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Biosorption of Heavy Metals by Powder of Green Coconut Shell

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Abstract: Alternative processing methods are being considered more seriously, sorption and/or complexation of dissolved metals based on the chemical activity of biomass, known as biosorption, is the base of the new technology for metal removal and recovery. Different types of biomass (dead and alive) like bacteria, yeast, bark, fungi, agricultural by-products, coconut shell, marine algae, peat, moss and aquatic mosses have been investigated for biosorption of heavy metals ions. Biosorption of each of the metal ions by coconut shell powder was investigated in this study. The biosorption capacities of coconut shell for cadmium, chromium, and arsenic were studied at different particle sizes (0.044–0.297 mm), initial metal concentration (20–1000 mg/L), and solution pH values (2–9) in batch mode, the experimental data obtained for each metal were evaluated and fitted using adsorption models. Also, analyses were made of biomass by SEM-EDS before and after the biosorption to confirm the presence of metal ions species.

Keywords: Biosorbent, metal removal, wastewater treatment, coconut shell

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INTRODUCTION

The increase of industrial activities has intensified environmental pollution problems and the deterioration of several ecosystems with the accumulation of many pollutants, such as toxic metals. These pollutants are introduced into the aquatic system significantly as a result of various industrial operations; heavy metal pollution usually derives from electroplating, plastics manufacturing, fertilizers, pigments, mining, and metallurgical process. Over the past few decades, the community has been devoting concentrated efforts for the treatment and removal of heavy metals in order to combat this problem.

The imposition of stricter regulations increases the demand for innovative treatment technologies to remove metals from wastewaters and to attain a day's toxicity-driven concentrations limits. Conventional technologies for removing metals from wastewaters are precipitation, coagulation, reduction and membrane process, ion exchange and adsorption. However, the application of these treatment processes is sometimes restricted due to technological or economical constraints.

The search for novel technologies has recently been directed to the application of biosorption, which constitutes an attractive alternative to common applied physical-chemical methods. In this general setting, the search for a new, economical, and effective heavy metal adsorbent focuses on the development of environmentally friendly techniques.

Biosorption can be defined as the removal of metal or metalloid species, compounds, and particulates from solution by biological material (1). Large quantities of metals can be accumulated by a variety of processes dependent and independent on metabolism. Both living and dead biomasses (and inactive biomasses) as well as cellular products such as polysaccharides can be used for metal removal. The advantages of biosorption lie in both the good performance in metal removal, often comparable with their commercial competitors (ion exchangers), and cost-effectiveness, making use of raw materials for fermentation and the agricultural process. This aspect can play an important role in improving a zero-wastes economic policy especially in the case of the re-use of biomasses coming from food, pharmaceuticals, and wastewater treatments. Metal ion uptake by biosorption may involve the contribution of diffusion, adsorption, chelation, complexation, coordination, or micro-precipitation mechanisms, depending on the specific substrate (biomass) (2–23).

Several investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of ions. Among the various resources in biological wastes, both dead and live biomass, exhibit particularly interesting metal-binding capacities. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean, and cottonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, orange peel, compost, humic substances, and leaves (6–24). The use of dead biomass eliminates the problem of toxicity and the economics aspects of nutrient supply and culture maintenance (10).

The aim of the present work was to investigate sorption of different heavy metals (As^{5+}, Cr^{3+}, Cr^{6+}, and Cd^{2+}) from aqueous solutions by using powder of coconut shell—*Cocos nucifera*. The use of coconut shell as a biosorbent material presents great potential due to its high content of lignin, about 35–45%, and cellulose, about 23–43% (11). The cellulose and lignin are biopolymers admittedly associated with the removal of heavy metals (12–23).

MATERIAL AND METHODS

Biosorbent Material

The powder of green coconut shells used in this work was supplied by Embrapa Tropical Agroindustry—Bioprocess Laboratory/Fortaleza, Ceará. The methodology used in the production of the powder is described in reference (15).

