Effects of swine manure biochar on sorption equilibrium of cadmium and zinc in sandy soils

Efectos del biocarbón hecho a base de estiércol porcino en el equilibrio de sorción de cadmio y zinc en suelos arenosos

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ABSTRACT

Swine manure is an agricultural waste that can increase soil fertility. However, this residue has a high content of heavy metals, particularly zinc (Zn) and cadmium (Cd), that are not only toxic to plants and soil organisms but they also pose a great threat to human health due to the potential accumulation of these metals through the food chain. Transforming swine manure into biochar and adding it to soils can improve the soil's capacity to retain heavy metals. The main objective of this research was to study the capacity of sandy soils mixed with different doses of swine manure biochar (SMB) to retain Cd and Zn as well as to evaluate the sorption equilibrium of these metals. Sorption essays were performed by adding solutions of Zn ($ZnCl_2$) or Cd ($CdCl_2$) at different concentrations (0, 2.5, 5, 10, 50 and 100 mg L^{-1}) to soil samples mixed with different doses of SMB (0, 0.25, 0.75, 1.5, and 3.0 % (w/w)). The data were modelled using both Langmuir and Freundlich adsorption isotherm models to describe the adsorption processes. The data were best represented by the Langmuir model ($R^2>0.97$), indicating a mono-layer sorption to the surface. Results showed that sorption capacity of Zn and Cd increased with the dose of SMB, improving metal retention. The Langmuir constant (K_L) for soil without SMB for Cd and Zn were 0.01 L mg^{-1} and 0.05 L mg^{-1}, respectively. With the highest dose of SMB, K_L increased to 9.86 L mg^{-1} and 1.26 L mg^{-1} for Cd and Zn, respectively. Results suggest that SMB has the potential to mitigate Zn and Cd contamination of sandy soils.

Key words: pyrolized carbon, agricultural wastes, sorption, heavy metals.

RESUMEN

El estiércol de cerdo es un residuo agrícola que puede aumentar la fertilidad del suelo. Sin embargo, este residuo tiene un alto contenido de metales pesados, principalmente zinc (Zn) y cadmio (Cd), los cuales no sólo son tóxicos para las plantas y los organismos del suelo, sino que también representan una gran amenaza para la salud humana por su potencial acumulación en la cadena alimentaria. Transformar el estiércol en biocarbón y agregarlo al suelo puede mejorar la capacidad del suelo para retener metales pesados. El objetivo principal de este trabajo fue estudiar la capacidad de suelos arenosos mezclados con diferentes dosis de biocarbón de estiércol porcino (BEP) para retener Cd y Zn, y evaluar el equilibrio de sorción de estos metales. Las pruebas de sorción se realizaron agregando soluciones de Zn ($ZnCl_2$) o Cd ($CdCl_2$) en diferentes concentraciones (0, 2.5, 5, 10, 50 y 100 mg L^{-1}) a muestras de suelo mezcladas con diversas dosis de BEP (0, 0.25, 0.75, 1.5, y 3.0% (w/w). Los datos fueron modelados de acuerdo con las isotermas de Freundlich y Langmuir para describir los procesos de adsorción. El modelo de Langmuir representó mejor los datos ($R^2>0.97$), lo que indica una absorción de monocapa a la superficie. Los resultados mostraron que la capacidad de sorción de Zn y Cd aumentó con la dosis de BEP, mejorando la retención de metales. La constante de Langmuir (K_L) para el suelo sin BEP para Cd y Zn fue 0.01 L mg^{-1} y 0.05 L mg^{-1}, respectivamente. Con las dosis más altas de BEP, K_L aumentó a 9.86 L mg^{-1} y 1.26 L mg^{-1} para Cd y Zn, respectivamente. Los resultados sugieren que el BEP tiene el potencial de mitigar la contaminación por Zn y Cd en suelos arenosos.

Palabras clave: carbono pirolizado, residuos agropecuarios, sorción, metales pesados.

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Introduction

Technological advances in agricultural practices and production systems allow for the expansion of agriculture into areas with sandy soils. Nowadays, agricultural production in this type of soil is extensive, particularly in the state of Mato Grosso in Brazil (IBGE, 2017) that is now considered a hub for agribusiness. Grain production in the area also stimulated the growth of animal husbandry, particularly pig and cattle farming. Integration of crop and animal production systems allows farmers to use animal manure as fertilizer. This practice reduces costs and increases soil nutrient content and water retention but, at the same time, it can have detrimental consequences if animal manure is applied in excess (De Vrieze *et al.*, 2019) since it has a high content of heavy metals such as copper (Cu), zinc (Zn), and cadmium (Cd).

Intensive application of swine manure can promote the accumulation of heavy metals in soils and the contamination of waterways through runoff and leaching (Zhang *et al.*, 2003; He *et al.*, 2005). This contamination can pose a risk to human health due to accumulation through the food chain (Scherer *et al.*, 2010). Soil remediation is based on the use of chelating agents to immobilize metals and avoid uptake by plant roots, as well as leaching. This process is usually expensive and time- and resource-consuming (Wuana & Okieimen, 2011; Yao *et al.*, 2012; Paz-Ferreiro *et al.*, 2014).

The organic matter of agricultural residues has the potential to act as a biosorbent, and, thus, it can help mitigate contamination from heavy metals in soils and water streams (Sud *et al.*, 2008; Liu *et al.*, 2018; Purakayastha *et al.*, 2019). Biosorbents can act through complex processes, such as ion exchange, adsorption on surface and into pores, complexation, chelation, etc. (Puls & Bohn, 1988; Sud *et al.*, 2008; Chen *et al.*, 2019). The management of this type of residues in tropical regions can be very challenging due to environmental conditions that increase the rate of soil organic matter mineralization and decomposition.

A potential solution for residue stabilization in these areas is the use of biochar. Pyrolysis provides a promising method for the treatment of animal manure with the advantages of destroying pathogens, breaking down antibiotics, producing value-added energy and biochar products, immobilizing heavy metals, and reducing the volume of waste stream (Tian *et al.*, 2019; Xu *et al.*, 2019).

