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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+}

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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
Escola Agrícola de Jundiaí, 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.

Resumo
Os materiais lignocelulósicos têm sido utilizados como bioadsorventes para remoção de contaminantes de efluentes industriais devido às suas propriedades físico-químicas, fonte renovável, baixo custo e eficiência que os tornam competitivos ao carvão ativado comercial. O objetivo deste trabalho é desenvolver um bioadsorvente eficiente e de baixo custo, reutilizando a casca da castanha de caju (*Anarcadium acidentale L*), CNS, para a remoção de íons metálicos (Cu^{2+} e Cr^{3+}).. O CCC foi caracterizado por microscopia eletrônica de varredura (MEV), Espectroscopia de infravermelho com transformada de Fourier (FTIR), o ponto de carga zero (pHpcz) e a titulação de Boehm foram medidos. Os experimentos de cinética e equilíbrio de adsorção foram realizados em sistema monoelementar e batelada. A cinetica de adsorção foi avaliada pelos modelos matemáticos de pseudo-primeira ordem, pseudo-segunda ordem e difusão intraparticula, enquanto, a isoterma de adsorção foi ajustada de acordo com os modelos de Langmuir, Freundlich e Redlich- Peterson. A porcentagem de remoção foi de 91% (Cu^{2+}) e 96% (Cr^{3+}) e a cinética de adsorção se ajustou melhor ao modelo de pseudosegunda ordem sugerindo a predominância da quimissorção. O ajuste da isoterma de Langmuir foi melhor para os dados experimentais dos íons de Cu^{2+} e Cr^{3+}, indicando a adsorção em monocamadas. Conclui-se que o bioadsorvente produzido a partir CCC apresenta elevado potencial para a remoção de metais, além de ser um produto abundante na natureza, renovável e biodegradável e sua reutilização contribui para a redução da poluição ambiental, da produção de resíduos e melhora a economia circular local através da valorização do subproduto.
Palavras-chave: Adsorção; Metais; Biomassa; Resíduos agroindustriais; Sustentabilidade.

Resumen
Los materiales lignocelulósicos se han utilizado como bioadsorbentes para remover contaminantes de efluentes industriales debido a sus propiedades físico-químicas, fuente renovable, barato y eficiencia. El objetivo de este trabajo es desarrollar un bioadsorbente eficiente y de bajo costo reutilizando la cáscara del anacardo (*Anarcadium accidentale L*), CNS, para la remoción de iones metálicos (Cu^{2+} y Cr^{3+}). La CCC se caracterizó por microscopía electrónica de barrido (SEM), espectroscopía infrarroja por transformada de Fourier (FTIR), se midieron el punto de carga cero (pHpcz) y la titulación de Boehm. Los experimentos de cinética y de equilibrio de adsorción se llevaron a cabo en un sistema monoelemental y discontinuo. La cinética de adsorción se evaluó mediante los modelos matemáticos de pseudo-primer orden, pseudo-segundo orden y difusión intrarticular, mientras que la isoterma de adsorción se ajustó según los modelos de Langmuir, Freundlich y Redlich-Peterson. El porcentaje de remoción fue 91% (Cu^{2+}) y 96% (Cr^{3+}) e la cinética de adsorción se ajustó mejor al modelo de pseudo-segundo orden, lo que sugiere el predominio de la quimisorción. El ajuste de la isoterma de Langmuir fue mejor para los datos experimentales de iones Cu^{2+} y Cr^{3+}, lo que indica adsorción en monocapas. Se concluye que el bioabsorbente producido a partir de CCC tiene un alto potencial para la remoción de metales, además de ser un producto abundante en la naturaleza, renovable y biodegradable y su reutilización contribuye a la reducción de la contaminación ambiental, la producción de residuos y mejora la economía. circulación local a través de la valorización del subproducto.
Palabras clave: Adsorción; Rieles; Biomasa; Residuos agroindustriales; Sustentabilidad.

1. 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 physiochemical and biological characteristics of water, which affects the environment and the ecosystem of the affected regions (Santos *et al.*, 2019).

