

Cadmium and lead adsorption and desorption by coffee waste-derived biochars

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ABSTRACT: Biochar derived from coffee waste has been reported as a promising material for heavy metal sorption. However, if the intended use is environmental remediation, knowing the extent to which desorption may occur is critical. Thus, the objective of this work was to evaluate the efficiency of spent coffee ground (SCG) and coffee parchment (CP) biochars pyrolyzed at 700 °C under laboratory conditions, in the sorption of Cd and Pb from aqueous solutions, in a pH range from 2 to 10, and their retention after an induced desorption process with a 2.9 pH acetic acid solution. Both biochars were alkaline, and the initial pH of the solution had a large effect on the sorption capacity of SCG but a small effect on the sorption capacity of CP. The Pb sorption capacity was higher for CP (18.6 mg·g⁻¹) than for SCG (11.4 mg·g⁻¹), while both biochars had low Cd retention capacities (1.18 mg·g⁻¹). Coffee parchment also showed the highest Pb retention (30% to 87%), while for Cd there was no difference between CP and SCG biochars. Our results showed that metal precipitation was the main mechanism for metal immobilization and CP biochar proved to be more reliable than SCG, mainly for Pb, due to its higher sorption capacity and lower metal release by desorption than SCG. These characteristics are particularly important for the use of biochar in environmental remediation. Besides that, the biochar production represents an eco-friendly destination for these feedstocks, contributing to the circular economy.

Key words: environmental contamination, heavy metals, remediation, biosorbents.

INTRODUCTION

The increase in environmental contamination by heavy metals due to anthropogenic activities is a global issue that requires attention. Heavy metals pose high environmental risks due to their high toxicity and bioaccumulative potential (Xu et al. 2018). Moreover, their persistence in the environment affects ecosystem productivity and the economy (Lahori et al. 2017). Heavy metals such as Zn and Cu are also nutrients; however, they become toxic at high levels. Other elements, such as Cd and Pb, do not have biological functions and are potentially toxic even at low levels (Nazir et al. 2015). Prolonged human exposure to Cd and Pb can damage the bones and kidneys and negatively affect the central nervous system and fertility (Kumar et al. 2020; Wang et al. 2018).

Chemical precipitation, membrane filtration, and ionic exchange are some of the traditional techniques utilized in the remediation of heavy metal-polluted areas and are usually expensive (Abdel-Raouf et al. 2017). Among alternative techniques, heavy metal sorption by different sorbents has proven to be an effective and low-cost approach (Tomczyk et al. 2019). Thus, using biochars as biosorbents has been widely reported in the scientific literature (Fdez-Sanromán et al. 2020; Jiang et al. 2016; Zhang et al. 2018). Sorption of heavy metals by biochars occurs due to their high aromaticity and surface area, functional groups, and alkalinity. These properties make biochars viable and effective materials to immobilize organic and inorganic pollutants (Bian et al. 2014).

Sorption occurs when the metal (sorbate) is retained on the biochar's solid surface (sorbent). This is a complex process and may involve different mechanisms, such as surface complexation (chemisorption), electrostatic attraction (physisorption), cation exchange, and precipitation (Hoslett et al. 2019). These mechanisms, in turn, are influenced by several factors associated with biochar properties. The high surface area of biochars contributes to metal retention and immobilization (Beesley et al. 2011). In addition, biochar is commonly alkaline, which influences heavy metal sorption by electrostatic interactions and precipitation (Wang S. et al. 2015). pH is one of the main factors that influences metal sorption because it alters metal speciation and the sorbent surface (Meng et al. 2018). pH also influences the desorption and reavailability of metals due to their greater mobility under acidic conditions. The influence of pH on sorption and desorption depends on the metal species, composition and characteristics of the adsorbent, mainly on surface charges (Nascimento et al. 2014).

Several feedstocks may be used for biochar production, such as agricultural residues, sewage sludge, animal manures, and others (Zeng et al. 2018; Zhao et al. 2018; Zhou et al. 2017). Nevertheless, from an environmental and economic point of view, using biomass with no defined final use seems more interesting. This is the issue of coffee industry waste, which is produced in large amounts (Veiga et al. 2017). It is estimated that approximately 1.1 ton of waste is generated for each ton of processed grains (Dias et al. 2014). Most coffee wastes are composed of coffee husks and spent coffee grounds (SCGs) (Blinová et al. 2017). Although coffee wastes are gaining other uses as byproducts (e.g., in the food industry) (Klingel et al. 2020), their proper final disposal is still challenging, and thus, the use of coffee wastes for biochar production to immobilize heavy metals becomes even more meaningful.

A significant reduction of uranium (U(VI)) in aqueous solution employing biochar, produced at 850 °C from coffee espresso waste, was observed by Paschalidou et al. (2020). López et al. (2020) evaluated biochar produced at 550 °C from coffee husks and verified the immobilization of Cd in aqueous solution mainly due to the effect of precipitation. Chwastowski et al. (2020) observed the efficiency of SCG biochar in the removal of Mn, Pb and Cd from aqueous solutions, which was more significant than that obtained for raw biomass. Stylianou et al. (2020), characterizing different biochars, found that SCG biochar had a high carbon content and aromaticity and was viable for environmental applications such as metal remediation.

