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REVIEW

Biosorption of Cu(II) and Pb(II) from aqueous solutions by chemically modified spent coffee grains

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Abstract In this research, spent coffee grains were modified with citric acid solutions (0.1 and 0.6 M) to increase the quantity of carboxylic groups improving its metal adsorption capacity. Added functional groups on modified and non-modified spent coffee grains were identified and quantified by attenuated total reflection Fourier transform infrared analyses and potentiometric titrations, respectively. These adsorbents were used for the removal of lead (II) and copper (II) from aqueous solutions at 30 °C and different pH in batch systems. In addition, adsorption–desorption experiments were conducted to evaluate the possibility of re-using the modified adsorbent. Potentiometric titrations data reveal that the quantity of carboxylic groups was increased from 0.47 to 2.2 mmol/g when spent coffee grains were modified with 0.1 and 0.6 M citric acid. Spent coffee grains treated with 0.6 M citric acid, achieved a maximum adsorption capacity of 0.77 and 1.53 mmol/g for lead (II) and copper (II), respectively, whereas non-modified spent coffee grains only reached 0.24 and 0.19 mmol/g for lead (II) and copper (II), respectively. Desorption of lead (II) and copper (II) achieved around 70 % using 0.1 N HCl for non-modified and modified spent coffee grains with 0.6 M citric acid. It is suggested that lead (II) and copper (II) species were adsorbed mainly on the carboxylic groups of modified spent coffee grains and these metals may be exchanged for hydrogen and calcium (II) ions during adsorption on non-modified spent coffee grains. Finally, the adsorption equilibrium was reached after 400 min for modified spent coffee grains with 0.6 M citric acid. Modified spent coffee grains are a promising option for removing metal cations from aqueous solutions due to its low cost and high adsorption capacity (about 10 times higher than the activated carbons).

Keywords Adsorption · Carboxylic groups · Heavy metals · Lignocellulosic biosorbents · Wastewater

Introduction

Industrial activities, such as electroplating, textile dyeing, storage batteries, ceramic, glass and metal-processing industries discharge metals-containing wastewater. These pollutants are dangerous for human health and living organism due to their high toxicity, non-biodegradability, and their accumulation in the biosphere (Kaim and Schwederski 1994).

In some industrial effluents, the concentration of heavy metals is higher than the safe permissible limits, which affects the biosphere, and thus, these pollutants must be removed. Several physicochemical processes have been studied to remove heavy metals from aqueous solutions including precipitation, electrochemical treatment, membrane filtration, ion exchange and adsorption (Guillard and Lewis 2001; Valverde et al. 2001; Matlock et al. 2002; Ng et al. 2002; Naiya et al. 2009a). Among these treatments, biosorption can be considered as an eco-friendly and

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economical wastewater treatment that has been proven to be highly efficient to remove low metal concentration, and in addition, the biosorbent can be easily regenerated (Chojnacka 2010). Several biosorbents have been tested such as algae, bacteria, fungi, yeast, and agro-waste materials (Romera et al. 2006; Ahluwalia and Goyal 2007; Kumar et al. 2007; Kumar et al. 2008; Sud et al. 2008; Basha et al. 2009; Garcia-Reyes and Rangel-Mendez 2009; Garcia-Reyes et al. 2009; Garcia-Reyes and Rangel-Mendez 2010; Cerino-Córdova et al. 2011a, b). Agro-waste materials can be considered as alternative adsorbents due to their low cost and physicochemical properties (Naiya et al. 2009b), besides these materials are widely available as by-products from industrial processes such as beverage, wood, and food industries, among others.

Among agro-waste materials, spent coffee grains (by-product of brewing coffee) have the potential to be used as biosorbent for removing heavy metals from aqueous solutions instead of being burned or disposed of. A number of authors have reported the use of coffee by-products to remove either organic (Boonamnuayvitaya et al. 2004; Oliveira et al. 2008) or inorganic (Utomo and Hunter 2006) pollutants from water.

Several researchers have used lignocellulosic materials as metal-cation adsorbents (Naiya et al. 2008), however, in some cases, their adsorption capacities are low in comparison with the commercial adsorbents such as activated carbon and polymeric resins. To overcome these shortcomings, researchers have modified lignocellulosic materials with numerous chemicals, for example, H_2SO_4 (Martin-Lara et al. 2010) and citric acid (Wartelle and Marshall 2000; Marshall and Wartelle 2003; Leyva-Ramos et al. 2005; Altundogan et al. 2007; Marshall et al. 2007; Zhu et al. 2008). The main purpose of such chemical treatments is to increase the quantity of functional groups on the adsorbent, which are capable of binding heavy metals from aqueous solutions. For instance, it was reported that lignocellulosic adsorbents improve its adsorption capacity when these are modified with citric acid.

In this research, to the best of our knowledge, citric acid modification on spent coffee grains have not been reported. In addition, researchers have reported generally the total quantity of functional groups incorporated after citric acid modification but, in this study, functional groups as well as their equilibrium constants were estimated using potentiometric titrations data. These results are helpful for understanding the chemical interaction between functional groups on modified adsorbent and metal cation species in aqueous solutions. Finally, most lignocellulosic adsorbents (modified with citric acid) are not regenerated opposite to this work. This issue is an important step to evaluate the possibility of re-using the spent adsorbent.

The aim of this research was to study lead and copper biosorption from aqueous solution by non-modified and chemically modified SCG. In addition, functional groups and their equilibrium constants were determined to explain the increase of metal adsorption capacity. Furthermore, adsorption mechanisms were proposed based on biosorbent characterization, adsorption–desorption experiments at equilibrium, and adsorption kinetics. This research was conducted at the Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, México during 2010–2011.

Materials and methods

Biosorbent

Spent coffee grains were collected as a by-product of brewing coffee, and washed with deionized water until obtaining a non-colored effluent. Subsequently, SCG were dried at 60 °C for 10 h and stored until chemical modification.

