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Evaluation of the Efficiency of Biosorption of Lead, Cadmium, and Chromium by the Biomass of Pequi Fruit Skin (*Caryocar brasiliense* Camb.)

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Effluents containing metals may come from different types of industries, including paper mills, petrochemical plants, inorganic reagents and fertilizers, petroleum refining, steel foundries and metal working, textile mills, leather tanning, and others. These industries produce large volumes of wastewater requiring efficient and low-cost treatment.Pequi (*Caryocar brasiliense* Camb.) is a fruit native to the Brazilian cerrado, and its skin, which represents about 60% by weight of the fruit, is often overlooked during processing. In this work, pequi skins were used as biosorbent material in solutions containing chromium, lead, and cadmium. Factors such as biomass dose, pH, and biomass size were studied using a factorial statistical design. The results showed that the metal with the highest biosorption in the biomass was lead, with anaverage biosorption of 16.78 mg.g^{-1} and up to 80% removal of the solution, while there was less removal of chromium and cadmium. The dose of biomass and pH were found to be the most important factors in the biosorption. The grain size, on the other hand, generally did not influence the adsorption and can be discounted among the factors that act in the process.

1. Introduction

The strong growth of consumption and exploitation of raw materials, along with population growthin the last few decades, have caused widespread devastation to the environment as well as contributing to the significant increase in contamination by metal ions in water (Silva Junior et al., 2008).

Contamination of water by heavy metals in industrial effluents is a serious environmental problem (Vieira et al, 2011). When heavy metal ions such as chromium, cadmium, and lead escape into the environment, they can accumulate in living organisms, especially in humans, which are at the top of the food chain. The World Health Organization (WHO) recommends that the maximum acceptable concentration levels of chromium, cadmium, and lead in drinking water are 0.05, 0.003, and 0.1 mg L^{-1}, respectively.

Although biosorption is a cheap and environmentally safe alternative to the use of traditional adsorbents, the suitability of a given biomass for this application needs careful evaluation (Lavecchia et al, 2010).

This study aims toinvestigate the adsorption capacity of chromium, cadmium, and lead ions in pequi skin, to analyze the influence of factors such as biomass, average particle size, and pH of the synthetic sewage, and to evaluate the efficiency of adsorption of each of these metal ions.

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2. Materials and Methods

2.1 Collection and preparation of biosorbent material

Pequi fruit was obtained at markets in Goiânia, in the state of Goiás. The skin was chopped, dried in an oven at 50 °C for 24 hours, and then crushed in a grinder. Through a screening process, two bands of material diameter were obtained, one with an average of 0.225 mm and the other with an average of 0.715 mm.

2.2 Preparation of solutions

Three synthetic effluents were prepared with concentrations of approximately 100.0 $mg.L^{-1}$ of a given metal ion. The pH was adjusted with the help of a pH meter (model Tecnal). It were used pure $PbCl_2$supplied by Vetec, $CrCl_3.6H_2O$ with minimum purity of 99% supplied by SIGMA, and $CdCl_2.H_2O$ supplied by PA.

2.3 Application of tests

Experiments to evaluate the biosorption capacity of the pequi skin were performed in random order for independence between observations. A planning matrix was set up to take account of the factors that could influence with responses, such as measurement of biomass, average particle size, and pH of the solution of metals at different levels. Table 1 shows the factors and levels chosen for the planning matrix. Table 2 shows the combinations of three levels of planning factors. The experiments were replicated to improve reliability of the data.

Table 1: Factors and levels for the biosorption experiments evaluated for each metal

Factor	Level	Level Value	Representation
Biomass dose	1	2 $g.L^{-1}$	-1
	2	10 $g.L^{-1}$	1
Particle size	1	0,225 mm	-1
	2	0,715 mm	1
pH	1	3	-1
	2	5*	1

**For chromium, a pH of 4 was used to avoid metal precipitation.*

Table 2: Factorial design carried out for biosorption of each metal studied

Experiment	Biomass Dose	Particle Size	pH
1	-1	-1	-1
2	-1	-1	1
3	-1	1	-1
4	-1	1	1
5	1	-1	-1
6	1	-1	1
7	1	1	-1
8	1	1	1

The experiments were performed in batches at 30 °C under constant stirring (150 rpm) for 24 h. 0.15 g(2 $g.L^{-1}$) or 0.75 g (10 $g.L^{-1}$) of metal was added to every 75 mL of solution. After this period, the liquid was filtered and diluted, and its concentration was determined by atomic absorption spectrometry.

