Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions

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Abstract

The objective of this work was to propose an alternative use for coffee husks (CH), a coffee processing residue, as untreated sorbents for the removal of heavy metal ions from aqueous solutions. Biosorption studies were conducted in a batch system as a function of contact time, initial metal ion concentration, biosorbent concentration and pH of the solution. A contact time of 72 h assured attainment of equilibrium for Cu(II), Cd(II) and Zn(II). The sorption efficiency after equilibrium was higher for Cu(II) (89–98% adsorption), followed by Cd(II) (65–85%) and Zn(II) (48–79%). Even though equilibrium was not attained in the case of Cr(VI) ions, sorption efficiency ranged from 79 to 86%. Sorption performance improved as metal ions concentrations were lowered. The experimental sorption equilibrium data were fitted by both Langmuir and Freundlich sorption models, with Langmuir providing the best fit ($R^2 > 0.95$). The biosorption kinetics was determined by fitting first and second-order kinetic models to the experimental data, being better described by the pseudo-second-order model ($R^2 > 0.99$). The amount of metal ions sorbed increased with the biosorbent concentration in the case of Cu(II) and Cr(VI) and did not present significant variations for the other metal ions. The effect of the initial pH in the biosorption efficiency was verified in the pH range of 4–7, and the results showed that the highest adsorption capacity occurred at distinct pH values for each metal ion. A comparison of the maximum sorption capacity of several untreated biomaterial-based residues showed that coffee husks are suitable candidates for use as biosorbents in the removal of heavy metals from aqueous solutions.
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1. Introduction

The removal of heavy metals from contaminated waters has become a major topic of research in recent years, due to the toxicological problems caused by the metal ions to the environment and to human health. Most of the research is directed to developing cost-effective technologies for the removal of metal ions from aqueous solutions. The production of sorbents (activated carbons) or the direct use as biosorbents for the removal of heavy metals from industrial wastewaters are two of the potential alternative uses for low-cost agricultural wastes that have been extensively studied in the last decade [1–9]. Bansal et al. [10] reviewed several criteria to be considered when selecting a potential precursor for the manufacture of activated carbon and Pollard et al. [1] pointed out that few materials would satisfy all the requirements, and that selection is often made on the basis of raw material availability. Furthermore, Evans et al. [2] stated that the manufacture of activated carbon should balance economic viability with performance, with the precursor materials being readily available and a minimum of resources being used in the process of conversion. Based on these criteria, the possibility of using raw agricultural waste that is readily available in significant amounts as biosorbents for the removal of heavy metals from industrial wastewaters seems rather appropriate. Additionally, if deemed necessary, the heavy metals can be easily recovered from the biosorbents for reuse. Therefore, coffee processing residues are potential candidates for use as biosorbents, since in major coffee-producing countries, such as Brazil, this type of residue satisfies the mentioned criteria.

The processing of coffee generates significant amounts of agricultural waste. Coffee husks (CH), comprised of dry outer skin, pulp and parchment, are probably the major residues from the handling and processing of coffee. For every ton of coffee beans produced, approximately 1 ton of husks are generated

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during dry processing, whereas for wet and semi-wet processing this residue amounts to more than 2 tonnes [11]. To our best knowledge, there are no profitable uses for this type of residue and its disposal constitutes a major problem. Although combustion of agricultural wastes is usually considered as an alternative source of energy, it has already been demonstrated that major problems are prone to happen, such as agglomeration, fouling and excessive emissions, due to the low melting point of the ash of burnt coffee husks and the significant amount of volatile organic matter present in the husks [11]. Furthermore, since sustainable development should be prioritized, the development of techniques for giving additional value and reusing this type of residue should be sought.

In view of the aforementioned, the objective of this study was to investigate the feasibility of using dry coffee husks as natural biosorbents for the removal of heavy metals from synthetic aqueous media.

2. Materials and methods

2.1. Samples

Dry coffee husks were acquired from Samambaia Farm, a coffee producer at Santo Antônio do Amparo, Minas Gerais State, Brazil. The husks were obtained from a dry processed coffee after de-hulling.

2.2. Biosorbent preparation and characterization

Coffee husks were washed with distilled water to remove dirt and color, and dried at 105 °C for 5 h in a convection oven. They were then treated with 2% formaldehyde solution in order to reduce organic leaching and avoid mould formation during batch sorption [12]. The point of zero charge (PZC) and surface functional groups were evaluated according to the titration procedures described by Valdés et al. [13]. Three aqueous solutions of different pH's (3, 6 and 11) were prepared. Several amounts of coffee husks (0.05%, 0.1%, 0.5%, 1.0%, 3.0%, 7.0% and 10.0% w/w) were added to 20 mL of each solution. The aqueous suspensions containing different amounts of the biosorbent were let to equilibrate for 24 h under agitation (100 rpm) at 25 °C. The pH of each solution was then measured using a digital pHmeter (Micronal, São Paulo, Brazil). The pzc was determined as the converging pH value from the pH versus biosorbent mass curve. Surface functional groups determination was based on the Boehm titration method. Solutions of NaHCO₃ (0.1 mol/L), Na₂CO₃ (0.05 mol/L), NaOH (0.1 mol/L), and HCl (0.1 mol/L) were prepared with deionized water. A volume of 50 mL of these solutions was added to vials containing 1 g of dry coffee husks and shaken (100 rpm) until equilibrium (24 h), then filtered. Five solution blanks (without the sorbent) were also prepared. The excess of base or acid was then determined by back titration using NaOH (0.1 mol/L) and HCl (0.1 mol/L) solutions [13].

