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Functionalized Charcoal as a Buffering Matrix of Copper and Zinc Availability

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ABSTRACT: High copper (Cu) and zinc (Zn) contents in soil can cause phytotoxicity to plants and contaminate surface and groundwater, with negative effects on agriculture and the environment. Functionalized charcoal (OCh) has high cation exchange capacity (CEC) and the ability to adsorb Cu and Zn and control their availability in the soil and water. An adsorption study at two pH levels was carried out to evaluate increasing Cu and Zn sorption capacity provided by the functionalization process of a charcoal. In addition, a kinetics study of competitive and non-competitive adsorption-desorption of Cu and Zn in OCh was also evaluated. The results showed that functionalized charcoal (Ch) increased CEC 8.7 times due to an increase in carboxyl and phenolic groups, without changing its specific surface area. The Cu and Zn kinetics study showed higher interaction of Cu with the OCh, with total adsorption capacity of 53.1 mg g^{-1}. From this amount, only 74.9 % was desorbed. However, competitive adsorption with Zn reduced the total amount of Cu adsorbed and decreased the Cu affinity for organic matter. This study shows the potential use of functionalized charcoal for control of Cu and Zn availability in the soil solution.

Keywords: adsorption, desorption, metals, remediation, biochar.

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INTRODUCTION

Intensive crop production systems have a high demand for Cu and Zn, and the addition of these micronutrients to poor soils is necessary to meet plant nutritional needs. However, the application of high rates of these micronutrients in the soil can cause phytotoxicity (Fortunati et al., 2005; Lamb et al., 2012), reduction of the soil microbial activity (Giller et al., 1998), and contamination of surface water and groundwater (Xiaorong et al., 2007). In addition, recent research has shown that continuous use of animal waste in agriculture (Girotto et al., 2010; Mallmann et al., 2012, 2014) and successive application of cupric fungicides (Flores-Vélez et al., 1996; Pietrzak and McPhail, 2004; Mirlean et al., 2005; Komárek et al., 2010) have increased Cu and Zn levels in soil and water, representing a potential source of contamination. These undesirable effects on agriculture and the environment are intensified in low pH soils and soils with low clay and organic matter content (Alva et al., 2000; Fernández-Calviño et al., 2010), as well as in soils naturally rich in Cu and Zn (Xu et al., 2016; Gloaguen and Passe, 2017).

The dynamics of Cu^{2+} and Zn^{2+} in the soil solution is governed by the sorption-desorption equilibrium (Arias et al., 2006) and is mainly influenced by physicochemical factors, such as cation exchange capacity (CEC) (Gomes et al., 2001; Fontes and Santos, 2010) and the nature of the colloid and solution pH (Sparks et al., 1995; Song et al., 2015). Due to the inherent characteristics of Cu^{2+}, there is preferential adsorption of Cu^{2+} in organic colloids compared to Zn^{2+} (Elliott et al., 1986); thus, Cu^{2+} competes with Zn^{2+} and reduces its adsorption (Arias et al., 2006). However, Zn^{2+} in several situations has greater affinity with mineral compounds compared to Cu^{2+} (Covelo et al., 2007).

The addition of organic compounds to the soil, such as sewage sludge (Long et al., 2010), biochar (Tang et al., 2013; Schweiker et al., 2014), charcoal, and functionalized charcoal (Jośko et al., 2013), is being studied to reduce the mobility, bioavailability, and toxicity of metals such as Cu and Zn. Functionalized charcoal or biochar is also used as a sorbent in the removal of potentially toxic substances in industrial wastes (Deb et al., 2013) and as a sorbent for contaminant management in soil and water (Ahmad et al., 2014; Rajapaksha et al., 2016) due to characteristics that favor adsorption, such as high specific surface area, pore volume, and CEC (Liu et al., 2007; Linhares et al., 2012; Araujo et al., 2014).

One approach to promote functionalization of the charcoal surface, enhancing the use of charcoal as a sorbent, is oxidation of the charcoal with HNO_3 (Trompowsky et al., 2005; Liu et al., 2007). This process increases specific surface area, pore volume, and the presence of carboxyl, amino, and phenolic groups (Chen and Wu, 2004; Shafeeyan et al., 2010). To promote the oxidation of *Eucalyptus grandis* charcoal, Paiva et al. (2012) used 4.5 mol L^{-1} HNO_3, followed by an alkaline treatment, and obtained a functionalized charcoal with CEC over 440 $cmol_c$ kg^{-1}. In a subsequent study, Guimarães et al. (2015) avoided this alkaline treatment and used only oxidation with 4.5 mol L^{-1} HNO_3, obtaining functionalized charcoal with CEC of 417 $cmol_c$ kg^{-1} but with a yield 8.4 times higher. This oxidation process increased the content of carboxylic, phenolic, and N-containing groups, contributing to an increase in CEC and, consequently, to improvement in the metal adsorption capacity of charcoal (Puga et al., 2015). In addition, it decreased the charcoal pH value from 6.8 to 2.7, due to functionalization of the charcoal surface, which showed functional groups in protonated form (Guimarães et al., 2015).