When applied to soils, biochar can have several beneficial properties. It can increase the amount of recalcitrant organic matter in soils, improve nutrient and water retention, decrease greenhouse gas emissions, and increase the soil capacity for heavy metal retention (Woolf & Lehmann, 2012; Bartoli *et al.*, 2020). Transforming agricultural residues into biochar can be useful for improving soil chemical and physical properties and mitigating soil contamination by heavy metals. However, more research is still needed in the use of biochar for heavy metal immobilization. Biochar properties vary depending on pyrolysis temperature and time, the biomass used to produce the biochar, and the dose and the type of soil that biochar is applied to (Zheng *et al.*, 2013; Abujabhah *et al.*, 2016). For example, Shen *et al.* (2020) indicate that the characteristics and speciation of heavy metals in the biochar produced from pig manure are affected by the pyrolysis temperature. Between 500°C and 700°C is the ideal temperature for improving the characteristics of the biochar structure. In addition, the pyrolysis process can immobilize heavy metals, transforming unstable fractions into more stable fractions, and reducing environmental risk.

This study focused on the use of biochar from swine manure, one of the main residues produced in agricultural systems in the state of Mato Grosso. Swine manure is heavily used as fertilizer in sandy soils as a potential mitigation strategy for zinc (Zn) and cadmium (Cd) contamination in this type of soil. Thus, this study aimed to evaluate the capacity of an Ustoxic Quartzipsamment soil and the mixture of soil with swine manure biochar to adsorb Zn and Cd, and the chemical changes conferred to the soil after adding the biochar.

Materials and methods

Soil collection and biochar production

Soil classified as an Ustoxic Quartzipsamment (91% sand, 4% silt, and 5% clay) (Soil Survey Staff, 2014) was collected from the 0-0.2 m layer from an agricultural area located in the city of Campo Verde, Mato Grosso, Brazil (15°13'55.2" S, 54°57'43.4" W). The soil was dried and sieved (2 mm) and its chemical properties were analyzed according to the methodology described by MAPA (2017) and Teixeira *et al.* (2017). Soil pH was measured with a pH meter in a soil solution of 1:2.5 distilled water. To determine the contents of sodium (Na^+) and potassium (K^+), the soil was extracted with a $NH_4CH_3CO_2$ buffer (pH = 7). Na^+ and K^+ were determined using a flame photometer (model Pegassvs II, Tecnow, Maringa, Brazil).

To determine the contents of manganese (Mn) and phosphorus (P), the soil was extracted with a 1:1 solution of

H_2SO_4. Mn was determined by measuring the solution's absorbance at 550 nm, and P was determined by measuring the absorbance at 660 nm. The contents of calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe^{3+}), zinc (Zn^{2+}), cadmium (Cd^{+2}) and copper (Cu^{2+}) were determined by acid digestion of the soil with HCl and metal concentrations were measured using an atomic adsorption spectrometer (SpectrAA 50 Varian, Mulgrave, Australia).

Swine manure biochar (SMB) was commercially produced (SPPT, Mogi Morim, São Paulo, Brazil) via slow pyrolysis at 400°C for 17 min. After pyrolysis, the biochar was sieved and homogenized to obtain a particle size of 0.5 mm. The chemical properties of SMB were determined following the methodology described above (MAPA, 2017; Teixeira *et al.*, 2017).

Soil density and porosity were analyzed according to the method described by Teixeira *et al.* (2017). For soil bulk density (ρ_d), 35 ml of dried soil was measured in a graduated cylinder, and Equation 1 was applied:

$$\rho_d = \frac{\mathrm{m}}{\mathrm{V}} f \tag{1}$$

where ρ_d is the soil bulk density (kg dm^{-3}), m is the mass of dried soil added to the cylinder (g), V is the volume of soil in the cylinder (cm^{-3}), and f is a correction factor for soil humidity.

Soil porosity was obtained using Equation 2:

$$P = 1 - \frac{\rho_d}{\rho_p} f \tag{2}$$

where *P* is the soil porosity, ρ_p is the difference between total porosity and volumetric humidity at field capacity (θcc), and ρ_d is the soil bulk density.

Soil-biochar mix characterization

Soil samples were incubated with different doses of SMB (0, 0.25, 0.75, 1.5 and 3% (w/w)) for 30 d. Soil moisture was kept constant at 60% of the soil water holding capacity, and temperature was maintained at 25°C (Souza *et al.*, 2007).

After the incubation period, the chemical properties of the mixture were determined using the methodology previously described by MAPA (2017) and Teixeira *et al.* (2017). Total organic carbon (TOC) was determined by wet combustion, following the methodology of Yeomans and Bremner (1988). Organic matter from soil was oxidized with a mixture of 10 ml of 0.167 potassium dichromate ($K_2Cr_2O_7$) and 20 ml of concentrated sulfuric acid (H_2SO_4) while stirring it to ensure good mixing of the soil with the reagents. The excess $K_2Cr_2O_7$ was then titrated with $(NH_4)_2Fe(SO_4)_2$ and TOC was estimated as the equivalent of $K_2Cr_2O_7$ that reacted with the soil. Labile carbon (LC) was determined using the method proposed by Blair *et al.* (1995) and adapted by Shang and Tiessen (1997) that consisted of the partial oxidation of soil carbon with $KMnO_4$ 0.033 M. The amount of oxidized C was calculated and considered as the labile component of soil organic C. Non-labile carbon (NLC) was determined as the difference between TOC and LC.

Sorption essays

Sorption essays were performed separately for each metal. Twenty ml of aqueous solutions of Cd ($CdCl_2$) and Zn ($ZnCl_2$) at different concentrations (0, 2.5, 5, 10, 50 and 100 mg L^{-1}) were added to 50 ml falcon tubes containing 2 g of soil or soil-biochar mixture. The samples were then agitated for 24 h at 120 rpm and subsequently centrifuged for 15 min at 9000 rpm and filtered. The temperature was kept constant at 25°C. Metal concentration in the supernatant was measured using an atomic absorption spectrophotometer (SpectrAA 50 Varian, Agilent technologies, CA, USA). Characterization tests and analyses were performed in four replicates within a completely randomized design.

