

Removal of Cd, Cu, Pb, and Zn from aqueous solutions by biochars

M. E. Doumer¹ · A. Rigol² · M. Vidal² · A. S. Mangrich¹

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Abstract Sorption and desorption of heavy metals (Cd, Cu, Pb, and Zn) was evaluated in biochars derived from sugarcane bagasse (SB), eucalyptus forest residues (CE), castor meal (CM), green coconut pericarp (PC), and water hyacinth (WH) as candidate materials for the treatment of contaminated waters and soils. Solid–liquid distribution coefficients depended strongly on the initial metal concentration, with $K_{d,max}$ values mostly within the range 10^3 – 10^4 L kg⁻¹. For all biochars, up to 95 % removal of all the target metals from water was achieved. The WH biochar showed the highest $K_{d,max}$ values for all the metals, especially Cd and Zn, followed by CE (for Cd and Pb) and PC (for Cd, Pb, and Zn). Sorption data were fitted satisfactorily with Freundlich and linear models (in the latter case, for the low concentration range). The sorption appeared to be controlled by cationic exchange, together with specific surface complexation at low metal concentrations. The low desorption yields, generally less than 5 %, confirmed that the sorption process was largely irreversible and that the biochars could potentially be used in decontamination applications.

Keywords Biochar · Waste biomass · Slow pyrolysis · Metal removal · Sorption · Desorption

Introduction

Heavy metals are among the pollutants found in water and soils that have most significant environmental impacts. They can be transported to uncontaminated environmental compartments, such as groundwater, and can be absorbed by plants, hence affecting the trophic chain and causing harmful effects to living organisms and the environment (Mohan et al. 2007). Therefore, it is necessary to develop low-cost and effective methods able to reduce the impact of heavy metal pollution in soil and water.

The use of non-toxic solid by-products, such as quarry waste, biosolids and sewage sludge, both in permeable reactive barriers and as amendment of soils, is an increasingly considered strategy for decontamination of metal-contaminated waters or immobilization of metals in contaminated soils, through the irreversible sorption of metals by the solid phase of the by-product (Mulligan et al. 2001; Guo et al. 2006). In this context, the use of biochars for the treatment of contaminated water and soils has recently received much attention (Mohan et al. 2014; Ahmad et al. 2014). Biochar is a carbon-rich pyrolytic material derived from the thermal decomposition of biomass in a closed system with little or no oxygen (Lehmann et al. 2006). It has been found that biochars derived from materials such as oak bark, crop straw, and manure may be more efficient for reducing heavy metal concentrations in water, compared to commercially available activated carbon (Mohan et al. 2007; Cao et al. 2011; Tong et al. 2011). Although biochars may have lower surface area (Han et al. 2013; Wang et al. 2015a) and lower degree of porosity than activated carbon, its higher content in acid functional

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✉ A. Rigol
annarigol@ub.edu

¹ Department of Chemistry, Federal University of Paraná-UFPR, 81531-990 Curitiba, PR, Brazil

² Department of Analytical Chemistry, University of Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

groups may explain this pattern (Han et al. 2013), as oxygen-containing functional groups (mainly phenolic, carboxylic, and hydroxyl groups) in biochar surface enhance metal sorption efficiency with respect to activated carbon (Bogusz et al. 2015; Frišták et al. 2015). However, the type of biomass from which biochar is obtained affects its intrinsic properties, such as the metal sorption capacity (Zhao et al. 2013; Frišták et al. 2015; Wang et al. 2015b; Venegas et al. 2015).

Metal sorption onto biochar is usually based on cation exchange (e.g., K, Ca, Mg) followed by complexation between oxygen functional groups and metal (Ding et al. 2014; Wang et al. 2015a; Frišták et al. 2015; Zhang et al. 2015). Additionally, precipitation of metals can occur in the presence of phosphate, hydroxide, and others anions released from biochars (Wang et al. 2015a).

There are numerous candidate materials for the production of biochars due to the high levels of generation of biomass wastes in many countries, which should be managed, revalorized, and reduced (IBÁ 2015; IBGE 2015; Bergier et al. 2012). As the metal sorption by biochars cannot be predicted, but it is extremely dependent on the biomass from which it is produced and on the target metal (Chen et al. 2011; Kim et al. 2014), the present work examines the capacity of five biochar materials produced from biomass of different origin, for the sorption and removal of heavy metals (Cd, Cu, Pb, and Zn) present in aqueous solutions, with the aim of recommending the most efficient materials for treatment of contaminated water.