Chemical modification

The chemical modification of SCG was carried out according to a similar method described by Zhu et al. (2008); 30 g of SCG was added to Erlenmeyer flasks containing 210 mL of 0.1 M or 0.6 M citric acid solutions. These suspensions were heated at 60 °C for 12 h and, afterwards, temperature was increased up to 100 °C until almost complete dryness (around 90 min), and then, solids were dried at 120 °C for 24 h. Modified spent coffee grains with 0.1 and 0.6 M citric acid (MSCG-0.1 M and MSCG-0.6 M, respectively) were washed with deionized water to eliminate the excess of citric acid not covalently bound to the biosorbent surface. To verify the complete elimination of citric acid, 10 mL of 0.1 M $Pb(NO)_3$ solution was added to 10 mL of the washing water until obtaining a colorless solution (Zhu et al. 2008). Modified spent coffee grains were dried at 100 °C for 24 h and stored in desiccators prior to characterization and adsorption experiments. To evaluate the effect of thermal treatment upon modification, a blank of SCG was prepared as previously mentioned using deionized water instead of citric acid solutions. Blank is going to be identified throughout the manuscript as non-modified spent coffee grains (NMSCG).

Biosorbent characterization

Functional groups quantity and their equilibrium constants of MSCG-0.1 M, MSCG-0.6 M, and NMSCG were estimated by potentiometric titration methodology proposed by Yun et al. (2001) and applied to agro-waste materials (Pagnanelli et al. 2008; Garcia-Reyes et al. 2009). In addition, to identify the functional groups on biosorbent surface (before and after adsorption and desorption experiments), attenuated total reflection infrared spectra (ATR-FTIR) were recorded in the range of 4,000–650 cm^{-1} (Perkin Elmer, Mod Spectrum One, USA). The pH at point of zero charge (pH_{pzc}) was determined using the procedure reported by Babic et al. (1999). In brief, 20 mL of 0.1 N NaCl was placed in volumetric flasks, different volumes of 0.1 N HCl or 0.1 N NaOH were added, and flasks were filled to 25 mL with 0.1 N NaCl. After that, 0.1 g of adsorbent (MSCG-0.1 M, MSCG-0.6 M or NSCG) was placed into flasks and stirred at 200 min^{-1} for 2 days at room temperature. A blank was carried out at the same conditions without adsorbent. Final pH was measured for samples and blanks and these values were plotted against the added volume of 0.1 N HCl and 0.1 N NaOH. With aid of that plot, surface charge distribution was obtained as follows:

$$q_{H^+} = \frac{C_N(V_b - V_s)}{m} \quad (1)$$

where q_H^+ (mmol/g) represents moles of released ions per mass of adsorbent (m, g), C_N is titrant solution concentration (mmol/L), V_s is titrant added volume at each pH in sample curve (L), V_b is titrant added volume at each pH in blank curve (L). Finally, pH_{pzc} was obtained at the point where surface charge distribution curve intersects with pH axis.

Chemicals

Copper and lead solutions were prepared dissolving $Cu(NO_3)_2 \cdot 5H_2O$ (analytical reagent grade JT Baker, México, MX) and $Pb(NO_3)_2$ (analytical reagent grade Fermont, Monterrey, MX) in deionized water at pH 4 to obtain a stock solution of 1,000 mg/L. Chemicals such as 0.1 N sodium hydroxide, 0.1 N nitric acid, 0.1 N chloride acid, and citric acid were obtained from LeMont (Illinois, USA) and sodium chloride from J.T. Baker (México, MX).

Equilibrium adsorption experiments

Biosorption experiments were carried out in 50-mL conic flasks containing 40 mL of metal solutions with different initial concentration [0.01–1.2 mmol/L for Pb(II) and 0.08–4.72 mmol/L for Cu(II)]. The MSCG and NMSCG were used as biosorbents of Pb(II) and Cu(II) separately as follows: 50 or 100 mg of biosorbents were added into 40 mL of metal solution of Pb(II) or Cu(II), respectively. Flasks were stirred at 200 min^{-1} and kept at 30 °C for 5 days to ensure that adsorption equilibrium was reached. Metal speciation diagrams (Fig. 1) were used to select the pH of metal adsorption experiments. For lead adsorption experiments, the pH solution was maintained at pH 3 and 4, whereas for copper adsorption experiments, pH 4 and 5 were chosen. During adsorption experiments, pH was kept constant by addition of 0.1 N HNO_3 or 0.1 N NaOH. Before and after experiments, aliquots were taken from solution to determine metal concentration by atomic absorption spectroscopy (Thermoscientific model ICE 3000, USA), at wavelength of 217 and 324.8 nm for Pb(II) and Cu(II), respectively. Based on these measurements, the metal biosorption capacity was calculated by Eq. (2).

$$q_e = \frac{V(C_o - C_e)}{m} \quad (2)$$

where V is volume solution (L), C_o and C_e are initial and final metal concentration (mmol/L), and m is adsorbent mass (g).

Desorption experiments

To verify the possibility of re-using the metal-laden biosorbent, adsorption experiments were conducted as

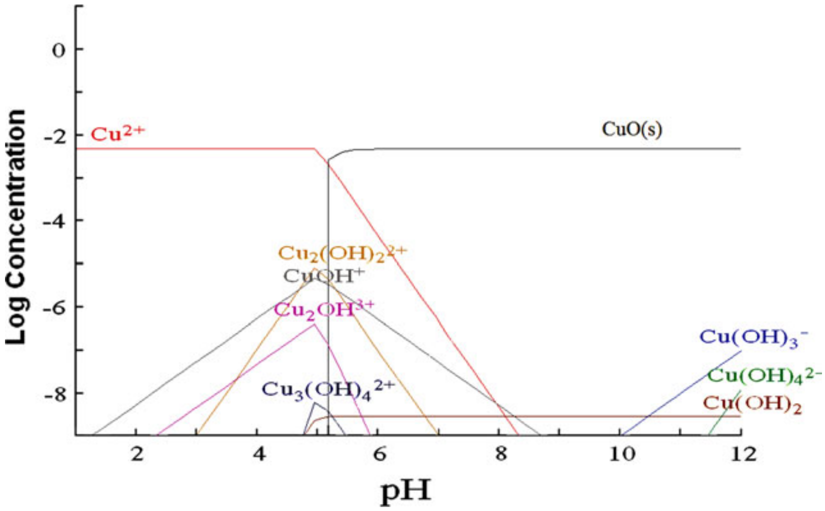

Fig. 1 Speciation diagram of **a** Pb(II) and **b** Cu(II) for a total concentration of 1.20 and 4.72 mmol/L, respectively

described in previous section and the experimental conditions are shown in Table 1. After 5 days, aliquots were taken to determine the equilibrium adsorption capacity. Subsequently, the used biosorbent were filtered and rinsed with 40 mL of deionized water at the same pH of the adsorption experiment. After that, biosorbent was added to flasks containing a selected volume of 0.1 M HCl for 48 h for metal desorption. At the end of the experiments, aliquots were taken to determine metal concentration by atomic absorption spectroscopy. The quantities of desorbed metal per gram of adsorbent (q_d) were calculated with the following equation:

$$q_{\mathrm{d}} = \frac{V_{\mathrm{f}} C_{\mathrm{f}}}{m} \tag{3}$$

where m is adsorbent mass (g), V_f represents volume solution (L) and C_f is final concentration (mmol/L).