The concentration of metals adsorbed in soil was calculated as the difference between the initial concentration of metals added and the concentration of metals that remained in the solution (Harter & Naidu, 2001), according to Equation 3.

$$Q_e = (C_o - C_e)\frac{Vol}{m} \tag{3}$$

where Q_e is the concentration of metals in soil (mg kg^{-1}); C_o and C_e are the initial concentration of metals and concentration of metals in the solution (in equilibrium), respectively (mg L^{-1}); Vol is the volume of the metal aqueous solution added to the falcon tube (L), and *m* is the amount of soil added to the falcon tube (kg).

Sorption efficiency was calculated using Equation 4.

$$Sorption\ efficiency = \frac{C_o - C_e}{C_o} \times 100\% \tag{4}$$

The Langmuir and Freundlich isotherms were then used to understand the equilibrium behind metal sorption to the surface. The equations are summarized in Table 1.

Although linear and non-linear models are mathematically equivalent, linearization often can introduce bias and increase the error distribution (Bolster & Hornberger, 2007). To avoid these errors, we fitted the Langmuir and Freundlich non-linear models using the R package 'PUPAIM' version 0.2.0 that provides a collection of isotherm models, and the software R version 4.0.3 and RStudio version 1.3.1093.

TABLE 1. Langmuir and Freundlich equations.

Isotherm model	Non-linear equation	Linear equation	
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{Q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$	(5)
Freundlich	$q_e = K_F C_e^{1/n}$	$InQ_e = \frac{1}{n} InQ_e + InK_F$	(6)

Q_e - concentration of sorbate adsorbed by the surface in the equilibrium (mg kg^{-1}); q_{max} - maximum sorption capacity (mg kg^{-1}); K_L - Langmuir distribution constant (L mg^{-1}); K_F - Freundlich distribution constant (mg kg^{-1}); C_e - sorbate concentration in the equilibrium solution (mg L^{-1}), and n - heterogeneity parameter.

Results and discussion

Soil-biochar chemical and physical properties

Biochar application had a significant effect on soil chemical and physical properties (Tab. 2). SMB addition increased soil pH. Soil without biochar had a pH of 5.3, and it increased to 7.9 with the highest SMB dose. Previous studies (Rondon *et al.*, 2006; Houben *et al.*, 2013) show that these changes can be attributed to the high ash content in biochar. Ash is mainly composed of alkaline metal oxides that can interact with the soil solution and release bases and other ions, increasing the pH (Steenari *et al.*, 1999; Glaser *et al.*, 2015). Another factor that may be related to the increase in pH is the alkalinity of the biochar caused by the presence of organic (-OH, -CO, -C=O, -COOH, -COH) and inorganic ($-PO_4^{3-}$, -Si-O-Si) functional groups, and inorganic halogens (KCl and $CaCl_2$). These groups belong to negatively charged surfaces (-COO- and -O-) that can capture protons from the solution (Tsai *et al.*, 2012; Martinsen *et al.*, 2014; Ding *et al.*, 2016). This may also explain the decrease in H^+ with the increase in the dose of biochar shown in TOC, LC and NLC also increased with the addition of SMB. As SMB is a substance with high carbon content (Wu *et al.*, 2012; Speratti *et al.*, 2017), the addition of biochar to the soil provides the necessary carbon sources for carbon cycling. Likewise, biochar can provide the soil with complex aromatic structures that increase NLC (Woolf & Lehmann, 2012) or labile compounds, such as aliphatic carbon compounds, increasing the LC content in the soil mixture.

Additionally, after SMB application there was a significant increase in the content of macro and micronutrients (P, Zn^{+2}, Cu^{+2}, Mn^{+2}, Na^+, K^+, Ca^{+2}, Mg^{+2}) (Tab. 2). This is due to the type of organic matter used for biochar production. Swine manure usually has a high concentration of these nutrients, so when SMB is produced, it inherits these compounds (Tsai *et al.*, 2012; Ding *et al.*, 2016; Subedi *et al.*, 2016).

Although there are many studies that show that biochar can increase soil porosity and improve water holding capacity and nutrient retention (Kuzyakov *et al.*, 2014; Ajayi & Horn, 2017), soil porosity did not change significantly with SMB while soil density decreased slightly with the increases in SMB doses (Tab. 3). One possible explanation is that, although the number of pores did not change, its distribution on the surface did. Speratti *et al.* (2017), using the same biochar as in this study, performed a BET analysis to obtain the pore size and distribution of swine manure biochar and found that SMB had a total surface area of 7.2 m^2 g^{-1} and a total pore volume of 0.0002 cm^3 g^{-1} (micropore area was 0.7 m^2 g^{-1} and mesopore area was 4.1 m^2 g^{-1}). Considering this, biochar particles could have changed pore characteristics like size, shape, connectivity,

TABLE 2. Soil chemical properties before and after swine manure biochar (SMB) addition.

SMB dose	pH H_2O	P	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+	TOC	LC	NLC	Fe	Zn	Cd	Mn	Cu
%w/w		mg dm^{-3}		cmol$_c$ dm^{-3}				g kg^{-1}			mg dm^{-3}				
0 (soil)	5.3	2.0	1.0	8.0	1.5	0.8	3.4	6.6	1.0	5.6	171.0	7.0	-	12.0	1.1
0.25	6.2	44.0	3.0	18.0	2.3	0.9	2.5	7.0	1.2	5.9	173.4	9.0	-	25.0	8.8
0.75	6.8	86.0	4.0	26.0	2.5	0.9	1.3	8.9	1.3	7.6	169.0	10.0	-	25.0	15.0
1.5	7.5	125.0	6.0	37.0	2.6	1.1	0.8	10.8	1.4	9.5	169.0	14.0	-	69.0	32.0
3.0	7.9	170.0	11..0	111.0	3.1	1.1	0.7	17.9	1.4	16.5	182.0	21.0	-	125.0	79.0
100 (SMB)	9.3	6536.0	52.0	421.0	137.4	46.3	-	32.2	3.0	29.2	230.0	136.0	-	9215.0	292.5

(-) Below the limit of detection. TOC - total organic carbon, LC - labile carbon, NLC - non-labile carbon.

and volume and, therefore, changed nutrient, water, and heavy metal retention. For example, Liu *et al.* (2006) report that small biochar particles could enter bigger soil particles, decreasing its size.

