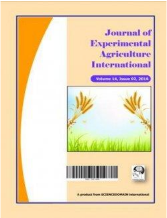

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Individual and Competitive Adsorption of Copper, Zinc and Lead in Soils with Contrasting Texture

Larissa Kummer[1*], Morgana Suszek Gonçalves[2], Adriana Zemiani[3], Vander de Freitas Melo[4] and Simone Damasceno Gomes[5]

[1]Department of Chemistry and Biology, Federal Technological University of Paraná (UTFPR), Curitiba, Paraná, Brazil.
[2]Federal Technological University of Paraná (UTFPR), Campo Mourão, Paraná, Brazil.
[3]Department of Environmental Engineering, Federal Technological University of Paraná (UTFPR), Londrina, Paraná, Brazil.
[4]Department of Soil Science and Agricultural Engineering, Federal University of Paraná (UFPR), Curitiba, Paraná, Brazil.
[5]Center of Exact and Technological Sciences, Western Paraná State University, (UNIOESTE/CASCAVEL/CCET/ PGEAGRI), Cascavel, Paraná, Brazil.

Authors' contributions

This work was carried out in collaboration between all authors. Author LK conducted the study, collected the soils in the field and did the analysis of the data coming from her thesis. Author AZ helped in the laboratory analysis. Author MSG reviewed the analyses of the study. Author SDG was the supervisor of the doctor thesis that originated the scientific article. Authors VFM was the co-advisor of the thesis, reviewed the first draft of the manuscript and collaborated in the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Waste is often disposed of in the soil, leading to contamination not only by a metal, but by two or more elements. The adsorption studies are a way of evaluating the behaviour of the different metals when in contact with the soils. This study aimed to evaluate the effect of adsorption of Cu, Zn and Pb, in an individual and competitive system, in soils with contrasting texture. To achieve the goals,

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**Corresponding author: E-mail: lkummer@utfpr.edu.br, larikummer@hotmail.com;*

two types of soils, typical of the state of Paraná (PR), Brazil were used. One of the samples (Soil A) were collected in the city of Francisco Beltrão, classified as a typical dystrophic Red Latosol (Oxisol) and the other (Soil B) were collected in the city of São Pedro do Paraná in the region of Paranavaí, classified as a Red-Yellow Argisol Abruptic eutrophic. The soils were characterised by chemical, granulometric, and mineralogical analyses. The metals adsorption were tested by the batch method. With these results, adsorption parameters derived from the Langmuir and Freündlich models were obtained. The adequacy of the Langmuir and Freündlich equations to the adsorption results did not occur in all situations but was satisfactory. Pb presented the highest values of maximum adsorption capacity estimated by the Langmuir model. Simultaneous adsorption reduced the adsorption of the three metals, with the highest reductions observed for Zn. Zn's lower competitive power, evidenced by the reduction of its adsorption capacity in the presence of other metals, makes this element very worrisome in more weathered tropical soils, since it indicates a greater predisposition of this element to the movement in the profile or in superficial waters.

Keywords: Langmuir; Freündlich; isotherm of adsorption; heavy metals; soil pollution.

1. INTRODUCTION

Heavy metals are the most toxic inorganic pollutants that occur in soils and may be natural or anthropic. The mechanisms of adsorption and desorption, with precipitation/ dissolution processes, are considered the main processes controlling the concentration of chemical species in the soil solution [1].

The soil ability to adsorb metal ions from aqueous solutions has direct relations with agriculture and environmental issues. A mechanism of soil remediation contaminated with heavy metals is the ability of this matrix in adsorbing pollutants. Therefore, knowing the behaviour of these elements and the adsorptive capacity of soils is essential to predict environmental disasters [2].

The soils, when polluted, are usually contaminated by many elements simultaneously. This competitive system can interfere with both the mobility in the soil as with the bioavailability of pollutants [3]. Metals that are adsorbed with more energy to soil charges may displace other ions of lower ionic potential and increase the potential for groundwater pollution. Thus, the competitive adsorption or multielement adsorption needs to be better investigated due to soils with contrasting physical and mineralogical characteristics as well as the comparison between the individual and competitive behaviours [4].

Metals more strongly adsorbed such as Pb and Cu, are less affected by the competition from more mobile metals such as Cd and Zn. The competition effect between the metals more mobile (as Cd, Ni and Zn), especially on organic soils, has been little studied [5]. In addition, the authors say that is still not entirely clear how the competitive adsorption of weakly adsorbed heavy metals affect their behaviour and their availability over time.