Adsorption kinetics

Adsorption kinetic experiments were conducted in stirred batch systems to determine the time required to achieve the equilibrium. Prior to adsorption kinetic experiments, 100 mg of adsorbent (NMSCG, MSCG-0.1 M or MSCG-0.6 M) was hydrated during 24 h with deionized water at pH 4 and 5 for Pb(II) and Cu(II), respectively, and these were kept constant with 0.1 N HNO_3 or NaOH solutions. The hydration step was performed to minimize pH solution variation during kinetic experiments and to swell the biosorbent.

After that, hydrated biosorbent was separated by filtration from the suspension. Afterwards, 250 mL of metal solution (around 1 mmol/L) was added to the flask with the hydrated biosorbent and the stirrer was turned on at 300 min^{-1}. Aliquots were taken at different times to determine the remaining metal concentration in solution by atomic absorption spectroscopy. The samples were carefully taken to avoid removing the adsorbent, and the adsorption capacity (q_t) was calculated taking into account the volume variation during the sampling. The pseudo-first- and pseudo-second-order kinetic models represented by Eqs. (4) and (5) were used to estimate parameters of kinetic models by non-lineal fitting of experimental adsorption data:

$$q_t = \frac{q_{\mathrm{e}}}{1 + e^{-k_1 t}} \tag{4}$$

$$q_t = \frac{k_2 q_{\mathrm{e}}^2 t}{1 + k_2 q_{\mathrm{e}} t} \tag{5}$$

where k_1 (1/min) and k_2 (g/mg·min) are the rate constants of pseudo-first- and pseudo-second-order adsorptions, respectively; q_t (mg/g) denotes the adsorption capacity at time t (min), and q_e (mg/g) is the adsorption capacity at equilibrium. For the pseudo-second-order kinetic model, initial adsorption rate ($h = \mathrm{k}_2\mathrm{q}_\mathrm{e}^2$) can be estimated using the parameters of the kinetic model. Initial adsorption rate refers to the quantity of metal adsorbed per unit mass of adsorbent and unit time. A high value of h means that metal ions, are quickly adsorbed in the first minutes of the adsorption process.

Table 1 Experimental conditions for desorption tests

Metal	Mass (mg)	Adsorption			Desorption
		initial concentration (mmol/L)	pH	Solution volume (mL)	0.1 M HCl volume (mL)
Pb(II)	50	1.00	4	100	100
Cu(II)	100	2.88	5	40	40

Results and discussion

Metal species in aqueous solutions

Figure 1 shows the speciation diagrams of lead and copper for a total concentration of 1.20 and 4.72 mmol/L, respectively. These diagrams were computed using MEDUSA software (Puigdomenech 2010) that is based on equilibrium reactions. Speciation diagrams allow selecting the pH for adsorption experiments to avoid metal precipitation and to identify the metal species in aqueous solution. According to the speciation diagrams (Fig. 1), adsorption experiments must be conducted below 5.2 and 5.6 for Cu(II) and Pb(II) species, respectively.

Chemical characterization

The results given in Table 2 and Fig. 2 showed that the chemical modification of coffee grains led to an increase in the quantity of carboxylic groups and a decrease in the point of zero charge on the biosorbent surface. Marshall and Wartelle (Marshall et al. 2003) found a similar result, however, the equilibrium constants were not reported. In the present research, the quantity of functional groups their equilibrium constants, and point of zero charge were estimated by potentiometric titrations, and these data are shown in Table 2 A high quantity of carboxyl groups (2.2 mmol/g) was determined for MSCG-0.6 M in comparison with MSCG-0.1 M (0.47 mmol/g). In addition, equilibrium constants of functional groups (3.99–4.25 and 7.02–8.36) could be associated with those reported for carboxylic groups of citric acid (3.13, 4.78, and 6.40) (Brown et al. 2005). Carboxylic groups were also identified by means of ATR-FTIR analyses at 1,740 cm^{-1} as shown in Fig. 2. This peak was increased when citric acid

Table 2 Functional groups (b_i, mmol/g) their equilibrium constants (pKa_i) and point of zero charge of non-modified (NMSCG) and modified spent coffee grains with 0.1 M and 0.6 M citric acid (MSCG-0.1 M and MSCG-0.6 M, respectively)

Biosorbent	b_1	pKa_1	b_2	pKa_2	pHpzc
NMSCG	0.92	7.14	0.82	10.46	5.5
MSCG-0.1 M	0.47	4.25	1.87	8.36	3.9
MSCG-0.6 M	2.20	3.99	2.49	7.02	2.8

concentration rose from 0.1 to 0.6 M, showing greater transmittance peaks than those of NMSCG. As mentioned previously, citric acid modification incorporates carboxylic groups to biosorbent, but these groups were not detected by potentiometric titrations on non-modified biosorbent, because calcium is bound to carboxylic groups and its releasing did not cause a pH changing along potentiometric titration (Garcia-Reyes et al. 2009).

Nitrogen-containing sites were detected by ATR-FTIR analyses at 1,650–1,600 cm^{-1} (Fig. 2) as well as by means of elemental analyses (1.4–2.2 % w/w). These functional groups could be used as adsorption sites, since nitrogen contains an electron pair available to form covalent bonds with positively charged species such as Cu(II) and Pb(II) (see Fig. 1). In addition, nitrogen-containing groups could be protonated, therefore, the biosorbent surface acquires a positive charge (see Fig. 3). At pH values below the point of zero charge (pH_{pzc}), adsorbent may uptake anionic species but may cause electrostatic repulsion with positive-charged species. The pH_{pzc} decreased as long as the citric acid concentration was increased, for instance, pH_{pzc} was 4.8 for NMSCG whereas the pH_{pzc} changed to 3.0 and 2.6 for MSCG-0.1 M and MSCG-0.6 M, respectively (see Fig. 3). This behavior could be explained due to the carboxylic groups covalently bound to the biosorbent surface as shown in Fig. 2 and Table 2.