Previous studies have shown that it is feasible to remediate metal-contaminated soils with biochar, reducing metals in the soil solution, consequently reducing risks of leaching and environmental impacts (Melo et al., 2016; Puga et al., 2016). Thus, functionalized charcoal has the potential for use in reducing the mobility, bioavailability, and toxicity of Cu and Zn in soil and water. However, the phenomenon of metal adsorption-desorption in charcoals is still poorly understood; in addition, the role of oxidation of charcoal to control the availability of Cu and Zn is not known. The purpose of this study was to evaluate Cu and Zn adsorption in functionalized charcoal in comparison to non-functionalized charcoal, and the effect of pH on the adsorption-desorption phenomenon. We also investigated the competitive and non-competitive Cu and Zn adsorption-desorption kinetics in the functionalized charcoal.

MATERIALS AND METHODS

Production of functionalized charcoal

The charcoal (Ch) used in this study was obtained from wood blocks of *Eucalyptus urophilla* carbonized in a laboratory oven at 350 °C for 8 h, which was crushed in an ultracentrifugal mill until its particle size was smaller than 74 μm and dried at 105 °C for 12 h, according to Guimarães et al. (2015). The Ch was functionalized with 4 mol L^{-1} HNO_3 at the proportion of 45 g L^{-1}, heated to boiling, and maintained under reflux for 4 h. After this time, the suspension was vacuum filtered using J. Prolab filter paper number 42. The residue in the filter was washed with deionized water, transferred to dialysis tubes (MWCO 12,400; Sigma-Aldrich), and submerged in deionized water to remove excess of acid and ions with successive water exchanges until electrical conductivity was below 2 μS. After dialysis, the functionalized charcoal (OCh) was dried at 60 °C, powdered with a mortar and pistil, and then sieved to <74 μm.

Characterizations

The chemical characterization of charcoal (Ch) and OCh consisted of elemental analysis in a Perkin-Elmer 2400 Series II CHNS/O Analyzer. The contents of C, H, and N were expressed in relation to ash free dry weight, while the O content was estimated by the difference (Table 1). Ratios were calculated from the C/N atomic mass. The pH of the charcoal/deionized water suspension was determined at a 1:10 (w/v) ratio and the CEC was determined by potentiometric titration with 0.1 M NaOH, assuming that it was derived from carboxyl groups from pH 3 to 8 and from phenolic groups from pH 8 to 10, according to Bowles et al. (1989) and Inbar et al. (1990).

The specific surface areas (SSA) of the materials were measured with a Micromeritics ASAP-2020 instrument and calculated by the Brunauer-Emmett-Teller (BET) method, measured by N_2 adsorption. The materials were pre-treated (degasification) by heating to 70 °C under vacuum until reaching a degassing pressure of less than 20 mmHg. The zeta potential of the materials was measured in a Zeta Potential Meter (Malvern-Zetasizer Nano-ZS) at pH ranging from 4 to 11. The FTIR Spectroscopy: Attenuated Total Reflection (FTIR-ATR) of the materials was obtained with a Perkin Elmer Spectrum 1000 spectrophotometer from 4000 to 400 cm^{-1}, with 32 scans and 4 cm^{-1} resolution. Material morphologies were analyzed by field emission scanning electron microscopy (FESEM, JEOL JSM 6701F operating at 2 kV).

Static adsorption experiments

Samples of 0.1 g of Ch or OCh were transferred to 50 mL polyethylene centrifuge tubes and 17.5 mL of 10 mmol L^{-1} K_2SO_4 solution was added, followed by adjustment to pH 6.5 or 2.7 with 1 mol L^{-1} H_2SO_4 or 1 mol L^{-1} KOH solution until pH stabilization. The pH of solutions was standardized at 6.5 and 2.7 to represent the original pH from Ch and OCh, respectively (Table 1). The charcoal suspension was then shaken in an orbital bench shaker at 50 rpm for 30 min. After that, 2.5 mL of Cu or Zn (16 mmol L^{-1}) prepared with $CuSO_4$ and $ZnSO_4$ salts was added. The salts were dissolved in the 10 mmol L^{-1} K_2SO_4 solution and pH was adjusted as previously described. The Cu or Zn solutions were also added to the 10 mmol L^{-1} K_2SO_4 solution at both pHs, without the addition of charcoal, as blank treatments. The final Cu or Zn concentration in the total volume (20 mL) inside

Table 1. Chemical and physical properties of charcoal (Ch), and oxidized charcoal (OCh)

Property	Ch	OCh
C (g kg^{-1})$^{(1)}$	735	574
H (g kg^{-1})$^{(1)}$	34	24
N (g kg^{-1})$^{(1)}$	9	30
O (g kg^{-1})$^{(1)}$	222	373
C:N (molar)	95	22
pH(H_2O)$^{(2)}$	6.5	2.7
Carboxyl groups ($cmol_c$ kg^{-1})$^{(3)}$	30	318
Phenolic groups ($cmol_c$ kg^{-1})$^{(3)}$	20	117
Total acidity CEC ($cmol_c$ kg^{-1})$^{(4)}$	50	436
Surface area (m^2 g^{-1})$^{(5)}$	30	29
Zeta potential (mV)$^{(6)}$	-23.5	-44.3

(1) In relation to dry matter free from ash. (2) Charcoal:water ratio of 1:10. (3) Estimated by potentiometric titration. (4) Sum of the carboxyl groups (pH 3.0-8.0) and phenolic groups (pH 8.0-10.0). (5) Estimated by N_2 adsorption. (6) Measured by suspensions of the charcoals.

the polyethylene centrifuge tubes was 2 mmol L^{-1}, an intermediate concentration used by Fernández-Calviño et al. (2010) in batch experiments.