Materials and methods

Materials

Five biochars, produced by slow pyrolysis of biomass, were used in this work. They were obtained from the following biomasses: sugarcane bagasse (SB), eucalyptus forest residues (CE), castor meal (CM), green pericarp of coconut (PC), and water hyacinth (WH) (*Eichornia crassipes*).

Details of the biomass origin, as well as the pyrolysis conditions used to obtain the biochars and the methods used to characterize them, are included in the [Supplementary material](#).

Determination of water-soluble metal content in biochars

The water-soluble metal contents were quantified in the extracts obtained after equilibrating known amounts of the materials with Milli-Q water for 16 h, using a liquid/solid ratio of 25 mL g⁻¹, with end-over-end shaking at room temperature.

The concentrations of elements in the extracts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass

spectrometry (ICP-MS). Details of the measurements are described in the [Supplementary material](#).

Sorption isotherms

Stock metal solutions containing 100 mmol L⁻¹ Cd, Cu, Pb, or Zn were prepared by dissolving a weighed amount of Cd(NO₃)₂·4H₂O, Cu(NO₃)₂·3H₂O, Pb(NO₃)₂, and Zn(NO₃)₂·4H₂O (Merck, Pro-Analysi) in Milli-Q water, respectively. Batch sorption tests were performed in 80 mL polypropylene centrifuge tubes. Two grams of the biochar samples was pre-equilibrated for 16 h with 45 mL of Milli-Q water, using end-over-end shaking. Then, suitable volumes of the corresponding stock solution were added in order to obtain initial metal concentrations within the 0.025–5 mmol L⁻¹ range (a minimum of seven different concentrations) after adjustment of the final volume to 50 mL. The resulting suspensions were shaken end-over-end for 24 h. The solid and liquid phases were then separated by centrifugation at 15,000 rpm for 10 min and the solutions were filtered through 0.45 μm Millipore filters. The filtered supernatants were immediately acidified to pH <2 with concentrated HNO₃ and kept at 4 °C until analysis.

In order to evaluate possible changes of pH and exchangeable cations caused by the addition of the target metal, control samples were generated in parallel by following the same procedure, but without the presence of the target metal.

Oxidizing digestion of the supernatants was carried out, as described in the [Supplementary material](#), for those highly colored solutions indicating high dissolved organic carbon (DOC) contents, as recommended in previous studies (Silva and Ciminelli 2009).

Desorption tests

The residues obtained from selected sorption experiments (those that used 0.025, 0.10, 0.30, and 1.75 mmol L⁻¹ initial metal concentrations) were employed in the desorption tests. The material remaining from the sorption procedure was dried at 105 °C for 48 h, 50 mL of Milli-Q water were added, and the resulting suspension was shaken end-over-end for 24 h. After attainment of equilibrium, the solid and liquid phases were separated by centrifugation at 15,000 rpm for 10 min and the solution was filtered through a 0.45-μm Millipore filter. The filtered supernatants were immediately acidified to pH <2 with concentrated HNO₃ and kept at 4 °C until analysis.

Data treatment and sorption isotherm fitting

The sorption and desorption parameters were calculated from the initial metal concentration in the contact solution (C_i , mmol L⁻¹), the equilibrium concentration in the supernatant after the sorption experiments (C_{eq} , mmol L⁻¹), and the

equilibrium concentration in the supernatant after the desorption experiments ($C_{eq,des}$, mmol L^{-1}), as follows:

- (a) Sorption solid–liquid distribution coefficient (K_d , L kg^{-1}):

$$K_d = \frac{[(C_i - C_{eq}) \times V] / m}{C_{eq}} \quad (1)$$

where V is the volume of the liquid phase (in L) and m is the biochar mass (in kg).