Biosorption Experiments

Batch experiments of biosorption were performed at constant temperature (27°C) in Erlenmeyer flasks, stirred in a reciprocal shaker (175 rpm) for 2 hours. One can observe that the equilibrium is reached significantly before two hours. In all sets of experiments 0.5 g of powder of coconut shells was thoroughly mixed into a 100 ml solution of metallic species. After shaking the flasks, the reaction mixtures were filtered to remove particulates and the filtrates were analyzed by an atomic absorption spectrophotometer for the concentration of metallic species. The experiments were carried out on a triplicate basis.

The stock solutions of metals were prepared in deionized water using, CrO_3, $Na_2HAsO_4 \cdot 7H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, and $CdSO_4$ 8/3 H_2O. The reagents used were of analytical grade supplied by Merck.

A first series of biosorption experiments was carried out with the following metallic species: Cr^{6+}, As^{5+}, Cd^{2+}, and Cr^{3+}, with an initial concentration of 20 mg L^{-1}. In these tests the optimal pH value of biosorption was determined for the metallic species. After this, the influence of particle size was also evaluated. Using HCl and NaOH solutions made all the pH adjustments.

The second series of experiments were performed at different concentrations (20 to 1000 mg/L) in order to evaluate the effect of initial concentration of metallic species on the biosorption process.

SEM and EDS Analyses

The morphological characteristics of coconut shell were evaluated by using DSN 960 Zeiss Scanning Electron Microscope. The samples of coconut shell powder were covered with a thin layer of gold and an electron acceleration voltage of 20 kV was applied. The EDS analyses of biomass were performed after and before biosorption experiments in order to identify the presence of metallic species.

RESULTS AND DISCUSSION

Effect of pH

pH has great importance on heavy metal biosorption, and tests were undertaken with different initial pH values of the solutions, using a constant concentration of coconut shell powder. The effect of initial pH on biosorption process is presented in Fig. 1 for the metals: Cr^{6+}, As^{5+}, Cd^{2+}, and Cr^{3+}.

The results presented show excellent removal capacities for Cd^{2+}, Cr^{3+}, and Cr^{6+} by using the powder of green coconut shell, where a similar profile of removal was observed. The cadmium removal increased from 69% at pH 4, to 98% at pH 7. At the above pH value of 7 the removal becomes constant until it reaches pH 9; at higher pH values cadmium ions precipitate as $Cd(OH)_2$ (16).

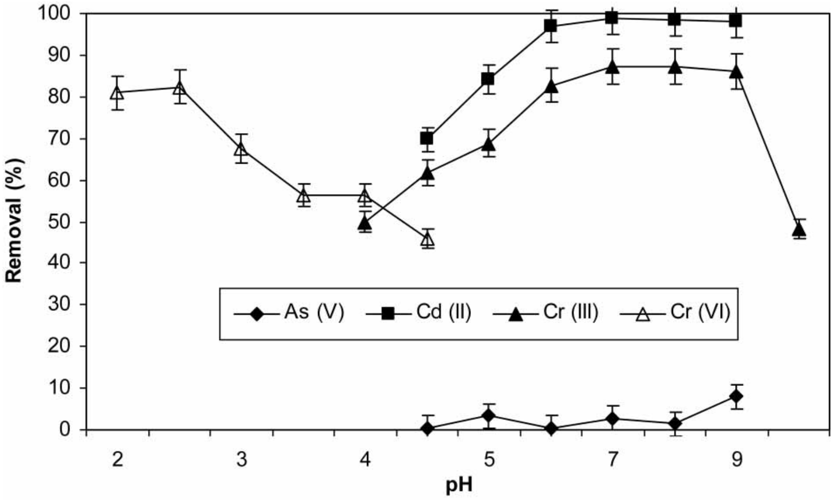

Figure 1. Removal of metals by powder of green coconut shell in function of pH. Initial concentration: 20 mg/L; agitation rate: 175 rpm; biomass concentration: 5 g/L; size particles: 200–297 μm; contact time: 2 hours.

