material. Therefore, research regarding lignocellulosic residues for the removal of contaminants have increased worldwide, as may be seen in Figure 1, which displays the increase in the number of articles containing the keywords "lignocellulosic + adsorbent" published in the last decade in indexed journals.

**Figure 1.** Published articles containing keyword "lignocellulosic + adsorbent" published from 2010 to 2020. The data were obtained from “Science Direct”.

As seen in Figure 1, the works related to the keywords “lignocellulosic + adsorption” have increased considerably in the last 10 years. In 2018, approximately 218 papers were published, in 2020 this number increased to 1304, drawing the attention of researchers and reinforcing the importance of the applicability of these by-products.

The fruit processing industry is constantly expanding, and normally the fruit shells are discarded, corresponding to about 30 to 43% of the fruit, generating large amounts of waste and causing environmental pollution due to excessive release to the environment. (Santiago et al., 2021). These materials are rich in lignocellulose and the cashew nut shell is a kind of these materials that comes from the processing of cashew (Anarcadium occidentale L). The culture of the cashew nut plays an important role in the Brazilian socioeconomic context, since the process of obtaining the nut may be carried out by
cooperatives of rural producers, small factories and even large industries, creating jobs for the local population (Coelho et al., 2014). In Brazil, the main producer is the state of Ceará, with an estimated production of 81.1 thousand tons. The state of Rio Grande do Norte, the third largest producer in Brazil, annually produces approximately 20.7 thousand tons of cashew nuts, of which 2 thousand tons are residue (CONAB, 2019). This residue may be reinserted in the firing process, in the boiler, or is often disposed incorrectly, causing damage to the soil due to the corrosivity and flammability of the cashew nut shell liquid (CNSL).

The creation of sustainable agro-industrial systems has united agricultural production chains and researchers in the search of socio-environmental solutions for the treatment of effluents using bioadsorbents, which may be reinserted in the production process in order to add economic value to these by-products. Therefore, the objective of this work is to develop an efficient and low cost bioadsorbent for the removal of metal ions (Cu$^{2+}$ and Cr$^{3+}$), reusing the biochar from the cashew nut shell, which has a great potential for use as a bioadsorbent. Besides, the use of this by-product favors the circular economy by reusing the waste generated in the process and, therefore, attributes an economic value and improves the local economy.

2. Methodology

Figure 2 presents the general flowchart of the experimental procedure used in this work.

![Figure 2. Experimental Procedure.](image-url)
In Figure 2, it can be seen, the material was pre-treated with NaOH to obtain the CNS that was characterized and submitted to the kinetic and isothermal studies that were carried out to evaluate the efficiency of the bioadsorbent. The description of these procedures will be detailed in the following sections.

2.1 Adsorbate preparation

For the adsorption studies, solutions of 100 mg/mL of Cu$^{2+}$ and Cr$^{3+}$ were prepared using nitrates (Cu(NO$_3$)$_2$.3H$_2$O P.A. ≥ 99% from VETEC and Cr(NO$_3$)$_2$.9H$_2$O P.A. ≥ 99% from SIGMA-ALDRICH). Further solutions at different concentrations were prepared from the dilution of the stock solution.

2.2 Bioadsorbent preparation

Cashew nut shell (Anacardium occidentale L) was obtained from the cashew processing at a cooperative located in the city of Serra do Mel, state of Rio Grande do Norte, Brazil. The shells were washed with distilled water, dried in an oven at 80 °C for 24 h and grounded in an industrial blender. After this process, a granulometric separation was carried out to select particles with diameter between 1.19 – 0.841 mm.

This method was carried out by Moreira et al. (2009). In erlenmeyers containing 3.0 g of biomass were added to 75 mL of 0.1 mol/L NaOH (VETEC, 99%) solution and were shaken at 25 °C for 6 h. NaOH excess was removed from bioadsorbent using distilled water until reaching a neutral pH. The biomass was dried in an oven at 80 °C for 24 h and the resulting material was named CNS.

2.3 Material characterization

The point of zero charge (pHpzc) characterizes the surface charge in the sample, where the variety of functional groups on the material surface determines the magnitude of pH. The pHpcz was determined according to the method developed by Babić et al. (1999), which uses 0.1 g of the material and 25 mL of a 0.1 mol/L KCl (VETEC, 99%) solution with pH varying from 1 to 12, adjusted with diluted HCl, 0.1 mol/L, or NaOH (0.1 mol/L). The systems were kept under constant agitation at room temperature for 24 h and then were filtered, so that the final pH values were obtained.