The morphological characteristics of the biosorbent surface, before and after sorption of heavy metals, was investigated by scanning electron microscopy – SEM (JSM-5410 Scanning Electron Microscope). Samples were covered with a thin layer of gold. Since the coffee husks were employed whole (no comminution), the average particle size was evaluated by an image analyzer software [14].

2.3. Preparation of solutions

The stock solutions of Cu(II), Zn(II) and Cd(II) were prepared by dissolving the specific sulfate salts in distilled water, and, for the stock solution of Cr(VI), $K_2Cr_2O_7$ was dissolved in distilled water. The test solutions were prepared by diluting a 1 g/L stock solution of each metal ion. The initial ion concentrations ranged from 50 to 100 mg/L.

2.4. Effect of contact time

Batch experiments of biosorption were performed in 250 mL Erlenmeyer flasks placed in a temperature-controlled orbital shaker (Nova Ética, São Paulo, Brasil), at 25 ± 2 °C, and stirred at 100 rpm for periods of time that ranged from 0.5 to 72 h. In all sets of experiments, 1 g of coffee husks was thoroughly mixed with 150 mL solution of the specific ion being sorbed. The solution pH was adjusted to 4 with HCl (0.1 mol/L) for the chromate salt solutions and H_2SO_4 (0.1 mol/L) for the sulfate salt solutions. All tests were performed in three replicates.

2.5. Analysis of metal ions

After the specified time period, 5 mL aliquots were taken from the Erlenmeyer flask, filtered (0.45 μm) and the concentration of the metal ions was determined using an atomic absorption spectrometer (GBC AVANTA 932 PLUS, Dandenong, Australia). Absorption readings were taken at 324.8 nm for copper, 213.9 nm for zinc, 228.8 nm for cadmium and 357.9 nm for chromium. Sample dilutions ranged from 10 to 100 times depending on the metal ion initial concentration. All samples were acidified with HNO_3 10% (v/v) prior to the analysis. The amount of metal sorbed was determined by taking the difference between the initial ion concentration and the concentration of the solution at the time of sampling. All determinations were performed in a total of three replicates per experiment and the average values were reported. Since the pH affects the state in which the metal ion will be present in solution, and, consequently, the mechanism by which the metal is sorbed, its value was monitored before and after the biosorption tests.

2.6. Sorption isotherms

Both Langmuir and Freundlich models were tested for equilibrium description. Langmuir equation, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface. It does not take into consideration interactions between adsorbed molecules. It can be represented by the equation:

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{1}$$

where Q_e corresponds to the amount adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is the solute concentration (mg/L) in the aqueous solution after equilibrium was reached, and Q_{max} and K_L are constants related to the maximum adsorption capacity (mg/g) and the adsorption energy (L/mg), respectively. The product of Q_{max} and K_L represents the constant for Henry's Law [15]. Freundlich's equation is an empirical model based on heterogeneous adsorption over independent sites and is given by:

$$Q_e = K_F C_e^{1/n} \qquad (2)$$

where K_F is related to binding energy and adsorption capacity and n is related to the intensity of adsorption [16].

2.7. Sorption kinetics

The controlling mechanism of the metal biosorption process was investigated by fitting first and second-order kinetic models to the experimental data. The linearized first-order kinetic model is given as [9]:

$$\log(Q_e - Q_t) = \log Q_e - 0.4342 k_1 t \qquad (3)$$

where Q_e and Q_t are the amounts of metal ions adsorbed per unit mass of biosorbent (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant for first-order adsorption (min^{-1}). The linearized second-order kinetic model is given as [9]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (4)$$

where k_2 is the rate constant for the second-order adsorption kinetics (g mg^{-1} min^{-1}). The straight-line plots of $\log(Q_e - Q_t)$ against t and of t/Q_t against t were used to determine the rate constants and correlation coefficients for the first and second-order kinetic models, respectively.

3. Results and discussion

3.1. Characterization of the biosorbent

The average dimensions of the coffee husks (±standard deviation) were determined as 9.71 ± 2.09 and 6.09 ± 1.75 mm for the major and minor diameters, respectively. The analysis was based on three randomly selected samples of 200 particles each and a photograph of a typical sample is displayed in Fig. 1. Physical characterization of the biosorbent before and after biosorption was carried out by SEM and the respective micrographs are presented in Fig. 2. Notice that there is an evident morphological difference between the surface of the husks before (Fig. 2a) and after biosorption of metals, and also between the surfaces with adsorbed copper (Fig. 2b) and chromium (Fig. 2c) ions. It is clearly seen that the surface of the coffee husks after biosorption of Cu(II) became smoother than it was before biosorption, corroborating the presence of the adsorbed metal on the surface. The non smooth patches represent oddly distributed abrasions in the husk skin. In regard
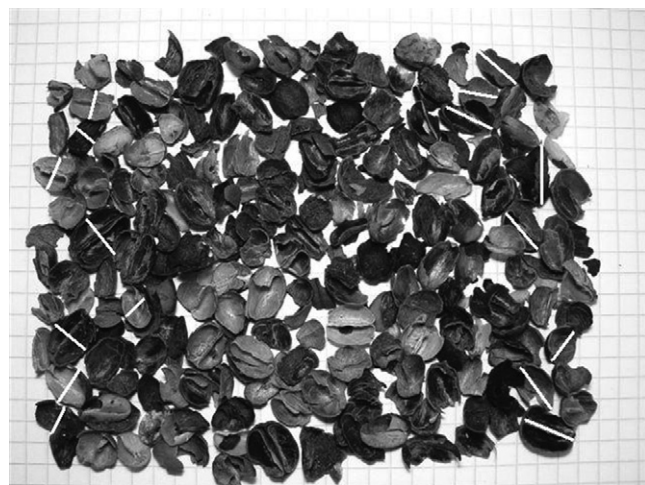