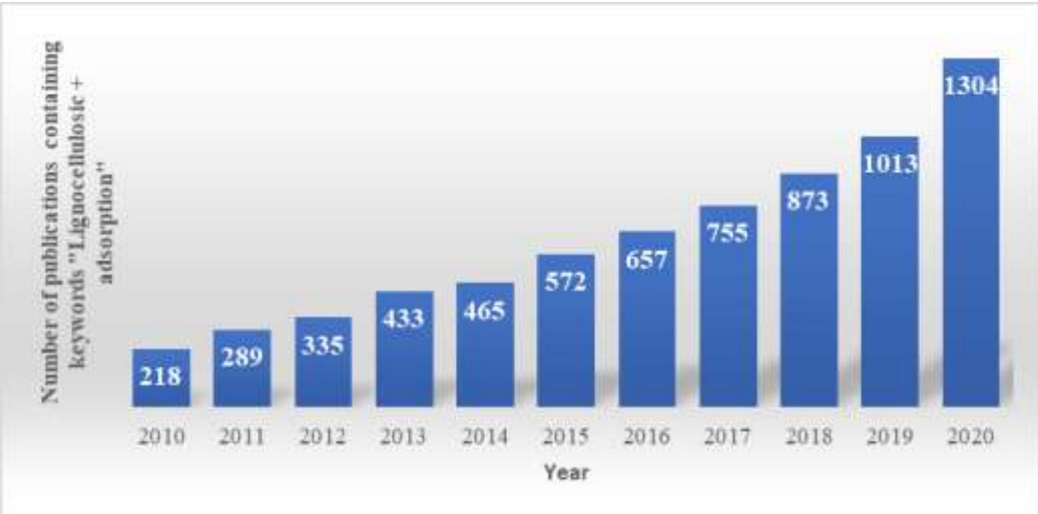
Water pollution by toxic metal ions has attracted attention due to its high toxicity, non-biodegradability, bioaccumulation in the food chain, as well as its carcinogenic and mutagenic potentials (Santos *et al.*, 2019). The most common heavy metals found in the environment are chromium (Cr), nickel (Ni), zinc (Zn), manganese (Mn), copper (Cu), cobalt (Co) and lead (Pb)(Soliman e Moustafa, 2020). Among these toxic metals, Cu^{2+} and Cr^{3+} 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".



Source: Adapted from Science Direct (2021).

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.

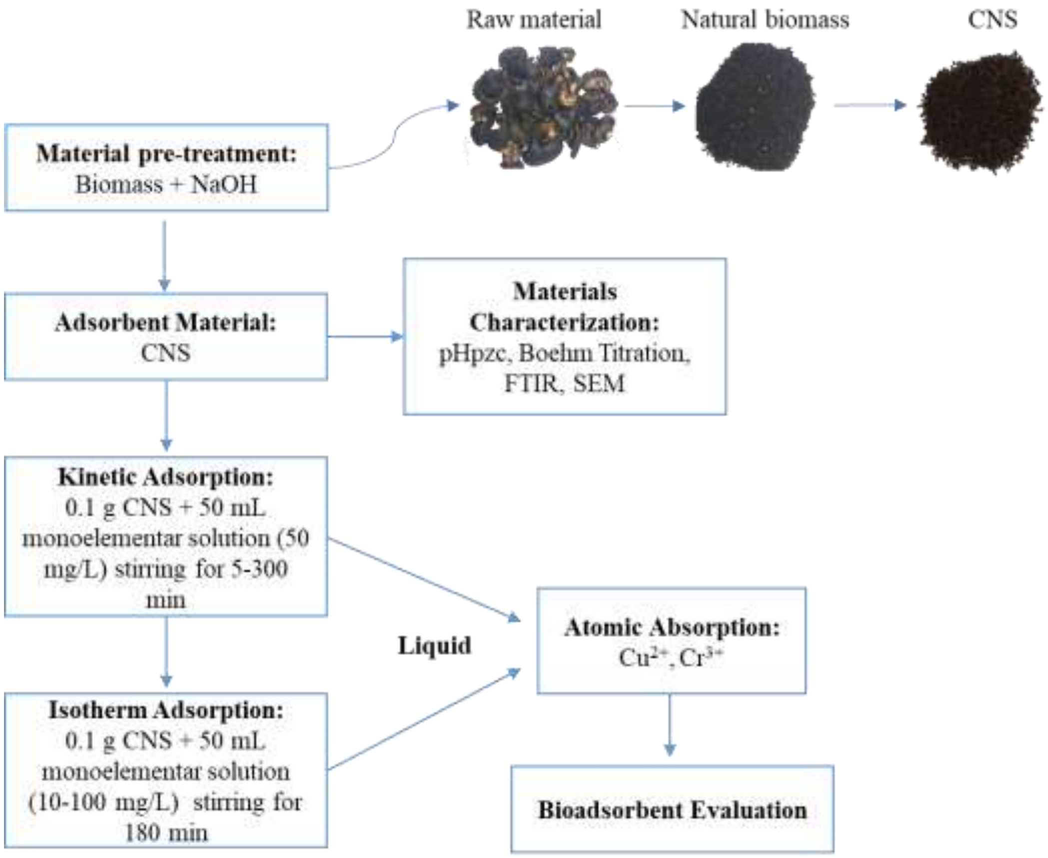
The fruit processing industry is constantly expanding, and normally the fruit shells are discarded, corresponding to about 30 to 43% of the fruit, generating large amounts of waste and causing environmental pollution due to excessive release to the environment. (Santiago *et al.*, 2021). These materials are rich in lignocellulose and the cashew nut shell is a kid of these materials that comes from the processing of cashew (*Anarcadium accidentale 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.