For chromium the same behavior is observed, an increase in the removal percentage from 61% at pH 4, to 88% at pH 7; after this value of pH the removal becomes constant until it reaches pH 9. For pH values above 9 the trivalent chromium ions precipitate as $Cr(OH)_3 \cdot nH_2O$. In the case of As^{5+}, very low removal percentages were obtained, showing a weak interaction among the metallic species and the biosorbent. The percent adsorption of Cr^{6+} increased up to 80% in pH 2 and thereafter decreased with further increase in pH.

The dependence of metal uptake on pH is related to both the surface functional groups present on the biomass and the metal chemistry in solution. At low pH, the surface ligands are closely associated with the hydronium ions (H_3O^+) and restricted the approach of metal cations as a result of the repulsive force (17, 18). Furthermore, the pH dependency on the metal ions uptake by biomasses can also be justified by the association-dissociation of certain functional groups, such as the carboxyl and hydroxyl groups present in the biomass. In fact, it is known that at a low pH, most of the carboxylic groups are not dissociated and cannot bind the metal ions in solution, although they take part in complexation reactions (19–23).

Based on these results, the following experiments were performed only with cadmium and chromium species; for Cd^{2+} and Cr^{3+} at pH 7, and for Cr^{6+} at pH 2.

The coconut shell powder had a good performance in biosorption process, the total removal percentage is 90%, 86%, and 99% for Cr^{3+}, Cr^{6+}, and Cd^{2+}, respectively, for an initial concentration of 20 mg/L; with a final concentration of 2.2, 2.3, and 0.2 mg/L for each metal respectively.

Sorption Isotherms

The equilibrium of a solute separated between the liquid and solid phases may be described by various models of sorption. In order to investigate the sorption capacity and isotherm, two equilibrium models are used frequently, Langmuir and Freundlich, which were fitted to the data obtained.

Initial concentrations of ions solutions were between 20 and 1000 mg/L, in all experiments 0.5 g of biomass was mixed into 100 ml solution of metallic species.

Langmuir Isotherm

The Langmuir model is probably the best known and most widely applied sorption isotherm. This model supposes a monolayer sorption with a homogeneous distribution of sorption sites and sorption energies, without interactions between the sorbed molecules. It has produced good agreement with a wide variety of experimental data and may be represented as follows (20):

$$q = \frac{q_{\max} b C_f}{1 + b C_f} \tag{1}$$

Where:

C is the equilibrium concentration ($\mathrm{m_{eq}/L}$).

q is the amount of copper ions sorbed ($\mathrm{m_{eq}/g}$).

$q_{\max}$ is a maximum amount of metal ion sorbed per unit weight of biomass to form a complete monolayer ($\mathrm{m_{eq}/g}$).

b is sorption equilibrium constant ($\mathrm{L/m_{eq}}$).

The Eq. (1) can be rearranged to the following linear form:

$$\frac{C}{q} = \frac{C}{q_{\max}} + \frac{1}{q_{\max} b} \tag{2}$$

Freundlich Isotherm

This empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by Eq. (3) (21). In contrast to the Langmuir model the Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity.

$$q = k_f C^{1/n} \tag{3}$$

Where:

C is the equilibrium concentration ($\mathrm{m_{eq}/L}$).

q is the amount of copper ions sorbed ($\mathrm{m_{eq}/g}$).

k_f and n are Freundlich's adsorption constants.

The Eq. (3) is frequently used in the linear form by taking the logarithm of both sides as:

$$\log q = \log k_f + \frac{1}{n} \log C \tag{4}$$

The data obtained from the adsorption experiments are shown in Figs. 2–4. All experiments were conduced at 27°C and all data experiments were fitted to Equations (2) and (3)

The linear form of Langmuir and Freundlich adsorption isotherms of each metal ion for coconut shell are shown in the Figs. 5 and 6, respectively. The Freundlich and Langmuir parameters are also given in Table 1.