Fig. 1. Coffee husks sample image displaying examples of measured dimensions. White solid lines at the right and left sides of the image correspond to major and minor diameter measurements, respectively.

to the surface with adsorbed chromium, the morphology resembles a network of interconnected veins. The morphological differences between the surfaces with adsorbed copper and with adsorbed chromium can be attributed to the differences in ionic species present in solution for each metal ion, i.e., divalent copper, zinc, and cadmium ions in comparison to oxygenated anionic species for chromium, and the respective sorption mechanisms, i.e., simple cation exchange for divalent metal ions or direct and indirect reduction for chromium oxyanions [8]. The same behavior observed for copper was also observed for zinc and cadmium metal ions with varying degrees of smoothness of the surface. The functional groups at the surface of the husks, characterized by the Boehm method, were predominantly phenolic (2.24 ± 0.03 mmol/g$_{sorbent}$), followed by lactonic (1.05 ± 0.03 mmol/g$_{sorbent}$), carboxylic (0.60 ± 0.02 mmol/g$_{sorbent}$) and basic (0.49 ± 0.01 mmol/g$_{sorbent}$) groups. The estimated amounts of functional groups depleted by the biosorption of metals ions, based on the difference of the functional groups at the surface determined by Boehm titration prior to and after sorption tests, are presented in Fig. 3. All functional groups were involved in the biosorption of all metal ions, with the relative affinities being defined by the amount depleted by the binding metal as follows: Zn(II) > Cu(II) > Cr(VI) > Cd(II) for carboxylic groups; Cr(VI) > Zn(II) > Cd(II) > Cu(II), for lactonic groups; Cr(VI) > Zn(II) > Cu(II), > Cd(II) for phenolic groups; and Cu(II), > Cr(VI) > Cd(II) > Zn(II) for basic groups. It was verified by atomic absorption analysis of the titrated solutions that the Boehm titration procedure did not lead to desorption of metal ions in any of the method steps.

3.2. Determination of PZC

The experimental titration curves for PZC determination are presented in Fig. 4. These results indicate PZC values in the range of 4.3–4.5 and therefore pH values should be maintained above 4.5 to ensure a predominant negatively charged surface.
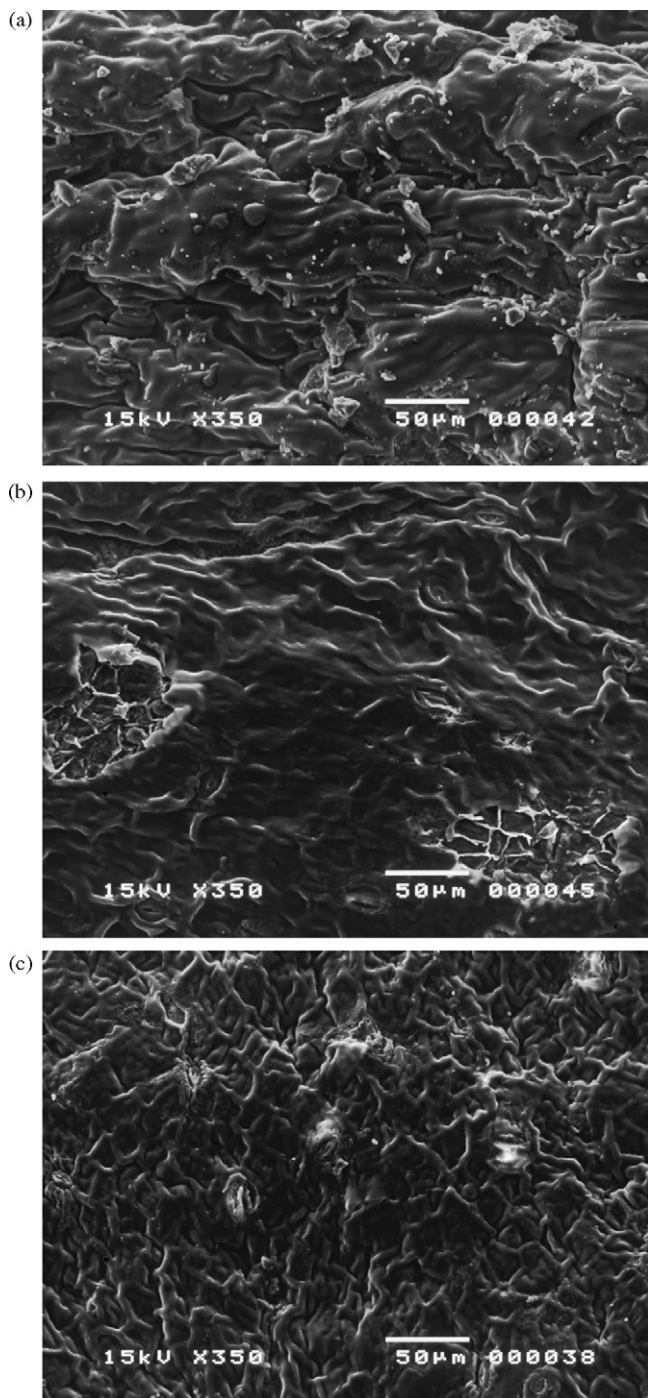
(a)