The Boehm titration method involves the selective neutralization of the functional groups on the surface of activated carbon by titration with different strength bases when they are acidic and with acidic solutions when they are basic. Carboxylic acids are neutralized by reaction with NaHCO$_3$; carboxylic acids and lactones are neutralized by Na$_2$CO$_3$ and all of these groups, including phenols, can be neutralized by NaOH (Moradi-Choghamaran, Moosavi e Baghernejad, 2019). The method consists in which 0.5 g of biomass is added in standard solutions of HCl (0.1 mol/L), NaOH (0.1 mol/L), NaHCO$_3$ (0.1 mol/L) and Na$_2$CO$_3$ (0.05 mol/L) in separated flasks of 150 mL. The flasks were sealed and kept under agitation at room temperature for 24 h in a shaking table. The solutions were filtered and the supernatant was back titrated with HCl (0.1 mol/L).

The functional groups detection was carried out by the Fourier Transform Infrared Spectroscopy (FTIR) technique, using the IRPrestige-2 from SHIMADZU, in the region between 400 and 4000 cm$^{-1}$ by transmittance with a KBr pellet.

Bioadsorbent’s morphology was observed through a Scanning Electronic Microscope (SEM) from SHIMADZU, model SSX-550 with a 15 kV tension, tungsten filament and equipped with secondary detectors. Samples were fixed in a metallic support with carbon tape and then coated with gold before the analysis.
2.4 Adsorption experiments

2.4.1 Adsorption kinetics

Erlenmeyers containing 0.1 g of the bioadsorbent and 50 mL of the metallic ions solutions (Cr\(^{3+}\) and Cu\(^{2+}\)) at 50 mg/mL and pH 5.0 were submitted to constant agitation in a thermostatic shaker. Aliquots were removed in time intervals of 5, 10, 15, 30, 45, 60, 90, 120, 150, 180, 240 and 300 min. Then, the samples were filtered, and the residual ions concentrations were determined by Atomic Absorption Spectroscopy in a SHIMADZU AA-6300, flame mode. An analytical standard of each concentration was submitted at the same samples conditions and analyzed.

2.4.2 Adsorption isotherms

Adsorption isotherms were obtained from the addition of 0.1 g of bioadsorbent in an Erlenmeyer of 125 mL containing 50 mL of the metallic ions (Cu\(^{2+}\) and Cr\(^{3+}\)) solutions at pH 5.0 and in a concentration range from 10 to 100 mg/L (Velazquez-Jimenez, Pavlick e Rangel-Mendez, 2013). The flasks were shaken in a thermostatic shaker at 150 rpm and room temperature for 2 h. After that, the samples were filtered with filter paper and the concentrations of the metallic ions were measured. The adsorbent efficiency (%R) was calculated by Equation 01 and the adsorbed amount (q\(_{eq}\)) by Equation 2:

\[
\%R = \frac{C_i - C_{eq}}{C_i} \times 100 \quad \text{Eq. 01}
\]

\[
q_{eq} = \frac{C_i - C_{eq}}{m} \times V \quad \text{Eq. 02}
\]

where \(C_i\) is the initial metal concentration (mg/L); \(C_{eq}\) is the metal concentration at equilibrium (mg/L); \(m\) is the adsorbent mass (g); \(V\) is the volume of the solution (L).

Table 1 summarizes all models and equations used for evaluation of adsorption in this article.
Table 1. Models used for the evaluation of adsorption of Cu$^{2+}$ and Cr$^{3+}$ ions in cashew nut shell.

| Model            | Equation                                                                 | Parameters                                                                 |
|------------------|--------------------------------------------------------------------------|---------------------------------------------------------------------------|
| **Isotherm models** |                                                                          |                                                                           |
| Langmuir         | $q_{eq} = \frac{q_{max}K_L C_{eq}}{1 + K_L C_{eq}}$                       | $q_{eq}$ (mg/g): sorption capacity at equilibrium                           |
|                  |                                                                          | $q_{max}$ (mg/g): maximum sorption capacity                                |
|                  | $RL = \frac{1}{(1 + K_L C_0)}$                                           | $K_L$ (L/mg): Langmuir’s constant                                          |
|                  |                                                                          | $C_{eq}$ (mg/L): concentration at equilibrium                              |
|                  |                                                                          | $R_L$: separation factor                                                   |
|                  |                                                                          | $C_0$ (mg/L): higher initial concentration                                 |
| Freundlich       | $q_{eq} = K_F C_{eq}^{1/n}$                                               | $K_F$ (mg/g)(L/mg)$^{1/n}$: Freundlich’s constant                          |
|                  |                                                                          | $n$: heterogeneity factor                                                  |
| Redlich-Peterson | $q_{eq} = \frac{K_{RP} C_{eq}}{1 + \alpha_{RP} q_{eq}^{\beta}}$          | $\alpha$: Redlich-Peterson’s parameter                                     |
|                  |                                                                          | $\beta$: Redlich-Peterson’s parameter                                      |
| **Kinetic models** |                                                                          |                                                                           |
| Pseudo first-order | $ln(q_{eq} - q_t) = ln q_{eq} - k_1 t$                                      | $q_t$ (mg/g): sorption capacity at time $t$                               |
|                  |                                                                          | $k_1$ (1/min): pseudo first-order’s constant rate                         |
| Pseudo second-order | $\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}$              | $k_2$ (1/min): pseudo second-order’s constant rate                         |
| Intraparticle diffusion | $q_t = k_d t^{0.5} + C$                                                  | $k_d$ (mg/min$^{1/2}$): intraparticle diffusion’s parameter               |
|                  |                                                                          | $C$ (mg/g): intercept                                                      |