Source: Authors (2021).

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 ($Cu(NO_3)_2.3H_2O$ P.A. ≥ 99% from VETEC and $Cr(NO_3)_2.9H_2O$ 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 ºC 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 ºC 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 ºC 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_2CO_3 and all of these groups, including phenols, can be neutralized by NaOH (Moradi-Choghamarani, 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_2CO_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:

$$\%R = \frac{C_i - C_{eq}}{C_i} \qquad \text{Eq. 01}$$

$$q_{eq} = \frac{C_i - C_{eq}}{m} \; x \; V \qquad \text{Eq. 02}$$

where Ci is the initial metal concentration (mg/L); Ceq 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
	$RL = \frac{1}{(1 + K_L C_o)}$	K_L (L/mg): Langmuir's constant C_{eq} (mg/L): concentration at equilibrium R_L: separation factor Co (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	$q_{eq} = \frac{K_{RP} C_{eq}}{1 + \alpha_{RP} C_{eq}^{\beta}}$	α: Redlich-Peterson's parameter β: Redlich-Peterson's parameter
	Kinetic models	
Pseudo first-order	$ln\left(q_{eq} - q_t\right) = ln\, q_{eq} - k_1 t$	q_t (mg/g): sorption capacity at time t k_1 (1/min): pseudo first-order's constant rate
Pseudo second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t$	k_2 (1/min): pseudo second-order's constant rate
Intraparticle diffusion	$q_t = k_d t^{0,5} + C$	k_d (mg/min$^{1/2}$g): instraparticle diffusion's parameter C (mg/g): intercept

Source: Adapted Almeida e Santos (2020).

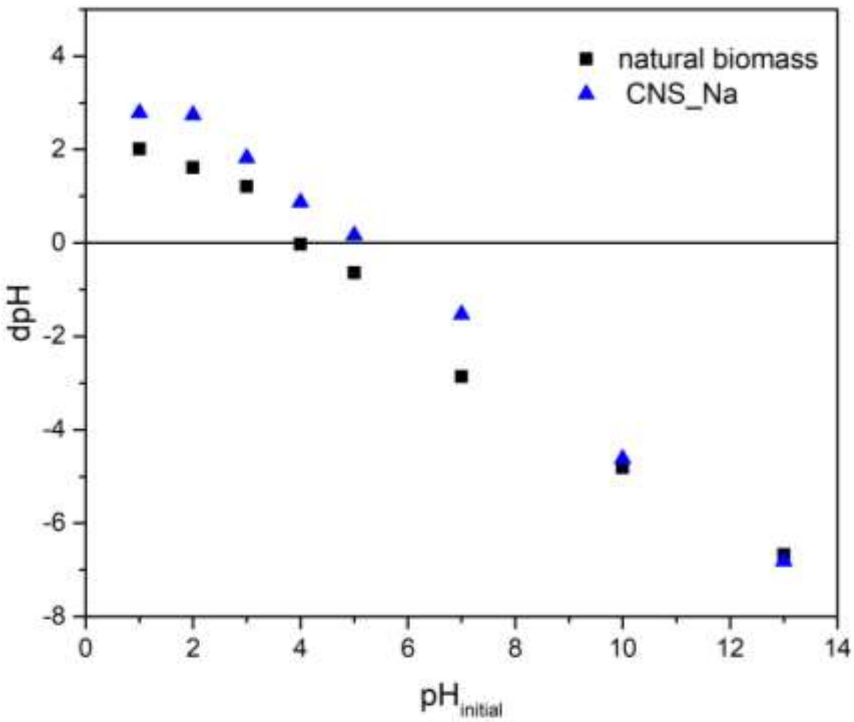
The models in Table 1 are to understand the sorption process of the experimental data, Langmuir, Freundlich and Redlich-Peterson isotherms models (Almeida e Santos, 2020) and kinetics models (pseudo first-order, pseudo second-order and intraparticle diffusion) (Schwantes *et al.*, 2018) were applied.

