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Biosorptive capacity of plant based biosorbents in removing Cr^{6+} from aqueous solutions – Insights into isotherm studies

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Abstract

The inappropriate discharge of effluents containing heavy metals leads to environmental contamination and the bioaccumulation of dangerous substances, threatening human and animal health. Metals such as chromium, needed in small quantities, become extremely toxic in their hexavalent form, causing serious health problems. Some plant species, such as *Taioba-brava* (TAB) and *Comigo-ninguém-pode* (CNP), can be used as alternative bioadsorbents for removing heavy metals. The objective of this work was to evaluate the adsorption isotherms of Cr^{6+} in aqueous solution by dehydrated TAB and CNP leaves. $K_2Cr_2O_7$ aqueous solutions, with different concentrations, were prepared and used in adsorption tests. The system was composed of 0.5 g of substrate with 50 mL of solution, under constant stirring for 960 min. After filtration, the resulting solution was quantified by UV-Vis spectroscopy. The results indicated that the samples treated with TAB reached an adsorption capacity value of 113.511 $mg.g^{-1}$, while when treated with CNP the adsorption capacity was 103.89 $mg.g^{-1}$. The Langmuir isotherm was the one that best fitted the samples treated with TAB, while the Freundlich isotherm was fitted with the system using CNP. The study determined the feasibility of using plant species as a viable alternative for the bioremediation of effluents contaminated by heavy metals.

Keywords: Bioadsorbents; Taioba-brava; Comigo-ninguém-pode; Isotherms.

1. Introduction

The use of heavy metals by industry, such as zinc (Zn), copper (Cu), chromium (Cr), and mercury (Hg), has caused serious environmental impacts with the advent of technologies and their innovations. The improper release of effluents containing these metals results in the contamination of water bodies and soils, promoting the bioaccumulation of harmful substances that pose significant risks to human and animal health, including potential carcinogenic and mutagenic effects [1]. At elevated levels, these metals compromise the ecological balance and can cause various pathologies. Particularly, chromium, which is necessary for cellular metabolism, becomes highly toxic in its hexavalent form (Cr^{6+}), accumulating in soil, plants, bodies of water, and in the flesh of animals, causing serious health problems such as nausea, damage to vital organs, and cancer. [2].

Adsorption can be quantitatively assessed through isotherms, which allow for the analysis of both the adsorption capacity and the strength of the bond between metals and a specific adsorbent. The graphical behavior of isotherms can manifest in different ways, providing relevant information about the adsorption mechanism, through fitting parameters obtained from mathematical models that describe them [3,4].

The *Taioba-brava* species (Colocasia antiquorum schot) is part of the Araceae family. It is a plant where all its parts are toxic (root, stem, and leaves) and it is native to the Tropical and Equatorial Americas, including Brazil [5]. The *Comigo-ninguém-pode* species (Dieffenbachia picta Schott) is a toxic plant belonging to the Araceae family. It appears as a subshrub with a cylindrical stem and large, shiny dark green leaves or green leaves with white spots. It is widely used as an ornamental plant in homes, schools, and public squares [6].

In this study, dehydrated leaves of the *Taioba-brava* and *Comigo-ninguém-pode* plants were used as biosorbents for the removal of hexavalent chromium from aqueous solutions, in order to evaluate the adsorption isotherms.

2. Materials and Methods

The leaves of the plant species Taioba Brava (TAB) and Comigo-ninguém-pode (CNP) were collected and washed with running water and then with distilled water. These were cut into small pieces and dehydrated in an oven at 105º C until a constant weight was reached. After drying, the bioadsorbents were crushed in a knife mill, sieved (100 MESH), and stored in polyethylene containers.

A solution containing Cr(VI) ions was prepared from the dissolution of potassium dichromate ($K_2Cr_2O_7$, Impex, 99.0%), and approximately 5.5 mL of sulfuric acid (H_2SO_4, LabQuimios, 98.08%) was added, resulting in a solution with a concentration of 10 mmol.L^{-1}. Dilutions were carried out to result in solutions with concentrations of 1, 3, 5, and 7 mmol.L^{-1}.

The adsorption tests were conducted by adding 0.50 g of the substrate to 50 mL of the $K_2Cr_2O_7$ solution. The system remained in contact under constant agitation (130 rpm) for 960 minutes. Next, the system was filtered through quantitative filter paper and quantified by spectroscopy in the UV-Vis region using a BEL, model UV-M51, UV-Visible spectrophotometer. The adsorption capacity (q) was determined using Equation 1.

$$q\ (\mathrm{mg.g^{-1}}) = \frac{(C_o - C_f).V}{m} \qquad (1)$$

Where: C_0 is the initial concentration of Cr(VI); C_f is the concentration of Cr(VI) after the adsorption process, V is the volume of the solution, and *m* is the mass of the substrate used.

The evaluation of the adsorption isotherms was carried out based on the (linearized) mathematical models of Langmuir and Freundlich, according to Equations 2 and 3, respectively.

$$q_e = \frac{q_{max} K_L C_e}{1 + q_{max} C_e} \qquad (2)$$

$$q_e = K_F . C_e^{1/p} \qquad (3)$$

Where: q_e is the capacity for adsorption (mg.g^{-1}); C_e the concentrations of Cr(VI) at equilibrium (g.L^{-1}); q_{max} is the constant related to energy and adsorption (L.mg^{-1}); K_L (L.g^{-1}) and K_F (mg.g^{-1}) as Langmuir and Freundlich constants, respectively; and p is an empirical parameter.