(b)

(c)

Fig. 2. SEM images showing surface morphologies of the coffee husk (a) before and after biosorption of (b) copper and (c) chromium ions.

However, sorption tests were initially performed at a selected pH value of 4, based on the fact that, within the metal ions concentration range used in this study: (i) copper introduces a limiting pH value of 4.5, above which its precipitation begins in the form of insoluble hydroxide [5,9,17]; (ii) the hydrolysis of Cr(VI) will predominantly produce anionic species at low pH values [6,17], thus, requiring a predominant positively charged surface for its efficient removal; and (iii) on the idea of working in a condition close to that naturally established by the medium, thus, not
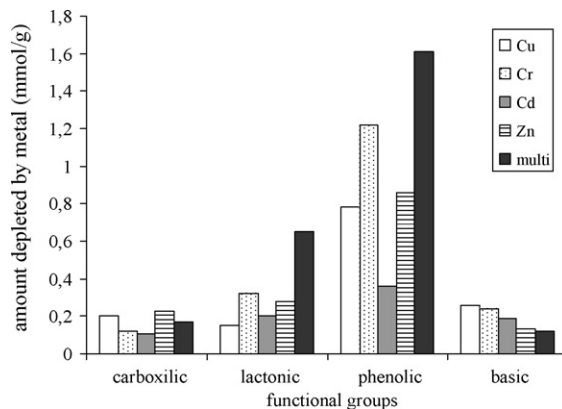

Fig. 3. Amount of functional groups at the surface depleted by the binding metal ions.

requiring significant modifications. Zinc will be predominantly present in the form of Zn(II) at pH < 7 [17,18] and, according to the cadmium speciation diagram [17], the predominant species at pH < 8 is Cd(II) [19]. Thus, at pH 4, sorption capacity for both cadmium and zinc were expected not to be as high as for copper and chromium ions if electrostatic forces are the main responsible for metal uptake.

3.3. Biosorption kinetics

The CH biosorption data, at room temperature and pH 4, showed that a contact time of 72 h assured attainment of equilibrium for all the metal ions studied, except for Cr(VI). The results obtained for the metal sorption tests are presented in Fig. 5. It can be readily observed that sorption occurred at faster rates in the first 6 h for all initial ion concentrations. For a sorption period of 6 h, the amount of adsorbed metal ion was in the range of 80–90% for all the initial ion concentrations. Results indicate that the time to reach equilibrium is slightly affected by the sorbate initial concentration, but it is rather influenced by the nature of the metal ion in solution, since equilibrium was not attained for Cr(VI) after 72 h contact time. Biosorption efficiency decreased as metal ion concentrations increased, indi-
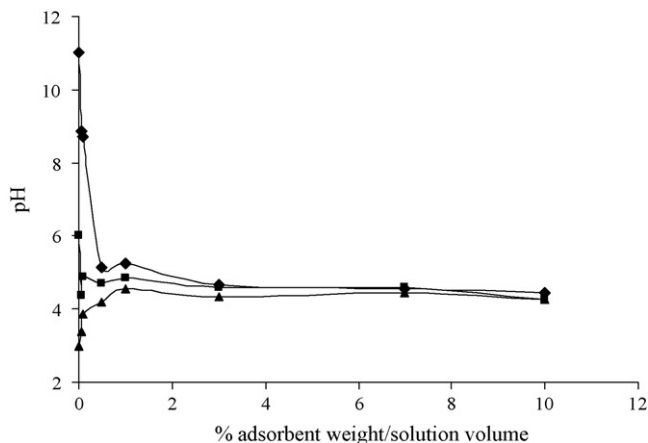

