COFFEE WASTE BIOCHARS: CHARACTERIZATION AND ZINC ADSORPTION FROM AQUEOUS SOLUTION

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ABSTRACT: The final disposal of organic wastes has become a major challenge with increasing industrialization and population growth. Coffee wastes can be converted into biochar and provide economic and environmental benefits, such as heavy metal remediation in different media. We produced biochars at 700 °C from spent coffee grounds and coffee parchment, characterized them physically and chemically and evaluated their Zn adsorption capacity from aqueous solution. Batch adsorption experiments were performed with six Zn concentrations using four replicates. The desorption process was performed sequentially with a pH 4.9 buffer acetic acid solution. Langmuir and Freundlich isotherms were fitted to the adsorption data using non-linear models. Results show that both biochars are alkaline and have high values of point of zero charge (PZC) (9.2 and 7.7 for coffee parchment and spent coffee grounds biochar). These characteristics indicate precipitation as the main mechanism of Zn immobilization and may have contributed to the low adsorption capacity obtained (0.056 and 0.792 mg g^{-1} for spent coffee ground and coffee parchment biochar, respectively). Although the biochars have shown low adsorption capacity, they bound Zn strongly and the adsorption process is not easily reversed.

Index terms: Heavy metal, coffee waste, recycling, remediation.

1 INTRODUCTION

Heavy metals are important environmental pollutants that may originate from several anthropogenic sources and are widespread (MA et al., 2014; HOU et al., 2016; HOU and Li, 2017). Mining and smelting activities generate tailings with high concentrations of heavy metals, such as zinc (Zn), lead (Pb), cadmium (Cd), copper (Cu), etc. These elements are characterized by high toxicity and long-term persistence, which can lead to harmful effects on the environment and human health, particularly when the metal enters the trophic chain (VENEGAS et al., 2015; XU et al., 2018). Usually, soils and sediments in mining areas present high concentrations of these elements that can transfer to plants or to water bodies.

Sustainable environmental remediation remains an enormous challenge for modern society (QI et al., 2017; ZHANG et al., 2017). The need to remediate contaminated areas with metals is justified by the possibility of restoring its functionality. Generally, the techniques used to recover these areas are costly and sometimes difficult to implement in the field (SANTOS, 2014), requiring alternative approaches. Biochar is a technology which can be easily deployed and is receiving increasing attention. Biochar is a carbon-rich material intended for soil amendment and produced from the thermal decomposition of biomass at medium temperatures (usually 400 to 700 °C) with little or no oxygen supply (LIN et al., 2017). Moreover, biochar has potential to constitute an effective, sustainable and low cost waste management solution (MELO et al., 2015; PUGA et al., 2015; PENIDO et al, 2019). The initial focus on biochar research was due to its potential to mitigate climate change, resulting in carbon sequestration (WOOLF et al., 2010). In the last years an increasing body of literature has been devoted to the use of biochar for multiple applications. Several works demonstrated the potential of biochar to improve soil fertility characteristics (LYCHUK et al., 2015; DING et al., 2016), in the remediation of heavy metal polluted soils (PAZ-FERREIRO et al., 2017; WANG et al., 2017) and heavy metal polluted water (DOUMER et al., 2016; KONKIENE and BALTRENAITE, 2016; PATRA et al., 2017).

Biochars have been prepared from many different feedstocks, including manures, ligno-cellulosic materials and sewage sludges (ZHAO et al., 2018). Much less attention has been paid to the residues of the coffee industry. This is surprising, particularly considering that coffee is the second most traded commodity in the world, after oil. Brazil is the largest coffee producer in the world (CONAB, 2019), and consequently,

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about 1.1 ton of wastes are generated for each ton of coffee grounds processed (DIAS et al, 2014). More specifically, coffee parchment and spent coffee grounds, which are organic wastes generate in vast quantities and have a limited number of applications. For instance, coffee parchment is occasionally processed in thermal facilities to recover energy (ADAMS and GHALY, 2007), while spent coffee grounds have been used as fertilizer, but it was hindered due to its low N content and high acidity (VEGA et al., 2015). Besides, spent coffee grounds have also been used as a fuel due to its high calorific value (ATABANI et al., 2018) or as precursors for activated carbons preparation (REFFAS et al., 2010), biodiesels (KONDAMUDI et al., 2008), or as sorbent materials for heavy metals (KIM et al., 2014).