2.4 Evaluation of the adsorption capacity

The samples were then diluted toa ratio of 1:20, enabling reading and analysis of the concentrations of metal ions using an atomic absorption spectrophotometer (GBC model). Thevalues of the percentage of metal adsorbed and the adsorption capacity were then calculated. The percentage of metal adsorbed was determined by:

$$\% \ Biosorbed = \left(\frac{C_i - C_{eq}}{C_i}\right).100$$

(1)

The adsorption capacity, Q, (mg metal/g biosorbent) was determined using Equation 2 (Inglezakis and Poulopoulos, 2007, cited by Ruthven, 1984):

$$Q = \frac{(C_i - C_{eq})V}{m}$$

(2)

where:
V: volume of solution; C_i: initial concentration of solution; C_{eq}: equilibrium or final concentration of solution; m: mass of biosorbent
The results were statistically analyzed with an analysis of variance (ANOVA) test and Tukey's test, both using the SAS software.

3. Results and Discussion

The experiments showed that the metal with the best adsorptive capacity was lead. The results of the tests and their replicates are shown in Table 3. These results initiated a discussion about different factors that can influence the adsorption—pH, biomass dosage, and particle size—which can be analyzed accurately. The biosorption capacities of cadmium and chromium are also shown in Table 3.

Table 3: Biosorption capacity of metals in the factorial design

Experiment	Lead		Cadmium		Chromium	
	Q	Q(replicate)	Q	Q(replicate)	Q	Q(replicate)
1	20.17	22.96	0.13	0.10	4.95	4.82
2	24.11	27.44	4.48	3.95	7.44	8.15
3	21.40	24.21	0.65	0.8	2.90	2.62
4	30.11	29.05	1.62	1.35	8.44	9.92
5	8.92	9.20	2.06	2.19	7.29	7.12
6	7.97	7.87	2.72	2.51	5.65	6.74
7	8.98	9.26	1.98	1.93	4.83	5.40
8	7.06	7.21	2.21	2.20	6.01	6.43

From Table 3, it appears that the adsorption capacity of lead decreased when the biomass dosage was increased. This observation is confirmed in Table 4 by the low Pr>F of this factor. This can be explained by the reduction of the electromotive force in the solution and the formation of larger aggregates of biosorbent particles. As the biosorption process occurs, the solution tends to become less concentrated, reducing the electromotive force. In the case of lead, it happens quickly and this contributes to the reduction of biosorption capacity. Although the percentage of ion removal was higher due to a higher number of active sites, the formation of aggregates of particles decreases the surface area and increases the diffusion of ions in solution, reducing the biosorption capacity.
Factors that influence the biosorption are those in which Pr>Fis less than 0.05 (5%), which is the confidence interval used in the analysis of variance.

Table 4: Analysis of variance (ANOVA) - Influence of the factors studied in metal biosorption. (a)Pb (R= 0.971395); (b) Cd (R = 0.989852); (c) Cr (R = 0.960168)

(a)

Sources of Variation	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr> F**
D	1	979.37702250	979.37702250	261.13	<0.0001
S	1	6.2250250	6.2250250	1.66	0.2336
D*S	1	10.3684000	10.3684000	2.76	0.1349
pH	1	1.6129000	1.6129000	0.43	0.5304
D*pH	1	19.3160250	19.3160250	5.15	0.0529
S*pH	1	0.2353350	0.2353350	0.06	0.8086
D*S*pH	1	1.7689000	1.7689000	0.47	0.5116
Error	8	3.750500			
Total	15				

(b)

Sources of Variation	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr> F**
D	1	1.39240000	1.39240000	50.54	0.0001
S	1	1.82250000	1.82250000	66.15	<0.0001
D*S	1	0.59290000	0.59290000	21.52	0.0017
pH	1	7.84000000	7.84000000	284.57	<0.0001
D*pH	1	4.24360000	4.24360000	154.03	<0.0001
S*pH	1	3.20410000	3.20410000	116.30	<0.0001
D*S*pH	1	2.40250000	2.40250000	87.21	<0.0001
Error	8		0.02755000		
Total	15				

(c)

Sources of Variation	**Degrees of Freedom**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr> F**
D	1	0.00330625	0.00330625	0.01	0.9164
S	1	1.96700625	1.96700625	6.98	0.0296
D*S	1	0.43890625	0.43890625	1.56	0.2473
pH	1	22.20765625	22.20765625	78.82	<0.0001
D*pH	1	21.32130625	21.32130625	75.67	<0.0001
S*pH	1	7.91015625	7.91015625	28.07	0.0007
D*S*pH	1	0.48650625	0.48650625	1.73	0.2253
Error	8		0.28175625		
Total	15				

D= dosage, S = particle size, pH =pH, *= combination

The Tukey test is applied to determine the mean difference between the two levels of the factors studied. The results of the Tukey test are summarized in Table 5, and it can be observed that the pH is a factor of great importance. Different data on the influence of pH on biosorption can be found in the literature. They indicate how the changes in the pH depend on the type of biomass and the type of metal ions (Ozdemir, 2004).