Fig. 4. Experimental curves for PZC determination. (▲) Initial pH 3; (■) initial pH 6; (♦) initial pH 11.
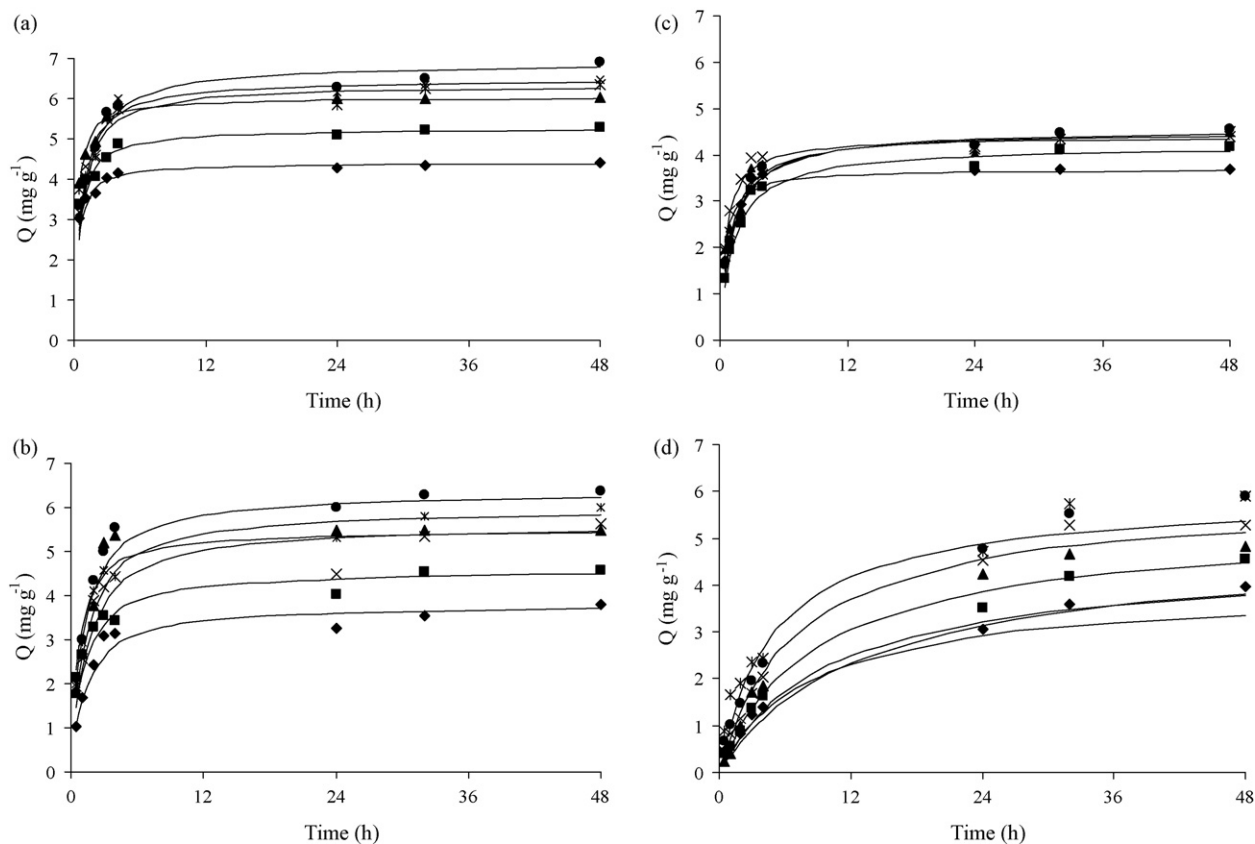
Fig. 5. Effect of contact time on metal sorption by coffee husks from single component solutions: (a) Cu(II); (b) Cd(II); (c) Zn(II); and (d) Cr(VI). ($\blacklozenge$) 50 mg/L; ($\blacksquare$) 60 mg/L; ($\blacktriangle$) 70 mg/L; ($\times$) 80 mg/L; ($\ast$) 90 mg/L; ($\bullet$) 100 mg/L. Solid lines correspond to pseudo-second-order kinetics model fits.

cating saturation. This was expected since, for lower metal ion concentrations, the ratio of surface active sites to total amount of metal ions is high, and, thus, all metal ions can more easily interact with the biosorbent and be removed from the solution. The biosorption efficiency was higher for copper ions than for all the other metals. Divalent zinc and cadmium ions presented lower values for biosorption efficiency when compared to divalent copper ions. This behavior can be attributed to the fact that, at pH 4 (lower than the biosorbent PZC), the electrostatic repulsion between Zn(II) and Cd(II) and the predominant positively charged surface of the biosorbent interfered with the sorption process. The low but effective biosorption of those ions at pH 4 can be attributed either to isolated clusters of negatively charged sites distributed over the surface, where neighboring positively charged functional groups are not strong enough to cause repulsion to the ions, or to ion-exchange mechanism with light metals comprising part of the husks composition. It is noteworthy to point out that, in the case of chromium, at a low pH range, the expected predominant species in solution is $HCrO_4^-$ for a wide range of chromium concentrations [20]. This was verified by constructing the speciation diagram for the experimental conditions employed in this study, using the software MEDUSA [17]. Due to its high reduction potential value (above +1.3 V), Cr(VI) is highly susceptible to undergo reduction to Cr(III) prior to its effective binding to the sorbent surface [21], with the carboxylic and hydroxyl groups at the surface acting as electron donors in the solution. Also, as pointed out by Park et al. [21],

the chromium bound to the biomass is likely to remain in the hexavalent state if there are a small number of electron-donor groups at the biosorbent surface or protons in the solution. The possibility of sorption by ion exchange should not be ruled out either, in the case where Cr(VI) is effectively reduced to Cr(III). The exact mechanism for the sorption of chromium cannot be ascertained from this work and further study is required if the mechanism is to be correctly determined.