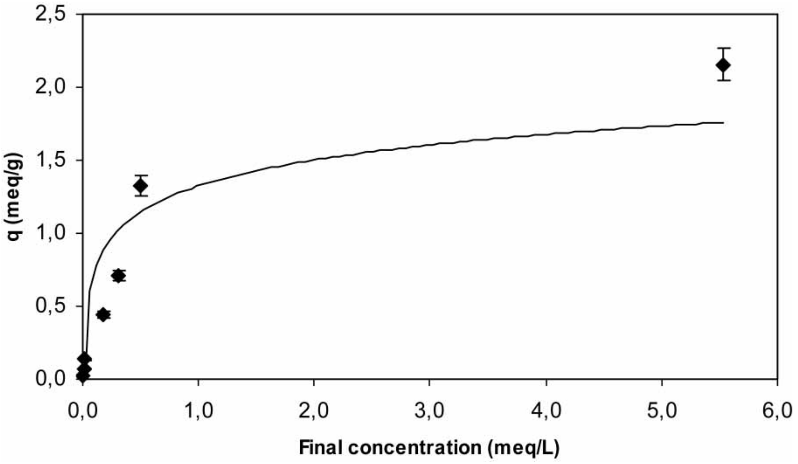

Figure 2. The Langmuir adsorption isotherms of Cd^{2+} by powder of green coconut shell. Experimental conditions: temperature 27°C; agitation rate: 175 rpm; biomass concentration: 5 g/L; size particle: 200–297 μm and pH 7.

It can be observed through the value of the correlation coefficient (R^2) presented in Table 1, that the Langmuir model adjusts the experimental data very well for the adsorption of cadmium by coconut fiber powder. In the case of the Freundlich model the values observed for R^2 fit best all the experimental dates, mainly for Cr^{3+} adsorption.

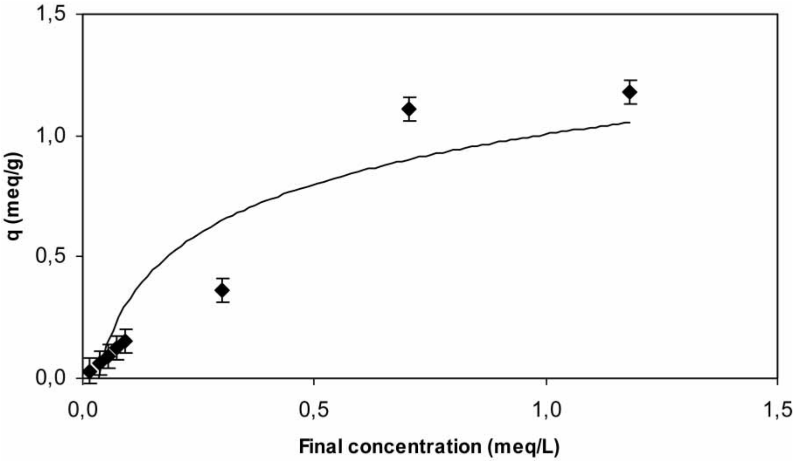

Figure 3. The Langmuir adsorption isotherms of Cr^{3+} by powder of green coconut shell. Experimental conditions: temperature 27°C; agitation rate: 175 rpm; biomass concentration: 5 g/L; size particle: 200–297 μm and pH 7.

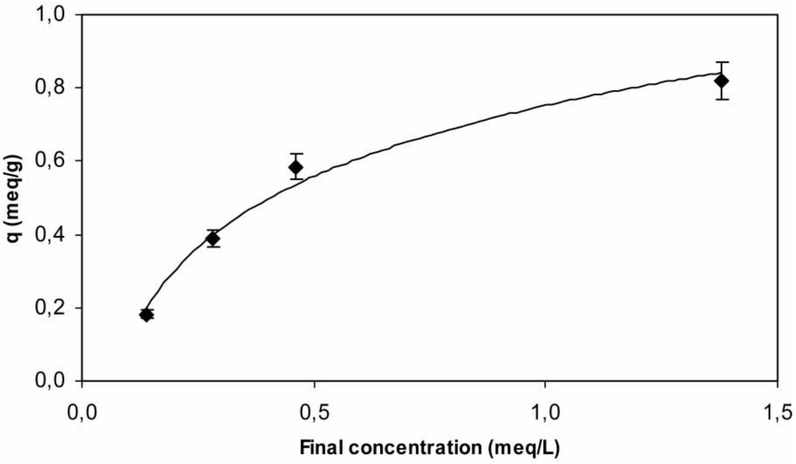

Figure 4. The Langmuir adsorption isotherms of Cr^{6+} by powder of green coconut shell. Experimental conditions: temperature 27°C; agitation rate: 175 rpm; biomass concentration: 5 g/L; size particle: 200–297 μm, pH 2.