TABLE 3. Soil physical properties before and after swine manure biochar (SMB) addition.

SMB dose (% w/w)	Soil density (kg m^{-3})	Total porosity (m^3 m^{-3})
0 (Soil)	1.66	0.40
0.25	1.63	0.39
0.75	1.61	0.38
1.5	1.58	0.38
3	1.55	0.39
100 (SMB)	-	-

Cadmium and Zinc sorption

Sorption isotherms

Results from the sorption assays showed that the amount of adsorbed metal to the surface increased with biochar application (Fig. 1). This effect was particularly evident for a higher concentration of the metal solutions (>50 mg L^{-1}) and higher SMB doses. Considering these data, Freundlich and Langmuir isotherms were used to evaluate metal sorption to soils with and without SMB addition. Table 4 summarizes the results obtained for the sorption essays.

The Langmuir model is based on the hypothesis that, when molecules are adsorbed into the surface, they form a single, uniform layer that covers the whole surface. The Langmuir constant (K_L) is a parameter related to the affinity of metal ions to the sorption sites, and q_{max} is the maximum absorption capacity of the material. The Langmuir model showed a good fit for soil with and without SMB (R^2 varied between 0.97 and 0.99, for both Cd and Zn). K_L and q_{max} increased with the dose of SMB for all the cases, except for soil without biochar in which q_{max} for Cd was almost 20 times higher than q_{max} for a SMB dose of 3%. So, K_L of 3% SMB was larger than K_L of soil for Cd, but q_{max} was larger for soil without SMB. Since higher K_L values indicate that the interaction between adsorbate and adsorbent is stronger, and lower K_L values indicate a weaker interaction, this could mean that, although the soil has more sorption sites for Cd, biochar binds Cd stronger than soil. This could also indicate that SMB application favors chemisorption (stronger interactions, monolayer adsorption) over physisorption (weaker interactions, multilayer adsorption) that could be explained by the increase in functional groups that can bind the Cd to the surface (Ho & McKay, 1998; Kołodyńska *et al.*, 2012; Wang *et al.*, 2020).

The Freundlich isotherm is valid for heterogeneous surfaces and considers a multi-layer adsorption to explain the relationship between sorbate and adsorbent. This model had a good fit for both metals and all the concentrations of SMB used (R^2>0.95). In the Freundlich isotherm, K_F is related to the adsorption capacity of the surface, and n is a parameter related to the intensity of adsorption. If 1/n<1, adsorption is favorable; if n = 1, the partition between the two phases is independent of the concentration; finally, if 1/n>1, it means that adsorption is cooperative (Komkiene & Baltrenaite, 2016).

For Cd, K_F increased with the dose of SMB (Tab. 4). Initially, the soil without SMB had a K_F = 472.66 mg kg^{-1} and

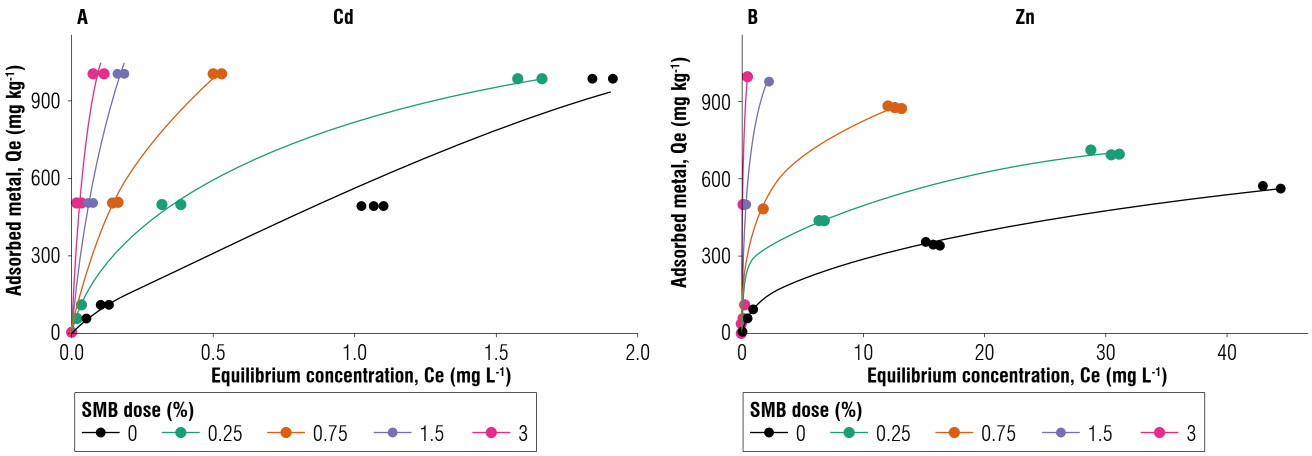

FIGURE 1. Equilibrium concentration (Ce, mg L^{-1}) vs. amount of adsorbed metal (Qe, mg kg^{-1}) for A) cadmium (Cd) and B) zinc (Zn) and for every dose of swine manure biochar (SMB) applied.

TABLE 4. Langmuir and Freundlich isotherm coefficients for Zn and Cd with and without swine manure biochar (SMB) addition to soil.