Biochar capacity to retain heavy metals is related mainly to the biomass type and to the pyrolysis temperature (GELL et al., 2011; ZHAO et al., 2018). Biochar produced at higher temperatures usually presents higher surficial area and porosity (BIRAR, 2014; SHAABAN et al., 2013), which contributes to the retention of organic and inorganic contaminants (BEESLEY et al., 2011). The mechanisms of heavy metals retention are complex and involve surface complexation, electrostatic interactions and cation exchange (HOSLETT et al., 2019). Besides the charge related surface effects, biochar is usually alkaline and has a liming effect that can cause significant metal precipitation (ALMAROAI et al., 2014).

Considering biochar heavy metal remediation potential and the importance of ecofriendly destination of organic wastes, this work aimed to physico-chemically characterize and to evaluate spent coffee grounds and coffee parchment biochars in the Zn adsorption from aqueous solution.

2 MATERIAL AND METHODS

Biochars production

Coffee parchment was obtained directly form a farm located at Tres Pontas, Minas Gerais state, Brazil. Spent coffee grounds from soluble coffee powder production was obtained from an industry located at Varginha, Minas Gerais State, Brazil. The two materials were air dried and the original granulometry was maintained. After dried, the materials were pyrolyzed in a reactor of continuous operation with production capacity of 2 t/day. Given the positive correlation between high pyrolysis temperature and retention of heavy metals, the pyrolysis occurred at a heating rate of 5 °C/min up to 700 °C with holding time of one hour, followed by a slow cool down to room temperature. The obtained biochars were used without further preparation.

Biochars characterization

Currently, there are no specific legislation that regulates biochar characterization for any use in Brazil. Thus, both materials were chemically characterized according to Resolution nº 375 from the Nacional environment Council (CONAMA, 2006) and according to the normative for soil conditioner from Ministry of Agriculture, Livestock and Supply (MAPA), as described bellow. Organic carbon (OC) was measured by titration after dichromate oxidation; Semi total Phosphorus was measured by ICP-OES after microwave digestion with nitric acid (EPA - 3051a) (US-EPA, 2007); pH was measured in water (1:10, solid: solution ratio); Volatile solids were measured by weight loss after heating to 500 ºC in muffle furnace; Ash content were determined as stated at the International Biochar Initiative guidelines (IBI, 2015). Briefly, 1.0 g was spread in ceramic crucibles and heated up to 750 °C under oxygen atmosphere. The remaining mass in the crucible was considered the ash content.

Cation exchange capacity (CEC) was obtained following the normative instruction nº 17 from MAPA (BRASIL, 2007), specific for soil conditioners and plant substrates. Briefly, the exchange sites are saturated with H^+ from HCl 0.5 mol L^{-1}, that are washed with calcium acetate 0.5 mol L^{-1}, followed by the titration with NaOH 0.1 mol L^{-1}, obtaining the CEC. Ultimate analysis (CHN) was obtained by combustion at 925 ºC using a Perkin Elmer CNH 2400 analyzer and the surface area was obtained by BET-N_2 method (BRUNAUER et al., 1938). Scanning electron microscopy (SEM) images were obtained using a Leo 440i model. Prior to measurements the samples were coated with a 200 Å thickness gold layer using a Sputter Coater EMITECH, K450 model. The SEM images were zoomed at 20 µm (500 x) for both biochar samples. Fourier transform infrared spectroscopy (FTIR) spectra was obtained using a Thermo Scientific, Nicolet 6700 model, in the transmission mode, with samples diluted in KBr, in the range of 4000-400 cm^{-1} with 4 cm^{-1} resolution.

Point of zero charge (PZC) of biochar samples was obtained as described by Yang et al., (2004), in triplicate. Initially, the samples were washings of with HCl 0.01 mol L^{-1} for 1 h under continuous stirring, followed by three consecutive water washes for 20 minutes and finally drying at 60 ± 5 °C. In sequence, 60 mg portions of each biochar were stirred for 24 h at 220 rpm with 20 mL $CaCl_2$ 0.01 mol L^{-1}, with initial pH adjusted to 2, 4, 6, 8 and 10. Finally, the samples were centrifuged and the final pH was measured in the supernatant. Then, the initial pH ($CaCl_2$ solution pH) was plotted against the final pH (measured after equilibrium) and the pH value where the line cross the curves of the initial pH and final pH was taken as PZC.