For the static experiment, the suspension was shaken for 24 h in an orbital shaker at 50 rpm at 25 °C. Then the samples were centrifuged at 3000 rpm for 20 min, and the supernatant was filtered through JP filter paper (J. Prolab) number 42. The concentrations of Cu or Zn solution were measured by atomic absorption spectrophotometry (VarianSpectrAA 220FS) and the content of Cu or Zn adsorbed by the Ch or OCh was then estimated by difference.

Adsorption was evaluated in a factorial arrangement consisting of two metals (Cu and Zn), two adsorbents (Ch and OCh), and two solution pHs (6.5 and 2.7), with three replications. Data were expressed as means and the significance of the treatment was determined by analysis of variance. The means were compared by the Games-Howell test ($p<0.05$).

Sorption and desorption kinetics

A second experiment was designed to evaluate the kinetics of competitive and non-competitive sorption/desorption of Cu and Zn in OCh at its natural pH of 2.7. After the adsorption phase reached equilibrium (i.e., there was no difference between the concentration of the solutions entering and leaving the chamber), the solution containing Zn and/or Cu was stopped and started to pass the background solution (10 mmol L^{-1} K_2SO_4) to evaluate Zn and/or Cu desorption from the OCh.

Kinetic studies were performed using a continuous stirred-flow system in which a solution is pumped into a reactor where the sorption/desorption occurs, as described by Fernández-Calviño et al. (2010). Briefly explained, in the stirred-flow system, a 17 mL Teflon reactor is connected to a quaternary piston pump (Thermo Ultimate 3000). The entering solution is injected at the bottom of the reactor (1 mL min^{-1} flow), passes through the reactor chamber containing the functionalized charcoal, and is constantly mixed by a magnetic stirrer (300 rpm). The solution leaves the reactor through an outlet located on the top of the cap of the reactor. The functionalized charcoal is kept inside the reactor chamber by a 25-mm diameter cellulose filter with 0.2 µm pores (Sartorius Biolab Products) placed right before the outlet on the top of the chamber. The solution leaving the reactor is collected by an automatic fraction collector every two minutes for a total of 320 min. After the sorption/desorption has ended, we quantify the amount of Zn and Cu in it.

For the sorption experiment, the reaction chamber was filled with 5 mL of a 5 g L^{-1} OCh suspension at pH 2.7 and ionic strength of 10 mmol L^{-1} K_2SO_4. After completing the volume with the background solution (10 mmol L^{-1} K_2SO_4 and pH 2.7), the reactor was closed, and 0.0787 mmol L^{-1} (5 mg L^{-1}) Cu or Zn solutions with pH adjusted to 2.7, as described by Fernández-Calviño et al. (2010), were passed through the system at a flow rate of 1 mL min^{-1}. The solutions were prepared from $CuSO_4$ or $ZnSO_4$ salts in the background solution. The competitive adsorption of Cu and Zn was also evaluated with solution containing 0.0394 mmol L^{-1} (2.5 mg L^{-1}) Cu and 0.0394 mmol L^{-1} (2.5 mg L^{-1}) Zn with pH adjusted to 2.7, prepared and evaluated in the same way as described above for non-competitive adsorption.

After 320 min of the sorption experiment, we stopped the flow of the Zn or Cu (or both) solutions and started to flow only the 10 mmol L^{-1} K_2SO_4 background solution with pH adjusted to 2.7 to evaluate the desorption of Cu and Zn adsorbed by OCh.

All the sorption-desorption experiments were evaluated in duplicates, and we also used blank controls in which the sorption-desorption experiments were the same, expect that there was no charcoal in the reaction chamber. The Cu and Zn in the solution leaving the reaction chamber was quantified by atomic absorption spectrometry. The sorption (Equation 1) and desorption (Equation 2) of Cu and/or Zn in the OCh were calculated according to Fernández-Calviño et al. (2010):

$$q(i) = \left\{ \sum_{j=1}^{i} \left[\frac{(C1(j) - C2(j))\Delta tJ}{Ve} \right] + [C1\ (i+1) - C2\ (i+1)] \right\} \frac{Ve}{m} \qquad \text{Eq. 1}$$

$$q(i) = \left\{ \sum_{j=1}^{i} \left[\frac{(C2(j) - C1(j))\Delta tJ}{Ve} \right] + [C2\ (i+1) - C1\ (i+1)] \right\} \frac{Ve}{m} \qquad \text{Eq. 2}$$

in which q(i) = adsorption or desorption (mg g^{-1}) accumulated in $i\Delta t$ time (min) (Δt = collection time of each aliquot); C1 (i) and C2 (i) = metal concentration in each aliquot in the absence and presence of OCh (mg L^{-1}), respectively; J = flow rate (L min^{-1}); Ve = the effective volume of the solution chamber (L); and m = mass of OCh (g).