However, most studies related to coffee waste-derived biochar did not evaluate if and to which extent metal desorption can occur. Knowledge of how much metal remains sorbed is ultimate if the intended use of biochar is environmental remediation. Toxicity characteristic leaching procedure (TCLP) is a soil sample extraction method for chemical analysis employed as an analytical method to simulate leaching through a landfill. It simulates a worst-case scenario under environmental conditions submitting the sample to an induced desorption process with a 2.9 pH acetic acid solution (USEPA 1992).

Thus, considering the high availability of coffee waste and the potential of its biochars in the remediation of metals, the objective of this study was to evaluate the efficiency of SCG and coffee parchment (CP) biochars in the sorption of Cd and Pb from aqueous solution in a pH range from 2 to 10, their retention after an induced sorption process by TCLP and after results comparison, to indicate the most promising one.

MATERIAL AND METHODS

Biochar production and characterization

The biomasses of SCGs and CP for the production of SCG and CP biochars, respectively, were obtained from the cities of Três Pontas and Varginha, respectively, in the state of Minas Gerais, Brazil. Pyrolysis was carried out in an electric drag bed thermochemical reactor, with six resistors. The pyrolysis process occurred at a heating rate of 5 °C·min⁻¹ to 700 °C and a holding time of 1 h, followed by slow cooling to room temperature. The biochars were then characterized in terms of their physicochemical characteristics, as briefly described below.

The pH was measured in a 1:10 (biochar:water) extract (Singh et al. 2017), and the elemental composition (C, N, H) was obtained by dry combustion in an elemental analyzer (IBI 2015). The ash content was determined at 750 °C in a muffle furnace (IBI 2015), and the organic carbon (OC) was obtained by digestion with dichromate and determined by titration (Nelson and Sommers 1996). The results of these analysis described above were expressed in % (m/m). The cation exchange

capacity (CEC) was measured by the modified procedure of ammonium acetate compulsory displacement, as described by Domingues et al. (2017). These analyzes were performed in triplicate.

The surface area and pore size distribution were obtained by BET- N_2 (Brunauer et al. 1938) and to illustrate the porous surface of the biochars, scanning electron microscopy (SEM) images were obtained using a Leo 440i model. The SEM images were zoomed at 100 μm (150 \times) for both biochar samples. More details on the biochars characterization can be seen in our previous study (Sertoli et al. 2019).

Sorption and desorption of Cd and Pb by biochars

The metal sorption capacity of the SCG and CP biochars was evaluated using two experiments. First, the effect of pH was tested, maintaining a fixed concentration of Cd or Pb and the desorption test was carried out in sequence in the metal-loaded-biochars. Second, a batch experiment was performed to obtain the maximum sorption of Cd or Pb for both biochars by Langmuir (1916) and Freundlich (1906) adsorption isotherms, with no pH adjustment. The metal concentration used in the experiments was determined by previous tests (data not shown) with literature support (Pathirana et al. 2019; Penido et al. 2019; Sertoli et al. 2019; Wang R.-Z. et al. 2018; Zhang et al. 2018).

pH effect on biochar sorption and desorption

To evaluate the influence of pH on the sorption of metals, Cd and Pb were tested separately in the pH range from 2 to 10 based on Penido et al. (2019) proposed assay for pH 2, 4, 6, 8 and 10. Cadmium and Pb solutions were prepared at 16 and 100 $\text{mg}\cdot\text{L}^{-1}$, respectively, using $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ dissolved in an electrolyte support solution of 0.01 $\text{mol}\cdot\text{L}^{-1}$ $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$. The pH of the solution containing Cd or Pb was adjusted using 0.1 $\text{mol}\cdot\text{L}^{-1}$ HCl or 0.1 $\text{mol}\cdot\text{L}^{-1}$ NaOH solutions, as necessary. Afterwards, 0.04 g of each biochar was added to 25 mL centrifuge tubes containing 10 mL of each metal-pH combination. The resulting sample was stirred for 24 h in a bench shaker. After the stirring time, samples were centrifuged at 5000 rpm for 10 min, and the supernatants were extracted with a syringe and filtered ($\phi = 0.22 \mu\text{m}$) to determine the final/equilibrium pH and the contents of Cd and Pb. A pH meter (model Orion Star A211) was used for pH measurement. The Cd and Pb concentrations in the supernatants were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in Varian Vista MPX^T equipment (axial view).

The contents of Cd and Pb sorbed by the biochars were calculated from the difference between their initial concentration and their equilibrium concentration after the sorption process (Uchimiya et al. 2011), as indicated by Eq. 1:

$$q_s = \frac{V_s}{m} (c_i - c_s) \quad (1)$$

where q_s ($\text{mg}\cdot\text{g}^{-1}$) is the amount of sorbed Cd and Pb, V_s (mL) is the volume added of the Cd and Pb solution, m (mg) is the added mass of biochar, and c_i and c_s ($\text{mg}\cdot\text{L}^{-1}$) are the initial and equilibrium concentrations of metals in solution, respectively.