SMB dose (%) w/w	Langmuir			Freundlich		
	K_L (L mg^{-1})	q_{max} (mg kg^{-1})	R^2	K_F (mg kg^{-1})	1/n	R^2
			Cd			
0.00	0.01	46360	0.99	472.66	1.14	0.99
0.25	1.44	1393.29	0.99	762.24	0.53	0.99
0.75	2.78	1677.02	0.99	1450	0.58	0.99
1.50	4.44	2325.48	0.98	3597.56	0.72	0.98
3.00	9.86	2045.82	0.98	5376.32	0.72	0.97
			Zn			
0.00	0.05	788.59	0.99	86.04	0.49	0.99
0.25	0.17	829.66	0.99	195.92	0.38	0.99
0.75	0.56	990.14	0.99	313.81	0.41	0.98
1.50	1.29	1310.38	0.99	616.55	0.58	0.96
3.00	1.26	2373.70	0.97	1582.91	0.81	0.95

K_L - Langmuir distribution constant (L mg^{-1}), q_{max} - maximum sorption capacity (mg kg^{-1}), K_F - Freundlich constant (mg kg^{-1}), n - heterogeneity parameter, R^2 - goodness of fit measure for each regression.

increased to 5376.32 mg kg^{-1} with the highest dose of SMB; this was an 11-fold increase in K_F. In the case of Zn, the same trend was observed. Soil without SMB had an initial K_F of 86.04 mg kg^{-1} and increased to 1582.91 mg kg^{-1} with 3% SMB (18-fold increase). When comparing the K_F for both metals, K_F for Zn was lower than K_F for Cd for every SMB dose (values 3-6 times higher for Cd than for Zn). Park *et al.* (2015) and Chen *et al.* (2019) also find that biochar increases the soil's capacity to retain heavy metals, and that adsorption is up to 6 times higher for Cd than for Zn.

The intensity of adsorption (n) of the metals also changed with biochar addition. For Zn, 1/n was always lower than 1, suggesting that adsorption of the metals to the surface was favorable. In the case of Cd, 1/n was higher than 1 without biochar, indicating cooperative adsorption (i.e., the amount of metal adsorbed to the surface had an effect on the adsorption of new metal ions to the surface). With the addition of biochar, 1/n was lower than 1, indicating that the adsorption was favorable. That difference in 1/n between the soil and the soil with SMB for Cd was also an indication of different mechanisms of interaction between Cd and the surface when SMB is present.

Although both models were able to explain the data, the Langmuir isotherm was slightly better than the Freundlich isotherm, particularly for higher doses of SMB. This effect has also been observed in other studies with biochar and is attributed to the monolayer adsorption that occurs in the biochar surface (binding sites in the surface over electrostatic interactions) (Kołodyńska *et al.*, 2012; Park *et al.*, 2015; Wang *et al.*, 2020).

Sorption efficiency

The sorption efficiency was used to evaluate the capacity of soil (with and without biochar) to retain Cd and Zn (Fig. 2). Soil without SMB addition was very efficient in removing Cd from the solution, even for high doses of the metal (efficiency = 97%). Sorption efficiency increased with biochar application. Doses of 1.5 and 3% SMB showed a sorption efficiency of ~100% for all the studied Cd concentrations (0, 2.5, 5, 10, 50 and 100 mg L^{-1}).

Sorption efficiency for Zn without SMB application was high for low metal concentrations (~90% for Zn concentrations of 0, 2.5, 5 and 10 mg L^{-1}). However, for higher concentrations of Zn (>50 mg L^{-1}), sorption efficiency to the surface decreased to ~50%. Soil-SMB mixture had a sorption efficiency of ~100% for lower Zn doses (≤10 mg L^{-1}) and it varied between 70-100% for higher SMB doses (depending on Zn initial concentration).

This increase in sorption efficiency with SMB application was expected, as biochar characteristics favor metal retention (Mohamed *et al.*, 2018). Particularly, SMB has different functional groups (*e.g.*, COOH, phenolic, etc.) that are sorption sites for cations by forming metallic complexes (Wuana & Okieimen, 2011; Rees *et al.*, 2014).

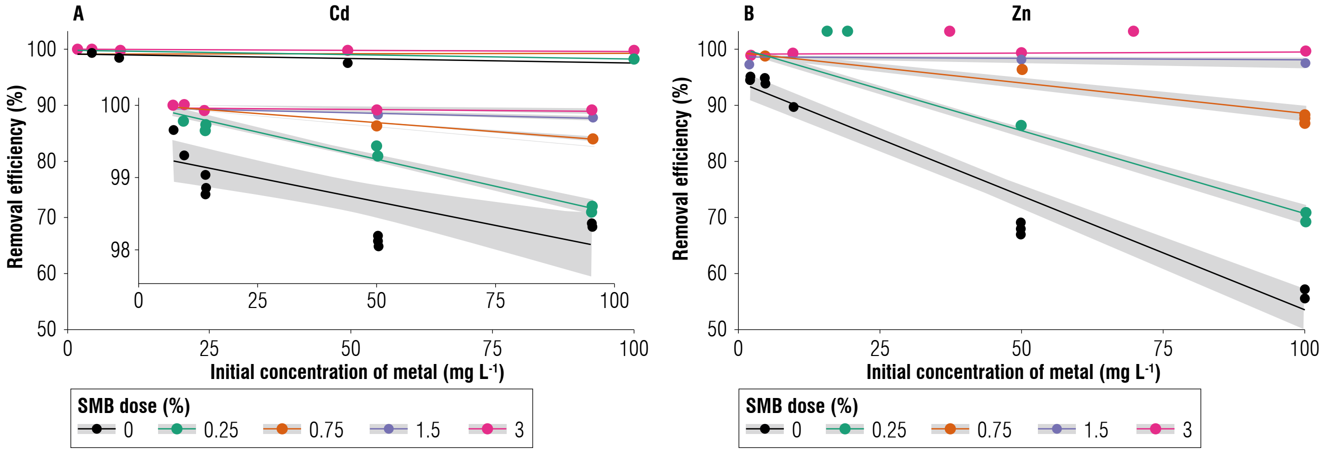

FIGURE 2. Sorption efficiency for A) cadmium (Cd) and B) zinc (Zn) for each dose of swine manure biochar (SMB) applied.