Adsorption and desorption of Zn

Deionized water (Milli-Q) was used for preparation of solutions and dilution of all liquid phases. A stock solution of $Zn(NO_3)_2.6HO$ (reagent grade, 98%) of 0.1 mol L^{-1} was prepared in $Ca(NO_3)_2$ 0.01 mol L^{-1} electrolyte solution. In previous tests, at higher doses of Zn, i.e, greater than 8 mg L^{-1}, no adsorption capacity of Zn was observed for both biochar samples. Thus, lower doses were used for the Zn adsorption study, which was carried out using six concentrations (0, 0.5, 1, 2, 4, 8 mg L^{-1}) with four replicates for both materials. No additional pH adjustment was made in the adsoption solutions.

The adsorption procedure was as follows: 500 mg of biochar were weighed and 40 mL of the solutions were added to 50 mL polypropylene centrifuge tubes. Afterwards, the tubes were agitated horizontally in an end-to-end Heidolph Unimax type shaker, at a speed of 200 rpm/min, with continuous shaking of 24 hours to achieve equilibrium. Several works showed that the kinetics of heavy metal adsorption is a fast process (less than 24h) (PENIDO et al., 2019; HUANG et al., 2018; HOSLLET et al., 2019). Thus, in this work it was assumed that equilibrium in adsorption process is reached within 24 h. The laboratory temperature was 25 ˚C (± 2 ˚C). The tubes were then centrifuged in Eppendorf A-4-44 centrifuge at 5,000 rpm for 5 min at 10 °C to decrease the suspended particles and to promote the separation of the biochar from the equilibrium solution. The solution pH was recorded and the solution was filtered (0.22 µm). The samples were kept under refrigeration at ~4 °C until Zn measurement by plasma emission spectrometry (ICP-OES). The Zn-loaded biochar was oven dried inside the centrifuge tubes for 18 h at 40 °C for further use in the desorption experiment. The amount of adsorbed Zn by the two biochar samples was calculated as described by UCHIMIYA et al. (2011):

$$q_s = \frac{V_s}{m}\ c_i - c_s$$

Where, q_s (mg g^{-1}) is the amount of Zn adsorbed by the biochar, V_s is the added volume of the solution (L), m is the mass of biochar (g) and c_i and c_s are respectively the initial and equilibrium Zn concentration (mg L^{-1})

Desorption was performed based on the Toxicity Characteristic Leaching Procedure (TCLP) of US-EPA (1992), method 1311. This method is used to determine the mobility of organic and inorganic analytes present in wastes either liquid, solid or multiphasic systems. The steps are described below: 200 mg of each Zn-loaded biochar were weighed and 20 mL of 0.1 mol L^{-1} acetic acid solution (pH of 4.9) were added and followed by 48 h stirring in the same shaker used in the adsorption experiment. The supernatant solution was filtered (0.22 µm) and Zn was determined by ICP-OES. The biochar retained on the filter was dried and stored for further analysis.

Isotherms

Langmuir (1916) and Freundlich (1906) isotherms were fitted to the experimental data using the non-linear models as shown by equation 1 and 2, respectively:

$$q_s = \frac{Q_{max} K_L Ce}{1 + K_L Ce}$$

$$q_s = K_F Ce^{\frac{1}{n}}$$

Where, q_s = amount of Zn adsorbed in biochar, in mg g^{-1}; Ce = Zn concentration in the equilibrium solution, in mg L^{-1}; Q_{max} = maximum adsorption capacity, in mg g^{-1}; K_L = Langmuir constant, indicating binding energy (mg^{-1}), K_F = Freundlich isotherm constant and 1/n = adsorption intensity.

Finally, the biochar samples used for the desorption studies were washed with deionized water in order to verify the existence of Zn in the form of surface precipitates. For this, the remaining mass of biochar from the desorption step was weighed into 50 mL-centrifuge tubes and 40 mL of deionized water was added, shaken for 24 hours, filtered (0.22 µm) and Zn concentrations were determined by plasma emission spectrometry (ICP-OES).

Statistical analyses

The pH data from the adsorption study was submitted to ANOVA analysis and fitted to linear regression. Mean values of four replicates were used to draw the isotherms and to calculate the adsorption isotherm constants. To obtain the isotherms, the StatSoft - Statistica v. 10 was used. The quality of fit in the isotherms was assessed by R^2 and the significance of the parameters ($p < 0.05$).