The controlling mechanism of heavy metal biosorption was investigated by fitting first and second-order models, given by Eqs. (3) and (4), respectively, to the experimental data for the biosorption dynamics. The results of the kinetic parameters for all studied metal ions are presented in Table 1. The low correlation coefficient values obtained for the pseudo-first-order model indicate that sorption is not occurring exclusively onto one site per ion. Based on the correlation coefficients, the biosorption for all metal ions is best described by the pseudo-second-order model (see solid lines in Fig. 5), which was developed based on the assumption that the rate limiting step may be chemisorption promoted by either valency forces, through sharing of electrons between biosorbent and sorbate, or covalent forces, through the exchange of electrons between the parties involved [22]. The values of the rate constant varied with initial concentration for all metals. Although consistency is expected for these values when a single controlling mechanism is assumed by the model, variations do occur for natural biosorbents and are usually attributed to the heterogeneous nature of the biosorbent surface [23]. The

Table 1
Pseudo-first-order and pseudo-second-order kinetic parameters for sorption of Cu(II), Cd(II), Zn(II) and Cr(VI) onto coffee husks

Ion	Concentration (mg/L)	Pseudo-first-order		Pseudo-second-order	
		k_1	R^2	k_2	R^2
Cu(II)	50	0.0509	0.8492	0.6613	0.9999
	60	0.0827	0.8854	0.4069	0.9998
	70	0.0564	0.6820	0.5762	0.9999
	80	0.0666	0.8608	0.2454	0.9996
	90	0.0440	0.8219	0.2415	0.9989
	100	0.0613	0.9051	0.1662	0.9983
Cd(II)	50	0.2764	0.7538	0.1942	0.9957
	60	0.0366	0.8890	0.2051	0.9971
	70	0.0801	0.6324	0.2650	0.9996
	80	0.0497	0.8684	0.1257	0.9901
	90	0.7162	0.9454	0.1294	0.9977
	100	0.1057	0.9456	0.1428	0.9996
Zn(II)	50	0.5642	0.6152	0.5937	0.9999
	60	0.0481	0.8814	0.1796	0.9982
	70	0.4122	0.8018	0.2218	0.9978
	80	0.0269	0.6533	0.3885	0.9997
	90	0.0343	0.8816	0.1959	0.9989
	100	0.0428	0.8851	0.1798	0.9992
Cr(VI)	50	0.0903	0.9389	0.0298	0.9881
	60	0.0866	0.9566	0.0219	0.9911
	70	0.0737	0.9895	0.0159	0.9881
	80	0.0744	0.9446	0.0215	0.9956
	90	0.1172	0.9337	0.0339	0.9894
	100	0.0698	0.9921	0.0238	0.9939

metal ions may be adsorbed at variable rates by different functional groups at the surface. Also, distinct ionic species might be present simultaneously in the solution, hence, each of them being adsorbed at variable rates as a function of their affinity to the individual functional groups and of the type of binding mechanism being taken place. Furthermore, in the case of chromium, if reduction of Cr(VI) to Cr(III) is occurring, the assumption of a single controlling mechanism may be detrimental to a good fit by the models herein used [21].

It is noteworthy mentioning that the pH of the metal ions solutions was monitored before and after biosorption tests, and no significant changes in pH value occurred for all tests. Similar behavior was also reported by Chubar et al. [24] for biosorption of Cu(II), Zn(II) and Ni(II) in cork biomass and for sorption of Cr(VI) in activated carbons derived from acid-treated coconut shells [6]. Also, the amount of potassium in solution was determined prior and after sorption to evaluate the intensity of its leaching from the husks since this material is known to contain expressive amounts of potassium oxide (~40% of the ash content) [11]. The determinations after sorption resulted in amounts of potassium in the chromium-depleted solution 2.5 times higher than the amount present in the initial solution with the dichromate salt. The same amount of leached potassium was found for a blank test with the sorbent in deionized water, assuring the inorganic nature of the leached potassium. Thus, it can be inferred that potassium can interact with the Cl⁻ ions in solution forming KCl which, in turn, will act as a buffering agent, hence, precluding a significant increase in pH. Buffering action by the
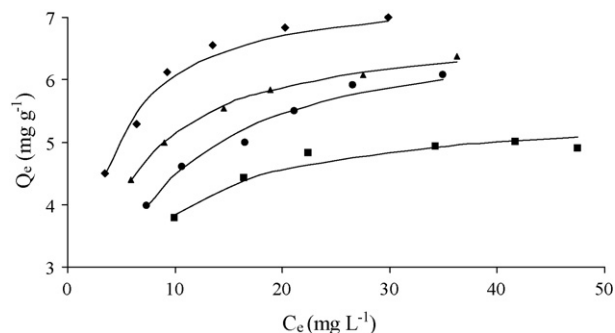

Fig. 6. Sorption isotherms of metal ions by coffee husks, pH 4; $T = 25\,^{\circ}C$. (◆) Cu(II); (▲) Cd(II); (■) Zn(II); (●) Cr(VI). Solid lines correspond to Langmuir fits.

acids used to adjust pH was also proposed by Dakiky et al. [25] as an explanation for the very small changes observed in pH for chromium sorption in a variety of biomaterials at low pH.