- (b) Removal rate from solution (R , %):

$$R\% = \frac{(C_i - C_{eq}) \times 100}{C_i} \quad (2)$$

- (c) Desorption solid–liquid distribution coefficient ($K_{d,des}$, L kg^{-1}):

$$K_{d,des} = \frac{[(C_i - C_{eq}) \times V + C_{eq} \times V_{sol,rem} - C_{eq,des} \times V] / m}{C_{eq,des}} \quad (3)$$

where C_{sorb} is the amount of sorbed metal (mmol kg^{-1}) and $V_{sol,rem}$ is the volume of solution (L) that remained in the residue after the sorption test.

- (d) Desorption rate (R_{des} , %):

$$R_{des}\% = \frac{C_{eq,des} \times V \times 100}{(C_i - C_{eq}) \times V + C_{eq} \times V_{sol,rem}} \quad (4)$$

The values of C_{sorb} and C_{eq} obtained at different initial metal concentrations were used for the construction of isotherms. The isotherms were then fitted using the Freundlich model:

$$C_{sorb} = K_F C_{eq}^N \quad (5)$$

where K_F is the Freundlich constant and describes the partitioning of the solute between the solid and the liquid phases, and parameter N provides information about the heterogeneity of the sorption sites and is indicative of the degree of linearity of the sorption isotherm.

Results and discussion

Characterization of biochar samples

Table 1 summarizes the main characteristics of the biochars, which mainly depended on the type of biomass used for their production. Most of them showed a neutral or basic pH, with the exception of the SB material, which was slightly acidic. All biochars had high contents of organic matter, as shown by

the high loss on ignition (LOI) and total organic carbon (TOC) values. The similar TOC (%) and C (%) values indicated that all the carbon content in the biochars was organic. The DOC contents of the biochars were in the range found in the literature ($0.1\text{--}110 \text{ g kg}^{-1}$) for biochars produced at low temperature (Gell et al. 2011), except for CM and WH with DOC above this range. Strong correlation was obtained between DOC and fulvic acid (FA) ($R^2=0.93$), as well as between DOC and humic acid (HA) ($R^2=0.92$).

The acid neutralization capacity (ANC) of CM and WH was similar to that found elsewhere for biochars (Venegas et al. 2015), but considerably higher than the one obtained for SB, CE, and PC. This can be attributed to a lower aromaticity and a higher abundance of carboxylic groups in CM and WH with respect of the rest of biochars, in agreement with the results of the ^{13}C -NMR analyses (see Table S1 in the Supplementary material). Moreover, ANC was correlated with cation exchange capacity (CEC) ($R^2=0.92$) and increased with the Ca+Mg content of the biochars, suggesting that the functional groups responsible for the buffering capacity of the biochars were those that participated in cationic exchange.

The total K, Ca, and Mg contents were highest for WH, being consistent with the highest ash content of this biochar (30 %). In the materials with the highest levels of total P, the soluble fractions of this element were 41 % for WH, 12 % for PC, and 5 % for CM. All the biochars contained high levels of Si, Al, and Fe, suggesting the presence of Fe oxides, aluminates, and silicates, in agreement with previous works (Abdel-Fattah et al. 2015; Zhang et al. 2015).

The total concentrations of Cd, Cu, Pb, and Zn were sufficiently low to be considered negligible for the sorption experiments, with water-soluble fractions lower than the C_{eq} obtained from the sorption isotherms.

Isotherms for metal sorption by the biochars

Description of the sorption isotherms and derived sorption parameters

Figure 1 shows the C_{sorb} vs. C_{eq} sorption isotherms for all the metal-biochar combinations examined. Three contrasted isotherm patterns were observed depending on the metal-biochar combination. CE-Cu and PC-Pb showed a linear behavior, indicating an almost constant K_d value for the whole range of concentrations assayed, which is consistent with the interaction of Cu and Pb with organic matter by complexation (Hinz 2001). PC-Cu, WH-Cu, and WH-Pb presented sigmoidal-shaped (S-type) isotherms, characterized by low slopes of C_{sorb} vs. C_{eq} at low surface coverage and higher slopes as the initial metal concentration increased. This type of isotherm suggests the occurrence of competition reactions during sorption processes at low metal concentrations (Hinz