When an adsorbent material is placed in an aqueous solution, the balance between adsorbent and adsorbate is not immediate, because the adsorbate molecules need to be transported from this aqueous solution to the outer surface of the adsorbent material and, after that, along the surface to its pore network; or it is still necessary for ionization of the functional groups at the surface of the adsorbent to occur, which can then interact with the ions of the solution. Thus, development of models for description of the kinetics of the adsorption process follow from these assumptions (Sontheimer et al., 1988). From the sorption-desorption curves, it was possible to analyze the kinetic of adsorption/desorption of the metals (Cu and/or Zn) in order to obtain the rate of metal adsorption by the functionalized charcoal. Thus, a pseudo-first-order model was used and can be represented by the equation 3:

$$\frac{dq_s}{dt} = k_s\,(q_{max} - q_s) \qquad \text{Eq. 3}$$

in which q_s (mg g^{-1}) is the concentration of metals adsorbed at time t, q_{max} is the maximum concentration of Cu or Zn adsorbed at equilibrium (mg g^{-1}), and k_s (min^{-1}) is the adsorption rate constant. For the reverse process, kd is the desorption rate constant, qd (mg g^{-1}) is the concentration of Cu or Zn desorption at time t, and q_{dmax} (mg g^{-1}) is the maximum concentration of Cu or Zn desorbed at equilibrium, as shown in equation 4.

$$\frac{dq_d}{dt} = k_d\,(q_{dmax} - q_d) \qquad \text{Eq. 4}$$

RESULTS AND DISCUSSION

Production and characterization of functionalized charcoal (OCh)

The OCh yield was 780 g kg^{-1} in relation to the initial charcoal weight (Ch), which is due to the loss of C as CO_2 and soluble compounds during the acid oxidation process. This process reduced C and H contents by 22 and 30 %, respectively (Table 1). However, it increased N and O contents by 33 and 68 %, respectively (Table 1), also reported in a previous study of our group (Guimarães et al., 2015). These changes decreased the OCh C:N ratio 4.2 times in comparison to the original Ch (Table 1). The increase in acidic groups on the surface of the functionalized charcoal makes it more hydrophilic, decreases its point of zero charge (PZC), and increases the negative surface charge density. Due to the increased carboxyl and phenolic groups in protonated form, OCh equilibrium pH in water decreased to 2.7 (Table 1), increasing its total acidity 8.7 times compared to Ch. Using nitric acid to functionalize almond charcoal, Moreno-Castilla et al. (2000) also found the same equilibrium pH (around 2.3) after the oxidation.

The amount of the carboxyl groups, estimated by potentiometric titration from pH 3 to 8 (Bowles et al., 1989; Inbar et al., 1990), were 2.7 times higher than the phenolic groups, which was estimated by potentiometric titration from pH 8 to 10. Since carboxyl groups are more acidic than phenolic groups, there was a decrease in the zeta potential, which was initially -23.5 mV and changed to -44.3 mV after functionalization of charcoal in both solutions and standardization at pH 2.7, although this did not cause any change in specific surface area (Table 1).

In terms of functional groups, FTIR-ATR analysis shows some differences between Ch and OCh (Figure 1). According to the spectra, there are basically two main bands that characterize the charcoal according to the vibrational energy of the molecules. The band between 3450 cm^{-1} corresponds to stretching of the O-H group (Huang et al., 2009), mainly in the carboxylic acid functional group. The band ranging from 1600 to 1700 cm^{-1} corresponds to stretching of the C=O to carboxylic acids or to lactones in phenolic groups (Zielke et al., 1996). Observing the FTIR-ATR spectrum, it cannot be stated conclusively that there were changes in the bands between 3450 cm^{-1} since these bands are highly influenced by the presence of water and also by the vibrations of the amine groups. However, it is in the regions between 1700-1600 cm^{-1} that more changes are observed for the OCh. These results clearly indicate that the functionalization by HNO_3 generates a large number of surface functional groups (Chen and Wu, 2004). A new band can be observed at 1691 cm^{-1} for free unsubstituted amide vibrations, and the band shift from 1596 cm^{-1} to 1589 cm^{-1} is due to a change in the chemical environment between the vibrations C=C of the aromatic ring related to the increase in the carboxylic and phenolic groups exhibited by OCh. In addition, there are changes in the bands at 1348 to 1368 cm^{-1}, corresponding to the OH of secondary alcohol and carboxylic acid and in the bands between 900 to 650 cm^{-1}, related to vibrations of the aromatic rings as a consequence of greater predominance of carboxylic and phenolic groups attached to aromatic rings (Silverstein et al., 2006).

The production of charcoal from eucalyptus wood produces a material that keeps the biological structures present in the plants (Figure 2a). Thermal decomposition of biomass forms an extensive pore network (Song and Guo, 2012). However, the acid functionalization of Ch broke down these structures, leaving behind smaller particles in the OCh (Figure 2b). Even though the structure has changed, the specific surface area of Ch and OCh did not change (Shamsijazeyi and Kaghazchi, 2010).