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 ΔpH versus pH_0 graph.

Figure 3. pH at point of zero charge (pzc) of natural biomass and pre-treated with NaOH (CNS).



Source: Authors (2021).

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 pHpcz 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).

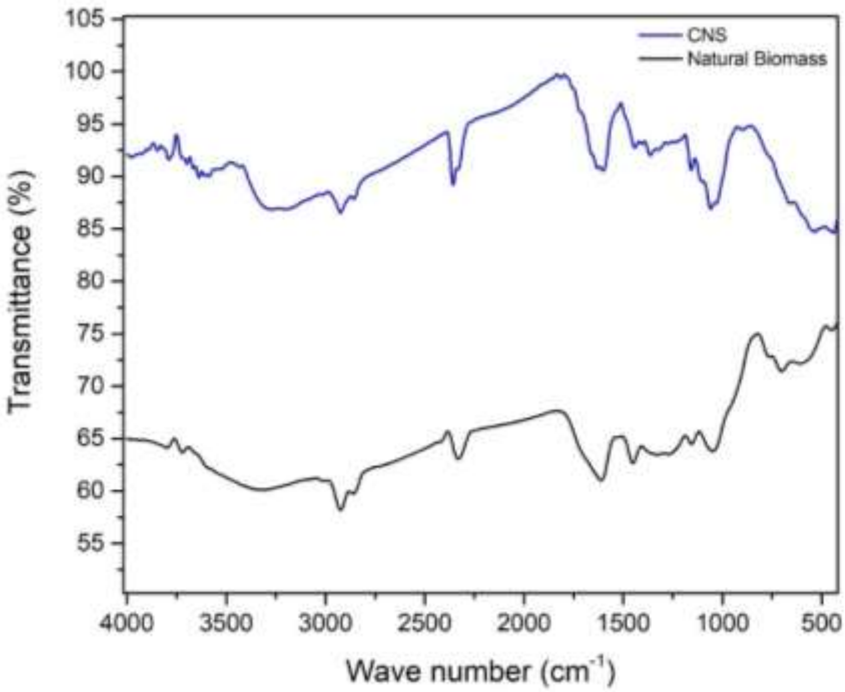
Sample	**Acid Groups (mmol/g)**			**Basic groups (mmol/g)**
	Carboxylic	**Lactonic**	**Phenolic**	
Natural biomass	0.114	0.408	0.355	0.261
CNS	0.053	0.326	0.203	0.316

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 pHpzc 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.



Source: Authors (2021).

The graphs (Figure 4) show the existence of bands, which that are characteristic of lignocellulosic materials as such as 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**
3791	3788	Axial deformation of the O-H group	Cellulose and lignin	(Tavares, Souza e Santos, 2020)
2924	2921	Axial deformation of the C-H group	Extractives and cellulose	(Coelho *et al.*, 2014)
2859	2849	Stretching $C\text{-}H_n$		
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)