Table 1 Main characteristics of the biochars

Parameter		CE	CM	PC	SB	WH
pH in water		7.2	7.3	8.9	6.0	9.2
PCZ		6.3	6.4	5.7	5.2	9.1
Moisture content (%)		5	5	3.5	3.5	2.5
N (%)		1	7	1	1	4
H (%)		4	6	4	4	3
C (%)		70	55	65	65	45
LOI (%)		95	90	90	87	70
TOC (%)		65	55	70	60	43
CEC (cmol _c kg ⁻¹)		9.5	24.5	13.7	6.7	37.6
DOC (g kg ⁻¹)		100	395	55	80	325
HA (%)		1	14	<0.5	0.9	5.7
FA (%)		5.5	9.7	3.0	5.2	9.2
Ash content (%)		4.5	10.5	5.5	5.0	30.5
ANC (meq kg ⁻¹)		154	322	181	129	773
Major and trace elements (mg kg ⁻¹)						
Si	TC	5600	18,940	5260	47,570	40,970
Al	TC	4730	14,140	43,040	15,150	7440
Fe	TC	850	3820	155	6600	5775
Ca	TC	12,496	12,685	2674	2041	136,580
	WS	320	680	21	225	925
Mg	TC	2735	6910	100	1165	83,615
	WS	348	607	73	96	5905
Mn	TC	900	260	18	210	2335
	WS	24	12	<lq	10	9
K	TC	6360	11,970	15,700	3515	117,260
	WS	1260	4630	9865	680	61,277
P	TC	920	9050	2160	435	5890
	WS	105	470	270	57	2410
Pb	TC	10	10.0	10.5	12.5	150
	WS	0.01	0.2	0.03	0.005	0.2
Zn	TC	50	180	50	60	160
	WS	0.15	2.2	0.30	0.15	2.0
Cd	TC	0.55	0.60	0.80	0.55	1.5
	WS	0.01	0.03	0.004	0.002	0.01
Ni	TC	10	7.2	15	20	40
	WS	0.2	0.3	0.04	0.06	0.4
Cu	TC	13	9.6	5.7	17	31
	WS	0.05	0.5	0.06	0.04	0.2
As	TC	0.3	0.2	0.7	0.5	15
	WS	0.02	0.08	0.03	0.02	0.3
Cr	TC	7.0	15	4.5	9.0	45
	WS	<lq	<lq	<lq	<lq	<lq

PZC point of zero charge, *LOI* loss on ignition, *TOC* total organic carbon, *CEC* cation exchange capacity, *DOC* dissolved organic carbon, *HA* humic acid, *FA* fulvic acid, *ANC* acid neutralization capacity, *CE* eucalyptus forest residues, *CM* castor meal, *PC* green pericarp of coconut, *SB* sugarcane bagasse, *WH* water hyacinth, *TC* total content, *WS* water-soluble, <lq lower than the quantification limit

2001). On one hand, the high concentrations of water-soluble Ca, Mg, and K in the WH biochar might affect metal sorption in the low concentration range. On the other hand, the

competition at low Cu loadings could be attributed to nitrogen and oxygen ligand groups of DOC that could form soluble complexes with Cu, even at low concentrations of DOC