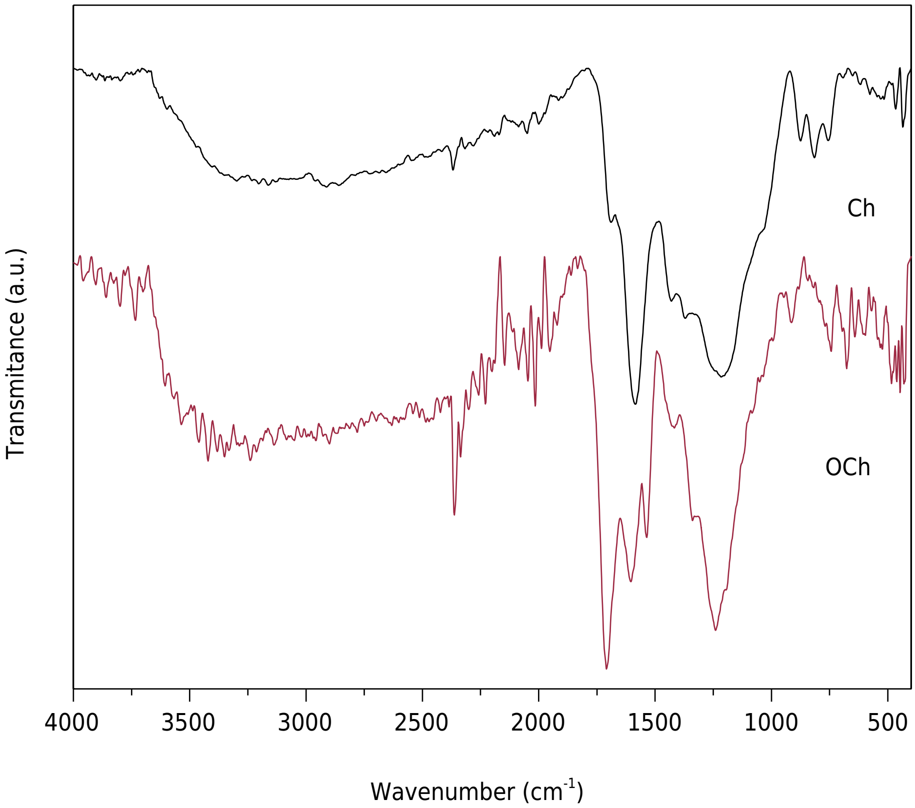

Figure 1. Infrared spectra of *Eucalyptus* charcoal (Ch) and of oxidized charcoal (OCh).

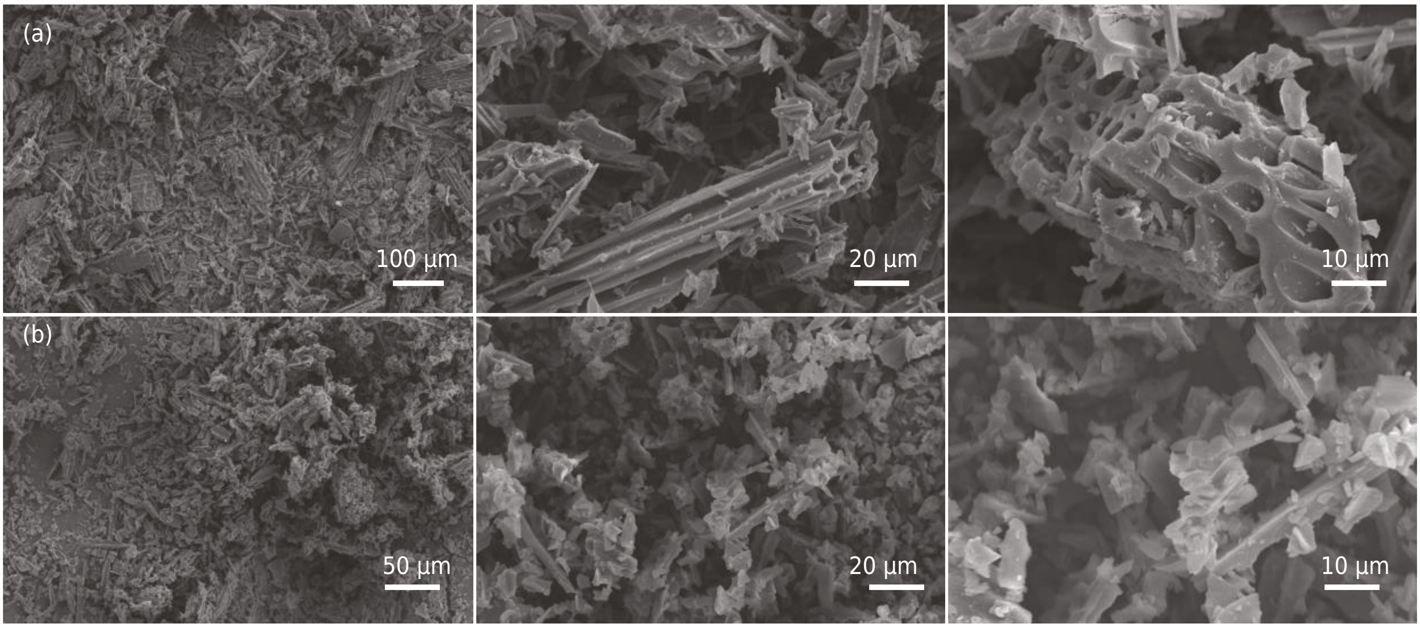

Figure 2. Scanning electron microscopy (SEM) images of *Eucalyptus* charcoal (Ch) (a) and of oxidized charcoal (OCh) (b).