Figure 2 also shows that the relationship between SMB dose and sorption efficiency is different for both metals. Efficiency for Cd was higher than that for Zn for all SMB doses and even for soil without SMB. This difference could be related to the chemical properties of each metal, such as electronegativity and ionic radius. Zn and Cd show electronegativity values of 1.66 and 1.46 and ionic radius values of 0.074 and 0.098, respectively (Liu *et al*., 2006). Puls and Bohn (1988) show that the retardation factor (*i.e.*, estimate of solute movement in the soil fraction) increases with the ionic radius and decreases with increasing electronegativity; this explains the highest retention for Cd over Zn. Another explanation could be related to the amount of Zn and Cd in the soil and in the biochar used for this study. The Cd concentration in the soil and in the biochar was below the limit of detection, whereas the initial concentration of Zn in the soil was 7 mg kg^{-1} and SMB had a Zn concentration of 136 mg kg^{-1} (Tab. 2).

As higher concentrations of Zn solution were added to the soil, the binding sites for Zn in the soil or soil-SMB surface become less available, and more Zn was left in the solution.

Additionally, as shown in Table 2, SMB increased soil pH. An alkaline pH can promote the precipitation of metal hydroxides and, therefore, can decrease the mobility of metal ions in the soil profile (Pierangeli *et al*., 2009).

Conclusions and implications of the use of SMB to retain heavy metals in sandy soils

The results show the high capacity of SMB to help in Zn and Cd sorption in sandy soils, potentially avoiding problems with bioaccumulation, contamination, and toxicity via leaching and runoff.

The data adjusted best to the Langmuir isotherm, particularly for higher SMB doses, suggesting a monolayer sorption to the surface. Additionally, with SMB application a stronger adsorbate-adsorbent interaction was observed (higher K_L) that could mean that SMB favors chemisorption over physisorption. On the other hand, soil without SMB showed weaker interactions with the metals.

Both SMB and the studied Ustoxic Quartzipsamment had a higher affinity towards Cd than Zn. This was related to the initial Zn content in both soil and SMB (7 and 136.25 mg kg^{-1}, respectively), as well as higher electronegativity and ionic radius of Zn.

Despite the greater adsorptive capacity observed with 3% SMB, it is important to also consider the high cost of biochar application and look for the best cost/benefit relationship. In that regard, SMB applied at 0.75% proved to be effective for the retention of both metals with high efficiency. At this dose, the K_F was about three times higher for Zn and Cd compared to the soil without the addition of SMB.

SMB addition to the soil increased the content of P, Na, K, TOC, NLC, LC, Zn, Mn, Cu and increased pH, making the soil more alkaline and more suitable for agriculture.

Although the results of this study are promising for Cd and Zn retention in sandy soils, more research is needed in the area. Particularly, more studies are necessary that focus on competition between Cd, Zn, and other heavy metals for the binding sites of SMB, metal desorption from the SMB-soil surface, and availability of the adsorbed metals to plants in order to evaluate if SMB addition is a good strategy for minimizing the risks associated with heavy metal pollution in sandy soils.

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Conflict of interest statement

The authors declare that there is no conflict of interest regarding the publication of this article.

Author's contributions

EGC, OLSW and EFGD designed the experiments. WSA carried out the field and laboratory experiments. ECN, BD, and WSA contributed to the data analysis, and ECN, BD and EGC wrote the article. All authors reviewed the manuscript.

Literature cited

Abujabhah, I. S., Doyle, R., Bound, S. A., & Bowman, J. P. (2016). The effect of biochar loading rates on soil fertility, soil biomass, potential nitrification, and soil community metabolic profiles in three different soils. *Journal of Soils and Sediments*, *16*, 2211–2222. https://doi.org/10.1007/s11368-016-1411-8

Ajayi, A. E., & Horn, R. (2017). Biochar-induced changes in soil resilience: effects of soil texture and biochar dosage. *Pedosphere*, *27*(2), 236–247. https://doi.org/10.1016/S1002-0160(17)60313-8

Bartoli, M., Giorcelli, M., Jagdale, P., Rovere, M., & Tagliaferro, A. (2020). A review of non-soil biochar applications. *Materials*, *13*(2), Article 261. https://doi.org/10.3390/ma13020261

Blair, G. J., Lefroy, R. D. B., & Lisle, L. (1995). Soil carbon fractions based on their degree of oxidation, and the development of a carbon management index for agricultural systems. *Australian Journal of Agricultural Research*, *46*(7), 1459–1466. https://doi.org/10.1071/AR9951459

Bolster, C. H., & Hornberger, G. M. (2007). On the use of linearized Langmuir equations. *Soil Science Society of America Journal*, *71*(6), Article 1796. https://doi.org/10.2136/sssaj2006.0304

Chen, R., Zhao, X., Jiao, J., Li, Y., & Wei, M. (2019). Surface-modified biochar with polydentate binding sites for the removal of cadmium. *International Journal of Molecular Sciences*, *20*(7), Article 1775. https://doi.org/10.3390/ijms20071775

De Vrieze, J., Colica, G., Pintucci, C., Sarli, J., Pedizzi, C., Willeghems, G., Bral, A., Varga, S., Prat, D., Peng, L., Spiller, M., Buysse, J., Colsen, J., Benito, O., Carballa, M., & Vlaeminck, S. E. (2019). Resource recovery from pig manure *via* an integrated approach: a technical and economic assessment for full-scale applications. *Bioresource Technology*, *272*, 582–593. https://doi.org/10.1016/j.biortech.2018.10.024

Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, L., & Zheng, B. (2016). Biochar to improve soil fertility. A review. *Agronomy for Sustainable Development*, *36*, Article 36. https://doi.org/10.1007/s13593-016-0372-z