A good way to study the behaviour of a metal in the soil is the use of physical and chemical adsorption models. In general, the relationship between the amount of a metal adsorbed by the soil solid phase (q) and its concentration in soil solution (C) is quantified by an isotherm (ratio q/C) which allows knowing more about the nature of the adsorption processes [6].

The two adsorption models often adopted for soil are the Langmuir and Freundlich. The Langmuir equation is adequate to be applied in describing the adsorption of ions in the soil, providing data for which the properties related to the surface phenomena can be interpreted [7]. The Langmuir theory is based on the fact that adsorption occurs in uniform sites with monolayer coverage and ion affinity regardless of the amount of adsorbed material [6]. The Freundlich model considers the non-uniformity of the surface, and when applied to soil describes well the ionic adsorption within certain concentration limits, but higher than these limits have difficulties to setting [7].

The aim of this work was to study the adsorption of Pb, Cu and Zn in two soils with contrasting texture in competitive and non-competitive systems.

2. MATERIALS AND METHODS

2.1 Study Area and Soil Sampling

Two types of soils were selected derived from different parent material; both were collected at 0-20 cm depth from sites belonging to areas of permanent preservation in Brazilian environmental legislation near water bodies (Fig. 1). One of the samples (Soil A) were collected in the city of Francisco Beltrão, classified as a typical dystrophic Red Latosol (Oxisol) (Latossolo Vermelho distroférrico típico, Brazilian Soil Classification System) (-26,086856ºS and 53,088951°W). This soil is typical from the south-west of Paraná state, developed from basaltic parent material from the "Serra Geral" Formation. The basalt is present in 53% of the Paraná area. The soil B was collected in the city of São Pedro do Paraná (-22,845222°S and -53,229028°W), in the region of Paranavaí, PR, classified as a Red-Yellow Argisol Abruptic eutrophic (Argissolo Vermelho-Amarelo Eutrófico abrúptico, Brazilian Soil Classification System). This soil was collected because is a typical soil from areas that have “arenito Cauá” as parent material, which occurs in 16% of the total area of Paraná state.

2.2 General Soil Characterisation

In the laboratory, soil samples were air dried and sieved with a 2-mm opening sieve and subjected to chemical and physical analyses [8]. Soil pH was determined in H_2O and in $CaCl_2$ 0,01 mol L^{-1}; exchangeable Ca^{2+}, Mg^{2+} and Al^{3+} were extracted with 1 mol L^{-1} KCl; exchangeable Na^+ and K^+ were extracted with Mehlich-1 and; H (non-exchangeable acidity) with 0.5 mol L^{-1} pH 7 Ca acetate. Element concentrations in the extracts were determined by atomic absorption spectroscopy (Ca^{2+}, Mg^{2+} and Al^{3+}), titration (H) and flame emission spectroscopy (K^+ and Na^+). Total organic carbon was determined by Walkley-Black method (0,167 mol L^{-1} $K_2Cr_20_7$ and concentrated H_2SO_4) and clay content by pipette method.

2.3 Mineralogical Analysis in the Clay Fraction

To study the minerals present in the clay fraction, around 20 g of each sample were mashed, submitted to a dispersion and sedimentation physical fractioning process, and the fractions sand, silt and clay were extracted. The clay fraction was analysed in the powder method by X-ray diffraction (XRD). Preparation and treatment of samples for determining the composition of the free clay fractions were performed according to Jackson [9]. The diffractograms were obtained with a XRD-7000 diffractometer Shimadzu, Cu Kα radiation at 50 kV and 20 mA, with an angular speed of 1º2Ө min^{-1} and horizontal scale ranging from 4 to 64°2θ. Sodium chlorite was used as an internal standard for correction of instrumental factors (position of the peaks). The mixture (about 50 mg g^{-1}) was made by grinding the sample in a mortar with added NaCl.