Adsorption isotherms

Langmuir adsorption isotherm model was tried to fit to the experimental adsorption data by non-lineal estimation based on least-square method and equation shown below:

$$q = \frac{q_{\mathrm{Max}} b C_{\mathrm{e}}}{1 + b C_{\mathrm{e}}} \tag{6}$$

where $q_{\max}$ is the maximum adsorption capacity (mmol/g), b is the relative energy of adsorption (L/mmol), C_e is the equilibrium concentration (mmol/L).

The Langmuir model fitted well the experimental data based on the obtained determination coefficients ($0.89 < R^2 < 0.99$) and isotherm parameters are shown in Table 3. Figures 4 and 5 show the adsorption isotherm of Pb(II) and Cu(II), respectively, on NMSCG, and MSCG with 0.1 and 0.6 M citric acid. Regardless of the pH of the solutions, MSCG-0.6 M achieved the maximum adsorption capacity for both metals (i.e., 0.77 mmol of Pb(II)/g at pH 4, and 1.53 mmol of Cu(II)/g at pH 5) followed by MSCG-0.1 M and NMSCG. This behavior is due to the chemical modification of the spent coffee grains that increased the quantity of carboxylic groups on the biosorbent surface (Table 2; Fig. 2). The maximum adsorption capacity of MSCG-0.6 M, obtained in this research for both metals, can be compared with other adsorbents' metal uptake as shown in Table 4. It can be observed that the MSCG-0.6 M had adsorption capacities for Pb(II) and Cu(II) of 5.24 and 8.79 times higher than the commercial activated carbon cloths, respectively (Kadirvelu et al. 2000). Nevertheless, Pb(II) adsorption capacity on MSCG-0.6 M was 56 % lower in comparison with *chlorella* sp. biomass (Almaguer-Cantu et al. 2008).

Decreasing the pH of the solution in one unit, the adsorption capacity of Pb(II) and Cu(II) on MSCG-0.6 M was reduced by 32 and 24 %, respectively, because protons

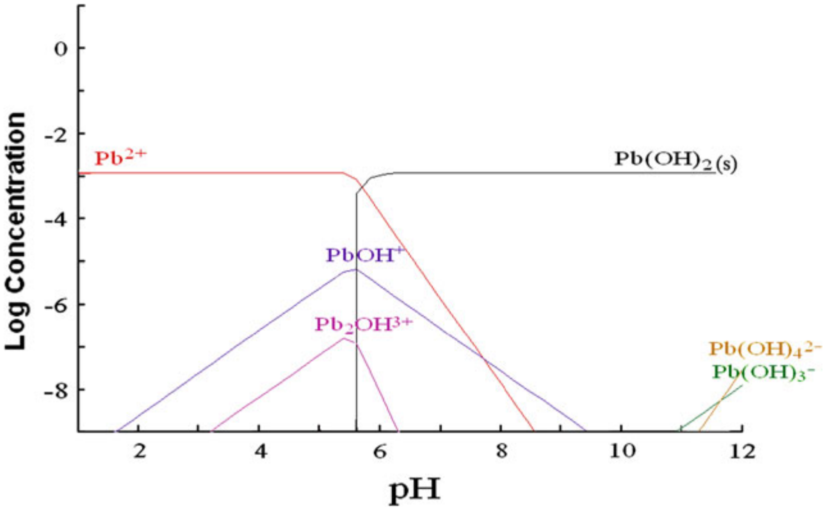

Fig. 2 ATR–FTIR spectra of non-modified spent coffee grains (NMSCG), and modified spent coffee grains with 0.1 M and 0.6 M citric acid (MSCG-0.1 M and MSCG-0.6 M, respectively)

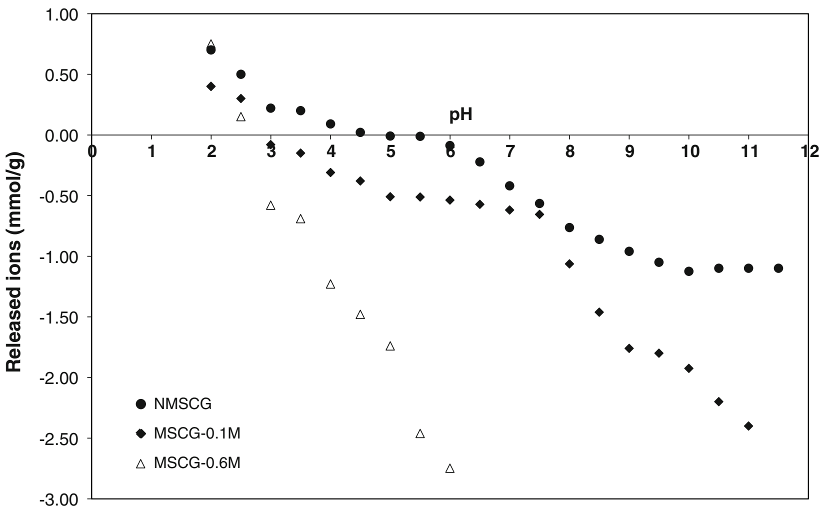

Fig. 3 Surface charge distribution of the tested biosorbents. Ionic strength was fixed with 0.1 N NaCl

Table 3 Langmuir isotherm parameters estimated with the equilibrium adsorption data at 30 °C

Biosorbent	pH	Lead (II)			pH	Copper (II)		
		$q^{a}_{\max}$ (mmol/g)	b[b] (L/mmol)	[c]R^2		$q_{\max}$ (mmol/g)	b (L/mmol)	[c]R^2
NMSCG[d]	3	0.42	0.51	0.99	4	0.11	104.27	0.98
	4	0.24	12.5	0.89	5	0.19	62.51	0.97
MSCG-0.1M[e]	3	0.38	1.19	0.93	4	0.32	44.39	0.98
	4	0.45	23.96	0.97	5	0.45	34.67	0.96
MSCG-0.6M[f]	3	0.52	24.99	0.98	4	1.15	6.75	0.98
	4	0.77	383.93	0.99	5	1.53	4.67	0.99

[a] Maximum adsorption capacity

[b] Relative energy of adsorption

[c] Determination coefficient

[d] Non-modified spent coffee grains

[e] Spent coffee grains modified with 0.1 M citric acid

[f] Spent coffee grains modified with 0.6 M citric acid

and metal species compete by the same adsorption sites (i.e., carboxylic groups). Carboxylic groups are partially protonated at pH 3 and 4 given that their equilibrium constants are around 3.99–4.25 (see Table 2). A number of researchers (Wartelle et al. 2000; Altundogan et al. 2007; Zhu et al. 2008) have reported that the metal-adsorption capacity, on citric acid modified lignocellulosic materials, decreased with decreasing the pH of the solution as presented in this study.