Source: Adapted Almeida e Santos (2020).

The models in Table 1 are to understand the sorption process of the experimental data, Langmuir, Freundlich and Redlich-Peterson isotherms models (Almeida e Santos, 2020) and kinetics models (pseudo first-order, pseudo second-order and intraparticle diffusion) (Schwantes et al., 2018) were applied.

3. Results and Discussion

3.1 Bioadsorbent characterization

The pH affects the adsorption process, as it determines the degree of distribution of chemical species. The pH intensity varies a lot and can be accentuated or not, since the surface loads depend on the composition and surface characteristics of the biomass (Appel et al., 2003). Figure 3 presents the graph for determining the pH at the point of zero charge, the data obtained were plotted on a $\Delta p\text{H}$ versus pH$_0$ graph.
Figure 3. pH at point of zero charge (pzc) of natural biomass and pre-treated with NaOH (CNS).

The point of intersection of the graph (Figure 3) obtained where pH0 = pHf was identified as the point at which the change in the pH of the solution was zero, hence the pHpzc value. The point of zero charge of the natural biomass and CNS was approximately 4.0 and 5.2, respectively, as shown in Figure 3, indicating surface acidity for the precursor material, caused by the residual existence of the CNSL (Cashew Nut Shell Liquid) which contains anacardic acid in its composition (Mazzetto, Lomonaco e Mele, 2009). The surface of CNS is protonated at a pH less than 5.2, favoring the adsorption of negatively charged compounds, and deprotonated at a pH greater than pHpzc, favoring the adsorption of cations. According to Sousa Neto et al. (2012) the increase in pHpzc of the treated material indicates a decrease in the number of positive charges, probably due to the dissociation of the functional groups carboxyl, carbonyl and phenol on the surface. Thus, each functional group on the surface may dissociate or associate protons from the solution depending on the properties of the adsorbent (Largitte et al., 2016).

The determination of the total acidic and basic sites determined by the Boehm titration, Table 2, shows that the total concentration of acidic sites is much higher than those of basic sites referring to the composition of lignocellulosic materials.
Table 2. Acid and basic surface groups present in the natural biomass and treated with NaOH (CNS).

| Sample          | Acid Groups (mmol/g) | Basic groups (mmol/g) |
|-----------------|----------------------|-----------------------|
|                 | Carboxylic | Lactonic | Phenolic |               |
| Natural biomass | 0.114       | 0.408   | 0.355    | 0.261         |
| CNS             | 0.053       | 0.326   | 0.203    | 0.316         |

Source: Authors (2021).

As seen the Table 2 may analyze the natural biomass surface has a high content of acid groups, especially phenolic groups, which are present in lignin and cellulose. However, after the modification the content of basic sites in CNS becomes higher than in natural biomass, as may be seen in the pHzpc value. This change that occurs after alkaline treatment indicates that the surface has more oxygenated functional groups with basic characteristics, such as hydroxyl, carbonyl and carboxyl that have amphoteric properties, along with the ketone, ether, pyrone and chromene groups (Šoštarić et al., 2018).

The Figure 4 shows the FTIR spectra, they were performed in the range of 400 to 4000 cm\(^{-1}\) for the natural cashew nut shell and pre-treated with sodium hydroxide (CNS).

Figure 4. Infrared Spectra of natural biomass and CNS.

The graphs (Figure 4) show the existence of bands, which that are characteristic of lignocellulosic materials as such carbonyls, carboxyls, phenols, esters and polysaccharides. Anionic groups may be responsible for the mechanism of adsorption of contaminants on the surface of the material. These bands can be confirmed in the Table 3, it summarizes the positions of the main peaks of both materials as well as its attributions.
Table 3. Peak position of FTIR spectra of natural biomass and treated with NaOH (CNS).