Afterwards, 0.04 g of Cd- or Pb-sorbed biochars (0.04 g) were dried in an oven at $60 \pm 5 \text{ }^\circ\text{C}$ for 24 h and submitted to the induced desorption process according to the TCLP (US-EPA 1992). After drying, the samples were stirred for 24 h in a bench shaker with 10 mL of 0.1 $\text{mol}\cdot\text{L}^{-1}$ acetic acid at $\text{pH } 2.9 \pm 0.1$. The supernatants were separated by centrifugation and the concentrations of Cd and Pb were determined by ICP-OES, as described before.

Isotherm experiment

Solutions containing 0, 1.0, 2.0, 4.0, 8.0 and 16.0 $\text{mg}\cdot\text{L}^{-1}$ Cd or 0, 20, 60, 100, 140 and 180 $\text{mg}\cdot\text{L}^{-1}$ Pb were prepared using the same electrolyte support solution and salts as described for the pH experiment. The sorption experiment was performed by the addition of 0.05 g of the biochars tested to 50 mL centrifuge tubes containing 40 mL of each metal solution (Sertoli et al. 2019). Stirring, filtration and metal determination in the supernatants were performed as described before. No pH adjustment was performed on the metal solutions or the resulting sample after biochar addition.

To obtain the adsorption isotherms for the biochars, batch sorption experiments were carried out. The amount of Cd and Pb sorbed by the SCG and the CP biochars was calculated by Eq. 1. The mean values of sorbed amounts for each concentration were fitted to the Langmuir (1916) and Freundlich (1906) nonlinear isotherms, indicated by Eqs. 2 and 3, respectively:

$$q_s = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_s = K_F C_e^{\frac{1}{n}} \quad (3)$$

where q_s ($\text{mg}\cdot\text{g}^{-1}$) is the amount of the sorbed metal, C_e is the metal concentration in the solution at equilibrium after the sorption process, q_{\max} ($\text{mg}\cdot\text{g}^{-1}$) and K_L are the maximum sorption capacity and the affinity constant of the Langmuir model, respectively, and K_F and $1/n$ are constants of the Freundlich model.

Data analysis

Sorption data as a function of the pH were subjected to analysis of variance to verify the effect of each pH on Cd or Pb sorption. When a significant effect of pH was identified, the mean values of the sorption and equilibrium pH data were submitted to regression analysis. ANOVA and means comparison by the Tukey's test were used for the desorption data experiment. The software StatSoft – Statistica v. 10 was used for Langmuir and Freundlich adsorption isotherm modeling for each metal, considering the values of R^2 and p ($p \leq 0.05$) as indicators of data fitting quality.

RESULTS AND DISCUSSION

Characterization of biochars

Both the SCG and CP biochars are alkaline with pH values of 9.5 and 9.6, respectively (Table 1). This is a common characteristic of biochar, especially those produced at higher pyrolysis temperatures, due to the formation of oxides, hydroxides, and carbonates of basic cations (Na, K, Ca and Mg) (Singh et al. 2010). In solution, the pH changes the speciation of metals (In this case, Pb and Cd) and the degree of protonation/deprotonation of functional groups present on the surface of biochars (Wu et al. 2019), which influences heavy metal mobility and availability (Lahori et al. 2017).

Table 1. Physical-chemical characteristics of the biochars.

Attribute	Biochar	
	SCG	CP
pH (water)	9.5 ± 0.3	9.6 ± 0.1
C (%)	62.3 ± 2.7	69.3 ± 1.6
N (%)	2.10 ± 0.23	1.57 ± 0.1
H (%)	1.48 ± 0.1	1.55 ± 0.1
Ashes (%)	37.7 ± 3.4	13.6 ± 0.5
OC (%)	31.9 ± 0.8	38.5 ± 1.8
H/OC	0.56 ± 0.1	0.48 ± 0.1
CEC ($\text{mmol}_c\cdot\text{kg}^{-1}$)	34.4 ± 0.1	275.8 ± 8.7

SCG = Spent coffee grounds; CP = Coffee parchment; OC = Organic carbon; CEC = Cation exchange capacity. Numbers after the ± signal indicate the standard deviation (n = 3).

The H/OC ratio is related to thermochemical changes in biochar since as lower it is, the biochar aromaticity of biochars increases, which in turn brings stability to the material (IBI 2015). For use in heavy metal remediation biochar stability is

an important characteristic as it assures remediation will last over time (Ronsse et al. 2013). The CEC was much higher for CP biochar than for SCG. A similar CEC value was also obtained by Domingues et al. (2020) with coffee husk biochar at 750 °C, which was indicated to improve soil fertility and have the potential for heavy metal immobilization.

The surface area varied from 32 to 45 m²·g⁻¹ for the CP and SCG biochars (Fig. 1a and b), with a predominance of mesopores (Figs. 1 and 2). The presence of mesopores favors ions transportation to active sorption sites (Cuong et al. 2019), increasing the effectiveness and speed of the sorption process (Hassan et al. 2021). The surface area plays an important role in metal sorption since this is a surface phenomenon (Nascimento et al. 2014) and can vary widely, even among close feedstocks. For example, the values described here for SCG and CP biochars are higher than the 1.53 and 5.0 m²·g⁻¹ reported by Stylianou et al. (2020) and Jagdale et al. (2019) respectively, for SCG biochars pyrolyzed at 550 and 700 °C. However, these values are close to the 34 m²·g⁻¹ reported for coffee ground biochar pyrolyzed at 400 °C (Liu and Huang 2018).