To compare the adsorption capacity of Pb(II) and Cu(II) on spent coffee grains, the same pH value must be selected, since the quantity of ionized functional groups depends on the pH of the solution. For example, at pH 4, the maximum adsorption capacity of Pb(II) on NMSG and MSCG-0.1 M was 2.18 and 1.4 times higher than Cu(II), respectively. However, the maximum adsorption capacity of Cu(II) on MSCG-0.6 M was around 1.5 times higher that the obtained for Pb(II). This metal-adsorption ratio [Cu(II)/Pb(II) = 1.5] was also reported for granular-activated carbon (Sulaymon et al. 2009). Similarly, a higher adsorption of Cu(II) than Pb(II) [Cu(II)/Pb(II) = 1.2] was obtained using activated carbon cloths as adsorbent (Kadirvelu et al. 2000).

In addition, Dubini-Radushkevich isotherm model (Eq. 7) was tried to fit to the experimental adsorption data by non-lineal estimation based on least-square method:

$$q = q_{\mathrm{m}} e^{-\beta\varepsilon^2} \tag{7}$$

where q_{m} is the Dubinin-Radushkevich monolayer capacity (mmol/g), β is a constant related to adsorption energy (mol^2/J^2), and ε is the Polanyi potential (J/mol) which is related to the equilibrium concentration (C_e, mol/L) as follows:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_{\mathrm{e}}}\right) \tag{8}$$

where R is the gas constant (8.314 J/mol K) and T is the absolute temperature.

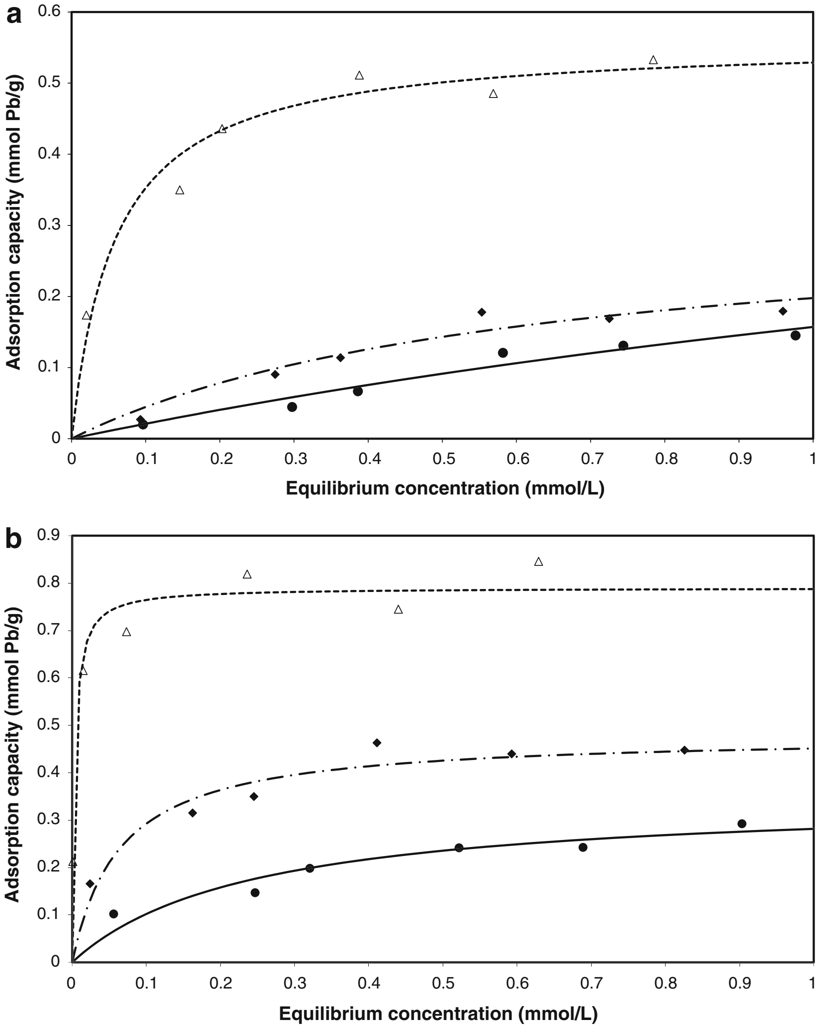

Fig. 4 Adsorption isotherm of Pb(II) at **a** pH 3 and **b** pH 4 on non-modified spent coffee grains (*filled circle* NMSCG), and spent coffee grains modified with 0.1 M and 0.6 M citric acid (*filled diamond* MSCG-0.1 M and *opened triangle* MSCG-0.6 M, respectively). *Symbols* and *lines* represent the experimental data and the predicted adsorption capacity with the Langmuir model, respectively

The constant β is related to the mean free energy of adsorption per mol of the adsorbate (E, kJ/mol) when it is transferred to the surface of the solid from infinity in the solution and E can be estimated as follows:

$$E = \frac{1}{\sqrt{2\beta}} \qquad (9)$$

Table 5 shows the Dubini-Radushkevich isotherm parameters for NMSCG, MSCG-0.1 M and MSCG-0.6 M at 30 °C. The high values of q_m shows high adsorption capacity in comparison to Langmuir isotherm. Moreover, the free energy of adsorption values (4–40 kJ/mol) suggests that physical adsorption process occurs at the adsorbent surface (MWH 2005).

Desorption experiments

Figure 6 shows the adsorption and desorption capacity of Pb(II) and Cu(II) on NMSCG and MSCG-0.6 M. Chemical modification enhanced the metal adsorption capacity (as previously discussed) and desorption capacity also increased because the quantity of the adsorbed metal allows releasing a higher amount of metal with 0.1 N HCl solutions. For instance, the desorption capacity of Pb(II) increased from 0.23 to 0.53 mmol/g for non-modified and modified (with 0.6 M citric acid) spent coffee grains, respectively.

Nevertheless, if the desorption percentage of Pb(II) and Cu(II) is compared, there are differences between the tested biosorbents. Desorption percentage decreased after chemical modification probably due to a chelation mechanism. Based on results shown in Fig. 6, desorption percentage of Pb(II) and Cu(II) for NMSCG was 85 and 93 %, respectively, and these percentages decreased 20 and 29 % when the biosorbent was modified with 0.6 M citric acid. If Pb(II) and Cu(II) percentage recovery on MSCG-0.6 M is compared, it is observed that these results are quite similar (around 64 %), because the stability constants for formation of bidentate complexes of citrate with Pb^{2+} (13.1) and Cu^{2+} (13.8) species are similar too (Stumm and Morgan 1995).