3 RESULTS AND DISCUSSION

Biochars characterization

The pH values observed in both biochar samples is within the range normally found in literature for coffee wastes prepared at similar pyrolysis temperature (TANGMANKONGWORAKOON, 2019) (Table 1). Usually, biochar obtained at high pyrolysis temperatures are alkaline due the progressive loss of surface acid groups (REEVES et al., 2007; SINGH et al., 2010). Overall, the carbon content was also in the same range of other coffee waste biochar (HOANG and MAEDA, 2018). The total carbon is significantly higher than the organic carbon (OC), which can be attributed to more resilient form of C, such as aromatic C, not mineralized by the dichromate oxidation procedure. The aromatic C content contributes to higher stability of biochar, making it persistent to degradation (SOHI et al., 2010), which is important to an effective, long-lasting remediation process.

Both biochars showed low P content, and even though they present N, this fraction is usually recalcitrant and therefore not available to plants (MCBEATH et al., 2015). The ash content was 13.6% and 37.7% for coffee parchment and spent coffee grounds, respectively and is related to the mineral fraction that is concentrated during the pyrolysis process and remain mainly in the biochar pores (SOHI et al., 2010; FERREIRA, 2012). Volatile solids indicate the presence of organic material with low stability, which represented about 50% of the biochars analyzed (45.5% and 54.6% for spent coffee grounds and coffee parchment, respectively). These results are in agreement with the carbon content, which is about 50% organic, and therefore subject to losses.

The CEC of both biochars can be considered low (41.3 and 58.3 $\text{mmol}_c\ \text{kg}^{-1}$ for spent coffee grounds and coffee parchment, respectively) when compared with values found in the literature for coffee waste biochar, such as 200 $\text{mmol}_c\ \text{kg}^{-1}$ in coffee husk biochar produced at 750 ºC (DOMINGUES et al., 2017). However, it should be highlight that the procedure used in this work was the one recommended by MAPA, which addresses the surface charge measurement directly after a cleaning and saturation step by a known amount of charged solution, while Domingues et al. (2017) used a modified ammonium acetate compulsory displacement method, adapted to biochars.

The values of surface area of coffee residues found in this work were similar to those found for other coffee waste biochars (DUME et al., 2015; LIU and HUANG, 2018) and the pore structure were evident in SEM (Figure 1). SEM analysis showed that the vegetable cellular structure was preserved for either materials despite pyrolysis and physical processes of coffee grounding. Metal adsorption is a surface phenomenon (NASCIMENTO et al., 2014), thus, high values of surface area and porosity are interesting.

Another analysis that gives information about the biochar surfaces is the spectra resulting from the FTIR analysis, which shows the bands associated with functional groups of each biochar (Figure 2). FTIR is a qualitative analytical technique and it is aimed to locate peaks referring to the chemical groups of higher (aromatic) and lower (aliphatic structures) recalcitrance, and both groups were verified for the biochars. For example, values between 1000 and 1200 cm^{-1} are attributed to the presence of oxygenated functional groups in open chains, for example, in hemicellulose and cellulose. Values in the range of 1200 and 1400 cm^{-1} correspond to oxygenated functional groups of lignin (NANDA et al., 2013), while the range of 1400 to 1600 cm^{-1} bands is characterized by double bonds aromatic rings. The 1625 cm^{-1} band is also assigned to the presence of aromatic rings, characterized by C=O and C=C (KOMNITSAS et al., 2014), which was highly evident for the coffee parchment. Peaks of aliphatic compounds appear at wavelengths between 3000 and 2800 cm^{-1} and the O-H stretch band characteristic of the hydroxyl and carboxylic acid groups is observed between

TABLE 1 - Physicochemical properties of the two biochar.

Biochar	pH	C	H	N	OC
	water (1:10)		%		
Spent coffee grounds	9.5 ± 0.1	62.3 ± 2.2	1.5 ± 0.0	2.1 ± 0.2	31.9 ± 0.7
Coffee parchment	9.6 ± 0.0	69.3 ± 1.3	1.6 ± 0.1	1.6 ± 0.0	38.5 ± 1.8
	P	Ashes	Volatile solids	Surficial area	CEC
		%		$m^2\ g^{-1}$	$mmol_c\ kg^{-1}$
Spent coffee grounds	0.16 ± 0.3	37.7 ± 3.4	45.5 ± 1,5	45.0 ± 0.0	41.3 ± 3.4
Coffee parchment	0.15 ± 0.2	13.6 ± 0.5	54.6 ± 1.3	32.0 ± 0.0	58.3 ± 6.9

OC = Organic carbon; CEC = cation exchange capacity.