3.4. Biosorption equilibrium

Sorption isotherms are presented in Fig. 6. The equilibrium sorption data for all metal ions produced convex upward curves, which are indicative of strong sorption [26]. The equilibrium capacity for metal ions sorption onto coffee husks increased upon increasing the initial metal ion concentration, due to the increase in the concentration gradient (driving force). Both Langmuir and Freundlich models were evaluated for description of metal sorption isotherms (Table 2). Heavy metal sorption from aqueous solutions by coffee husks was better described by Langmuir model (see solid lines in Fig. 6) in comparison to Freundlich model. A characteristic of the Langmuir isotherm is the definition of a dimensionless factor r, called separation factor:

$$r = (1 + K_L Q_{max})^{-1} \qquad (5)$$

Sorption is considered favorable when $r < 1$ [26] which was the case for all metal ions in all tests (Table 2). Metal uptake capacity, represented by Q_{max} in Langmuir equation, was higher for copper ions followed by chromium and cadmium, and was the lowest for zinc ions. A comparison of the metal ions uptake capacities of coffee husks with other untreated biomaterial-based sorbents is presented in Table 3. A direct comparison is not possible because the differences in metal uptake capacities are due to a variety of parameters and conditions employed in each referenced work. Aside from the differences in experimental conditions, differences in the properties of each sorbent such as structure, functional groups and surface area, do not allow

Table 2
Langmuir and Freundlich constants for sorption of metals by CH

Metal	Langmuir				Freundlich		
	Q_{max} (mg/g)	K_L (L/mg)	r	R^2	K_F	n	R^2
Cu(II)	7.496	0.4232	0.24	0.9783	3.702	5.01	0.9025
Cd (II)	6.854	0.3024	0.33	0.9972	3.188	5.05	0.9728
Zn (II)	5.565	0.2238	0.45	0.9524	2.721	6.07	0.8421
Cr (VI)	6.961	0.1805	0.44	0.9821	2.353	3.65	0.9810

Table 3
Langmuir based maximum adsorption capacity of several untreated biosorbents for heavy metal adsorption at ambient temperature

Biosorbent Cu(II)	Q_{max} (mg/g) (T (°C)/pH)	Ref.	Biosorbent Zn(II)	Q_{max} (mg/g) (T (°C)/pH)	Ref.
Papaya wood	19.9 (25/5)	[27]	*Tectona grandis* L.f. leaves	16.4 (30/5)	[9]
Tectona grandis L.f. leaves powder	15.4 (25/5)	[9]	Papaya wood	13.5 (25/5)	[26]
Wheat shell	8.3 (25/5)	[28]	Peanut hull	9.0 (25/6.7)	[28]
Peanut hull	8.0 (25/7)	[29]	Coir	8.6 (25/5.6)	[37]
Coffee husks	*7.5 (25/4)*	*This study*	*Coffee husks*	*5.6 (25/4)*	*This study*
Olive mill solid	5.0 (25/4)	[30]	Cocoa shell	2.9 (22/2)	[32]
Banana peel	4.8 (25/6–8)	[31]			
Orange peel	3.7 (25/6–8)	[31]			
Cocoa shell	2.9 (22/2)	[32]			
Cd(II)			**Cr(VI)**		
Papaya wood	17.2 (25/5)	[27]	Almond shells	10.6 (30/2)	[25]
Olive cake	10.6 (35/4.5)	[33]	Cactus leaves	7.1 (30/2)	[25]
Rice polish	9.7 (20/8.6)	[34]	*Coffee husks*	*7.0 (25/4)*	*This study*
Rice husk	8.6 (28/6.6)	[35]	Maple sawdust	5.1 (25/5)	[38]
Coffee husks	*6.9 (25/4)*	*This study*	Jatropha oil cake	0.8 (25/2)	[39]
Peanut hull	6.0 (25/6.7)	[29]	Sugarcane bagasse	0.6 (25/2)	[39]
Wheat bran	0.7 (30/8.6)	[36]	Maize corncob	0.3 (25/2)	[39]

for direct comparisons. However, qualitatively, it is evident that the metal uptake capacity of coffee husks, in general, exceeds or is comparable to those for other sorbents presented in Table 3. These results reinforce the feasibility of employing coffee husks as biosorbents for metal ions removal from aqueous solutions, since they present good adsorption capacity in comparison to other low-cost sorbents. Aside from the metal uptake capacity, the major advantage of coffee husks as low-cost sorbents is that they are readily available in large quantities (at least in Brazil) and do not present an alternative profitable use. Also, after metal sorption, the metal-laden husks can be used as a source of energy through combustion [11]. The main disadvantage is that, for the conditions used in this study, the metal ion sorption kinetics for untreated coffee husks is slow compared to other sorbents discussed in the literature [29,35,39].

3.5. Effect of biosorbent concentration

Fig. 7 shows the effect of biosorbent concentration on the amount of copper and chromium ions biosorbed. It is clear that the amount of metal ions sorbed varied with the biosorbent con-
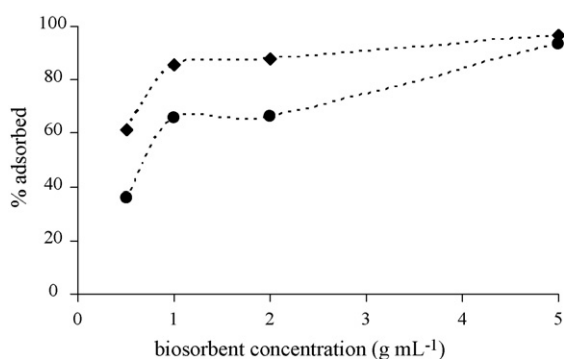

Fig. 7. Effect of biosorbent concentration on metal biosorption on CH, pH 4; $T = 25$ °C. (♦) Cu(II); (●) Cr(VI).

centration and that the amount sorbed increased with an increase in biosorbent dosage. The resulting effect can be easily explained by an increase in surface area (more availability of active adsorption sites) with the increase in biosorbent mass. Similar behavior for the effect of sorbent concentrations on metal sorption capacity was observed and discussed in the literature for a variety of sorbents [5,9,18]. The effect of increasing biosorbent concentration on the amount of cadmium and zinc sorbed was not significant, presenting only a slight increase in amount sorbed with an increase in biosorbent concentration, and hence was not included in Fig. 7.