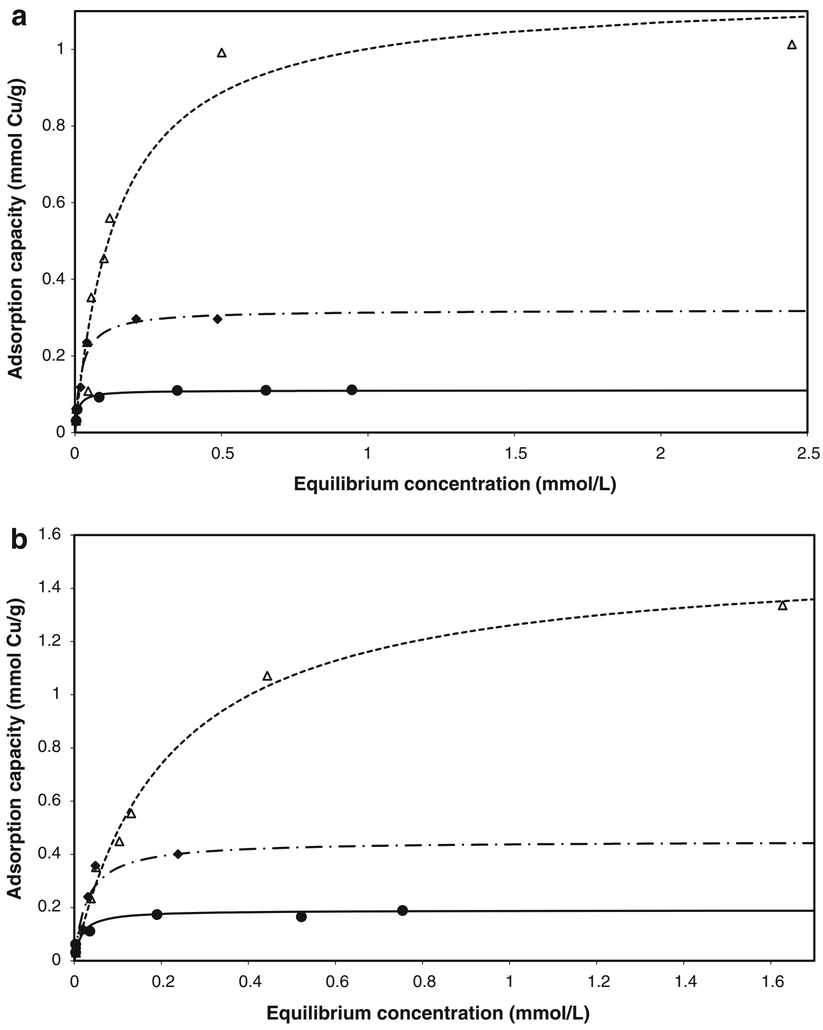

Fig. 5 Adsorption isotherm of Cu(II) at **a** pH 4 and **b** pH 5 on non-modified spent coffee grains (*filled circle* NMSCG), and spent coffee grains modified with 0.1 M and 0.6 M citric acid (*filled diamond* MSCG-0.1 M and *opened triangle* MSCG-0.6 M, respectively). *Symbols* and *lines* represent the experimental data and the predicted adsorption capacity with the Langmuir model, respectively

Taking into account that a high quantity of adsorbed metal (35 %) was not released to the solution in the desorption process, it could reduce the number of adsorption–desorption cycles in a continuous operation. In addition a high-concentration solution of HCl as eluent is not recommended due to the structure damage of biosorbent, which affect the biosorbent metal adsorption capacity.

Adsorption kinetics

Figures 7 and 8 show the adsorption kinetics of Pb(II) and Cu(II) on NMSCG and MSCG-0.6 M. A higher adsorption rate was observed in the first hour for both adsorbents but this rate decreased with time. Chemical modification affected the required time to achieve equilibrium; for example, MSCG-0.6 M needed more time in comparison with the NMSPG for both metals, due to the increment of carboxylic groups on MSCG-0.6 M (see Table 2). Adsorption equilibrium for NMSCG was approximately achieved in 120 and 200 min for Pb(II) and Cu(II), respectively, whereas for MSCG-0.6 M was 400 min for both Cu(II) and Pb(II). Similar results had been obtained using other adsorbents (Shin et al. 2007; Ofomaja 2010).

The kinetic models of pseudo-first order and pseudo-second order were tested to fit the experimental data. The pseudo-second-order kinetic model (Eq. 5) was selected to predict experimental kinetic data for both metals based on its determination coefficient ($0.897 < R^2 < 0.985$), since these values were higher than those obtained for the pseudo-first-order model ($0.611 < R^2 < 0.753$). Table 6 shows the estimated constants of the pseudo-first- and pseudo-second-order kinetic models. The rate constant of the pseudo-second-order model (k_2) of Cu(II) at pH 5 for MSCG-0.6 M was about 2.5 times lower than that estimated for NMSCG. Furthermore, the equilibrium adsorption capacity were almost similar for MSCG-0.6 M (i.e., 0.403 mmol Cu(II)/g and 0.502 mmol Pb(II)/g), because the final solution pH in kinetic experiments was similar for both metals (around 3.3).

It is important to mention that the initial adsorption rate (h) of Cu(II) was higher than that found for Pb(II) on MSCG-0.6 M. On the contrary, initial adsorption rate of Cu(II) was 6.25 times lower that that of Pb(II) on NMSCG.