Glaser, B., Wiedner, K., Seelig, S., Schmidt, H. P., & Gerber, H. (2015). Biochar organic fertilizers from natural resources as substitute for mineral fertilizers. *Agronomy for Sustainable Development, 35*, 667–678. https://doi.org/10.1007/s13593-014-0251-4

Harter, R. D., & Naidu, R. (2001). An assessment of environmental and solution parameter impact on trace-metal sorption by soils. *Soil Science Society of America Journal*, *65*(3), 597–612. https://doi.org/10.2136/sssaj2001.653597x

He, Z. L., Yang, X. E., & Stoffella, P. J. (2005). Trace elements in agroecosystems and impacts on the environment. *Journal of Trace Elements in Medicine and Biology, 19*(2–3), 125–140. https://doi.org/10.1016/j.jtemb.2005.02.010

Ho, Y. S., & McKay, G. (1998). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environmental Protection*, *76*(4), 332–340. https://doi.org/10.1205/095758298529696

Houben, D., Evrard, L., & Sonnet, P. (2013). Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. *Chemosphere*, *92*(11), 1450–1457. https://doi.org/10.1016/j.chemosphere.2013.03.055

IBGE. (2017). *Levantamento sistemático da produção agrícola*. Instituto Brasileiro de Geografia e Estatística. https://www.ibge.gov.br/estatisticas/economicas/agricultura-e-pecuaria/9201-levantamento-sistematico-da-producao-agricola.html?=&t=resultados

Kołodyńska, D., Wnętrzak, R., Leahy, J. J., Hayes, M. H. B., Kwapiński, W., & Hubicki, Z. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal*, *197*, 295–305. https://doi.org/10.1016/j.cej.2012.05.025

Komkiene, J., & Baltrenaite, E. (2016). Biochar as adsorbent for removal of heavy metal ions [Cadmium(II), Copper(II), Lead(II), Zinc(II)] from aqueous phase. *International Journal of Environmental Science and Technology*, *13*, 471–482. https://doi.org/10.1007/s13762-015-0873-3

Kuzyakov, Y., Bogomolova, I., & Glaser, B. (2014). Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific ^{14}C analysis. *Soil Biology and Biochemistry*, *70*, 229–236. https://doi.org/10.1016/j.soilbio.2013.12.021

Liu, C. L., Chang, T. W., Wang, M. K., & Huang, C. H. (2006). Transport of cadmium, nickel, and zinc in Taoyuan red soil using one-dimensional convective-dispersive model. *Geoderma*, *131*(1–2), 181–189. https://doi.org/10.1016/j.geoderma.2005.03.020

Liu, L., Li, W., Song, W., & Guo, M. (2018). Remediation techniques for heavy metal-contaminated soils: principles and applicability. *Science of the Total Environment*, *633*, 206–219. https://doi.org/10.1016/j.scitotenv.2018.03.161

MAPA. (2017). *Manual de métodos analíticos oficiais para fertilizantes minerais, orgânicos, organominerais e corretivos*. Ministério da Agricultura, Pecuária e Abastecimento.

Martinsen, V., Mulder, J., Shitumbanuma, V., Sparrevik, M., Børresen, T., & Cornelissen, G. (2014). Farmer-led maize biochar trials: effect on crop yield and soil nutrients under conservation farming. *Journal of Plant Nutrition and Soil Science*, *177*(5), 681–695. https://doi.org/10.1002/jpln.201300590

Mohamed, I., Ali, M., Ahmed, N., Abbas, M. H. H., Abdelsalam, M., Azab, A., Raleve, D., & Fang, C. (2018). Cow manure-loaded biochar changes Cd fractionation and phytotoxicity potential for wheat in a natural acidic contaminated soil. *Ecotoxicology and Environmental Safety*, *162*, 348–353. https://doi.org/10.1016/j.ecoenv.2018.06.065

Park, J. H., Cho, J. S., Ok, Y. S., Kim, S. H., Kang, S. W., Choi, I. W., Heo, J. S., DeLaune, R. D., & Seo, D. C. (2015). Competitive adsorption and selectivity sequence of heavy metals by chicken bone-derived biochar: batch and column experiment. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, *50*(11), 1194–1204. https://doi.org/10.1080/10934529.2015.1047680

Paz-Ferreiro, J., Lu, H., Fu, S., Méndez, A., & Gascó, G. (2014). Use of phytoremediation and biochar to remediate heavy metal polluted soils: a review. *Solid Earth*, *5*, 65–75. https://doi.org/10.5194/se-5-65-2014

Pierangeli, M. A. P., Nóbrega, J. C. A., Lima, J. M., Guilherme L. R. G., & Arantes, S. A. C. M. (2009). Sorção de cádmio e chumbo em Latossolo Vermelho Distrófico sob efeito de calcário e fosfato. *Revista Brasileira de Ciências Agrárias*, *4*(1), 42–47. https://doi.org/10.5039/agraria.v4i1a7

Puls, R. W., & Bohn, H. L. (1988). Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions. *Soil Science Society of America Journal*, *52*(5), 1289–1292. https://doi.org/10.2136/sssaj1988.03615995005200050013x

Purakayastha, T. J., Bera, T., Bhaduri, D., Sarkar, B., Mandal, S., Wade, P., Kumari, S., Biswas, S., Menon, M., Pathak, H., & Tsang, D. C. W. (2019). A review on biochar modulated soil condition improvements and nutrient dynamics concerning crop yields: pathways to climate change mitigation and global food security. *Chemosphere*, *227*, 345–365. https://doi.org/10.1016/j.chemosphere.2019.03.170

Rees, F., Simonnot, M. O., & Morel, J. L. (2014). Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. *European Journal of Soil Science*, *65*(1), 149–161. https://doi.org/10.1111/ejss.12107

Rondon, M. A., Molina, D., Hurtado, M., Ramirez, J., Lehmann, J., Major, J., & Amezquita, E. (2006, July 9–15). *Enhancing the productivity of crops and grasses while reducing greenhouse gas emissions through bio-char amendments to unfertile tropical soils* [Conference presentation]. Eighteenth world congress of soil science, Philadelphia, PA, United States.