| Waveleght (cm\(^{-1}\)) | Natural biomass | CNS | Functional groups | Attribution | Reference |
|--------------------------|-----------------|-----|-------------------|-------------|-----------|
|                          |                 |     | Axial deformation of the O-H group | Cellulose and lignin | (Tavares, Souza e Santos, 2020) |
| 3791                     | 3788            |     |                  |             |           |
| 2924                     | 2921            |     | Axial deformation of the C-H group | Extractives and cellulose | (Coelho et al., 2014) |
| 2859                     | 2849            |     | Stretching C-H\(_n\) |             |           |
| 1612                     | 1601            |     | Stretching vibration C-O | Hemicellulose and lignin | Šoštarić et al. (2018) |
| 1454                     | 1447            |     | OH bound | Phenol and alcohol | Moradi-Choghamarani et al. (2019) |
| 1150                     | 1157            |     | Streching C-O-C | Hemicellulose and lignin | Santos et al. (2019) |
| -                        | 1103            |     | Deformation O-H | Phenol and alcohol | Velazquez-Jimenez et al. (2013) |

Source: Authors (2021).

Bands between 3800 to 3400 cm\(^{-1}\) are present in the materials and are attributed to the vibrational stretching of the O-H bonds, due to the adsorbed water and the presence of hydroxyl groups (OH-) of alcohols, carboxylic acids and phenols, widely found in lignocellulosic materials (Guimarães et al., 2020). There are two distinct peaks in the region between 2600 and 3000 cm\(^{-1}\) that refer to the axial deformation of the C-H bond of alkane and aliphatic acid groups (Coelho et al., 2014). Three bands found at CNS between 1150-1050 cm\(^{-1}\) are associated with the C-O stretching of phenols and O-H of alcohols (Neris, Luzardo, Francisco Heriberto Martinez, et al., 2019). After the alkaline pretreatment there was a decrease in peak intensity between 900-500 cm\(^{-1}\) characteristic of the deformation of aromatic C-H bond, due to the solubilization of lignin in the solution (Šoštarić et al., 2018).

It is important to note that the presence of oxygen-containing groups, such as carboxylic acids, lactones, phenols, carbonyls, ethers or quinones on the surface of the activated carbon determines the acidity or basicity of the surface and influences its properties, depending on the pH of the aqueous solution (Guimarães et al., 2020). The chemical characterization of the surface of the bio-absorbent produced from the cashew nut shell showed the existence of several functional groups such as -OH (hydroxyl), -CH (carboxylate) and -C = O (carbonyl), which are considered as good indicative for the adsorption of metals, as they act as active sites, contributing to a good performance of the material.

The SEM imagens allow the observation of the microstructure of different bioadsorbents. The microstructures of the natural cashew nut shell and CNS are represented in Figure 5 and Figure 6, respectively.
After pretreatment (CNS) an irregular morphology was evidenced as seen in Figure 6. With the use of alkaline agents there is a swelling in the fiber causing its rupture, and this process favors the appearance of pores; however, in Figure 6 it is not possible to observe the superficial porous channels as was observed at CNS. It may be concluded that the surface of the bioadsorbent has a spongy, irregular and heterogeneous structure. According to Rubio et al. (2013) these aspects favor the adsorption of metals in aqueous solution.

### 3.2 Adsorption Kinetics

The adsorption kinetics of metal ions in the monoelementary solution was evaluated according to the variation of the adsorption capacity as a function of time as present in Figure 7.

The adsorption kinetics of metal ions in the monoelementary solution was evaluated according to the variation of the adsorption capacity as a function of time and is represented in Figure 7, representing time versus material adsorption capacity.
From the results of the kinetic experiment (Figure 7), it was possible to verify that the adsorption equilibrium time is fast, occurring in approximately 90 min for all metal ions, and after this time the adsorption occurs slowly up to 180 min. The adsorption kinetics is rapid initially (physisorption), occurring mainly on the external surface of the material, while the next step is slower because the process occurs on the internal surface of the adsorbent (chemisorption), until it reaches the equilibrium (Zimmer et al., 2020). A great advantage of a fast adsorption, in practice, is the use of a column, which requires an equipment with a smaller volume, ensuring a good efficiency and economy for the process (Moreira et al., 2009).

Some kinetic models were evaluated aiming a better understanding of the kinetic process of metallic ion adsorption by describing the behavior of the adsorption process as a function of time and, consequently, correlating the models to the limiting steps of the process. The parameters obtained in the model adjustment are reported in Table 4 and, for data interpretation, the correlation coefficient ($R^2$) determines the best fit and $Q_{eq}$ must be the closest to the experimental value ($Q_{eq(exp)}$) (Febrianto et al., 2009).
According Table 4, the pseudo second-order model adjusted well to the experimental data and for this reason is the model the best explains the adsorbent/adsorbate relation of the analyzed species. The $R^2$ values of the referred model were 0.999 for both Cu$^{2+}$ and Cr$^{3+}$. In addition, the experimental adsorption capacity obtained in the kinetic study is in agreement to the theoretical one calculated with this model.