Static adsorption experiments

Table 2 shows the adsorption of Cu and Zn in charcoal (Ch) or functionalized charcoal (OCh) at pH 6.5 or 2.7, respectively. The functionalization of Ch led to a significant increase in its ability to adsorb both Cu and Zn, especially under the more acidic pH condition. This result can be attributed to the presence of negative charges even at low pH (such as 2.7), due to the lower PZC of OCh. Adsorption of Cu increased 174 times with the functionalization of charcoal at pH 2.7; however, this increase was only 2.7 times at pH 6.5. This increase can be attributed to the increase of 8.7 times in CEC due to the carboxylic acidity promoted by charcoal functionalization (Table 1). The adsorption capacity of charcoal increases even without any change in specific surface area. According to many authors (Bautista-Toledo, 1994; Leon et al., 1994; Shamsijazeyi and Kahazachi, 2010), the surface chemistry of the adsorbent is, in general, more important for the adsorption process than the surface area and pore distribution of the adsorbent. In a study conducted by Xu and Liu (2008), it was observed that activation of charcoal with HNO_3 increased Pb^{2+} removal, due to an increase in its cation exchange capacity (CEC), but not due to structural properties.

The pH had a greater effect on Cu adsorption capacity in the Ch than in the OCh. This effect may be related to the greater variation in pKa values observed for the OCh, ranging from 1.2 to 9.6, as described by Guimarães et al. (2015). At a pH lower than the PZC (such as pH 2.7), Ch has protonated adsorption sites, which ultimately reduces its adsorptive capacity. In contrast, OCh showed a smaller difference in Cu adsorption within the same pH change due to the lower PZC. In contrast, the adsorption of Zn in OCh was more dependent on pH than adsorption of Cu. Whereas Ch showed greater adsorption of Zn than Cu, the reduction of pH 6.5 to 2.7 inhibited Zn adsorption by Ch. There was greater affinity for adsorption of Cu on the surface for both charcoals (OCh and Ch), especially at lower pH, corroborating the results from Elliott et al. (1986). At pH 2.7, OCh showed a greater ability to adsorb Cu, with only a slight increase at pH 6.5. However, Zn adsorption in OCh increased approximately three times at the increased pH level. This result was expected, due to the inherent characteristics of the Cu, which has high affinity to and specific adsorption with organic compounds (Guilherme and Anderson, 1998). The large increase in Zn adsorption when pH went from 2.7 to 6.5 showed the big influence of surface charges on Zn adsorption in OCh.

Sorption kinetics

The sorption of Cu in OCh was fast, the sorption rate increased up to 60 min, and maximum sorption capacity of 54.66 mg g^{-1} was achieved in 180 min (Table 3 and Figure 3). In a study performed by Sparks (2003), it also observed that Cu affinity by the organic matter surface decreased with the increase in the total adsorbed. From all this Cu sorbed, only 71.9 % was desorbed within 320 min (Table 3). This is due to the strong interaction between Cu and the OCh surface. According by Strawn and Baker (2008), Cu can form mainly inner-sphere complexes with organic matter, which promote irreversible adsorption. Cupper adsorption by OCh in the stirred-flow chamber method was four times higher than in the static method. Cupper adsorption tended to be greater in the flow systems, possibly because of precipitation or reduced competition between the solutes and desorbed antecedent species (Usepa, 1992).

The non-competitive adsorption and desorption of Zn on the OCh surface in the period of 320 min is shown in figure 4. As expected, Zn adsorption was lower than Cu adsorption.

Table 2. Adsorption of Cu or Zn (mg g^{-1}) in charcoal (Ch) and oxidized charcoal (OCh) at pH 2.7 and 6.5 in the static adsorption experiment. Values within the table followed by the same letter do not differ significantly by the Games-Howell test at p<0.05

Element	pH	Ch	OCh
		mg g^{-1}	
Cu	2.7	0.066 (0.018*) e	12.174 (0.126) b
	6.5	4.685 (0.829) c	12.914 (0.237) a
Zn	2.7	0.001 (0.000) f	4.567 (0.203) c
	6.5	1.185 (0.201) d	13.016 (0.220) a

Triple interaction was significant (p<0.001). * Confidence intervals.

Table 3. Non-competitive and competitive parameters of Cu or Zn adsorption and desorption by oxidized charcoal (OCh) at pH 2.7 performed using a continuous stirred-flow system. Mean values reported from two replicates, with standard deviations in parentheses

Samples	Adsorption			Desorption		
	q_{max}	k_s	R^2	q_{dmax}	k_d	R^2
	mg g^{-1}	min^{-1}		mg g^{-1}	min^{-1}	
Non-competitive						
Cu	54.66 (6.38)	0.62 (0.000)	0.99	39.31 (2.70)	0.29 (0.005)	0.99
Zn	8.34 (0.67)	0.12 (0.029)	0.96	9.09 (1.26)	0.11 (0.025)	0.97
Competitive						
Cu	28.54 (1.23)	0.40 (0.00)	0.98	29.04 (1.97)	0.22 (0.009)	0.99
Zn	7.76 (1.23)	0.09 (0.052)	0.97	7.24 (1.60)	0.05 (0.004)	0.97

q_{max} = maximum amount of Cu or Zn adsorbed; k_s = constant related to the adsorption rate; q_{dmax} = maximum amount of Cu or Zn desorbed; k_d = constant related to the desorption rate.