Scherer, E. E., Nesi, C. N., & Massotti, Z. (2010). Atributos químicos do solo influenciados por sucessivas aplicações de dejetos suínos em áreas agrícolas de Santa Catarina. *Revista Brasileira de Ciência do Solo*, *34*, 1375–1383. https://doi.org/10.1590/s0100-06832010000400034

Shang, C., & Tiessen, H. (1997). Organic matter lability in a tropical oxisol: evidence from shifting cultivation, chemical oxidation, particle size, density, and magnetic fractionations. *Soil Science*, *162*(11), 795–807. https://doi.org/10.1097/00010694-199711000-00004

Shen, X., Zeng, J., Zhang, D., Wang, F., Li, Y., & Yi, W. (2020). Effect of pyrolysis temperature on characteristics, chemical speciation and environmental risk of Cr, Mn, Cu, and Zn in biochars derived from pig manure. *Science of the Total Environment*, *704*, Article 135283. https://doi.org/10.1016/j.scitotenv.2019.135283

Soil Survey Staff. (2014). *Keys to soil taxonomy* (12th ed.). United States Department of Agriculture, Natural Resources Conservation Service.

Souza, R. S., Chaves, L. H. G., & Fernandes, J. D. (2007). Isotermas de Langmuir e de Freundlich na descrição da adsorção de zinco em solos do Estado da Paraíba. *Revista Brasileira de Ciências Agrárias, 2*(2), 123–127. https://doi.org/10.5039/agraria.v2i2a785

Speratti, A. B., Johnson, M. S., Sousa, H. M., Torres, G. N., & Couto, E. G. (2017). Impact of different agricultural waste biochars on maize biomass and soil water content in a Brazilian Cerrado Arenosol. *Agronomy*, *7*(3), Article 49. https://doi.org/10.3390/agronomy7030049

Steenari, B. M., Schelander, S., & Lindqvist, O. (1999). Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB – a comparative study. *Fuel*, *78*(2), 249–258. https://doi.org/10.1016/S0016-2361(98)00137-9

Subedi, R., Taupe, N., Ikoyi, I., Bertora, C., Zavattaro, L., Schmalenberger, A., Leahy, J. J., & Grignani, C. (2016). Chemically and biologically-mediated fertilizing value of manure-derived biochar. *Science of the Total Environment*, *550*, 924–933. https://doi.org/10.1016/j.scitotenv.2016.01.160

Sud, D., Mahajan, G., & Kaur, M. P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – a review. *Bioresource Technology*, *99*(14), 6017–6027. https://doi.org/10.1016/j.biortech.2007.11.064

Teixeira, P. C., Donagemma, G. K., Fontana, A., & Teixeira, W. G. (Eds.). (2017). *Manual de métodos de análise de solo*. Embrapa.

Tian, R., Li, C., Xie, S., You, F., Cao, Z., Xu, Z., Yu, G., & Wang, Y. (2019). Preparation of biochar via pyrolysis at laboratory and pilot scales to remove antibiotics and immobilize heavy metals in livestock feces. *Journal of Soils and Sediments*, *19*, 2891–2902. https://doi.org/10.1007/s11368-019-02350-2

Tsai, W. T., Liu, S. C., & Hsieh, C. H. (2012). Preparation and fuel properties of biochars from the pyrolysis of exhausted coffee residue. *Journal of Analytical and Applied Pyrolysis*, *93*, 63–67. https://doi.org/10.1016/j.jaap.2011.09.010

Wang, S., Kwak, J. H., Islam, M. S., Naeth, M. A., Gamal El-Din, M., & Chang, S. X. (2020). Biochar surface complexation and Ni(II), Cu(II), and Cd(II) adsorption in aqueous solutions depend on feedstock type. *Science of the Total Environment*, *712*, Article 136538. https://doi.org/10.1016/j.scitotenv.2020.136538

Woolf, D., & Lehmann, J. (2012). Modelling the long-term response to positive and negative priming of soil organic carbon by black carbon. *Biogeochemistry*, *111*, 83–95. https://doi.org/10.1007/s10533-012-9764-6

Wu, W., Yang, M., Feng, Q., McGrouther, K., Wang, H., Lu, H., & Chen, Y. (2012). Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass and Bioenergy*, *47*, 268–276. https://doi.org/10.1016/j.biombioe.2012.09.034

Wuana, R. A., & Okieimen, F. E. (2011). Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *International Scholarly Research Notices Ecology*, *2011,* Article 402647. https://doi.org/10.5402/2011/402647

Xu, Y., Qi, F., Bai, T., Yan, Y., Wu, C., An, Z., Luo, S., Huang, Z., & Xie, P. (2019). A further inquiry into co-pyrolysis of straws with manures for heavy metal immobilization in manure-derived biochars. *Journal of Hazardous Materials*, *380*, Article 120870. https://doi.org/10.1016/j.jhazmat.2019.120870

Yao, Z., Li, J., Xie, H., & Yu, C. (2012). Review on remediation technologies of soil contaminated by heavy metals. *Procedia Environmental Sciences*, *16*, 722–729. https://doi.org/10.1016/j.proenv.2012.10.099

Yeomans, J. C., & Bremner, J. M. (1988). A rapid and precise method for routine determination of organic carbon in soil. *Communications in Soil Science and Plant Analysis*, *19*(13), 1467–1476. https://doi.org/10.1080/00103628809368027

Zhang, M., He, Z., Calvert, D. V., Stoffella, P. J., & Yang, X. (2003). Surface runoff losses of copper and zinc in sandy soils. *Journal of Environmental Quality*, *32*(3), 909–915. https://doi.org/10.2134/jeq2003.9090

Zheng, H., Wang, Z., Zhao, J., Herbert, S., & Xing, B. (2013). Sorption of antibiotic sulfamethoxazole varies with biochars produced at different temperatures. *Environmental Pollution*, *181*, 60–67. https://doi.org/10.1016/j.envpol.2013.05.056