The pseudo second-order model describes the process of chemical adsorption involving donation or sharing of electrons between the adsorbent and the adsorbate, such as covalent or ionic binding forces. The disadvantage of this type of adsorption is that the material regenerating process is difficult, due to the strong interaction between the adsorbent-adsorbate. The molecules in this type of adsorption are not attracted by the entire surface of the solid, but specifically by activated sites to form initially a monolayer, with the possibility of the formation of another layer by physisorption (Cardoso et al., 2020; Tural, Tarhan e Tural, 2016).

The adsorption process for other metallic ions using lignocellulosic bioadsorbents such as rice straw (Rocha et al., 2009), coconut dregs (Kamari et al., 2014), wheat straw (Liu e Fan, 2018), corn stalk (Liu et al., 2019) also follows the kinetic model of pseudo second-order.

### 3.3 Adsorption Isotherm
To a better understanding of the interaction and distribution of the metallic ions Cu$^{2+}$ and Cr$^{3+}$ on the surface of the CNS adsorbent, the monoelementary isotherms were built from the experimental data and then the adjustments of the Langmuir, Freundlich and Redlich-Peterson models were obtained through a non-linear regression using the Origin 8.0 © software. The graphs are represented in Figure 8 compare the fits of the Langmuir, Freundlich and Redlich-Peterson Models.
Figure 8. Comparison of the fits of the Langmuir, Freundlich and Redlich-Peterson models for the monoelement adsorption experimental data for the Cu\textsuperscript{2+} (a) and Cr\textsuperscript{3+} (b) metal ions.

The graphics obtained (Figure 8) result in the parameters of the adsorption isotherms, as seen in Table 5, it shows the values of the adjustment parameters of the Langmuir, Freundlich and Redlich-Peterson models for the monoelement adsorption experimental data for the metal ions studied. For all adjustments, the regression coefficients, $R^2$, were calculated, so that it is possible to identify the best fit.

Table 5. Adjustment parameters of the Langmuir, Freundlich and Redlich-Peterson models for the monoelementary adsorption experimental data for the metal ions Cu\textsuperscript{2+}(a) and Cr\textsuperscript{3+}(b).

| Model              | Parameters | Cu\textsuperscript{2+} | Cr\textsuperscript{3+} |
|--------------------|------------|-------------------------|-------------------------|
| Langmuir           | $q_{\text{max}}$ (mg/g) | 49.8                    | 41.17                   |
|                    | $K_L$      | 0.059                   | 0.377                   |
|                    | $R_L$      | 0.13 – 0.63             | 0.02 - 0.16             |
|                    | $R^2$      | 0.942                   | 0.984                   |
| Freundlich         | $n$        | 1.42                    | 3.29                    |
|                    | $K_F$      | 8.13                    | 14.99                   |
|                    | $R^2$      | 0.896                   | 0.856                   |
| Redlich-Peterson   | $K_{RP}$   | 5.12                    | 12.52                   |
|                    | $\alpha_{RP}$ | 1.81                    | 0.21                    |
|                    | $\beta$    | 1.85                    | 1.12                    |
|                    | $R^2$      | 0.981                   | 0.988                   |

Source: Authors (2021).
The Redlich-Peterson model is quite versatile and may be applied to adsorption processes in active sites that are heterogeneous or homogeneous on the surface, and it is viable when the parameter $\beta$ from Redlich-Peterson value is less than 1. The closer to zero, the greater the degree of heterogeneity on the adsorption surface, while being equal to the unit, the model is converted to that of Langmuir (Nascimento et al., 2019; Neris, Luzardo, Francisco H.M., et al., 2019). However, in the adjustment of the experimental data for Cu$^{2+}$ and Cr$^{3+}$, the $\beta$ value was greater than 1 (Table 5), invalidating the use of this model. Therefore, when evaluating the other models, it was evidenced that the Langmuir isotherm best describes the Cu$^{2+}$ ($R^2 = 0.942$) and Cr$^{3+}$ ($R^2 = 0.984$) systems, indicating that the adsorption occurs in monolayer. The Freundlich model presented the worst performance in the correlation data, with $R^2 = 0.896$ for Cu$^{2+}$ and 0.856 for Cr$^{3+}$.

The $q_{\text{max}}$ values obtained with Langmuir model are interpreted as milligram of the metal ion adsorbed per gram of the adsorbent. According to Table 5, the maximum adsorption capacities of Cu$^{2+}$ and Cr$^{3+}$ proposed by the Langmuir model were 49.8 mg/g and 41.77 mg/g, respectively, and the removal percentage was 91% (Cu$^{2+}$) and 96% (Cr$^{3+}$). It may be noted that copper was the metal with the highest adsorption capacity. The $K_L$ value indicates the interaction strength between the adsorbent and the adsorbate and is relevant in the study of adsorption. Low $K_L$ values show that the bonding energy between the metal and the adsorbent is weak, so there is a possibility that the percentage of ion desorption is high (Coelho et al., 2014). The separation factor $R_L$ calculated from the Langmuir constant was less than 1.0, so the values are between zero and one ($0 < R_L < 1$) indicating a favorable adsorption for all metal ions.