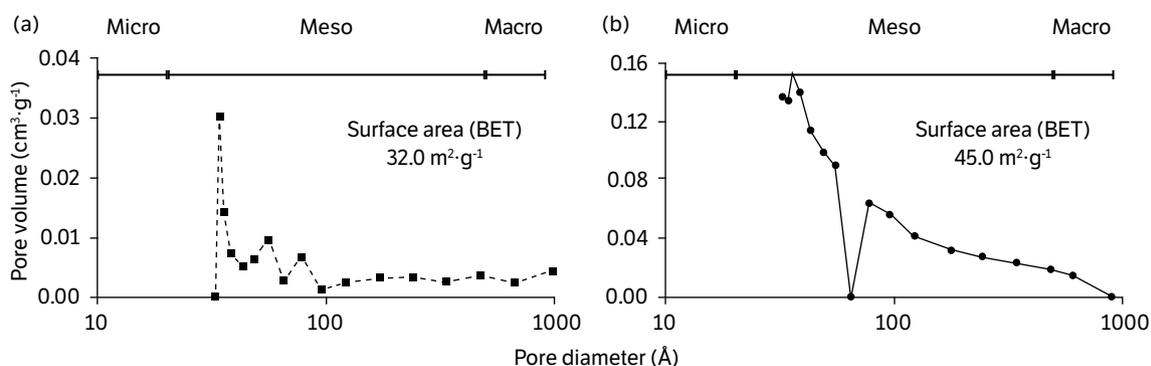


Figure 1. Surface area (BET) and pore size distribution for CP (a) and SCG (b) biochars.

Source: Elaborated by the authors.

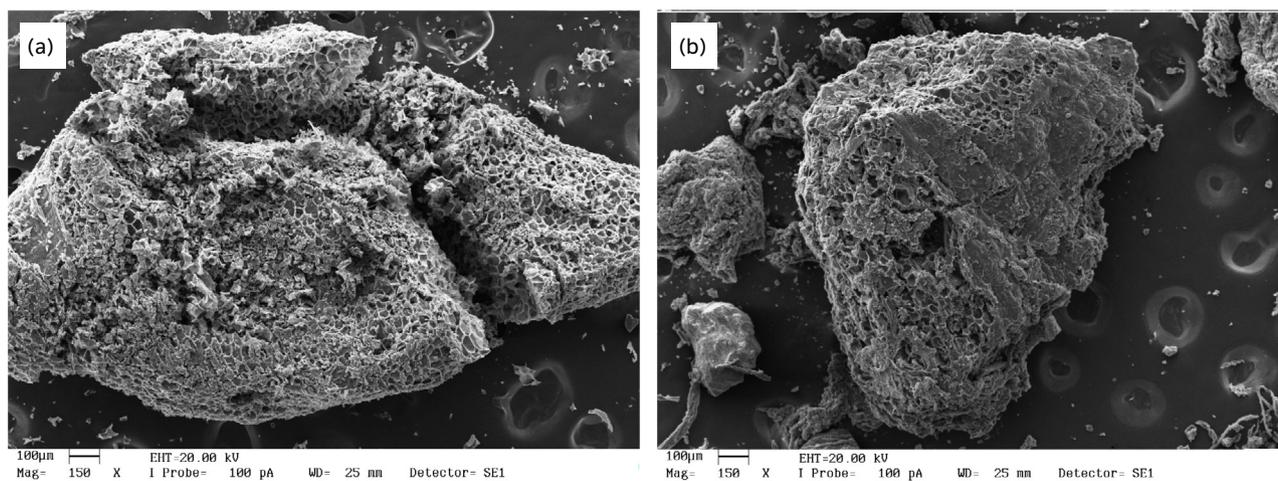


Figure 2. SEM images with a zoom of 150× for the CP (a) and the SCG (b) biochars.

Source: Elaborated by the authors.

In addition to the surface area size, the characteristics of this surface, such as the presence of chemical functional groups, have a substantial effect on the biochar sorption capacity for heavy metals. In our previous study (Sertoli et al. 2019), we found that the both biochars have oxygenated groups, but CP showed more aromatic structures, which is consistent with its H/OC ratio. Therefore, these characteristics increase the stability and contribute to the resistance to the decomposition of this material (Sohi et al. 2010). Nevertheless, these structures present lower polarity than aliphatic structures, which results in a lower density of negative charges on the biochar surface (Uchimiya et al. 2011). Thus, it is possible to infer that CP biochar tends to present a lower negative charge density than SCG biochar.

