

Use of residual ash for removal of Copper II from effluents by adsorption

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Abstract

The present work evaluated the use of residual ash as bioadsorbent for the removal of copper (II) from synthetic aqueous effluents. The samples were characterized using X-ray fluorescence (XRF) and the BET method for analyze the specific surface area, obtaining a value of 35.5 m²/g. Initially, the experimental methodology involved determining the optimal pH of the solution within the range from 1 to 7. For an aqueous copper (II) solution with a concentration of 50 mg/L, 100% removal was achieved, regardless of the solution's pH. Subsequently, the kinetics and adsorption equilibrium at 298 K were measured. The data modeling indicated that the pseudo-first-order model best described the adsorption kinetics. For the adsorption isotherm, the Langmuir model proved to be the most suitable, with a maximum adsorption capacity of 91.045 mg/g. The results suggest that the ash has significant potential as a bioadsorbent for the removal of copper ions from wastewater. Furthermore, the use of these ashes adds value to the industrial waste generated by the Red Ceramic industries, promoting a more sustainable approach to the management of effluents and industrial waste.

Keywords: bioadsorbent; agro-industrial waste; heavy metals; industrial effluents.

1. Introduction

Heavy metals are among the most harmful pollutants to both the environment and human health. Even at low concentrations, they exhibit extreme toxicity. Industrial activities are directly linked to the significant increase in metal ion concentrations in water, which poses a severe contamination risk to aquatic ecosystems. This increase represents a significant source of contamination of aquatic bodies, especially considering the potential for the spread of these ions through the food chain [1].

Some metals are essential for proper functioning of metabolic pathways, but most are harmful when consumed in excessively high concentrations, as they tend to accumulate in living organisms. Metals are difficult to eliminate from the human body, which can lead to illness or poisoning. These highly toxic substances are incompatible with most current biological effluent treatment methods and, therefore, should not be discarded into the public

sewer system for treatment alongside domestic sewage. In this context, copper (II) was chosen for study because it is a toxic metal, challenging to treat, and often found in considerable concentrations in industrial effluents, such as those from metallurgical and galvanizing processes [1].

Considering the problem described above, it is necessary to employ treatment methods to reduce or eliminate the presence of heavy metals as pollutants in effluents and watercourses. Methods such as ion exchange, membrane filtration, chemical precipitation and adsorption have been studied. However, due to the significant variation in the composition of industrial effluents, there is no universal treatment method that meets all the demands encountered. As a result, many studies are being conducted to improve existing technologies.

Adsorption is considered a promising alternative method for the treatment of metal effluents, offering significant advantages over conventional techniques, such as the ability to remove pollutants even at low concentrations and the potential to use

natural residues as bioadsorbents. Activated carbon is widely used due to its versatility in removing metal ions. However, given the high cost associated with the synthesis and regeneration of the adsorbent, the use of a variety of alternative adsorbents that are similarly efficient, inexpensive, and derived from natural materials has been extensively studied [2].

In the Brazilian Northeast, cashew cultivation has developed significantly, with the fruit and its derivatives serving as an important source of income for the region. One of the economic activities in the interior of Rio Grande do Norte is the ceramic industry, which uses cashew wood, along with algaroba wood, as a source of energy [3].

In this context, the present work evaluated the use of algaroba and cashew ash as bioadsorbent for the removal of copper (II) from aqueous solutions.

2. Materials and methods

2.1 Materials

Residual ash of algaroba and cashew was collected in a ceramic plant located in the Açú Valley, in the city of Itajá-RN. After collection, the material was sieved and samples with Tyler 200 (75 µm) size were selected. The samples were evaluated for their potential as bioadsorbent.

2.2 Characterization

The adsorbent was characterized by x-ray fluorescence (XRF) and nitrogen adsorption isotherms at 77 K (BET).