The adsorption capacity values (K_f) for Cd^{2+}, Cr^{3+}, and Cr^{6+} obtained from the Freundlich model were 9.780, 2.048, and 4.182 respectively; these values indicated that the coconut shell powder had a good affinity for these metallic species.

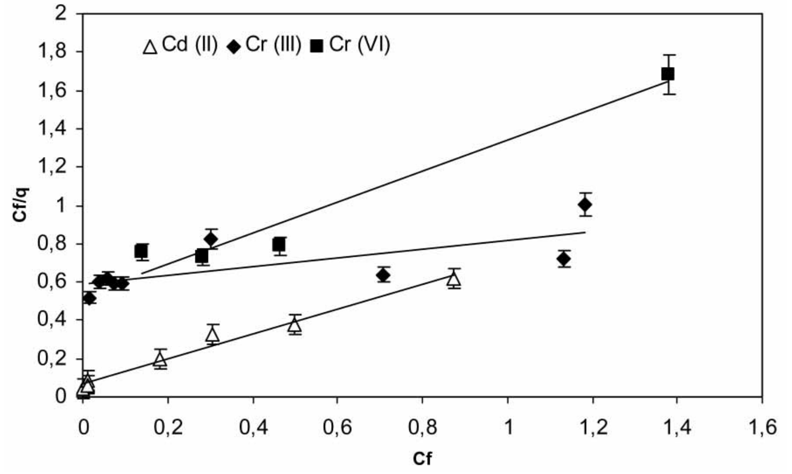

Figure 5. The linearized Langmuir adsorption isotherms of Cr^{3+}, Cr^{6+}, and Cd^{2+} by powder of green coconut shell. Experimental conditions: temperature 27°C; agitation rate: 175 rpm; biomass concentration: 5 g/L; size particle: 200–297 μm.

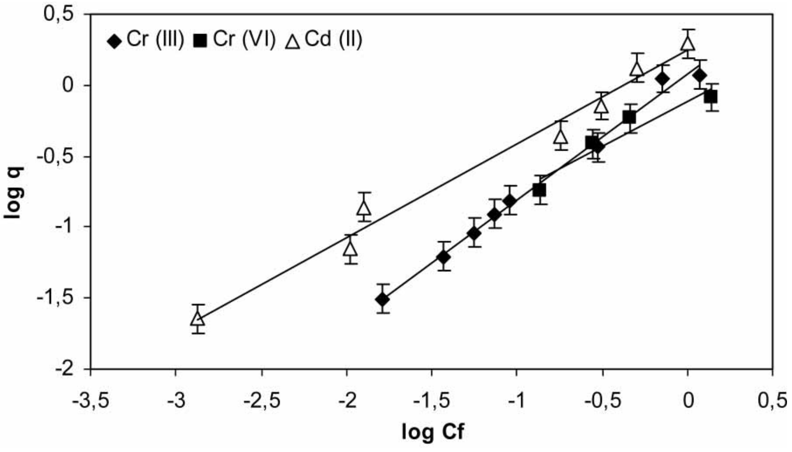

Figure 6. The linearized Freundlich adsorption isotherms of Cr^{6+}, Cr^{3+}, and Cd^{2+} by coconut shell. Experimental conditions: temperature 27°C; agitation rate: 175 rpm; biomass concentration: 5 g/L; size particle: 200–297 μm.