Table 5: Tukey test

Lead*					
Biomass Dose (D)		Particle Size (S)		pH	
Level	Q ($mg.g^{-1}$)	Level	Q ($mg.g^{-1}$)	Level	Q ($mg.g^{-1}$)
-1	25.2475 a	-1	16.3963 a	-1	15.9538 a
1	8.3088 b	1	17.1600 a	1	17.6025 a
Cadmium**					
Biomass Dose (D)		Particle Size (S)		pH	
Level	Q ($mg.g^{-1}$)	Level	Q ($mg.g^{-1}$)	Level	Q ($mg.g^{-1}$)
-1	1.1763 a	-1	2.0925 a	-1	1.1300 a
1	2.2250 b	1	1.3088 b	1	2.2713 b
Chromium***					
Biomass Dose (D)		Particle Size (S)		pH	
Level	Q ($mg.g^{-1}$)	Level	Q ($mg.g^{-1}$)	Level	Q ($mg.g^{-1}$)
-1	4.991 a	-1	4.791 a	-1	3.754 a
1	5.490 a	1	5.690 a	1	6.728 a

Means with dissimilar letters are statistically different by the Tukey test at 5% significance level.
Least significant difference: * 2.0095, ** 0.6898, *** 3.0014

The effect of pH on lead biosorption is linked to the measurement of biomass as observed (Factor D*pH). For a smaller dose, a higher pH yields a better biosorption capacity than a lower pH. On the other hand, in higher dosage, increased pH results in reduced biosorption capacity. Particle size does not affect the biomass biosorption and is a factor that can be disregarded for lead biosorption in pequi skin.

Cadmium exhibits a different behaviour to that observed for lead. ANOVA and Tukey's test (see Tables 4 and 5, respectively) show that all the factors proposed in the factorial design interfered in biosorptive capacity. The effect of dosage is relatively significant in cadmium biosorption, as can be seen in Table 3. Increased biomass dosage provides a greater removal of metals and causes an increase in biosorptive capacity, the opposite effect to that observed for lead. This can be explained by the rate of biosorption: in the case of lead, the biosorption rate is higher, so the electromotive forces decrease sharply and decrease the efficiency of biosorption at higher dosage.

With respect to cadmium, a higher dosage of biomass increases the number of functional groups that can act in the metal biosorption, which occurs at a slower rate, resulting in a milder reduction of the electromotive force and increasing the biosorption capacity. Therefore, the decision to increase the amount of biomass needs to be evaluated so that the metal concentration does not decrease much, reducing the adsorption capacity. The effects of pH and particle size are discrete but important.

The biosorption capacity of chromium is not significant. Individually, the factors do not influence the biosorption.

These results demonstrate the higher biosorbent affinity for lead than for other metals studied.

According to McBride (1994), cadmium retention occurs mainly through electrostatic forces of negatively charged particles, which makes it highly dependent on the cation exchange capacity (CEC). For lead, interactions with the particles are predominantly more specific and less dependent on surface charge (Pierangeli et al, 2001).

For lead, the analysis shows that these factors are a combination of biomass, biomass dosage, and pH, as shown in Table 4. Cadmium shows a low adsorption capacity, but all factors show interference in the adsorption process. With regard to chromium, adsorption capacity is low and no factor shows a significant difference at 5%.

Modelling equations show the biosorption capacity of the pequi skin in relation to different metals according to the factor levels. Note that the highest coefficients are related to the factors that most influence the efficiency of adsorption. The equations are:

$$Q_{(Pb)} = 16,77813 - 8,46937*D + 0,38188*S + 0,82438*pH - 0,56313*D*S - 1,60563*D*pH + 0,37312*S*pH - 0,58438*D*S*pH \quad (3)$$

$$Q_{(Cd)} = 1,70063 + 0,52438*D - 0,39188*S + 0,57063*pH + 0,24688*D*S - 0,38563*D*pH - 0,43938*S*pH + 0,37938*D*S*pH \quad (4)$$

$$Q_{(Cr)} = 5,24063 + 0,24938*D + 0,44937*S + 1,48688*pH - 0,48437*D*S - 0,91938*D*pH + 0,47812*S*pH - 0,28063*D*S*pH \quad (5)$$

4. Conclusions

The factorial design was essential for the analysis of influence in this work. The metal that proved to be best for biosorption in the pequi skin was lead (Pb^{2+}), with an average of 16.78 $mg.g^{-1}$ and up to 80% removal from the solution. Less removal was observed for the metals chromium and cadmium. The biomass dosage is also of great importance in this process, since it determines the ionization states of active sites, solution components, and impurities that may exist in the biosorbent. The particle size generally did not influence the biosorption and can be discounted among the factors that act in this process under the conditions analysed. The experiments showed that the pequi skin can be used as a viable alternative to remove metals such as lead and chromium with relative efficiency, depending on conditions. The pequi skin is not used industrially and is discarded as waste. Thus, the adoption of this material as a biosorbent would be cheap and sustainable, which are highly desirable features in industrial bioprocesses.

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