2.3 Adsorption Experiments

The stock solution of Cu²⁺ was prepared by dissolving Copper Nitrate II Trihydrate (Cu(NO₃)₂·3H₂O), with 98% purity, in deionized water. The effect of the solution pH on metal ion adsorption was studied in the pH range from 1 to 7. The capacity of residual ash adsorption at different contact times with metal ion solution (2, 4, 6, 8, 10, 15, 20, 30, 45, 60, 75 and 90 minutes) was also studied. In both cases, the initial concentration (100 mg/L), volume 30 mL, mass of 0.1 g of residual ash and temperature (298 K ± 0.5) of metal ion solutions were kept constant. All experiments were performed in triplicate, carried out to the shaker with 160 rpm stirring, centrifuged for 5 minutes and filtered with 0.45 µm opening syringe filter to be

read on the Rapid sequential atomic absorption spectrometer. Similarly for the isotherm, varying the initial concentrations (10, 25, 50, 100, 200, 300 and 500 ppm) in contact by the equilibrium time discovered in the kinetics.

The amount of metal adsorbed per mass unit of the adsorbent and the adsorption efficiency shall be calculated by Equations 01 and 02.

$$q = \frac{(C_0 - C_e)V}{m} \quad (01)$$

$$\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (02)$$

The kinetic and isothermal modeling was performed by using linear regression methods and non-linear method of adjustment by least squares method and Origin 8.5 for presentation of the graphs. The mathematical models adjusted to the experimental data, for adsorption kinetics, were pseudo-first order, pseudo-second order, intra-particle diffusion and Avrami. For the isotherms were the models of Langmuir and Freundlich.

The selection of the most appropriate model was performed by minimizing the Akaike Information Criterion (AIC and AICc), which allows to evaluate the probability that the model is the best to describe the experimental data, considering the collection of models, through the values of Akaike weight (wi).

3. Results and discussion

3.1 Characterization

3.1.1 X-ray fluorescence (XRF)

The results of the analysis of the chemical composition of residual ash by X-ray fluorescence are presented in Table 1.

Table 1 - Chemical composition of residual ash by X-ray fluorescence.

Óxidos	Composição (%) da CR
CaO	36.098
K ₂ O	21.623
SiO ₂	16.869
Al ₂ O ₃	6.225
SrO	5.275
MgO	4.897
Fe ₂ O ₃	3.304
Outros óxidos	5.709

Similar results were found by Melo et al. [4].

3.1.2 Surface Area Determination (BET)

The surface area of the residual ash studied is 35.5 m²/g, with mean pore diameter of 51.37 Å and total volume of single-point adsorption pores 0.05 cm³/g. According to IUPAC, the material is macro porous when it has mean pore diameter above 50 Å.

3.2 Adsorption Experiments

3.2.1 Effect of solution pH

Table 2 shows the percentage of removal as a function of pH of the solution.

Table 2 - Assessment of the influence of pH.

pH	Final Cu ²⁺ concentration (mg/L)	Removal percentage (%)
1	0,000	100
2	0,693	98
3	0,037	100
4	0,000	100
5	0,000	100
5,5	0,029	100
6	0,002	100
7	0,008	100

It is possible to observe that there was no variation in the percentage of copper removal in relation to pH, so we can consider natural pH (5.5) as optimal pH.

3.2.2 Kinetic study

The kinetic models of pseudo-1st order, pseudo-2nd order, intra-particle diffusion and Avrami were adjusted to the experimental data. Figure 2 shows the evolution of the adsorption kinetics of copper in the residual gray adsorbent and the model that best fitted to the experimental data.

It is possible to verify that the amount of adsorption of Cu²⁺ increases rapidly in the initial stage and, from there, slowly increases until reaching equilibrium in 20 min.

3.2.3 Adsorption Isotherms

Table 3 shows the parameters obtained from the adjustment of the Langmuir and Freundlich models to the experimental data for adsorption of Cu²⁺.

With the information in Table 3, we identified that the Langmuir model is more likely to adequately describe the experimental data, with q_{max} of 91.045 mg/g, as shown in Figure 2.