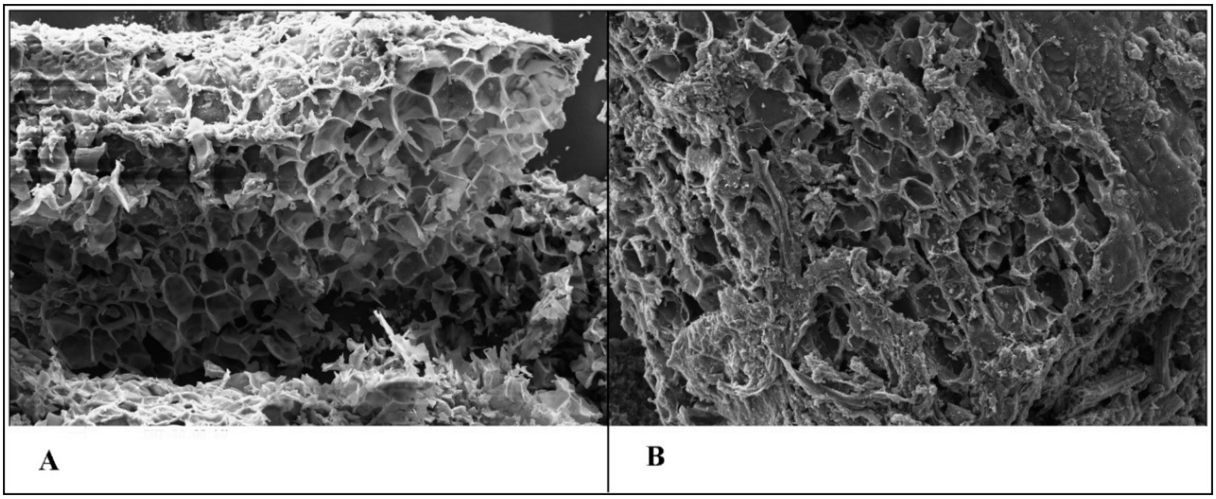

FIGURE 1 - SEM images for coffee parchment (A) and spent coffee grounds (B) biochars. (Zoom of 500x).

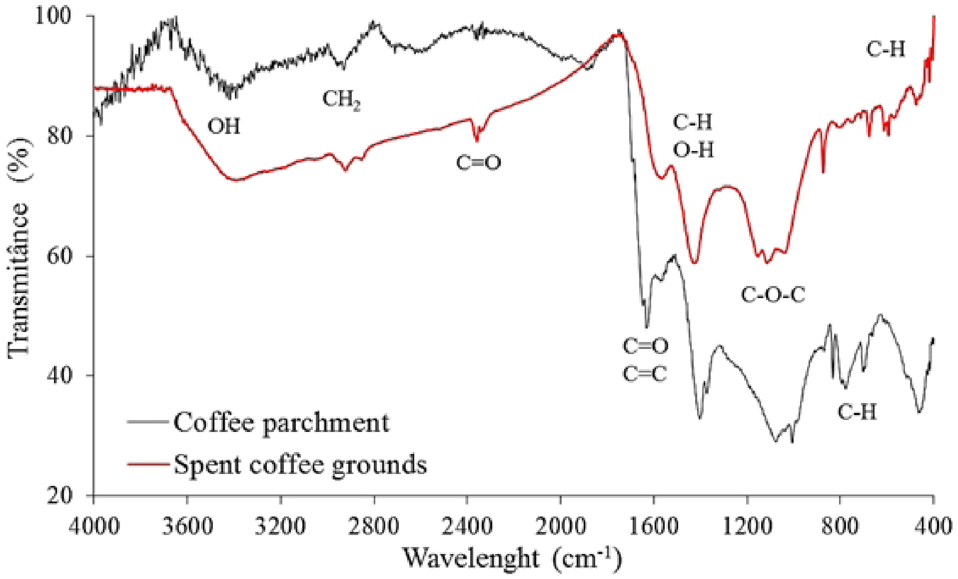

FIGURE 2 - FTIR spectra for the coffee parchment and spent coffee grounds biochars.