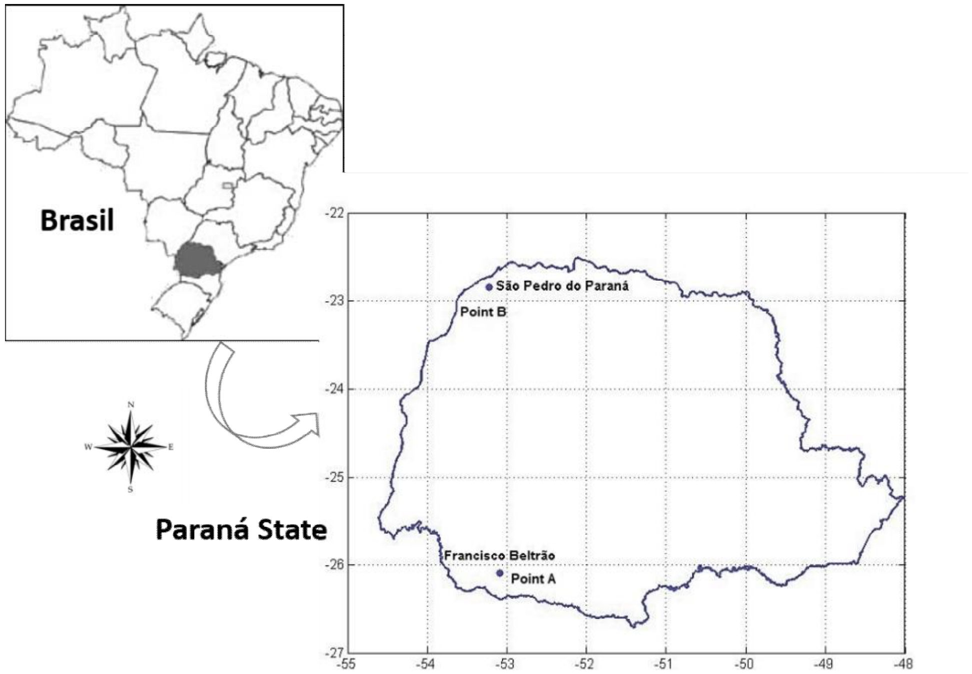

Fig. 1. Location of the study region

Content and chemical composition of iron oxides of low and high crystallinity were respectively determined by the 0.2 mol L^{-1} pH 3.0 ammonium oxalate (AO) [10] and citrate-bicarbonate-dithionite (CBD) [11] methods. Fe was determined by atomic absorption spectrophotometry.

2.4 Adsorption of Cu, Zn and Pb

To 2.0 g of fine soil (in triplicate) 20 mL of a metallic solution (Cu, Pb and Zn) in different initial concentrations were added. These solutions were prepared with the metals in nitrate salts ($Pb(NO_3)_2$, $Cu(NO_3)_2$ and $Zn(NO_3)_2$) in solution of 0,01 mol L^{-1} $NaNO_3$ (relation soil: solution = 1:10). The initial concentration of metals ranged between 50 and 2.000 mg L^{-1}. The experiments were performed with the addition of monometalic solution (Non-Competitive System - SNC) and with the solution containing the three metals together, multimetalic condition (competitive system - SC). The spiking of soils with heavy metals were carried out in polyethylene flasks of 50 ml that were shaken (200 rpm) for 24 h at 25 °C. After that, they were centrifuged at 5000 rpm for 10 min and the metals were determined in the supernatant by atomic absorption spectrophotometry (Shimadzu model AA 6030). Metal adsorption (q) was estimated by subtracting the value determined in the solution from the quantity initially placed in the equilibrium solution (Ce). Adsorption isotherms were constructed from the data obtained experimentally, plotting the quantity of the metal adsorption in y and the equilibrium concentration in x axis. The non-linear isotherm of Langmuir is given by the Equation 1 where: q_e = quantity of adsorbed metal per unit mass of soil (mg kg^{-1}); K_L = Langmuir constant related to the connection energy of the metal to the soil (L mg^{-1}); b = maximum adsorption (mg kg^{-1}); C_e = metal concentration in the balance solution (mg L^{-1}).

$$q_e = \frac{C_e K_L b}{1 + K_L C_e} \qquad (1)$$

The non-linear Freündlich equation is presented in Equation 2, where q_e = amount of metals adsorbed per unit mass of soil (mg kg^{-1}); K_F = Freündlich adsorption constant (L mg^{-1}); n = is a dimensionless parameter, which indicates the soil affinity for the solute (dimensionless); C_e = metal concentration in the balance solution (mg L^{-1}) [6].

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (2)$$

The statistical significance of the coefficient of determination (R^2), found for the Langmuir and Freundlich models, was tested at 5% level of significance.

3. RESULTS AND DISCUSSION

3.1 Soil Characterisation and Mineralogical Analysis

The soil texture and chemical characteristics of the soils involved in this study are showed in Table 1.