The amount adsorbed at equilibrium concentration of 50 mg/L and 298 K was compared

with the capacity of different agro-industrial wastes, see Table 4.

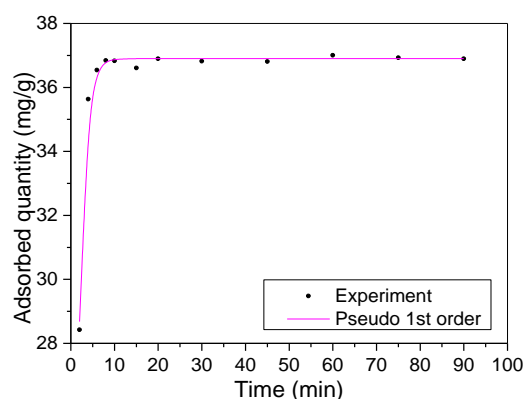


Figure 1 - Evolution of the adsorption kinetics of Cu²⁺ onto the residual ash adsorbent.

Table 3 - Parameters of Cu²⁺ adsorption models.

Model	Model parameters	Temperature
		298 K
Langmuir	q _{max} (mg/g)	91.045
	k _L (L/mg)	3.301
	W1	0.9930
Freundlich	k _F (mg/g)	37.371
	n	5.483
	W1	0.0070

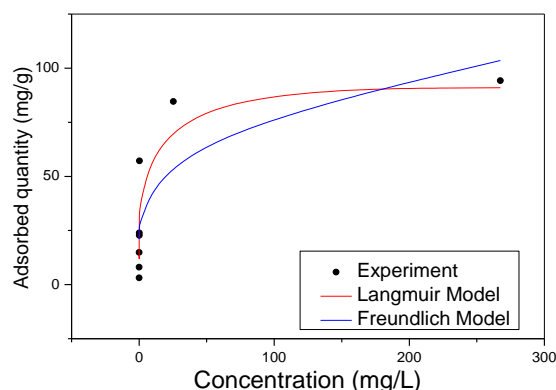


Figure 2 - Adsorption isotherm and Langmuir and Freundlich models.

Table 4 - Adsorbed amount of Cu²⁺.

Bioadsorbent	Sample	Q _{ads} (mg/g)	Source
Residual ash	-	79.73	Studied
Eucalyptus oil residue	-	35.51	[5]
Biochar seaweed	SW300	93.38	[6]
Rice husk	-	0.021	[7]
Buriti stone	-	10.19	[8]

Macadamia nut	SGCI	0.80	[9]
and guava seed	EMCI	2.79	

The values of adsorption capacities of different agro-industrial residues are in the range of 0.021-35.51 mg/g, which is lower compared to the adsorption capacity of residual ash (79.73 mg/g), only behind the biochar (93.38 mg/g). In addition, to improve the adsorption properties of some materials, their modification was carried out in different ways. The main advantage of the adsorbent used in this work is that the residue was directly subjected to adsorption experiments, without any process of purification and chemical modification of the surface of the adsorbent before measurements. These facts indicate that the residual ash studied in this work shows good adsorption capacity of copper ions under relatively neutral pH conditions (pH 5.5) and potentially can be used in the purification of contaminated effluents.

4. Conclusion

The adsorption equilibrium of copper ions was achieved in only 20 min and with a maximum single-layer adsorption capacity in aqueous copper solution of 91.045 mg/g, with pH of 5.5 and temperature of 298 K.

The residual ash presented great potential for removal, especially when it is considered the simultaneous removal of metal ions combined with no need for prior treatment or modification for its use, which considerably reduces the costs of the adsorbent, mainly because it is an industrial waste. In addition to these advantages, the use of residual ash with heavy metal adsorbent in contaminated effluents adds value to the industrial waste from the process of the Red Ceramic Industries, as it also contributes to minimize the negative environmental impacts of the waste from these effluents in the environment.

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