3.6. Influence of initial pH

The pH of the aqueous medium not only affects the solubility of the metal ions but also the ionic form in which it will be present in the solution and the type and ionic state of the functional groups at the biosorbent surface [40]. The choice of pH range (4–7) evaluated in the present study was based on the fact that it represents the normal pH range in natural waters. Also, at lower pH levels (<4), leaching of organic matter was observed, even with the 2% formaldehyde treatment. The effect of pH on the biosorption efficiency of metal ions is depicted in Fig. 8. The amount of copper ions sorbed by CH increased with the increase in pH from 4 to 6, followed by a decrease from pH 6 to 7. From the speciation diagram for copper [17] in between pH 4 and 5, copper is mainly present in the form of Cu(II), with smaller amounts in the form of CuOH$^+$. From pH 5 to 6, the situation is reversed, with an increase in CuOH$^+$ concentration and a sharp decrease in Cu(II) concentration. At pH 6, CuOH$^+$ concentration reaches a maximum and Cu(II) concentration becomes almost zero. Hence, from pH 4 to 6, the increase in the amount of copper ions biosorbed by CH is justified by the biosorbent surface becoming more negatively charged above pH at PZC value of 4.5 and, thus, establishing a
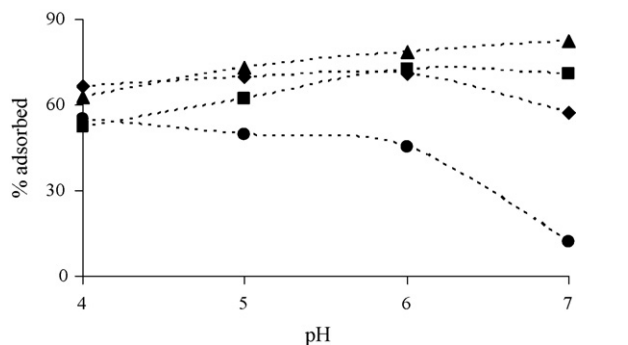
Fig. 8. Effect of initial solution pH on metal biosorption on CH. (♦) Cu(II); (▲) Cd(II); (■) Zn(II), (●) Cr(VI).

more favorable condition for the positively charged copper ions to be removed from the solution. In between pH 5 and 6, there is a sharp increase in insoluble $Cu(OH)_2$ concentration, and a further increase in pH from 6 to 7 promotes a decrease in the amount biosorbed, since, in this range, the concentration of positively charged copper ions in the solution undergoes a sharp decrease. The amount of chromium ions sorbed decreased from pH 4 to 7, since chromium is predominantly present in anionic form in solutions within that pH range and the surface becomes more negatively charged as the pH is increased above the PZC value. Both cadmium and zinc ions presented an increase in the amount sorbed with and increase in pH from 4 to 7. This is easily explained by the fact that, in that pH range, both metals will be mostly present in solution either in their divalent ionic form or as a positively charged hydroxide $(Me(OH)^+)$ [17], making it favorable for biosorption in an increasingly negatively charged surface.

4. Conclusions

A study of the feasibility of using dry coffee husks as untreated biosorbents for the removal of metal ions from aqueous solutions was successfully carried out. Coffee husks presented better sorption performance for low concentrations of metal ions. After increasing the initial metal concentration from 50 to 100 mg/L, the adsorption efficiency decreased in 9%, 8%, 40%, and 24% for Cu(II), Cd(II), Zn(II) and Cr(VI), respectively. The biosorption efficiency was higher for copper ions than for all the other metals, at pH 4. Biosorption kinetics was best described by a pseudo-second-order model. Equilibrium was attained after 72 h of contact time, except for Cr(VI). Sorption isotherms were better described by Langmuir model in comparison to Freundlich. Coffee husks maximum sorption capacity (evaluated based on Langmuir fit) was higher than other untreated residues such as sugarcane bagasse, cocoa shell, banana and orange peel, and peanut hulls. It was observed that, for Cu(II) and Cr(VI), the amount of metal ions sorbed increased with the biosorbent concentration due to the consequent increase in surface area. The effect of the initial pH in the biosorption efficiency was verified in the pH range of 4–7, and it was demonstrated that the highest adsorption capacity occurs at distinct pH values for each metal ion. Also, the pH of the metal ions solution was

monitored before and after sorption tests, and no significant variations were observed, herein attributed to a buffering action by leached potassium. The experimental data demonstrated coffee husks to be a suitable candidate for use as biosorbents in the removal of heavy metals of aqueous solutions such as industrial wastewaters.

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