3440-3300 cm^{-1} (GUILHEN, 2018).

Aromatic structure gives the product high chemical stability and contributes to the long-term persistence of biochars in soils (SOHI et al., 2010). However, aromatic structure shows less polarity compared to the aliphatic and, consequently, less charge on the surface (UCHIMIYA et al., 2011, BIBAR, 2014). Therefore, considering that the coffee parchment biochar showed stronger peaks of aromatic groups (Figure 2), it is expected that this biochar presents less charge than spent coffee grounds biochar and thus lower performance as a complexant. The presence of surface charge is also controlled by the PZC analysis, which is characterized by the pH condition (pH_{PZC}) that charge amounts of acidic and basic functional groups are equal (ARAÚJO et al., 2018). In the condition of pH below the pH_{PZC}, the surface presents negative net charge, while in pH above pH_{PZC} the net positive charge predominates (BORBA et al., 2019). In this work, both biochar have high pH_{PZC} (9.2 and 7.7 for coffee parchment and spent coffee grounds biochar respectively) (Figure 3). These data are consistent with the results reported by Banik et al., (2018), who evaluated influence pyrolysis temperature on surface charge and functional group chemistry of biochars. They showed that biochars pyrolyzed at higher temperatures (≥ 700) presented consequently higher pH_{PZC}. The higher pH_{PZC} of the coffee parchment biochar implies in the presence of negative charges only in conditions when the pH is higher than 9.2, which supports the premise of less abundance of net negative charge than the spent coffee grounds biochar.

Adsorption and desorption of Zn

The Isotherms obtained for the biochars were L-shaped and characterized by a decreasing slope as concentration increases, which is an indication that vacant adsorption sites decrease as the adsorbent becomes saturated (Figure 4). The q_s value of the coffee parchment biochar was significantly higher than for the spent coffee grounds biochar (Table 2). The fits of both isotherm models (Langmuir and Freundlich) showed a high R^2, indicating affinity of the metal to the biochar. This may be related to uniformity of the pore surface and to similar adsorption sites. Thus, according the to Langmuir model, adsorption occurs with only one molecule per site, forming a monolayer.

The parameter q_{max} indicates the maximum adsorption that can be achieved with these materials, while the K_L values indicates the binding energy. Although the adsorption capacity of coffee parchment was higher (0.792 mg g^{-1}), the spent coffee grounds exhibited a stronger binding energy (9.81). For the Freundlich isotherm, K_F is the constant of Freundlich, which indicates the sample adsorption capacity and 1/n is related to

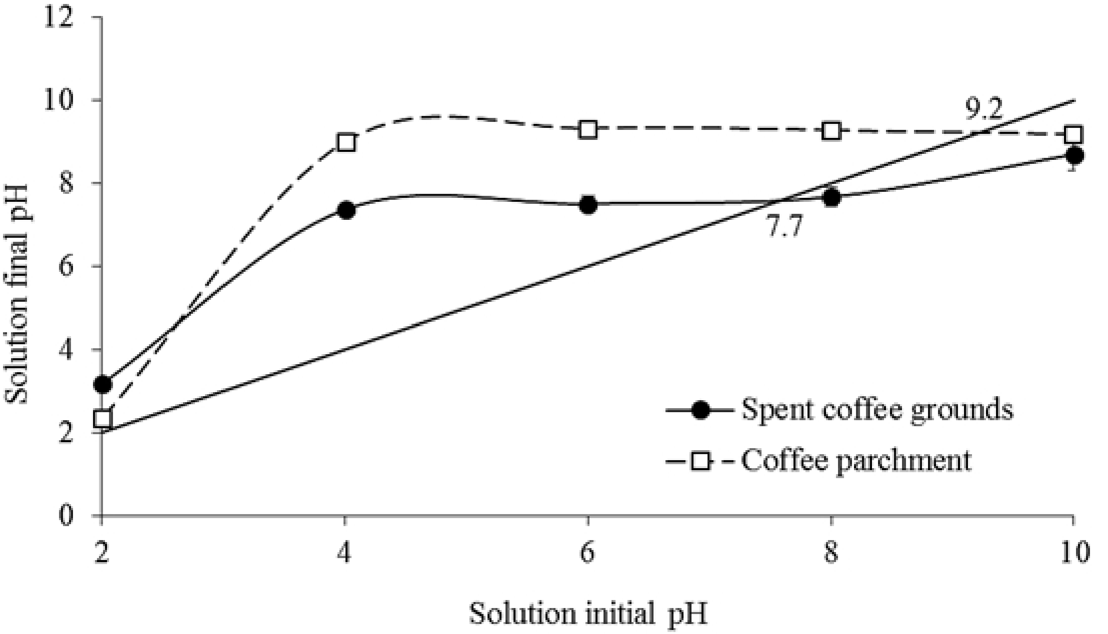

FIGURE 3 - Point of zero charge (PZC) for the spent coffee grounds and coffee parchment biochars.