Sorption and desorption of Cd and Pb by biochars

pH effect on biochar sorption and desorption

Cadmium and Pb sorption were directly proportional to the pH increase (Fig. 3), and both biochars were efficient in the removal of both metals, with significant linear adjustment. Coffee parchment biochar showed a higher Pb and Cd sorption capacity than SCG biochar (Fig. 3a and b), except for pH 10. The final solution pH (Fig. 3c and d) has a direct relation with the results of metal sorption. The values of metals sorbed for the final pH between 2 and 4, can be related to the presence of carboxylic groups in biochar that dissociate even in acidic pH (Kulikowska et al. 2015) and therefore can immobilize metals. Nevertheless, a buffering effect of CP biochar can be observed when compared to SCG biochar. Except for pH 2, CP biochar maintained the solution pH at approximately 8.0, unlike the SCG biochar, which presented a final solution pH proportional to the initial pH for both heavy metals. This neutralization effect was also observed by Huang et al. (2018) with chicken manure biochar pyrolyzed at 700 °C, and they attributed the buffering capacity to the presence of alkaline ions PO_4^{3-} and CO_3^{2-} in the biochar.

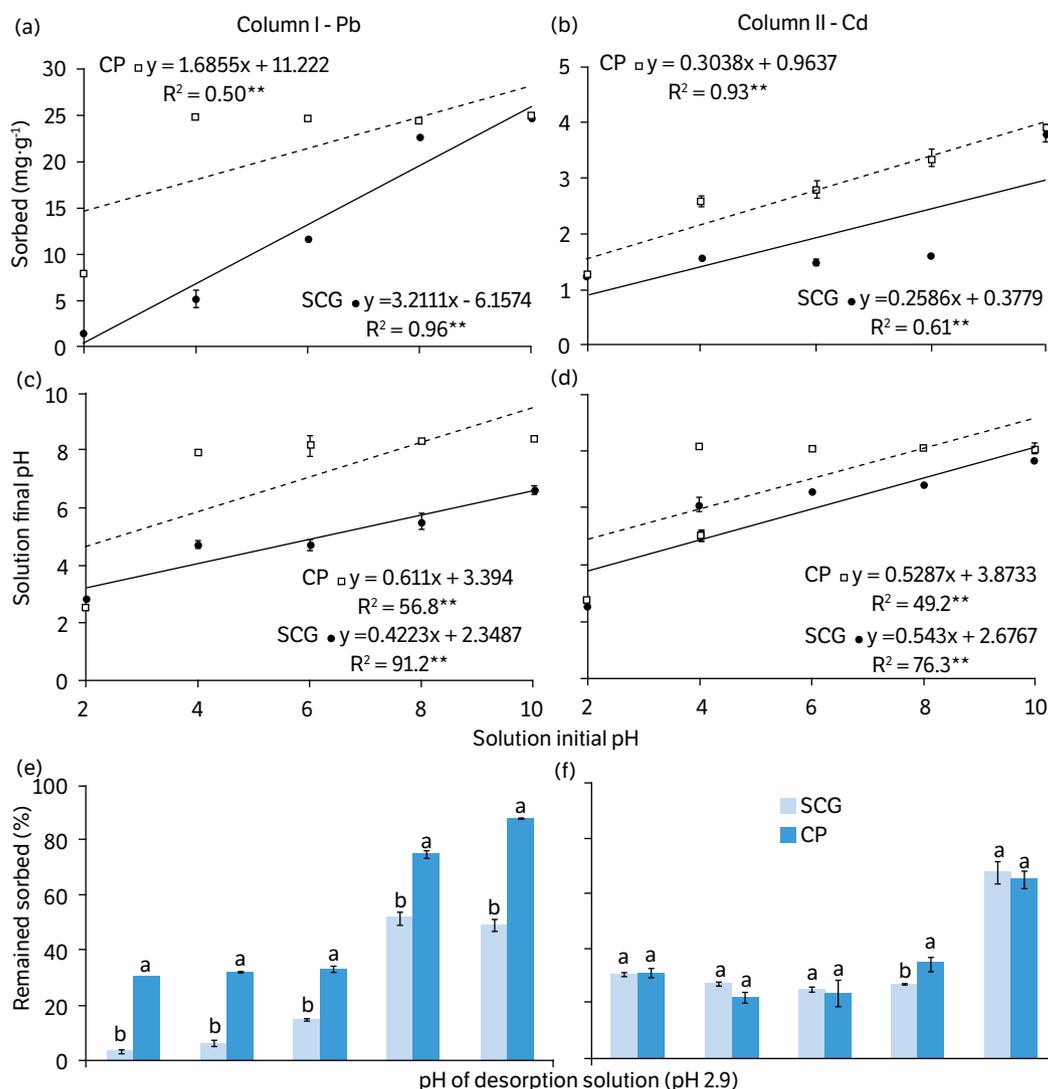


Figure 3. Amounts of lead and cadmium sorbed (a and b, respectively) and their respective final pH in solution (c and d) as a function of the initial pH. Amounts of lead and cadmium that remained sorbed after desorption test (e and f).

Note. ** Significant regression ($p \leq 0.05$). Horizontal columns with the same letter are not different for each metal by Tukey's test ($p \leq 0.05$). Bars indicate the standard deviation ($n = 3$). Source. Elaborated by the authors.