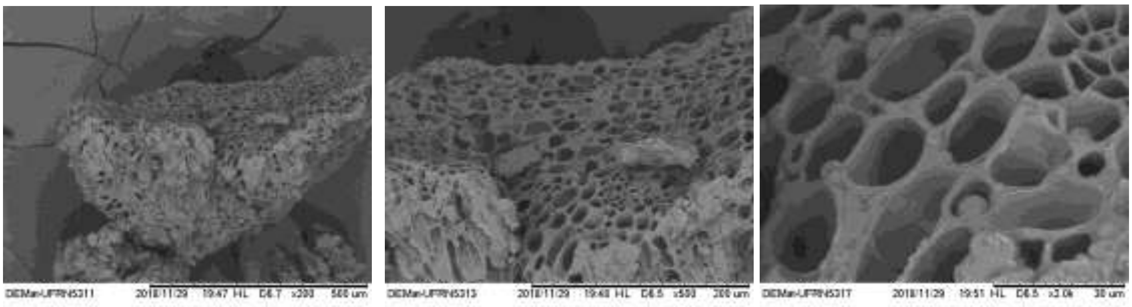
Source: Authors (2021).

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.

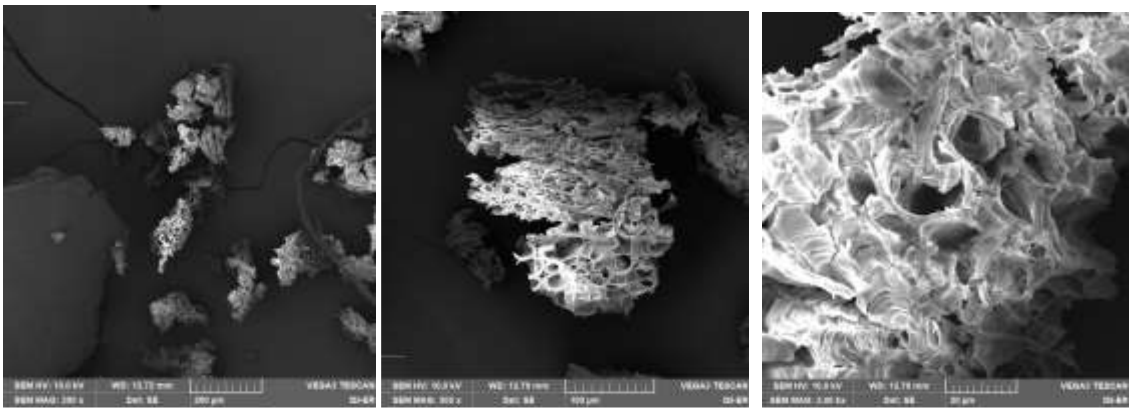
Figure 5. Scanning electron microscopy image of the natural biomass, in magnification of 200 (a), 500 (b), 2000 (c) times.



(a) (b) (c)

Source: Authors (2021).

Figure 6. Scanning electron microscopy image of the bioadsorbent material treated with NaOH (CNS) in magnification at 200 (a), 500 (b), 2000 (c) times.



(a) (b) (c)

Source: Authors (2021).

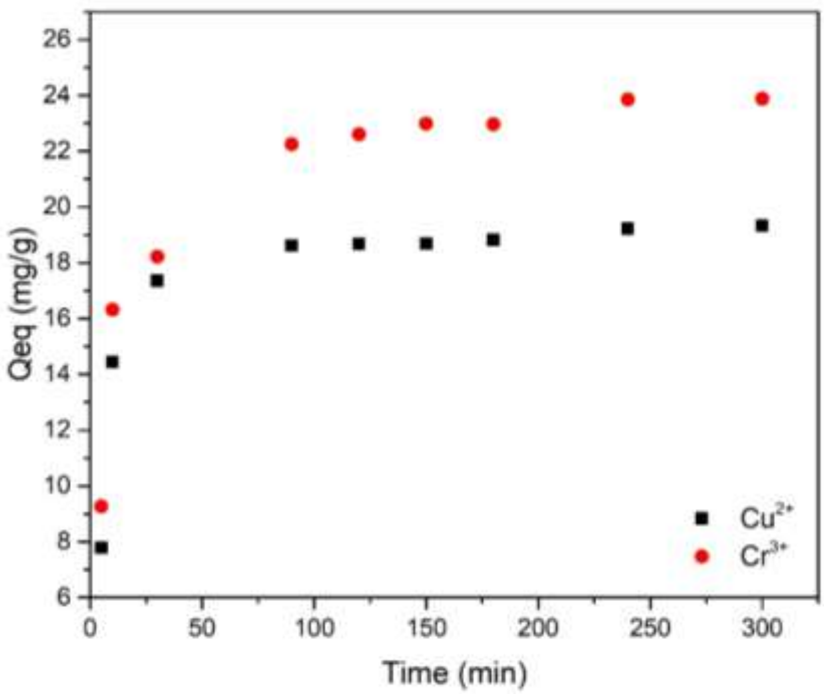
After pretreatment (CNS) an irregular morphology was evidenced as seen in Figure 6. With the use of alkaline agents there is a swelling in the fiber causing its rupture, and this process favors the appearance of pores; however, in Figure 6 it is not possible to observe the superficial porous channels 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.