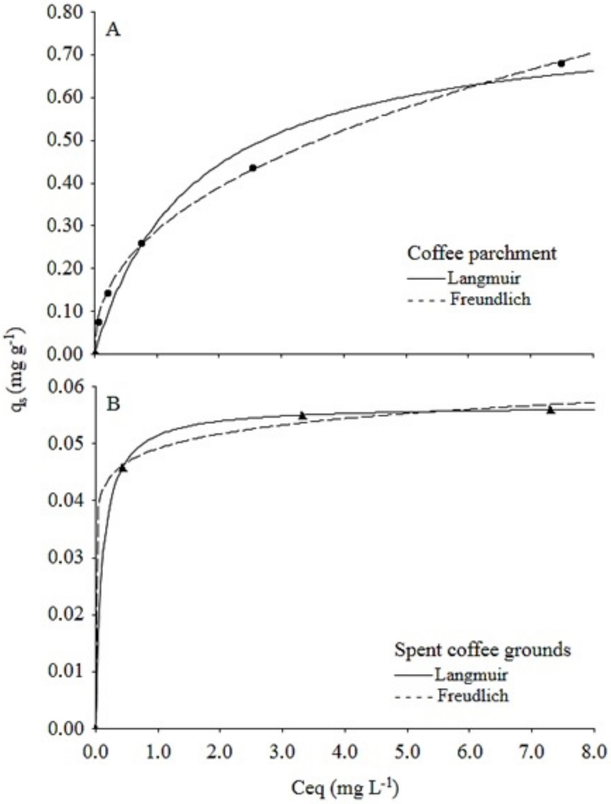

FIGURE 4 - Langmuir and Freundlich isotherms for adsorption of Zn by coffee parchament (**A**) and spent coffee grounds (**B**) biochars.

TABLE 2 - Parameters from Langmuir and Freundlich isotherms for the Zn adsorption by the two biochars.

Biochar	Langmuir			Freundlich		
	R^2	q_{max}	K_L	R^2	K_F	1/n
Coffee parchment	0.97	0.792	0.63	0.99	0.290	0.43
Spent coffee grounds	0.99	0.056	9.81	0.99	0.049	0.07

q_{max}= maximum adsorption capacity; K_L= Langmuir constant; K_F= Freundlich constant; 1/n= adsorption intensity;

affinity with the surface of the adsorbent.

The values obtained for these parameters followed the same trend of the Langmuir isotherm parameters. Coffee parchment showed a higher isotherm constant (0.290 mg g^{-1}), however, spent coffee parchment showed a lower value for the 1/n constant (0.07). The lower is the 1/n value the higher is the interaction between the adsorbent (biochar) and the adsorbate (Zn) (NASCIMENTO et al., 2014), indicating favorable adsorption.

In general, adsorption values reported in our study were lower than those found in literature. For example, corn straw pyrolyzed at 600 °C showed a maximum adsorption capacity of Zn of 11 mg g^{-1}, while hardwood biochar prepared at 450 ˚C showed a Zn retention capacity of 4.54 mg g^{-1} (CHEN et al., 2011). Bogusz et al. (2015) found a maximum adsorption capacity of Zn of 48.08 mg g^{-1} for *S. hermaphrodita* biochar obtained at 700 °C with a surface area of 27.1 m^2 g^{-1}. Nevertheless, Konkiene & Baltrenaite (2016), observed a value as low as 0.107 mg g^{-1} for the maximum adsorption capacity of Zn for scots pine biochar. These differences in the adsorption capacity by spent coffee grounds and coffee parchment biochars were influenced by their characteristics. Spent coffee grounds biochar has the higher surface area, which means more room for Zn retention (Table 1). However, besides the surface area, the presence of functional groups is a desirable characteristic for heavy metals remediation effectiveness by the biochar (HUANG et al., 2018; YU et al., 2018). We showed in the spectra from FTIR analysis that the spent coffee grounds presented more surficial aliphatic groups (Figure 2), and therefore a higher adsorption capacity was expected for this biochar. Nevertheless, the higher adsorption capacity of Zn was verified for the coffee parchment biochar. One possible explanation for this result is the higher pH in the equilibrium adsorption solution for coffee parchment when compared with spent coffee grounds (Figure 5). The pH values in the solution for both biochars are lower than their pH_{PZC} values, mainly for coffee parchment. Thus Zn will be repelled by the surface positive charges and precipitation may have occurred as the main mechanism of Zn immobilization.