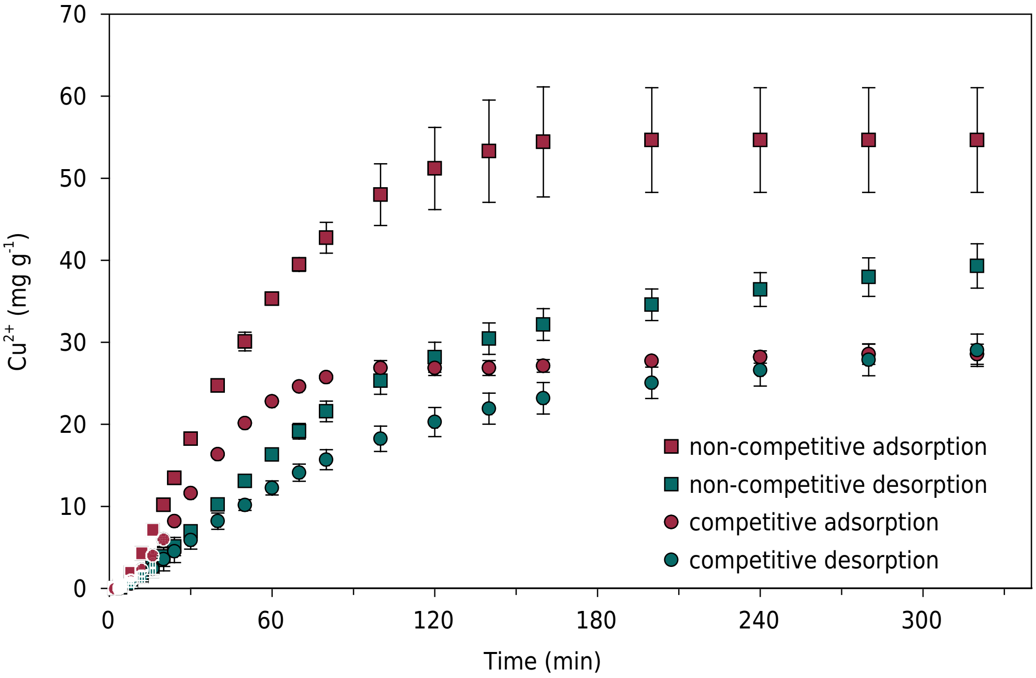

Figure 3. Cumulative non-competitive and competitive Cu adsorption and desorption by oxidized charcoal at pH 2.7 in stirred-flow experiments. Data shown as the mean values of duplicates with bars to indicate the standard error of the mean.

In addition, Zn adsorption stabilized faster, at 8.34 mg g^{-1}, after 120 min (Table 3). These results confirm the lower affinity for Zn than for Cu by the organic matter surface. This behavior was also observed by Fernández-Calviño et al. (2010). Despite the lower Zn adsorption, all the Zn adsorbed was desorbed up to 320 min, showing a lower interaction with the OCh surface, compared to Cu. The total desorption of Zn can be attributed to Zn mainly forming outer-sphere complexes with the adsorbent particles (Diesing et al., 2008). Similar to that observed for Cu, adsorption of the Zn in OCh was two times higher by the stirred-flow chamber compared to the static adsorption method.

The interaction of Cu and Zn ions in the solution, as well as competition for adsorption sites on the OCh surface eventually reduced Cu and Zn adsorption. However, this reduction was greater for Cu, from 54.66 to 28.54 mg g^{-1}, whereas for Zn, it was 8.34 to 7.76 mg g^{-1} (Table 3). These results suggest that Cu has more influence on this competition than Zn.