The clay fraction is prevalent in soil A and in soil B is prevalent sand fraction. In both of cases the silt/clay ratio is low (0.42 and 0.52). The low silt/clay ratio in Oxisols is related to its advanced stage of weathering [12]. Silva et al. [13] also found low ratio when studied soils originated from metabasalt in another region of Brazil.

The highest levels of Fe_{CBD} (extraction CBD) and Fe_{AO} (extraction with AO) were for clay fraction of soil A originated from basalt weathering (Table 2). In addition to presenting higher levels of Fe_2O_3, the soil A showed high clay content (Table 1). More acidic rocks such as rhyolite and dacite, give to soils lower values of Fe_{CBD} than basic rocks such as basalt [14]. Ghidin et al. [15], also in soils derived from basalt, found Fe_2O_3 concentrations above 200 g kg^{-1}. Horizons with Fe_2O_3-CBD content lower than 50 g kg^{-1} are considered poor in Fe [16], what happens to the soil B. The source material of the region (sandstone) is poor in primary minerals structural with Fe. The soil B showed only 94 g kg^{-1} of clay (Table 1).

Table 1. Soil texture and chemical characteristics of the soils

Soil	Sand	Silt	Clay	pH	pH H_2O	OM[1]	SB[2]	CEC[3]	P	K	Mg	Ca	Al^{+3}	BS[4]
	-------- g kg^{-1} --------			$CaCl_2$		g dm^{-3}	$cmol_c$ dm^{-3}		mg dm^{-3}	--------$cmol_c$ dm^{-3}------				%
Soil A	49	361	690	4.6	5.5	33.5	7.5	13.7	6.1	0.43	2.8	4.2	0.14	54.6
Soil B	866	40	94	4.5	5.0	10.7	3.5	6.7	3.0	0.15	1.4	1.9	0.06	52.4

[1] OM – organic matter; [2] SB – sum of bases; [3] CEC – cation exchange capacity; [4] BS – base saturation

Table 2. Fe_2O_3 content extracted with citrate-bicarbonate-dithionite (CBD) and ammonium oxalate (AO) and ratio $Fe_2O_{3\,AO}$ / $Fe_2O_{3\,CBD}$ in the soil clay fraction

Soil	Fe_2O_{3CBD}	$Fe_2O_{3\,AO}$	$Fe_2O_{3\,AO}$ /$Fe_2O_{3\,CBD}$
	---------------- g kg^{-1} ---------------------		
Soil A	113.8	11.4	0.1002
Soil B	48.0	5.3	0.1104

FeAO levels are extremely low when compared to FeCBD, which can be confirmed by the low ratio FeAO/FeCBD (maximum value of 0.11), evidencing the predominance of more crystalline forms of Fe oxides, typical characteristic of soils in advanced stage of weathering [17]. In the B-horizon of soils with a high degree of weathering, it is common to find values for this relation inferior to 0.01 [18]. Another factor that contributes to the predominance of crystalline Fe oxides is the good drainage of the soils, not occurring hydromorphism [15]. Silva et al. [13] also found higher levels of Fe_{CBD} in soils originated from basic rocks.

The XRD revealed the presence of Fe oxides of high crystallinity (hematite - Hm) in the clay fraction of soil A (Fig. 2). The Hm is formed preferentially in soils formed of rocks rich in Fe (basalt) and under warm weather conditions [19]. Therefore, the high content of Fe_2O_3 in soil A was the result of the dissolution of Hm of the clay fraction. In addition to Hm in this sample, the characteristic peaks of Quartz (Qz), Caulinite (Ct), and Gibbsite (Gb) are observed. Silva et al. [13] also found these minerals in large amounts in oxisoils. In soil B there is predominance of Qz and mica (Mi), as well as characteristic reflections of secondary mineral 2:1 (2:1), Ct and Gb. In this sample it was not possible to observe the presence of Hm. The source sandstone is rich in Qz, which facilitated its large occurrence in the clay fraction. Other authors have observed Qz in the clay fraction of different soil classes in Brazil [20,21]. The presence of secondary 2:1 clay minerals in weathered soils is usually in the form of smectite with Al-hydroxy interlayers [15]. The presence of Al-hydroxy islands increases the stability of the 2:1 mineral, which makes possible its co-existence with Gb in the clay fraction. The contrasting texture and mineralogy of the clay fraction is a reflection of the different source materials of the soils [22].