Although the precipitation seems to be the main mechanism of Zn immobilization, the desorption test showed that a small portion of Zn was released, which is promising aiming its use for remediation purposes. The highest desorption rate was 9% for the spent coffee grounds at the dose of 2 mg L^{-1} and 21% for the coffee parchment at the dose of 4 mg L^{-1} (Figure 6). After the desorption process, in the washing step of biochar to verify formation of precipitated Zn, very low values were obtained in the solution. Thus, although the

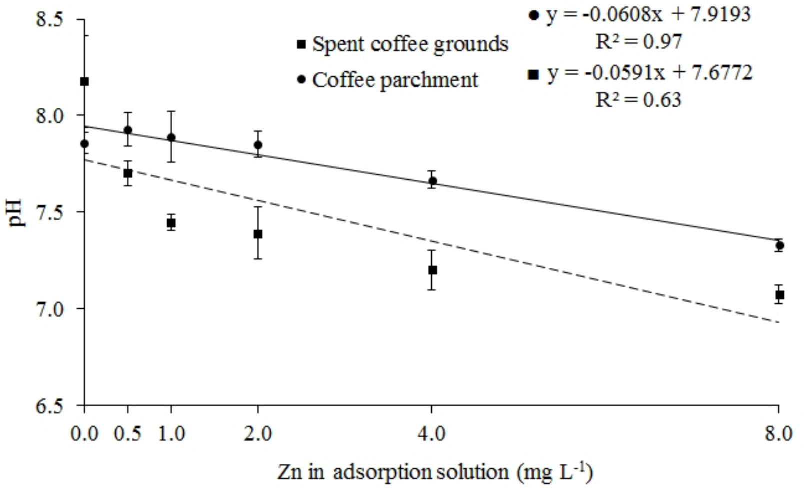

FIGURE 5 - Mean of the pH values in the solution after the adsorption process for the biochars at each metal concentration.

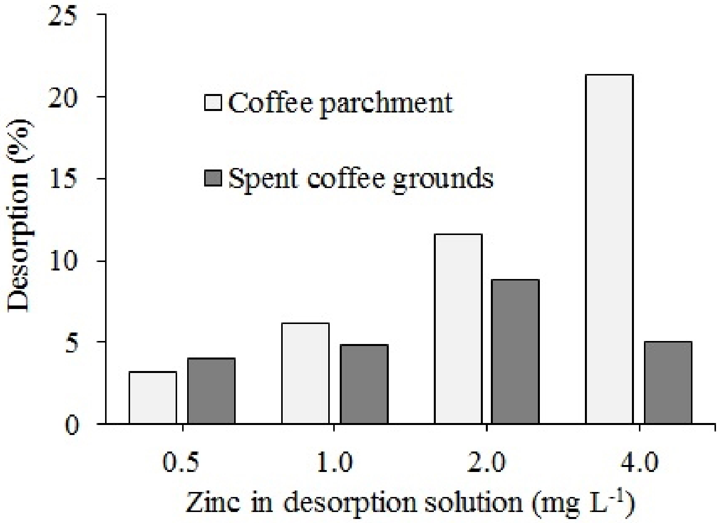

FIGURE 6 - Average rate for Zn desorption by the two biochar.

biochars did not possess a very high adsorption rate, the fraction adsorbed is strongly bonded.

4 CONCLUSIONS

Biochars presented low adsorption capacity. Nevertheless, both biochars bound Zn strongly and had low desorption rates. This results indicates that these materials have potential to remediate wastewater contaminated with Zn. Further studies using real contaminated matrices are needed to prove the effectiveness of these coffee waste biochars for remediation purposes.

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