Freundlich's model assumes that the material's surface is composed of many active sites and that adsorption occurs in multilayers, unlike the model proposed by Langmuir. The Freundlich constant ($K_F$) indicates the intensity of the adsorption, and $1/n$ characterizes whether the process is favorable or unfavorable. When the value of $1/n$ is less than an unit, the process is favorable; therefore we may say that the process was favorable for Cu$^{2+}$ and Cr$^{3+}$ in this study (Lima, de et al., 2018).

Table 6 shows the comparison of the maximum adsorption capacity of lignocellulosic bioadsorbents for the ions studied in this work. Pretreatment with sodium hydroxide doubled the material’s adsorption capacity for copper, as SenthilKumar et al. (2011) studied the natural biomass and obtained a $q_{\text{max}}$ of 20.00 mg/g, using 0.3 g of biomass and 100 mL of ions solution of different initial concentrations (10-50 mg/L) at a pH value of 5,0 and contact time of 30 min. Therefore, CNS has a great capacity for adsorption, possessing a great potential for the treatment of industrial effluents.

| Biosorbent                                | Adsorbate | $q_{\text{max}}$ (mg/g) | Reference                      |
|-------------------------------------------|-----------|--------------------------|-------------------------------|
| Cashew nut shell treated with NaOH        | Cu$^{2+}$ | 49.80                    | This research                 |
|                                           | Cr$^{3+}$ | 41.17                    |                               |
| Cashew nut shell                          | Cu$^{2+}$ | 20.00                    | Senthil Kumar et al., 2010    |
|                                           | Cr$^{3+}$ | 20.00                    | Senthil Kumar et al., 2010    |
| Barley straw with citric acid             | Cu$^{2+}$ | 31.71                    | Pehlivan et al. 2012          |
| Sunflower hulls                           | Cu$^{2+}$ | 57.14                    | Witek-Krowiak, 2012           |
| Sugarcane bagasse ash                     | Cu$^{2+}$ | 36.32                    | Ferreira et al., 2015         |
|                                           | Cr$^{3+}$ | 41.31                    |                               |
| modified materials of pinus               | Cr$^{3+}$ | 18.34                    | Schwantes et al. 2018         |
| Water hyacinth                            | Cr$^{3+}$ | 27.3                     | Hashem et al., 2020           |

Source: Authors (2021).
Lignocellulosic materials are very attractive for the study as bioadsorbents, obtaining a good efficiency in removal metal ions, as well as a great adsorption capacity as seen in the Table 6. Several treatments can be used to improve the adsorption capacity of these materials and they can be reinserted in the industrial process or even commercialized.

4. Conclusion

The use of the cashew nut shell (*Anacardium accidentale* L) pre-treated with NaOH as a bioadsorbent for the removal of Cu$^{2+}$ and Cr$^{3+}$ proved to be quite efficient, being able to remove approximately 91% (Cu$^{2+}$) and 96% (Cr$^{3+}$), in which the maximum adsorption capacity was 49.80 mg/g and 41.77 mg/g for Cu$^{2+}$ and Cr$^{3+}$, respectively. The characterization of CNS showed favorable properties for the adsorption of toxic metals, including basic sites such as hydroxyl, carbonyl and carboxyl. The kinetic analysis showed that the removal time was the same for both metal ions, 90 min. The pseudo second-order model indicates the predominance of chemisorption as an adsorption mechanism. Langmuir isotherm best described the systems for the Cu$^{2+}$ ($R^2 = 0.942$) and Cr$^{3+}$ ($R^2 = 0.984$) ions, indicating that the adsorption occurs in a monolayer.

The cashew nut shell treated with sodium hydroxide intensified the material's properties, favoring its use in the adsorption of metal ions. Therefore, the bioadsorbent studied may be applied in several liquid industrial effluents, optimizing the cost of the process, improving the quality of the material for disposal or reuse, in addition to contributing to the reduction of environmental pollution and waste production, which may be reinserted in the production process in order to add economic value to this subproduct.

For future work, a more detailed study of operating parameters such as temperature and pH is recommended. In addition, it is important to study adsorption in multi-element metallic solutions including other heavy metals toxic to the environment. Finally, it is suggested to apply the bioadsorbent in a real industrial effluent to validate the effectiveness of the new material.

Acknowledgments

This research was supported by the Brazilian National Counsel of Technological and Scientific Development (CNPq) and by the Coordination of Improvement of Higher Education Personnel – Brazil (CAPES). The authors are grateful to the LabTam, Petrobras and UFRN for all the support for the development of this research.