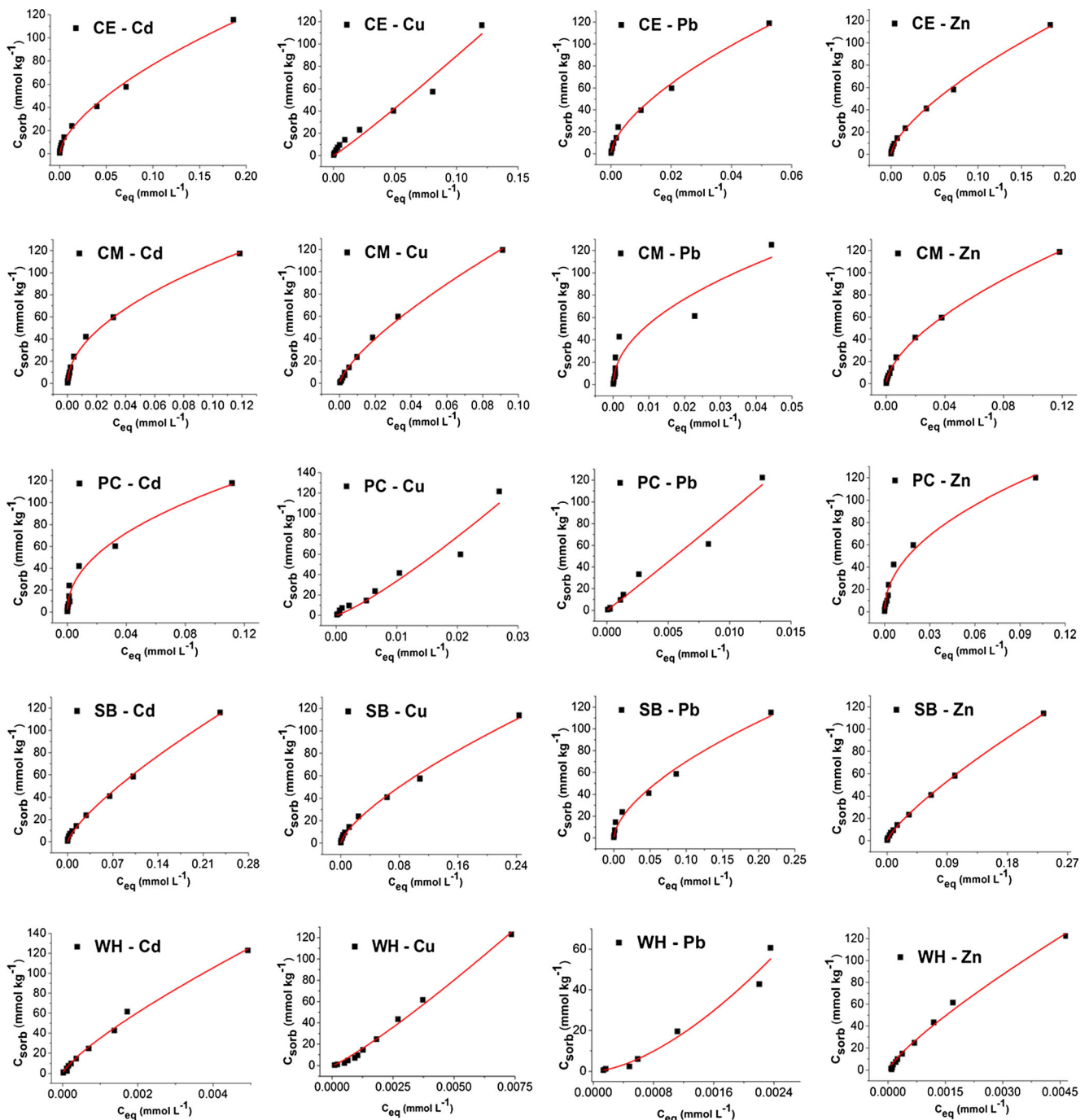


Fig. 1 Isotherms for the sorption of Cd, Cu, Pb, and Zn by the biochars. The red lines indicate the Freundlich fitting (CE eucalyptus forest residues, CM castor meal, PC green pericarp of coconut, SB sugarcane bagasse, WH water hyacinth)

(40 mg L⁻¹). This pattern agrees with the fact that the affinity of DOC for Cu is known to be stronger than for other metals such as Cd, Ni, and Pb (Christensen et al. 1999; Khokhotva and Waara 2010). The rest of isotherms could be classified as high-affinity (H-type) isotherms (Hinz 2001). This reflects a very high affinity of the biochars for the metals at low metal concentrations, with the affinity decreasing at higher metal concentrations. Such behavior suggests the formation of

inner-sphere surface complexes at low metal loadings, mainly due to the presence of phenolic and carboxylic groups, whereas ionic exchange may be the main mechanism at higher metal concentrations (Essington 2004; Ahmad et al. 2012).