Figure 7. Adsorption kinetics in the monoelementary solution of Cu^{2+} and Cr^{3+} metal ions.



Source: Authors (2021).

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).

Table 4. Kinetic parameters for metal ions Cu^{2+} and Cr^{3+}.

Parameters / adsorbent		**Cu**	**Cr**
	K_1 (1/min)	-0.016	-0.016
Pseudo first-order	**Q_{eq} (mg/g)**	1.721	1.813
	R^2	0.883	0.887
	K_2 (1/min)	0.002	0.002
Pseudo second-order	**Q_{eq} (mg/g)**	19.604	24.473
	R^2	0.999	0.999
	K_i (mg/g. $min^{1/2}$)	0.556	0.805
Intraparticle diffusion	**C (mg/g)**	11.440	12.231
	R^2	0.625	0.778

Source: Authors (2021).

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.

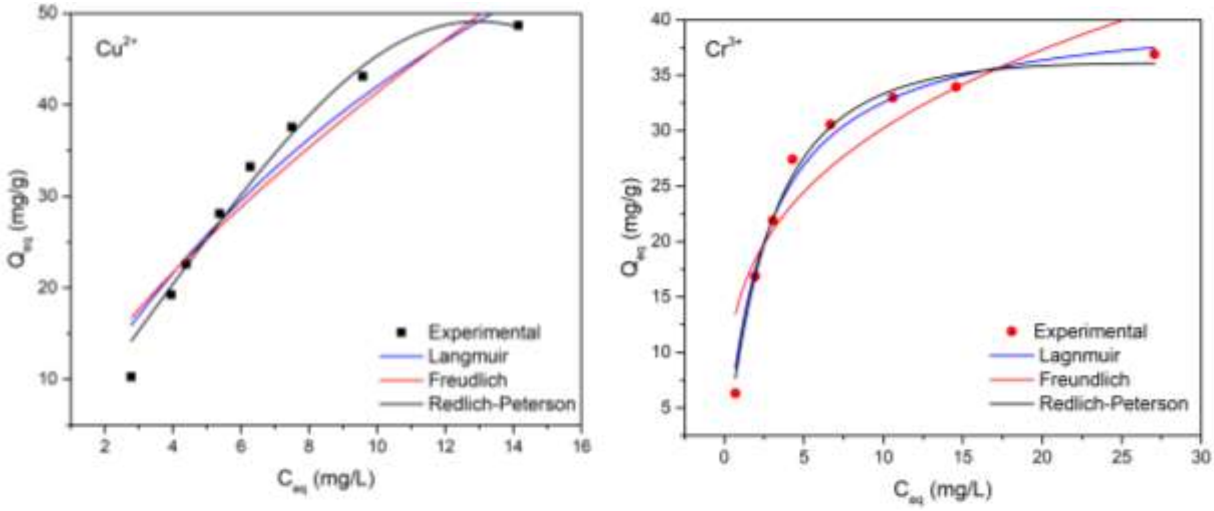
The pseudo second-order model describes the process of chemical adsorption involving donation or sharing of electrons between the adsorbent and the adsorbate, such as covalent or ionic binding forces. The disadvantage of this type of adsorption is that the material regenerating process is difficult, due to the strong interaction between the adsorbent-absorbate. 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 Lnagmuir, 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^{2+} (a) and Cr^{3+}(b) metal ions.



(a)

(b)

Source: Authors (2021).

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^{2+}(a) and Cr^{3+}(b).

Model	Parameters	Cu^{2+}	Cr^{3+}
Langmuir	q_{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
	α_{RP}	1.81	0.21
	β	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 β 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 β 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_{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_{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.

Table 6. Adsorption capacity of several lignocellulosic bioadsorbents.

Biosorbent	**Adsorbate**	**q_{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
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 (*Anarcadium 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.

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