3.2 Adsorption of Pb, Cu and Zn in Soils

In the graphs of the adsorption isotherms, the points represent the experimental data, and the curves refer to the Langmuir and Freündlich models (Figs. 3 and 4). The quantitative parameters of adjustment of the adsorption reaction are shown in Table 3.

There was a rapid increase of Cu and Pb adsorption at lower concentrations (Figs. 3 and 4), with a subsequent decrease in the curve slope (L-type isotherm). This behaviour occurs whenever the available sites for the adsorption are decreasing, that is, the coating of the adsorption surface ends. At low concentrations, the surface has high affinity for the adsorbed substance, and this affinity decreases in higher concentrations [23]. Linhares et al. [24] also obtained L-type isotherms for Pb in highly weathered soils. In addition to L-type isotherms, these authors also adjusted H-type isotherm for Cu adsorption. The H-type isotherm is often the result of a second layer of ions, retained by the surface in high concentration in the solution [25].

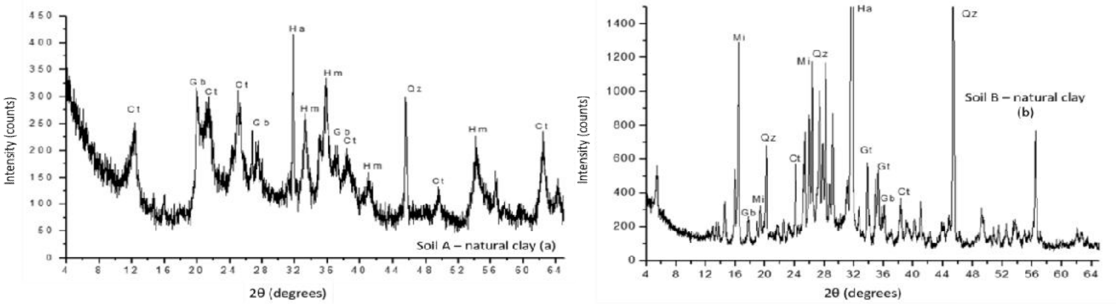

Fig. 2. X-ray diffraction (CuKα radiation) of clay fraction of soil A (a) and soil B (b)

Ct - caulinite, 2:1 - secondary mineral 2:1, Hm - hematite, Qz - quartz, Gb - gibbsite, Ha - halite, Mi - mica, Gt - goethite