Table 4 Comparison of maximum adsorption capacity of Pb(II) and Cu(II) on different adsorbents

Metal cation	Adsorbent	$q_{\max}^{a}$ (mmol/g)	pH	References
Pb(II)	*Aspergillus terreus*	0.174	5.2	Cerino-Córdova et al. 2011b
	Mansonia wood sawdust	0.25	6	Ofomaja et al. 2010
	Activated carbon cloth (CS1501)	0.147	5^{b}	Kadirvelu et al. 2000
	Chlorella sp. biomass	1.38	5^{b}	Almaguer Cantu et al. 2008
	Rice straw	0.117	5	Singha and Das 2012
	Rice bran	0.099	5	Singha and Das 2012
	Rice husk	0.103	5	Singha and Das 2012
	Coconut shell	0.117	5	Singha and Das 2012
	Neem leaves	0.108	5	Singha and Das 2012
	Hyacinth roots	0.120	5	Singha and Das 2012
	Granular activated carbon	0.064	NR^{c}	Sulaymon et al. 2009
	Modified spent coffee grains	**0.77**	**4**	This study
Cu(II)	*Aspergillus terreus.*	0.24	6	Cerino-Córdova, et al. 2011b
	Modified soybean straw	0.77	5	Zhu et al. 2008
	Treated flax/cotton	1.18	4.8	Marshall et al. 2007
	Mansonia wood sawdust	0.67	6	Ofomaja et al. 2010
	Activated carbon cloth (CS1501)	0.174	5^{b}	Kadirvelu et al. 2000
	Granular activated carbon	0.092	NR^{c}	Sulaymon et al. 2009
	Modified spent coffee grains	1.53	**5**	This study

[a] Maximum adsorption capacity

[b] Initial pH

[c] Not reported

Table 5 Dubini–Radushkevich isotherm parameters estimated with the equilibrium adsorption data at 30 °C

Adsorbent	pH	Lead (II)				pH	Copper (II)			
		q_{m}^{a} (mmol/g)	$\beta^{b} \times 10^{9}$ (mol^2/J^2)	E^{c} (kJ/mol)	$^{d}R^{2}$		q_{m}^{a} (mmol/g)	$\beta^{b} \times 10^{9}$ (mol^2/J^2)	E^{c} (kJ/mol)	$^{d}R^{2}$
NMSCG^{e}	3	2.32	8.93	7.482	0.95	4	0.0175	1.38	19.04	0.90
	4	0.966	3.97	11.22	0.95	5	0.0349	1.85	16.44	0.94
MSCG-0.1M^{f}	3	1.29	6.16	9.01	0.90	4	0.0663	2.14	15.30	0.86
	4	1.06	2.50	14.15	0.93	5	0.113	2.50	14.16	0.83
MSCG-0.6 M^{g}	3	1.22	2.46	14.25	0.94	4	3.05	7.80	8.00	0.91
	4	1.28	1.15	20.81	0.89	5	0.405	4.03	11.14	0.97

[a] Theoretical saturation capacity

[b] Constant related to the mean free energy of adsorption per mol of adsorbate

[c] Energy of adsorption

[d] Determination coefficient

[e] Non-modified spent coffee grains

[f] Spent coffee grains modified with 0.1 M citric acid

[g] Spent coffee grains modified with 0.6 M citric acid

When SGC were modified with citric acid 0.6 M, the equilibrium adsorption capacity of copper and lead (Table 6) was increased 3.83 and 2.10 times, respectively. These results can be explained by the augmentation of carboxylic groups on adsorbent surface (Table 2) after chemical modification with citric acid.

Adsorption mechanisms

The adsorption mechanism is a difficult task due to the complex nature of the adsorbent. However, considering the carboxylic groups covalently bound to the biosorbent surface after citric acid modification (Table 2 and Fig. 2) and,

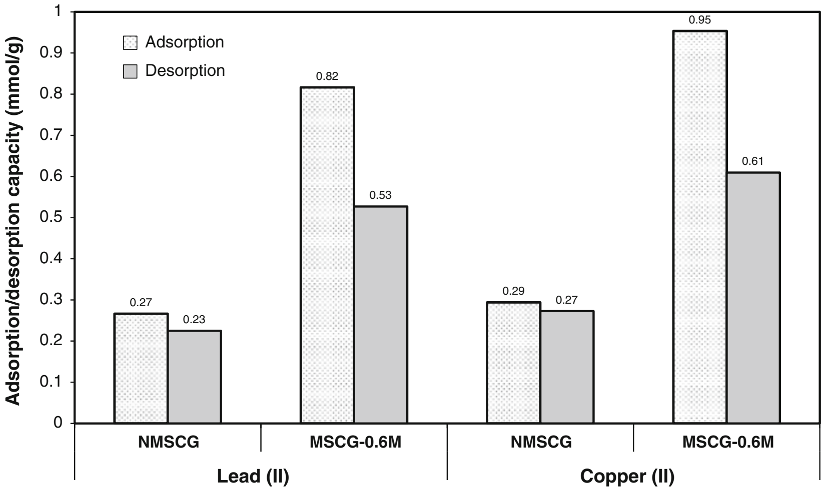

Fig. 6 Adsorption and desorption capacities of Pb(II) and Cu(II) on non-modified spent coffee grains (NMSCG), and spent coffee grains modified with 0.6 M citric acid (MSCG-0.6 M)

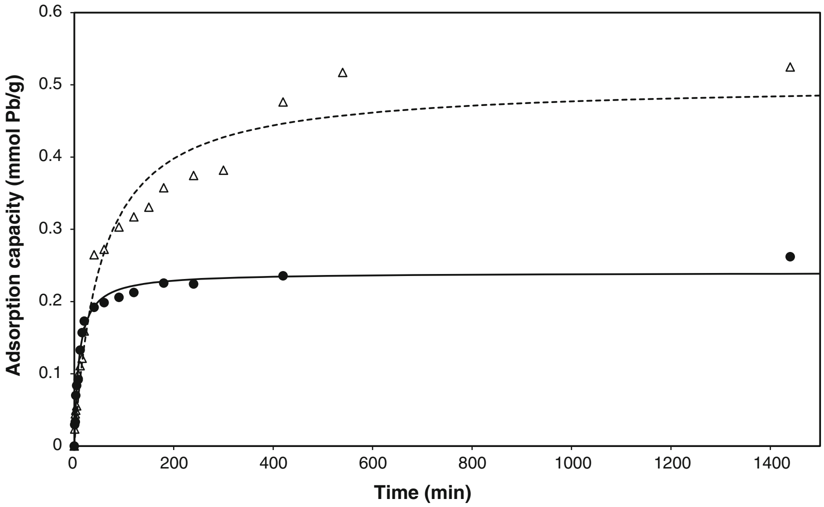

Fig. 7 Adsorption kinetics of Pb(II) on non-modified spent coffee grains (*filled circle* NMSCG), and modified spent coffee grains with 0.6 M citric acid (*opened triangle* MSCG-0.6 M). Experimental conditions were: $C_o = 1$ mM, initial pH 4, 300 min^{-1}, and 30 °C. *Symbols* and *lines* represent the experimental data and the predicted adsorption capacity with the pseudo-second-order model, respectively

also taking into account the Pb(II) and Cu(II) species present in aqueous solutions (Fig. 1), the following mechanisms based on exchange of protons (H^+) and divalent metal cations (Me^{2+}) are proposed:

$$\equiv 2\text{R--COOH} + \text{Me}^{2+} \leftrightarrow \equiv \text{R--COO--Me--OOC--R} \equiv + 2\text{H}^+ \tag{10}$$