The performance of many biosorbents in the removal of metal species from aqueous solutions has been extensively studied. For instance, $q_{\max}$ of a group of nine marine algae was reported to be mainly in the range 1.64–2.32 m_{eq}/g for cadmium adsorption, and the corresponding b value was 8.4–12 L/m_{eq}. Six different species of *Sargassum* biomass exhibited maximum uptake capacity ranging from 1.32–1.8 m_{eq}/g. The corresponding b values for cadmium ranged from 10.38 to 43 L/m_{eq}. Although a direct comparison is difficult due to the different physicochemical environments (18).

Particle Size

Another important parameter studied was the influence of the particle size of coconut shell used for uptake of metals. This parameter presents an important influence in the process cost. The results presented in Table 2 show a reduction

Table 1. Sorption isotherm coefficients of Langmuir and Freundlich models applied to Cd^{2+}, Cr^{3+}, and Cr^{6+} adsorption by coconut shell powder

	Langmuir			Freundlich		
Metal	q_{max}	b	R^2	K_f	n	R^2
Cd^{2+}	2.30	2.44	0,9806	9.780	1.748	0,9729
Cr^{3+}	4.35	0.4	0,5416	2.048	1.113	0,9914
Cr^{6+}	1.23	1.52	0,9555	4.182	1.567	0,9092

Table 2. Percentage removal of Cd^{+2}, Cr^{+3}, and Cr^{+6} by powder of green coconut shells for different range of particle size. $C_o = 100$ ppm, $\omega = 175$ rpm, $C_{biomass} = 5$ g/L

	Removal (%)		
Range of particle size (mm)	Cd^{2+}	Cr^{3+}	Cr^{6+}
0.074 a 0.044	81.8	68.6	88.8
0.105 to 0.074	82.2	73.3	88.5
0.210 to 0.105	82.4	83.4	90.0
0.297 to 0.210	98.2	89.4	74.8

in the adsorption of Cd^{2+} and Cr^{3+} with the decrease of the particle size of the biomass.

It is important to stress that larger particles with spherical shapes, in general, present higher external mass transfer than smaller particles (22–25). In this case, higher metal adsorption from these particles is attributed to mass transport inside the sorbent particles.

SEM and EDS

Scanning Electron Microscope evaluated the morphological characteristics of coconut. The micrographs of coconut shell powder before metal uptake and the respective EDS analyses are presented in Figs. 7 and 8, respectively.

The scanning electron micrographs of coconut shell powder are shown in Fig. 8. The morphology of this material can facilitate the adsorption of metals,

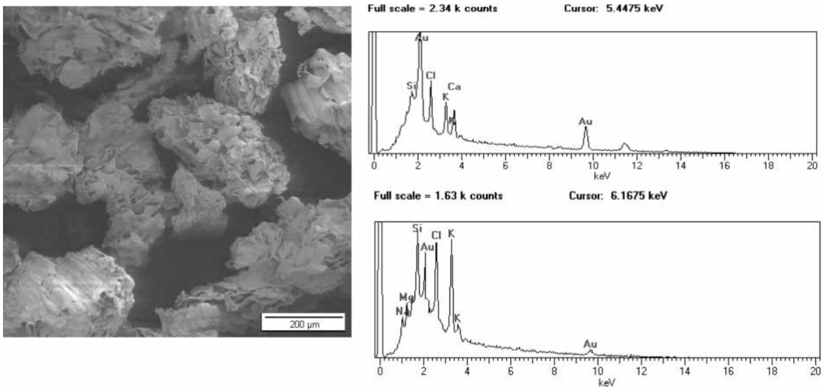

Figure 7. Scanning electron micrograph and EDS diffract grams for powder of green coconut shell before metal uptake − 100 times of magnification.