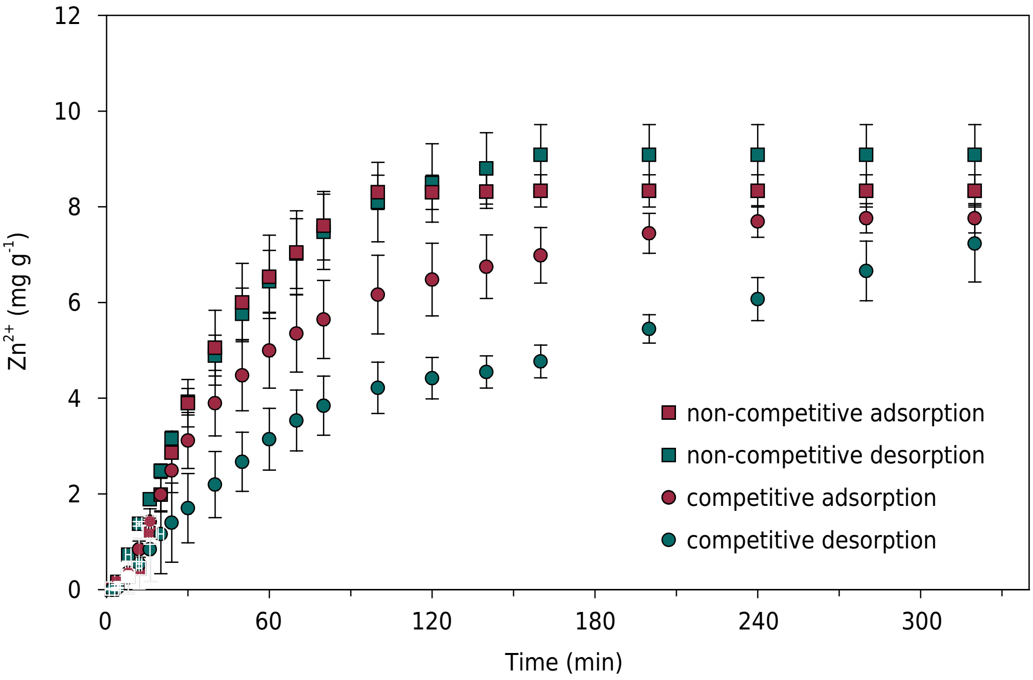

Figure 4. Cumulative non-competitive and competitive Zn adsorption and desorption by oxidized charcoal at pH 2.7 in stirred-flow experiments. Data shown as the mean values of duplicates with bars to indicate the standard error of the mean.

However, all the Cu adsorbed in the competitive test with Zn was desorbed over the period of 320 min. This result suggests that the interaction between Cu and Zn reduced the interaction force of Cu on the OCh surface, allowing 100 % of adsorbed Cu to be released in the same period (Table 3). In addition, the lower Cu concentration in the competitive experiment may have favored complete desorption of the Cu. Similarly, Zn desorption occurred more slowly in relation to the non-competitive experiment; however, all the Zn was desorbed from the OCh surface in the same period. The study of Arias et al. (2006) tends to support these findings because they also observed a higher desorption of Cu in the presence of Zn, which was explained by the Zn competition for sites in the soil. Thus, it can be seen that the adsorption and desorption behavior of Cu and Zn are influenced by the competitive interaction between these ions.

The data of the maximum amount of Cu and Zn adsorbed and desorbed in OCh (q_{max} and q_{dmax}) by non-competitive and competitive experiments is presented in table 3. For noncompetitive adsorption, the OCh surface exhibited higher affinity for Cu (q_{max} = 54.66 mg g^{-1}) compared to Zn (q_{max} = 8.34 mg g^{-1}), followed by the kinetics constant (k_s) of 0.62 (0.00) and 0.12 (0.029) min^{-1}. The higher affinity for Cu compared to Zn and the specific adsorption of Cu with organic binders is due to the higher electronegativity of Cu compared to Zn. In addition, Cu can form a coordination complex that increases interaction with the charcoal surface and forms mainly inner-sphere complexes with its ligands (Strawn and Baker, 2008), whereas Zn forms mainly outer-sphere complexes (Diesing et al., 2008).

Electronegativity is a measure of the attraction exerted on the electrons of a bond, and is related to atomic radius. The smaller the size of the atom, the greater the force of attraction, since the distance between the nucleus and the electrosphere is smaller. There are scales that relate the electronegativity of the elements; the Pauling scale is the most used, and from it we have Cu > Ni > Cd > Zn (Basta and Tabatabai, 1992).

The higher Cu rate constant in both (competitive and noncompetitive adsorption) experiments also confirms the affinity for Cu by the OCh surface, which was demonstrated by its greater capacity to adsorb Cu compared to Zn. However, Zn decreases the affinity of OCh for Cu, both reducing the amount adsorbed and facilitating its desorption.

Competitive adsorption of metals has been reported by many researchers for decades. The adsorption of Cu, Zn, and Cd in some acid soils was studied by Kuo and Baker (1980), and the authors observed that the Cu was preferentially adsorbed in relation to the others and that the presence of this metal interfered with retention of Cd and Zn. The same result was obtained by McBride and Blasiak (1979) in the Cu-Zn binary system. Competitive adsorption isotherms of Cd, Cu, Zn, Ni, and Pb as a function of the pH of two soils were obtained and increased competition as the initial concentrations of the metals increased was observed by Basta and Tabatabai (1992). In general, the affinity of both soils for the metals was in the following order: Pb > Cu > Ni > Cd-Zn. In the same way, Echeverría et al. (1998) also used isotherms to explain the competitive performance of these metals in three soils and concluded that Cu and Pb were adsorbed in large quantities and mainly with a higher bond strength compared to Cd, Ni, and Zn. Competition among the elements varied in magnitude, as shown by soil type and organic matter content.

CONCLUSION

The oxidizing process of charcoal led to an increase in Cu and Zn adsorption capacity on the OCh surface due to the increase in functional groups and, consequently, in the CEC of the charcoal. The adsorption of Zn by functionalized charcoal was more highly at a higher pH value, whereas Cu adsorption did not change when the pH was more basic. The competitive effect between Cu and Zn led to a considerable decrease in adsorption of Cu. Furthermore, 100 % of the Zn adsorbed on the OCh surface was released in water much faster than the Cu was. In addition, the OCh had higher retention of Cu than Zn, especially in the noncompetitive condition. This study indicates that functionalized charcoal is an efficient strategy for controlling Cu and Zn availability, which can reduce negative effects on agriculture and on the environment.

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