Table 2 shows the $K_{d,min}$ and $K_{d,max}$ values for all the metal-biochar combinations tested. Differences between the $K_{d,max}$ and $K_{d,min}$ values often exceeded 1 order of magnitude. On the basis of the $K_{d,max}$ values, the WH biochar showed the highest

Table 2 Sorption parameters of the biochars and fitting parameters derived from the Freundlich equation

Biochar	Metal	$K_{d,min}$ (L kg ⁻¹)	$K_{d,max}$ (L kg ⁻¹)	R_{min} (%)	R_{max} (%)	K_F	N	$K_{d,Freundlich}^a$	$K_{d,Linear}^b$
CE	Cd	620	16,760	96.3	99.9	310	0.62	3290	3850
	Cu	970	3380	96.8	99.3	1050	1.06	725	1840
	Pb	2250	16,550	99.2	99.9	730	0.62	7745	10,420
	Zn	635	8200	96.3	99.7	350	0.67	2720	2490
CM	Cd	990	7595	97.6	99.7	360	0.51	7565	6560
	Cu	1300	2260	98.2	99.1	700	0.73	3750	2920
	Pb	2810	14,115	99.1	99.9	540	0.49	12,850	15,450
	Zn	1000	4450	97.6	99.5	350	0.67	2720	3730
PC	Cd	1040	16,330	97.8	99.9	310	0.46	8890	9830
	Cu	4020	8210	99.2	99.7	8410	1.20	2430	8180
	Pb	4555	12,745	99.4	99.8	12,210	1.06	8770	8870
	Zn	1200	15,300	98	99.9	370	0.48	9370	5870
SB	Cd	480	11,660	95.3	99.8	330	0.76	1465	1240
	Cu	470	5060	95.1	99.5	310	0.72	1765	1600
	Pb	530	6910	95.7	99.7	275	0.59	3400	5390
	Zn	490	2220	98.2	98.9	360	0.79	1330	960
WH	Cd	20,500	62,100	99.9	>99.9	8500	0.79	31,350	42,970
	Cu	4850	16,780	99.5	99.9	37,115	1.16	13,640	9315
	Pb	4500	25,795	99.5	>99.9	878,295	1.60	21,100	18,915
	Zn	6410	40,230	99.6	99.9	10,140	0.81	33,025	54,800

CE eucalyptus forest residues, CM castor meal, PC green pericarp of coconut, SB sugarcane bagasse, WH water hyacinth

^a $K_{d,Freundlich}$ was calculated at $C_{eq}=0.002$ mmol L⁻¹

^b $K_{d,linear}$ was calculated for the linear region at low metal concentration of the isotherms

affinity for all the metals studied, with a very high value for Cd, followed by CE (for Cd and Pb) and PC (for Cd, Pb, and Zn). The removal percentages deduced from the $K_{d,min}$ (R_{min} , %) and $K_{d,max}$ (R_{max} , %) values were always higher than 95 %, thus confirming the efficiency of the biochars for the treatment of metal-contaminated waters. The K_d values obtained in this work were generally higher than the range reported in the literature (see Table S2 in the Supplementary material), especially for Cd (for all biochars) and for the WH biochar (for all metals). The high metal affinity of the WH biochar could be explained by its high pH and ANC, as well as its high CEC and elevated Ca+Mg content, which could enhance ionic exchange-based sorption mechanisms. The inner-sphere sorption mechanism was also favored in the case of the WH biochar, which presented the highest relative concentrations of phenolic and carboxylic functional groups among the biochars examined (Table S1 in the Supplementary material). Moreover, the unexpected high value of K_d (Cd) with respect to the K_d of less mobile metals such as Cu or Pb, for most biochars, but especially for WH, might be attributed to the formation of insoluble Cd salts such as K_4CdCl_6 as suggested by Zhang et al. (2015). The high content of water-soluble phosphorus in WH might also enhance metal phosphate