3. Results and Discussion

Figure 1 shows the adsorption capacity values (q) of Cr^{6+} by dehydrated TAB and CNP leaves as a function of the initial concentrations of the $K_2Cr_2O_7$ solution.

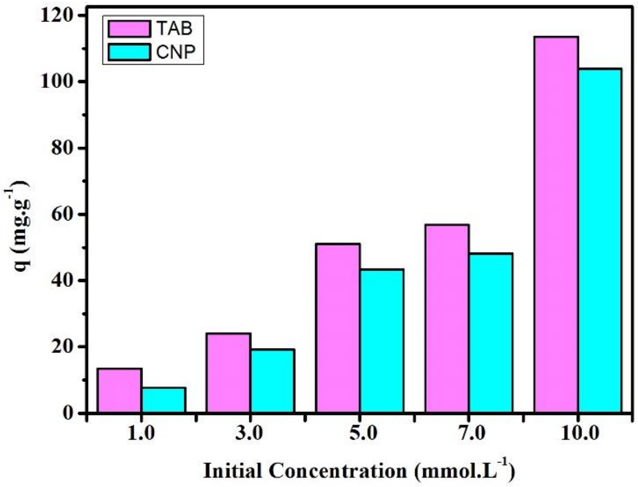

Fig. 1. Adsorption capacity of Cr^{6+} by dehydrated leaves of TAB and CNP.

The data showed that the samples treated with TAB exhibited the highest q results across all studied concentrations, with the maximum value reaching 113.511 mg.g^{-1} at a concentration of 10 mmol.L^{-1}, while the sample treated with CNP showed a value of 103.89 mg.g^{-1} at the same concentration.

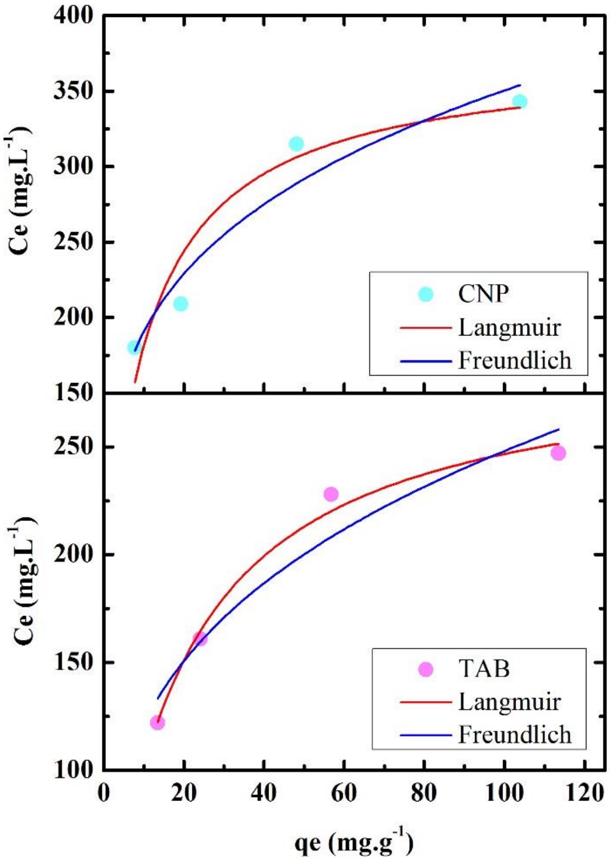

Fig. 2. Adsorption isotherms of Cr^{6+} by dehydrated leaves of TAB and CNP.

Starting from the adsorption isotherms (Fig. 2), it was possible to determine the values of the Langmuir adsorption constants (q_{max}, K_L) and Freundlich. (K_F, p). These parameters are essential for verifying the best fit of the adsorption data in relation to the two mathematical models. In relation specifically to the Langmuir model, the values of the adsorption constants allow for the determination of the equilibrium parameter (R_L).

The data presented in Table 1 showed that for the Langmuir model, the equilibrium parameter or separation factor (R_L) exhibited values between 0 and 1 for both substrates under study. In turn, for the Freundlich model, the parameter p showed values between 1 and 10. [7].

Table 1. Adsorption parameters of Cr^{6+} by dehydrated leaves of TAB and CNP for the Langmuir and Freundlich models.

		Langmuir		
Sample	q_{max} ($L.mg^{-1}$)	K_L ($L. g^{-1}$)	R_L	R^2
TAB	293.15	0.05	0.06	0.9862
CNP	373.96	0.09	0.03	0.8704
		Freundlich		
Sample		K_F ($mg.g^{-1}$)	p	R^2
TAB		59.53	3.23	0.9047
CNP		103.76	3.78	0.9108

In the Langmuir model, the movement of adsorbed ions occurs uniformly, forming a monolayer that covers the entire surface of the adsorbent. While the Freundlich model assumes that there is a logarithmic distribution of active sites, resulting in multilayer adsorption [8].

According to the data presented in Table 1, both mathematical models are favorable for the adsorption of the systems under study. However, based on the correlation coefficient values from the graphs (R^2), the Langmuir model was the one that best fit the samples treated with TAB, while the Freundlich model was more suitable for the system using CNP as a bioadsorbent.

4. Conclusion

The Langmuir and Freundlich isotherms indicated that the adsorption process of Cr^{6+} ions by dehydrated TAB and CNP leaves can occur in both monolayers and multilayers, with the Langmuir model fitting better for TAB, while the Freundlich model was more suitable for CNP. Thus, the results obtained demonstrate the feasibility of using bioadsorbents as a viable and sustainable alternative for the bioremediation of effluents contaminated by heavy metals.

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