Given the aromaticity and other characteristics of these biochars in the implications for the availability of negative charge, mainly for CP (Sertoli et al. 2019), when comparing with other sorption mechanisms, precipitation may have played a key role in the Cd and Pb sorption observed, which relates to solution speciation that is pH dependent. For cadmium, Cd^{2+} ions are the predominant species below pH 8.0, when they start to precipitate as CdCO_3 and represent up to 60% of the Cd species in solution at pH 9.0 (Wu et al. 2019). For lead, the free Pb^{2+} species predominates up to pH 6.0, when the PbOH^+ ion starts to form (Huang et al. 2017). However, from pH 7.0 Pb starts to precipitate as PbCO_3 , reaching 80% of the species in solution at pH 8.5 (Wu et al. 2019). The precipitated form $\text{Pb}(\text{OH})_2$ also starts to be formed at pH 8.0 (Huang et al. 2017). Therefore, increasing the solution pH favored precipitation and might explain the higher metal sorption capacity of CP than SCG biochar (Fig. 3a and b). The pH increase reduces the mobility of heavy metals in contaminated soil and water after treatment with coffee waste biochars (Kim et al. 2014). Chromium and Cd removal in the solution by precipitation caused by rice straw biochar has also been observed by other authors (Qian et al. 2016).

Thus, considering a greater effect of precipitation on the sorption of Cd and Pb by the biochars, mainly CP, the release of metals due to the acidification of the medium can occur through desorption (Uchimiya et al. 2011). In this work, the content of Pb that remained sorbed after desorption at pH 2.9 ranged from 2.7% to 51% and from 30% to 87% for the SCG and CP biochars respectively (Fig. 3e). For the Cd, the content ranged from 24% to 67% SCG and from 21% to 64% for the SCG and CP biochars respectively (Fig. 3f). Therefore, the highest desorption rates for Pb were obtained for SCG biochar (Fig. 3e), and for Cd there was practically no difference between the biochars (Fig. 3f).

In these results, there is a clear effect of the equilibrium pH of the medium (Fig. 3c and d) on the content of the metals that remained sorbed after acidification in the desorption step (Fig. 3e and f), mainly for Pb. Given the principle of precipitation, it can be seen that a portion of the complexes formed in basic or alkaline pH did not dissociate in acid pH (2.9). It is more evident for the CP biochar in relation to Pb, in which at least 30% remained absorbed which increases to 87% when the initial sorption occurred at basic pH. It is also noted, however, that at least about 20% of the Cd remained immobilized by both biochars. Metals sorbed by precipitation and complexation are desorbed less intensely than those that are retained by simple electrostatic attraction, ion exchange or physical sorption (Bandara et al. 2020).

The probable cause of Pb to have remained immobilized more intensely may be related to the species formed during sorption on biochar surface. Anions associated with minerals remaining on the biochars' surface (i.e., CO_3^- , PO_4^{3-} , SO_4^{2-} and OH^-) may allow the formation of compounds with the metals, favoring precipitation (Wang et al. L. 2019; Wu et al. 2019), which in turn is influenced by the pH of the medium. Such ions are often found in high pH biochar ashes. For example, Pb precipitates (e.g., PbCO_3 and $\text{Pb}(\text{OH})_2$) at pH values below those observed for Cd, which remains as Cd^{2+} even in alkaline medium (Wu et al. 2019). In addition, PbSO_4 , which remains precipitated even at acidic pH, can also be formed, and PbCO_3 has an almost tenfold lower solubility constant (K_{sp}) (1.5×10^{-13}) than CdCO_3 (5.2×10^{-12}) (Sengupta et al. 2017), which might contribute to some extent. Furthermore, Cd is known to be more soluble and mobile, preferring exchangeable fractions (Tabelin et al. 2018). Zama et al. (2017) observed a higher desorption rate for Cd due to the retention mechanisms involved in precipitation and electrostatic attraction, while for Pb precipitation, the formation of stable complexes with functional groups caused greater Pb stability and reduced desorption.

These results are very important from an environmental perspective, since even under acidity conditions, in which the mobility of metals is greater, part of the Cd and Pb remained sorbed by the biochars. Uchimiya et al (2011) evaluated the sequential desorption of Cu using synthetic rain water (pH 4.5) and acetate buffer solution (pH 4.9) in soils with and without the presence of biochar derived from broiler litter manure, pyrolyzed at 700 °C. The authors found that acetic acid provided the highest desorption rates and that this rate was reduced in the presence of biochar. In the present study, desorption was carried out at an even lower pH (2.9) and the fraction that remained absorbed was proportional to the increase in the initial pH of the medium (Fig. 3e and f). Based on these results and considering that the biochars evaluated are alkaline and have a characteristic buffer effect, mainly of CP, the metals tend to remain sorbed by the biochars applied in remediation processes. This characteristic is particularly important and advantageous in cases such as acid mine drainage, which are one of the main environmental problems around the planet due to the high acidity, metal content and the challenges involved in the treatment (Naidu et al. 2019).