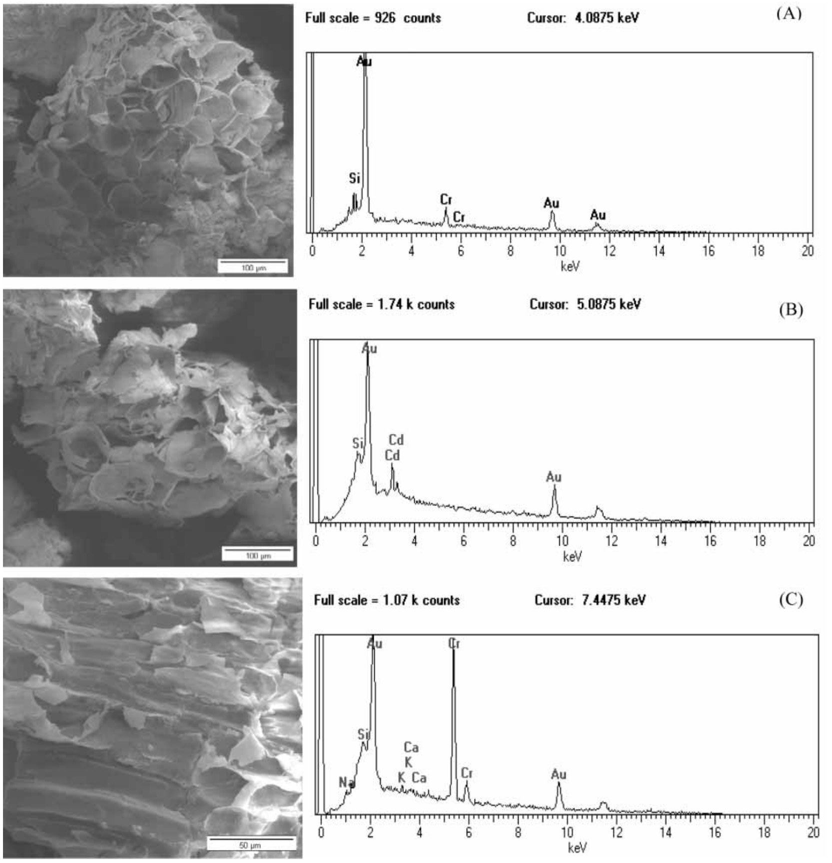

Figure 8. Scanning electron micrograph and EDS diffractograms for powder of green coconut shell. (A) after Cr^{6+} biosorption – 200 times of magnification; (B) after Cd^{2+} biosorption – 200 times of magnification; (C) after Cr^{3+} biosorption − 500 times of magnification.

on the coconut shell particles due to the irregular surface. The presence of metal ions over the surface of the biomass was confirmed by EDS analyses.

The EDS analysis obtained also shows the presence of Cl, K, Na, Mg, and Ca as natural species on the coconut shell, as already expected (15). The presence of these elements could influence on the adsorption mechanism through ionic exchange interactions.

The EDS analysis after the biosorption process shows the absence of Cl, K, Na, and Mg bands in the biomass particles loaded with the different metal ions, that can suggest a possible involvement of different mechanism on the removal of metallic species, like ion exchange, complexation, coordination, and microprecipitation. Due to the complexity of biomass used it is quite possible that at least some of these mechanisms are acting simultaneously (23).

CONCLUSIONS

The results presented in this work show that the powder of the coconut shell presents a great potential for application in the removal of the metals Cd^{2+}, Cr^{6+}, and Cr^{3+}.

The study of adsorption isotherms revealed that the Langmuir model adjusts the experimental data very well for the adsorption of cadmium by coconut fiber powder. In the case of the Freundlich model the values observed for R^2 fit best all the experimental dates, mainly for Cr^{3+} adsorption.

The analyses accomplished by SEM-EDS indicated the presence of the metals in the biomass particles after biosorption.