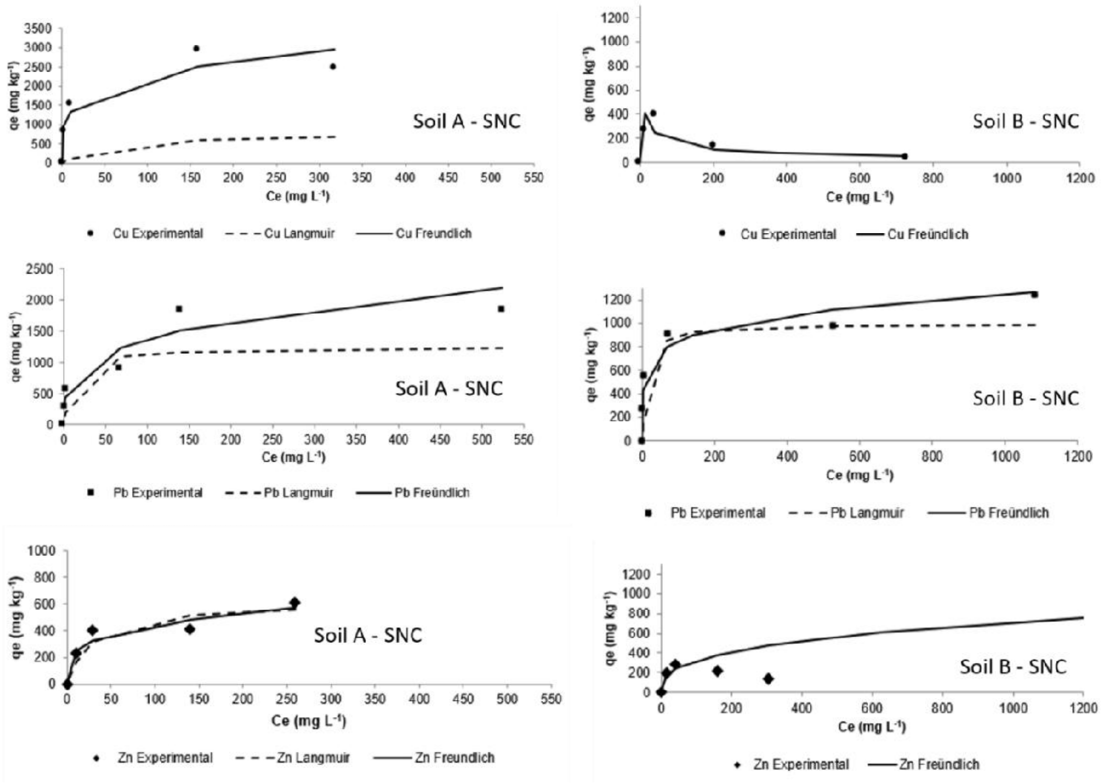

Fig. 3. Cu, Pb and Zn adsorption isotherms in a non-competitive system for clayey soil (Soil A) and sandy soil (Soil B)

C_e: equilibrium concentration (mg L^{-1}); q_e: amount adsorbed at equilibrium (mg kg^{-1})

Table 3. Langmuir and Freündlich parameters for adsorption of metals in both types of soils evaluated, in competitive and non-competitive systems

Metal	Soil	Langmuir			Freündlich		
		K_L	b_L	R^2	K_F	1/n	R^2
		L mg^{-1}	*mg g^{-1}*		*L mg^{-1}*		
				Non-competitive system (SNC)			
Pb	Soil A	0.0988	1.25	0.98	370.94	0.284	0.89
	Soil B	0.0885	1.00	0.98	391.74	0.168	0.88
Cu	Soil A	n.a.	n.a.	n.a	813.21	0.223	0.91
	Soil B	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Zn	Soil A	0.0338	0.63	0.93	134.74	0.260	0.82
	Soil B	n.a.	n.a	n.a.	n.a.	n.a.	n.a
				Competitive system (SC)			
Pb	Soil A	0.0851	2.50	0.98	367.28	0.384	1.00
	Soil B	0.0483	1.00	0.99	166.34	0.324	0.86
Cu	Soil A	0.0565	1.43	1.00	302.55	0.276	1.00
	Soil B	0.1393	0.29	0.99	250.61	0.039	0.13
Zn	Soil A	0.0173	0.63	0.99	45.95	0.436	0.95
	Soil B	n.a.	n.a	n.a.	n.a.	n.a.	n.a.

K_L- Langmuir isotherm constant; b_L- maximum monolayer coverage capacity; R^2 – coefficient of determination; K_F- Freündlich isotherm constant.