References

Almeida, N. P., Santos, K. G. Ensino do Laboratório de Engenharia Química baseado em projeto: ad sorção de gasolina empregando casca de banana. *Research, Society and Development*.

Appel, C., Ma, L. Q., Rhue, R. D., Kennelley, E. Point of zero charge determination in soils and minerals via traditional methods and detection of electroacoustic mobility. *Geoderma*.

Babić, B. M., Milonjić, S. K., Polovina, M. J., Kaladievič, B. V. Point of zero charge and intrinsic equilibrium constants of activated carbon cloth. *Carbon*.

Badsha, M. A. H., Khan, M., Wu, B., Kumar, A., LO, I. M. C. (2020). Role of surface functional groups of hydrogels in metal adsorption: From performance to mechanism*Journal of Hazardous Materials*.

Bhatnagar, A., Sillanpää, M. A review of emerging adsorbents for nitrate removal from water*Chemical Engineering Journal*.

Cardoso, C. K. M., Santana, R. S. G. De, Silva, V. L. Da, Meirelles, A. C. L. E., Mattedi, S., Moreira, Í. T. A., Lobato, A. K. De C. L. Kinetic and equilibrium study of petroleum adsorption using pre-treated coconut fibers. *Research, Society and Development*.

Coelho, G. F., Gonçalves, A. C., Tarley, C. R. T., Casarin, J., Nacce, H., Francziskowski, M. A. Removal of metal ions Cd (II), Pb (II), and Cr (III) from water by the cashew nut shell *Anacardium occidentale* L. *Ecological Engineering*.

CONAB. Acompanhamento da Safra Brasileira 2019/20. Acompanhamento da Safra Brasileira de Grãos 2019/20.

Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y. H., Indraswati, N., Ismadji, S. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: *A summary of recent studies* *Journal of Hazardous Materials*.
Ferreira, P. P. L., Braga, R. M., Teodoro, N. M. A., Melo, V. R. M., Melo, D. M. A., Melo, M. A. F. Adsorption of Cu²⁺ and Cr³⁺ in waste water using bagasse fly ash | Adsorção de Cu²⁺ e Cr³⁺ em efuentes líquidos utilizando a cinza do bagaço da cana-de-açúcar. *Ceramica*.

Guimarães, B., Silva, J. T. T., Santos, K. G., Vieira Neto, J. L. (2020). Sequencing of unit operations for integral and sustainable peanut processing. *Research, Society and Development, 9*, e67963449.

Hashem, M. A., Hasan, M., Momen, M. A., Payel, S., Nur-A-Tomal, M. S. (2020). Water hyacinth biochar for trivalent chromium adsorption from tannery wastewater. *Environmental and Sustainability Indicators*.

Kamari, A., Yusoff, S. N. M., Abdullah, F., Putra, W. P. (2012). Biosorptive removal of Cu(II), Ni(II) and Pb(II) ions from aqueous solutions using coconut dregs residue: Adsorption and characterisation studies. *Journal of Environmental Chemical Engineering*.

Largitte, L., Brudey, T., Tant, T., Dumesnil, P. C., Lodewyckx, P. (2016). Comparison of the adsorption of lead by activated carbons from three lignocellulosic precursors. *Microporous and Mesoporous Materials*.

Lima, F. M. De, Andrade Borges, T. De, Braga, R. M., Araújo Melo, D. M. De, Martinelli, A. E. Sulfur removal from model fuel by Zn impregnated retorted shales and with assistance of design of experiments. *Environmental Science and Pollution Research*.

Liu, L., Fan, S. Removal of cadmium in aqueous solution using wheat straw biochar: effect of minerals and mechanism. *Environmental Science and Pollution Research*.

Liu, L., Huang, Y., Zhang, S., Gong, Y., Su, Y., Cao, J., Hu, H. Adsorption characteristics and mechanism of Pb(II) by agricultural waste-derived biochars produced from a pilot-scale pyrolysis system. *Waste Management*.

Ma, H., Yang, J., Gao, X., Liu, Z., Liu, X., Xu, Z. Removal of chromium (VI) from water by porous carbon derived from corn straw: Influencing factors, regeneration and mechanism. *Journal of Hazardous Materials*.

Mazzetto, S. E., Lomonaco, D., Mele, G. Oleo da castanha de caju: Oportunidades e desafios no contexto do desenvolvimento e sustentabilidade industrial. *Química Nova*.

Moradi-Choghamarani, F., Moosavi, A. A., Baghernejad, M. Determining organo-chemical composition of sugarcane bagasse-derived biochar as a function of pyrolysis temperature using proximate and Fourier transform infrared analyses. *Journal of Thermal Analysis and Calorimetry*.