Sorption isotherm experiment

Langmuir and Freundlich isotherms showed a favorable shape for Pb sorption (Inglezakis and Pouloupoulos 2006) (Fig. 4a) and, for both CP and SCG biochars, a significant fit in the models was obtained ($p \leq 0.05$) (Table 2). The favorable isotherms indicate that a large adsorbate mass (metal) is retained by a unit mass of adsorbent (biochar) (Nascimento et al. 2014). The best fit for Pb was obtained by the Langmuir model, with an R^2 of 0.98 for both biochars, which suggests a relatively homogeneous sorption surface and a monolayer when saturated (Araújo et al. 2018). The interaction between the metals and the biochars can be inferred by the K_L and $1/n$ constants of the Langmuir and Freundlich models, respectively, which are related to the bonding energy. The higher the K_L value is, the higher the affinity between the biochar and metal, while for the $1/n$ constant, values lower than 1 indicate a strong interaction between the metal and the biochar (Nascimento et al. 2014). Lead sorption by biochar also fitted the Freundlich model, resulting in a complex process; thus, the process is not limited to a monolayer system (Park et al. 2013).

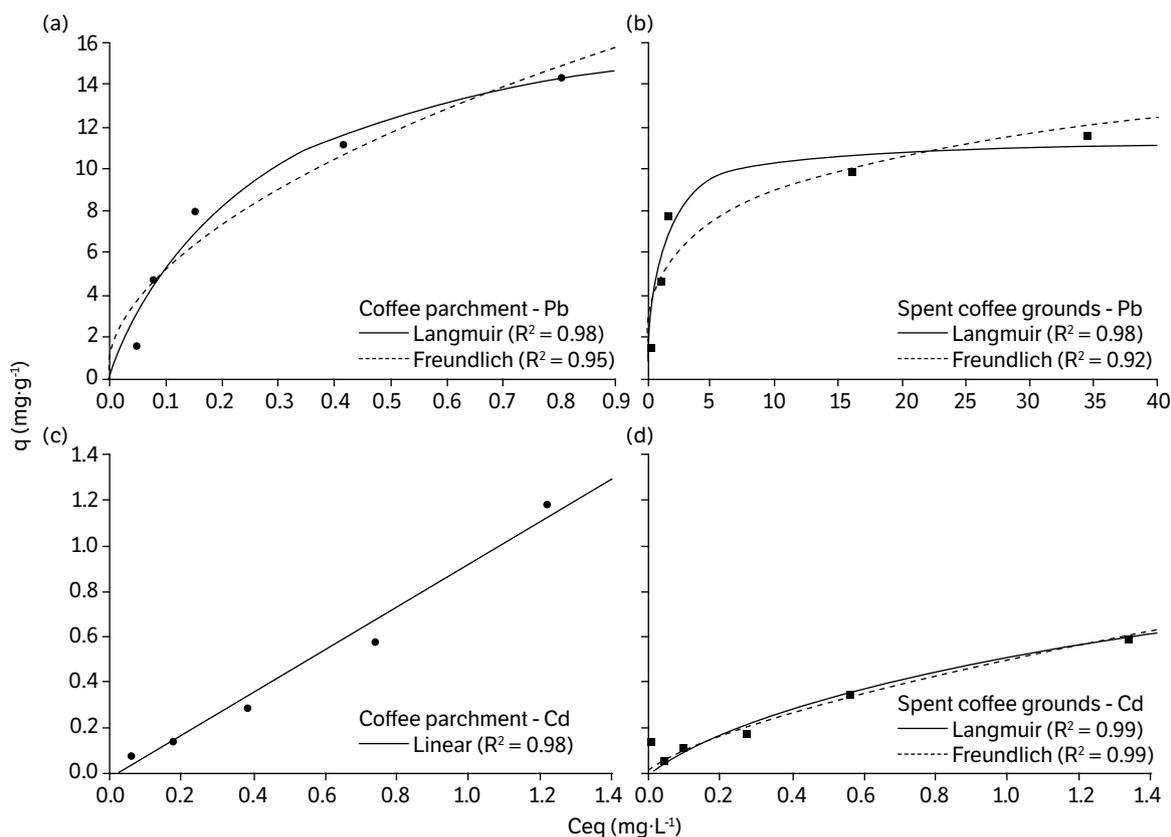


Figure 4. Lead and Cd adsorption isotherms for the CP (a and c) and SCG (b and d) biochars, respectively.

Source. Elaborated by the authors.

Table 2. Langmuir and Freundlich isotherm parameters for Cd and Pb sorbed by the biochars.

Biochar	Pb					
	Langmuir			Freundlich		
	R^2	q_{max}	K_L	R^2	K_f	$1/n$
SCG	0.98	11.41**	0.99**	0.92	5.13**	0.24**
CP	0.98	18.61**	4.02**	0.95	16.58**	0.49**
Biochar	Cd					
	Langmuir			Freundlich		
	R^2	q_{max}	K_L	R^2	K_f	$1/n$
SCG	0.99	1.18**	0.12**	0.99	0.14**	0.67**
CP	Linear; $R^2 = 0.98$					

SCG = Spent coffee grounds; CP = Coffee parchment; **Significant parameters ($p \leq 0.05$).