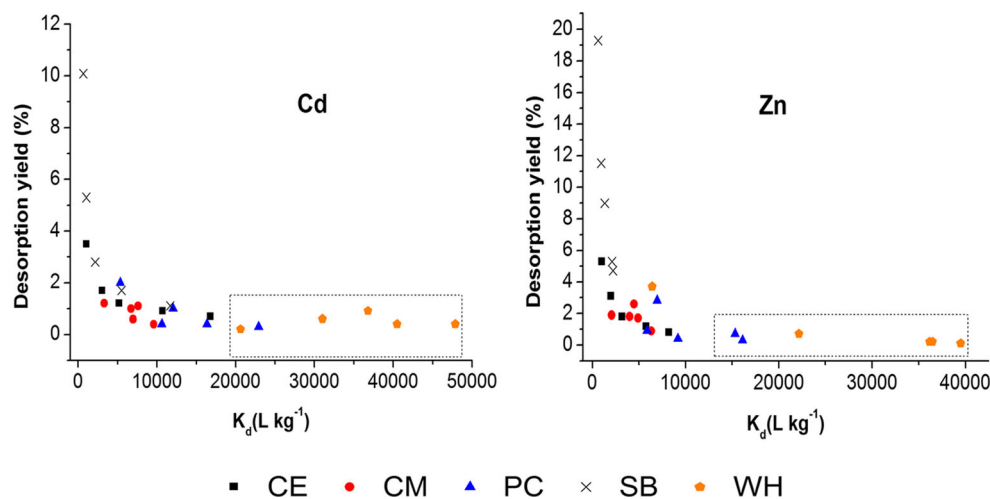
precipitation in the solid phase, especially for Pb (Kolodyńska et al. 2012; Inyang et al. 2012). Tong et al. (2011) also observed that high phosphorus contents in biochars may lead to the formation and precipitation of Cu phosphate.

Fitting of sorption isotherms

The Freundlich model was selected to fit the experimental data, as described previously for the sorption of metals by other sorbents (Pellera et al. 2012; Shaheen et al. 2013). The results of the fitting exercise are shown in Table 2 (N and K_F parameters) and Fig. 1 (fitted curves). In general, the Freundlich model provided a satisfactory description of the metal sorption, with values of the correlation coefficients often higher than 0.9. The values of N obtained from the fitting corroborated the deductions made above from the shapes of the isotherms: $N \approx 1$ and a value of K_F close to K_d for CE-Cu and PC-Pb, which is consistent with linear isotherms; $N > 1$ for PC-Cu, WH-Cu, and WH-Pb, in agreement with S-type isotherms; and $N < 1$ for the rest of biochar-metal combinations.

Due to the low C_{eq} in the obtained isotherms (lower than 1 mM), the K_F values were always extrapolated. Thus, K_F values were lower than the $K_{d, min}$ for the high-affinity

Fig. 2 Relation between desorption yields and K_d , for Cd and Zn. The dotted frames indicate the most efficient points for the sorption process with high K_d and low reversibility (CE eucalyptus forest residues, CM castor meal, PC green pericarp of coconut, SB sugarcane bagasse, WH water hyacinth)



isotherms ($N < 1$), whereas they were higher than the $K_{d, \max}$ for the sigmoidal-shaped isotherms ($N > 1$). Because the K_F values are only fully comparable when the N values are the same (Coles and Yong 2006) and they often relate to a metal concentration too high to be representative of environmental scenarios, two additional sorption parameters were thus calculated here in order to improve the comparison. Considering that the isotherms showed linearity between C_{sorb} and C_{eq} , at low C_{eq} , $K_{d, \text{linear}}$ values were derived from the slopes of the linear regressions in the region of low metal concentrations. In addition, a $K_{d, \text{Freundlich}}$ value was calculated at a C_{eq} of $0.002 \text{ mmol L}^{-1}$, being a concentration level of environmental interest within the range of maximum metal concentration thresholds often applied to drinking water ($4 \cdot 10^{-5}$ and 0.08 mmol L^{-1} , depending on the metal considered) (U.S.EPA 2011). Values of $K_{d, \text{linear}}$ and $K_{d, \text{Freundlich}}$ are also shown in Table 2. Good correlation was obtained between the $K_{d, \text{Freundlich}}$ and $K_{d, \text{linear}}$ values ($R^2 = 0.90$), and the these two sorption parameters were also reasonably correlated with $K_{d, \max}$ ($R^2 = 0.83$ with $K_{d, \text{Freundlich}}$ and $R^2 = 0.79$ with $K_{d, \text{linear}}$). This indicated that both $K_{d, \text{Freundlich}}$ (at a moderate metal concentration of $0.002 \text{ mmol L}^{-1}$) and $K_{d, \text{linear}}$ satisfactorily described the sorption capacities of the biochars, and permitted to identify those with the maximum sorption capacity at metal concentrations of environmental interest. Thus, WH and PC had the highest (or second highest) $K_{d, \text{Freundlich}}$ and $K_{d, \text{linear}}$ for all of the metals examined.