Moreira, S. A., Sousa, F. W., Oliveira, A. G., Nascimento, R. F. B., Brito, E. S. DE. Remoção de metais de solução aquosa usando bagaço de caju. *Química Nova*.

Nascimento, J. De L., Magalhães Júnior, G. A., Portela, R. R., Sousa Neto, V. De O., Buarque, P. M. C., Oliveira, M. De S., Moura, C. P. DE. Aplicação de processo adsorptivo para desulfurização de combustíveis utilizando fibra de coco como adsorvente. *Materia*.

Neris, J. B., Lázaro, Francisco H.M., Santos, P. F., Almeida, O. N. De, Velasco, F. G. Evaluation of single and tri-element adsorption of Pb 2+, Ni 2+ and Zn 2+ ions in aqueous solution on modified water hyacinth (Eichhornia crassipes) fibers. *Journal of Environmental Chemical Engineering*.

Neris, J. B., Lázaro, Francisco Heriberto Martinez, Silva, E. G. O. Da, Velasco, F. G. Evaluation of adsorption processes of metal ions in multi-element aqueous systems by lignocellulosic adsorbents applying different isothers. *A critical review* *Chemical Engineering Journal*.

Pehlivan, E., Altun, T., Parlayıcı, S. Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution. *Food Chemistry*.

Rocha, C. G., Zaia, D. A. M., Afaya, R. V. Da S., Afaya, A. A. DA S. Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents. *Journal of Hazardous Materials*, 166(1), 383–388.

Rubio, F., Gonçalves, A. C., Meneghel, A. P., Teixeira Tarley, C. R., Schwantes, D., Coelho, G. F. Removal of cadmium from water using by-product Crambe abyssinica Hoehst seeds as biosorbent material. *Water Science and Technology*.

Santos Silva, A. K. Dos, Alfaya, A. A. DA S. Use of rice straw for the removal of Cu(II) from aqueous solution: Adsorption and characterization studies. *Journal of Environmental Chemical Engineering*.

Schwantes, D., Gonçalves, A. C., Campagnolo, M. A., Tarley, C. R. T., Dragunski, D. C., Varenes, A. De, Santos Silva, A. K. Dos, Conradi, E. Chemical modifications on pine bark for adsorption of toxic metals. *Journal of Environmental Chemical Engineering*.

Senthil Kumar, P., Ramalingam, S., Senthuramari, C., Niranjanaa, M., Vijayalaikshmi, P., Sivanesan, S. Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*.

Senthilkumar, P., Ramalingam, S., Sathyaselvabala, V., Kirupha, S. D., Sivanesan, S. Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination*, 266(1–3), 63–71.

Soliman, N. K., Moustafa, A. F. Industrial solid waste for heavy metals adsorption features and challenges, a review *Journal of Materials Research and Technology*.

Šoštarič, T. D., Petrović, M. S., Pastor, F. T., Lončarević, D. R., Petrović, J. T., Milojković, J. V., Stojanović, M. D. Study Of heavy metals biosorption on native and alkali-treated apricot shells and its application in wastewater treatment. *Journal of Molecular Liquids*.

Sousa Neto, V. De O., Carvalho, T. V., Honorato, S. B., Gomes, C. L., Barros, F. C. F., Araújo-Silva, M. A., Freire, P. T. C., Nascimento, R. F. Coconut bagasse treated by thiourea/ammonia solution for cadmium removal: *Kinetics and adsorption equilibrium* *BioResources*.
Tavares, F. P., Souza, D. L. De, Santos, K. G. Dos. Biossorção de Azul de Metileno empregando serragem do gênero Apuleia Leiocarpa. Research, Society and Development.

Tural, S., Tarhan, T., Tural, B. Removal of hazardous azo dye Metanil Yellow from aqueous solution by cross-linked magnetic biosorbent, equilibrium and kinetic studies. Desalination and Water Treatment.

Velazquez-Jimenez, L. H., Pavlick, A., Rangel-Mendez, J. R. Chemical characterization of raw and treated agave bagasse and its potential as adsorbent of metal cations from water. Industrial Crops and Products.

Witek-Krowiak, A. Analysis of temperature-dependent biosorption of Cu2+ ions on sunflower hulls: Kinetics, equilibrium and mechanism of the process. Chemical Engineering Journal.

Zhang, L., Zeng, Y., Cheng, Z. Removal of heavy metal ions using chitosan and modified chitosan: A review. Journal of Molecular Liquids.

Zimmer, T. R., Silva, J. M., Rocha, D. H. De A., Teles, H. L., Barbosa, D. S., Freitas, F. F., Seolatto, A. A. Removal of the pesticide methomyl contained in simulated effluent from equipment washing by adsorption in residual orange bagasse. Research, Society and Development.