The maximum sorption capacity (q_{\max}) of Pb varied from 11.4 to 18.6 mg·g⁻¹ for the SCG and CP biochars, respectively. These values found for SCG and CP biochars are higher than 7 mg·g⁻¹ obtained for barley straw biochar (Jazini et al. 2018), and the result for CP biochar is close to 22.3 mg·g⁻¹, found for Pb removal in aqueous solution by SCGs biochar pyrolyzed at 700 °C (Chwastowski et al. 2020). However, both values are lower than 28.9 mg·g⁻¹ for corn straw biochar (Chi et al. 2017) and substantially lower than the 109 mg·g⁻¹ found for wheat straw (Kwak et al. 2019). For Cd, CP biochar followed a linear trend, and it was not possible to obtain a significant fit in the Langmuir and Freundlich isotherms (Fig. 4c), while for SCG biochar, both isotherm models fit the data ($R^2 = 0.99$) (Table 2) and resulted in a maximum sorption capacity of 1.18 mg·g⁻¹. The amount of Cd absorbed by the biochars was also substantially lower than those reported in previous works. Chwastowski et al. (2020) found a sorption capacity of 19.4 mg·g⁻¹ for Cd by SCG biochar pyrolyzed at 700 °C. The sorption capacity presented by Yin et al. (2019) for *Pennisetum* sp. straw biochar was 41.8 mg·g⁻¹. Li et al. (2017), who also studied straw-derived biochar pyrolyzed at 600 °C, found a high value of 149 mg·g⁻¹ for maximum sorption capacity.

The high degree of aromaticity and high point of zero charge (PZC) (Sertoli et al. 2019) might explain the relatively low metal retention by these coffee waste biochars when compared with other biochars in the literature. The lower negative charge density due the aromatic structure of the biochars is supported by the high PZC values (7.7 and 9.2 for SCG and CP respectively) (Sertoli et al. 2019). Such results imply a net negative charge on the biochars' surface only when the pH of the medium is higher than the PZC (Borba et al. 2019), limiting the attraction and sorption of metallic ions. The higher CEC (Table 1) and higher buffering capacity of CP compared to SCG biochar (Fig. 3) might explain the higher Pb retention of CP biochar. A greater affinity for Pb over Cd was also observed for biochars derived from vegetable residues and chicken manure (Park et al. 2013) and for sesame straw biochar pyrolyzed at 700 °C in either competitive or noncompetitive sorption systems (Park et al. 2016). In addition to biochar characteristics, its lower sorption capacity for Cd in relation to Pb may also be related to the metallic ions themselves. The size of their ionic radii (0.95 and 1.19 Å, respectively) may have contributed to the observed difference. Species with larger ionic radii have smaller hydrated radii and are consequently preferentially sorbed when in solution (Park et al. 2016). In addition to a smaller hydrated radius, Pb (2.33) is more electronegative than Cd (1.69), and it is a borderline Lewis acid, which favors a greater electrostatic attraction with Lewis hard bases, such as oxygenated functional groups remaining on the surface of the biochars (Oliveira et al. 2018). The hydroxyl and carboxylic acid groups still remained in the biochars (Sertoli et al. 2019), with the latter considered the most important groups for Pb sorption (Pathirana et al. 2019).

Although complexation of metals with oxygen functional groups is important, precipitation as carbonate and hydroxide seems to be the main sorption mechanism according to the experimental results and biochars characteristics, mainly for CP biochar. However, in this work, the separate contributions of each mechanism were not addressed.

CONCLUSION

Precipitation as the main sorption mechanism was observed; nevertheless, complexation by functional groups and cation exchange may also have contributed to the sorption of Pb and Cd by the biochar.

The Pb sorption capacity was higher for CP than for SCG, while both biochars had low Cd retention capacities. In addition to the higher sorption, CP also showed the higher content of Pb that remained sorbed after desorption (30% to 87%) than SCG (2.7% to 51%), even under conditions of intense acidity (pH 2.9).

Coffee parchment biochar proved to be more reliable than SCG, mainly for Pb, due to the higher sorption capacity and lower metal release by desorption. These characteristics make CP biochar a viable alternative for environmental use in remediation, especially in conditions of high acidity and metal content such as the mine drainages. Besides that, the biochar production represents an eco-friendly destination for these feedstocks, contributing to the circular economy.

AUTHORS' CONTRIBUTION

Conceptualization: Carnier R. and Abreu, C. A.; **Data Curation:** Carnier R.; Formal Analysis, Carnier R.; **Funding Acquisition:** Abreu, C. A.; **Investigation:** Carnier R.; **Methodology:** Carnier R., Coscione A. R., Abreu, C. A., Melo L. C. A. and Silva A. F.; **Project Administration:** Abreu, C. A.; **Resources:** Coscione A. R.; **Supervision:** Coscione A. R.; **Validation:** Carnier R.; **Visualization:** Carnier R., Coscione A. R., Melo L. C. A. and Silva A. F.; **Writing – Original Draft:** Carnier R.; **Writing – Review and Editing:** Carnier R., Coscione A. R., Abreu, C. A., Melo L. C. A. and Silva A. F.

DATA AVAILABILITY STATEMENT

All dataset were generated and analyzed in the current study.

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