This adsorption mechanism was also suggested by other researchers (Leyva-Ramos et al. 2005), who modified the corncob with citric acid and adsorbed cadmium from aqueous solutions. Other authors have reported the same adsorption mechanism for trivalent chromium on protonated alginate beads (Ibanez and Umetsu 2004) and agro-waste biosorbents (Garcia-Reyes et al. 2009). It is important to mention that this adsorption mechanism seems to be the most probable, since pH of solution decreases (i.e., protons were released to the solution due to the ion-exchange process) during the equilibrium and kinetic adsorption experiments. In the equilibrium experiments, a known volume of 0.1 N NaOH was added to the solution to keep constant the pH value. In addition, equilibrium constants of carboxylic groups (covalently bound to the MSCG) allow the interaction between metal cations and the ionized carboxylic groups.

On the contrary, non-modified spent coffee adsorbed a considerable quantity of Pb(II) or Cu(II), even higher than the commercial granular-activated carbon (Sulaymon et al. 2009) and activated carbon cloths (Kadirvelu et al. 2000) although this adsorption cannot be explained completely by a proton-exchange mechanism as shown in Eq. 10. Carboxylic groups on NMSCG were not detected by potentiometric titrations, because calcium release did not cause a changing in solution pH that is essential for potentiometric analyses. Nonetheless, carboxylic groups on NMSCG were identified in ATR-FTIR spectra (Fig. 2) and metal cations were adsorbed on NMSCG (Figs. 4 and 5). Therefore, a calcium-exchange mechanism seems to be feasible as proposed by other authors (Reddad et al. 2002):

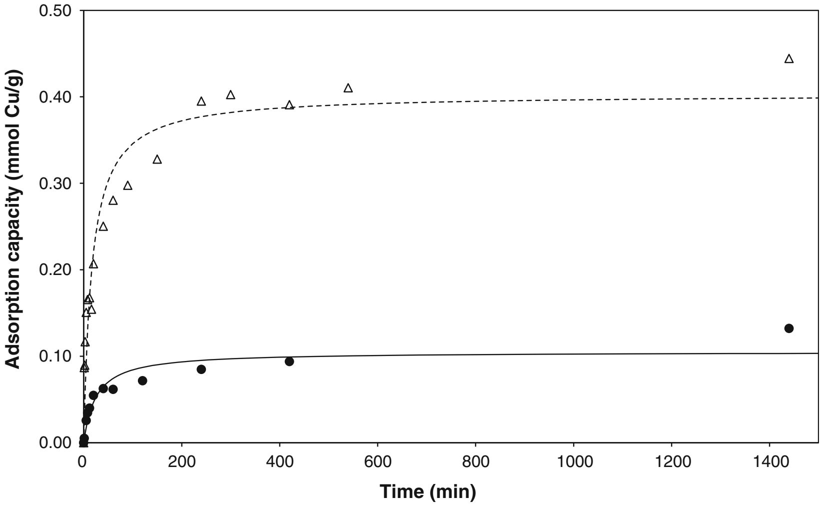

Fig. 8 Adsorption kinetics of Cu(II) on non-modified spent coffee grains (*filled circle* NMSCG), and spent coffee grains modified with 0.6 M citric acid (*opened triangle* MSCG-0.6 M). Experimental conditions were: $C_o = 1$ mM, initial pH 5, 300 min^{-1}, and 30 °C. *Symbols* and *lines* represent the experimental data and the predicted adsorption capacity with the pseudo-second-order model, respectively

Table 6 Pseudo-first- and pseudo-second-order model parameters estimated using the experimental data of the adsorption kinetics at 30 °C

Adsorbent	Metal	Initial pH	Pseudo-first-order model			Pseudo-second-order model			
			q_e^a	k_1^b	$^cR^2$	q_e^d	k_2^e	h^f	$^cR^2$
NMSCG	Pb(II)	4	0.203	0.053	0.710	0.240	0.429	0.025	0.985
	Cu(II)	5	0.086	0.015	0.611	0.105	0.385	0.004	0.897
MSCG-0.6 M	Pb(II)	4	0.362	0.015	0.631	0.502	0.038	0.010	0.966
	Cu(II)	5	0.355	0.018	0.753	0.403	0.150	0.024	0.919

[a] Adsorption capacity of the pseudo-second-order model (mmol/g)

[b] Rate constant of the pseudo-first-order model (1/min)

[c] Determination coefficient

[d] Quantity of metal ions adsorbed at equilibrium of the pseudo-second-order model (mmol/g)

[e] Rate constant of the pseudo-second-order model [g/(mmol·min)]

[f] Initial sorption rate calculated with parameters of the pseudo-second-order model [mmol/(g·min)]

$$\equiv 2\text{R--COO--Ca} + \text{Me}^{2+} \leftrightarrow \equiv \text{R--COO--Me--OOC--R} \equiv + \text{Ca}^{2+} \quad (11)$$

Conclusion

When spent coffee grains are modified with 0.6 M citric acid solutions, its cation adsorption capacity is improved significantly. The Langmuir isotherm model adequately predicts equilibrium adsorption data and the maximum adsorption capacity for MSCG-0.6 M is 0.77 mmol Pb(II)/g and 1.53 mmol Cu(II)/g at pH 4 and 5, respectively. These adsorption capacities are 3.2 and 8.1 times (for Pb(II) and Cu(II), respectively) higher than that found for non-modified spent coffee grains, respectively. Adsorption kinetic data are predicted well with the pseudo-second-order model and more than 2 h are needed to achieve the adsorption equilibrium. Desorption percentage data vary from 64 to 93 % using 0.1 M HCl solution. Undoubtedly, carboxylic groups play the major role in the adsorption of Pb(II) and Cu(II) species from aqueous solutions on modified adsorbent. Ion exchange between protons of carboxylic groups (bound to the modified adsorbent) and heavy-metal cations are suggested as the most probable adsorption mechanism. In summary, this modified low-cost adsorbent can be a promising way of removing metal cations from aqueous solutions.

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