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REFERENCES

1. Gadd, G.M. (1990) *Biosorption, Chemistry and Industry*, v.2; 421–426.
2. Churchill, S.A., Walters, J.V., and Churchill, P.F. (1995) Sorption of heavy metals by prepared bacterial cell surface. *J. Environ. Eng.*, 121 (10): 706–711.
3. Kuyucak, N. and Volesky, B. (1988) Biosorbents for recovery of metals from industrial solutions. *Biotechnol. Lett.*, 10 (2): 137–142.
4. Espósito, A., Pagnanelli, F., Lodi, A., Solisio, C., and Veglio, F. (2001) Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentration. *Hydrometallurgy*, 60: 129–141.
5. Pino, G.A.H. (2005) Biosorption of heavy metals using powder of green coconut shell. Master's Thesis, Catholic University of Rio de Janeiro: Brazil. (In Portuguese).
6. Chandra, K., Kamala, C.T., Chary, N.S., and Anjaneyulu, Y. (2003) Removal of heavy metals using a plant biomass with reference to environmental control. *International Journal of Mineral Processing*, 68: 37–45.
7. Dornellas de Barros, M.A., et al. (2000) Remoção de metais em água utilizando diversos adsorventes. *Revista Tecnológica*, Ed especial. 65–72.
8. Gaballah, I., Goy, D., Kilbertus, G., and Thauront, J. (1994a) Decontamination of industrial effluents for environment protection and recycling of metals. *Resources, Conservation and Recycling*, 10: 97–106.
9. Schneider, I., Rubio, J., and Smith, R. (2001) Biosorption of metals onto plant biomass: exchange adsorption or surface precipitation? *International Journal of Mineral Processing*, 62: 111–120.
10. Gomes, F.J., Minelli, M.F., Andrade, M.C., and Gomes, L.N.L. (1995) Use of biosorbents in the effluent treatment containing heavy metals. *Metalurgia e Materiais*, Outubro, 892–895. (In Portuguese).
11. Carrijo, O.A., Liz, R.S., and Makishima, N. (2002) Fibra da casca de coco verde como substrato agrícola. *Horticultura brasileira. Brasília*, 20: 533–535.

12. Gaballah, I. and Kilbertus, G. (1994b) Elimination of As, Hg and Zn from synthetic solutions and industrial effluents using modified barks. In *Separation Process: Heavy Metals, Ions and Minerals*. Misra, M. (ed.), The Minerals, Metals & Materials Society.
13. Gaballah, I., Goy, D., Allain, E., Kilbertus, G., and Thauront, J. (1997) Recovery of copper through decontamination of synthetic solutions using modified barks-*Metallurgical and Materials Transactions B*, 28B: 13–23.
14. Hunt, S. (1986) *Diversity of Biopolymer Structure and its Potential for Ion-Binding Applications*. Eccles, H. and Hunt, S. (eds.), Ellis Horwood Limited Publishers: London, United Kingdom.
15. Rosa, M.F., Santos, F.J.S., Montenegro, A.A.T., et al.. (2001) Characterization of powder of green coconut shell used as agricultural substratum embrapa tropical agroindustry. Official Technical Report, 54, 6, (In Portuguese).
16. Scorzelli, I.B. (1999) Removal of cadmium and zinc from very dilute solutions by ion flotation. PhD Diss., Catholic University of Rio de Janeiro: Brazil. (In Portuguese).
17. Aksu, Z. (2001) Equilibrium and kinetic modeling of cadmium(II) biosorption by *C.* v ulgaris in a batch system: effect of temperature. *Separation and Purification Technology*, 21 (3): 285–294.
18. Sheng, P.X., et al.. (2004) Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *Journal of Colloid and Interface Science*, 275: 131–141.
19. Chubar, N., Carvalho, J.R., and Neiva, M.J. (2004) Cork biomass as biosorbent for Cu(II), Zn(II) and Ni(II). *Colloids and Surfaces A: hysicochem. Eng. Aspects*, 230: 57–65.
20. Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40: 1361–1403.
21. Freundlich, H. (1907) Ueber die Adsorption in Loesungen. *Z. Phisik. Chem.*, 57: 385–470.
22. Leusch, A. and Volesky, B. (1995) The influence of film diffusion on cadmium biosorption by marine biomass. *Journal of Biotechnology*, 43: 1–10.
23. Wase, J. and Forster, C. (1997) *Biosorbents for Metal Ions*, 1st edition; Taylor and Francis: London, UK.
24. Tipping, E. (2002) *Cation Binding by Humic Substances*, 1st Edition; Cambridge Environmental Chemistry Series: Cambridge, UK.
25. Texeira, C. and Arruda, M. (2003) Biosorption of heavy metals using rice milling by-products. Characterization and application for removal of metals from aqueous effluents. *Chemosphere*, 54: 987–995.