Sorption mechanisms

In order to further understand the mechanisms of sorption of the metals by the biochars, measurements of pH and the concentrations of Ca, Mg, and K were conducted for selected equilibrium solutions (from the experiments with C_i of 0.1, 1, and 5 mmol L^{-1}). An increase in the initial metal concentration generally led to a decrease in the pH of the equilibrium

solution, compared to the control solution without addition of the metal (see Table S3 of the Supplementary material). For several metal-biochar combinations, the difference ranged from tenths of a pH unit (for the lowest metal concentration) to nearly 3 pH units (for the highest metal concentration).

In addition, there was a general increase in the Ca+Mg and K concentrations in the equilibrium solutions when the initial metal concentrations of the sorption solutions were higher, which could be explained by a displacement of these cations from the solid phase due to ionic exchange-based heavy metal sorption. These results are shown in Table S3 of the Supplementary material. For the WH biochar, with an extremely high initial K concentration in the solution, the effect was negligible for this cation and could not be observed. These results were in agreement with those observed previously for biochars and other organic materials (Sastre et al. 2007; Mohan et al. 2007). With the exception of the WH biochar, the ratio between the amount of sorbed metal and the net increase in the concentrations of Ca+Mg and K released to the solution tended towards 1, for an initial metal concentration of 1 mmol L^{-1} . This supported the role of cationic exchange as the predominant sorption mechanism, together with a contribution of metal sorption due to the formation of inner-sphere surface complexes at the low metal concentration range (Fiol et al. 2006; Mohan et al. 2007), suggested in the previous section. For a few metal-biochar combinations, the ratios tended to increase at high heavy metal loadings (5 mmol L^{-1}), indicating that other sorption mechanisms, such as precipitation, could not be disregarded (Mohan et al. 2007; Kołodyńska et al. 2012).

Evaluation of sorption reversibility

Desorption parameters such as desorption solid–liquid distribution coefficient ($K_{d, \text{des}}$) and desorption yield (R_{des}) were calculated from the desorption tests. The values of these

parameters are summarized in Table S4 of the Supplementary material. The $K_{d,des}$ values were systematically higher than the corresponding K_d values, exceeding 10^6 L kg⁻¹ in many cases, hence confirming that the sorption process was essentially irreversible. The $K_{d,des,max}$ and, thus, the minimum desorption yields ($R_{des,min}$, %) generally corresponded to the material residues obtained from the sorption tests carried out using lower initial metal concentrations, with most values below 2 %, while the desorption yields increased up to 19 % ($R_{des,max}$, %) for the sorption residues derived from the tests at the highest C_i .

It is difficult to predict desorption data from sorption parameters. However, for the Cd and Zn isotherms, with N values clearly lower than 1, indicating site heterogeneity, an inverse relation was observed between the desorption yields and the K_d values (Fig. 2). An explanation is that at low concentrations, sorption occurred at specific sites, with low reversibility, while at higher concentrations, the metal was mainly sorbed at low-affinity sites, with higher reversibility. However, for other metals such as Pb and Cu, with N values generally close to 1, the desorption yields were independent of the K_d values.

The desorption results were in agreement with previous reports (Regmi et al. 2012; Trakal et al. 2014). The data confirmed that sorption of the metals by the biochars was largely irreversible and was controlled by inner-sphere sorption mechanisms, especially at low initial metal concentrations. Therefore, metal sorption by the biochars examined here was characterized not only by a relatively high K_d but also by low sorption reversibility.

Conclusions

The biochars examined in this work presented high sorption of the target metals investigated, with removal rates from solution exceeding 95 % for the whole range of concentrations assayed, and even higher than 99.9 % for the low metal concentration range. Thus, the high sorption capacity of the biochars tested, together with low sorption reversibility, confirms them as suitable materials for the treatment of water contaminated with heavy metals. In addition, sorption K_d values higher than 10^4 L kg⁻¹ were obtained for all metals in the case of water hyacinth and green coconut pericarp, and for a few metals in the rest of biochars. These high K_d values indicate that the addition of these biochars as amendments in soils contaminated with metals can contribute, besides improving the quality of the soil, to soil remediation.

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