n.a. - the model does not fit the experimental data

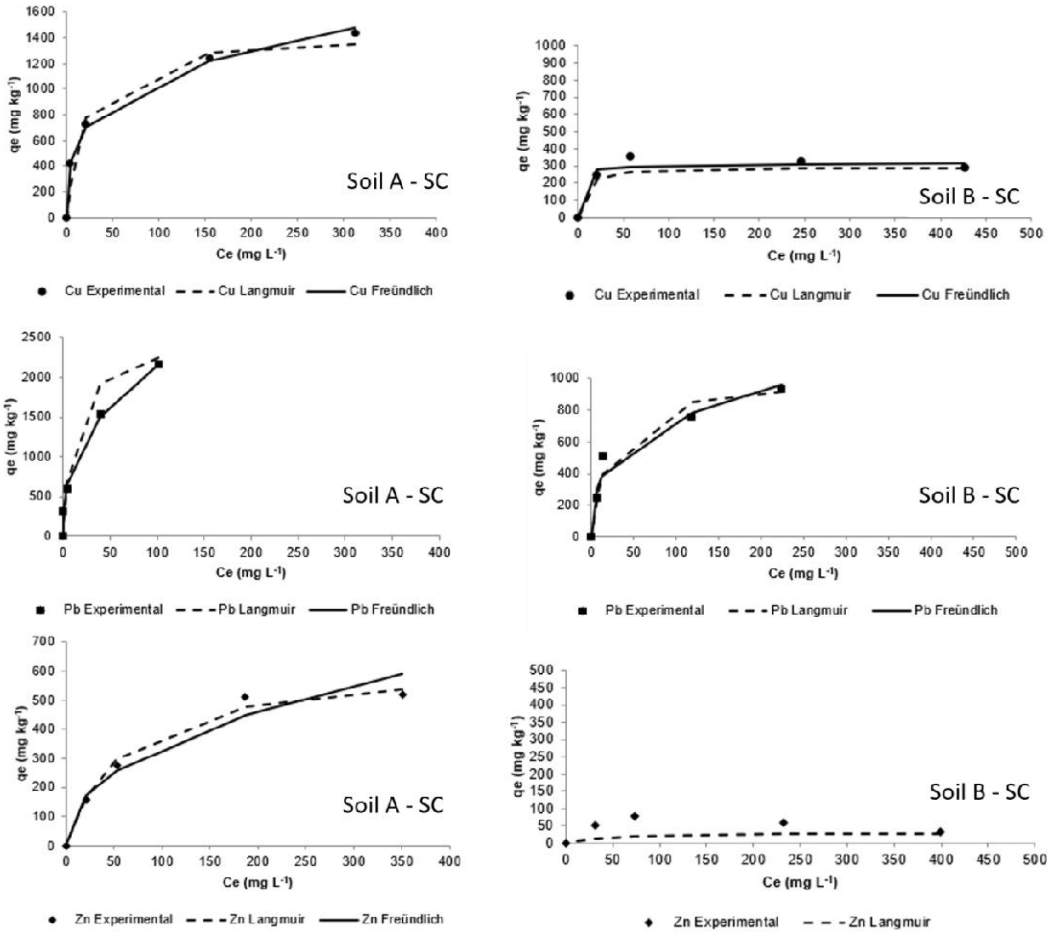

Fig. 4. Cu, Pb and Zn adsorption isotherms in a competitive system for clayey soil (Soil A) and sandy soil (Soil B)

In the competitive system, it is observed that both the Langmuir and Freündlich models had adequate adjustments to the experimental data in soil A (Fig. 4). In the case of soil B, only the Freündlich model did not fit Zn correctly. The retention of metals is a competitive process between the ions in solution and those adsorbed on the soil surface. Consequently, the ionic composition of the solution exerts a great effect on the adsorption of these ions in the soil particles. Due to several factors, such as adsorbate type and experimental conditions, different affinity sequences may arise, and it is practically impossible to establish a universal sequence [26]. The same author evaluated the competitive adsorption of Cd, Cu, Ni, and Zn in soils of different compositions and verified that, as the initial concentration increased, competition occurred between the metals, which affected the adsorption of all the metals in different proportions. Fontes and Gomes [27] evaluated the competitive adsorption of Cu, Cr, Pb, Ni, Zn, and Cd in tropical soils and found that some, such as Cu, Cr, and Pb, showed a high affinity with the surface of the soil colloids, while Ni, Zn, and Cd were displaced from the adsorbent surfaces. This difference occurs due to the type of metal-surface interaction of the soil. According to McBride [3], Ni, Zn and Cd are more dependent elements of electrostatic interactions with the solid phase exchange sites, while Cu is more dependent on covalent interactions with the structures of the minerals.

In all cases, either in SC or SNC, the highest adsorption was always in the clayey soil, regardless of the type of metal (Figs. 3 and 4). The reactions that promote the retention of heavy metals always occur in the finer fractions and coarse texture soils favor the mobility of these metals [24,28,29].

Cu, Zn, and Pb showed different behaviours in the adsorption process, which indicates that different mechanisms can be involved in the adsorption of each metal of the solution. Pb was always the metal with the highest adsorption potential, followed by Cu and Zn. Sipos et al. [30] also found this sequential. In clayey soil, Cu had higher potential than Zn, and in SC's sandy soil the situation was reversed, but with very close values (Table 3). Oliveira et al. [31] observed that the adsorption sequence of the metals was different due to the granulometry of the soil and of the minerals present. The adsorption of Cu and Zn was greater in relation to Pb for more clayey soils and was the opposite for more sandy soils.

The Langmuir equation b parameter has been used to estimate the maximum adsorption capacity (MAC) for various chemical elements present in soils [28,32]. Soil A always showed higher MAC than soil B for the three metals analysed. This difference is due to the physical and chemical characteristics between soils (Table 1). It can be inferred that the high clay content of soil A, as well as its high organic matter content, should be the main responsible for the metals adsorption phenomenon. In the study by Linhares et al. [33], the organic matter content and the crystalline iron oxides correlated significantly with the Pb MAC, showing that these constituents are probably one of the most active lead adsorption sites. The high affinity of the Pb element is shown by most functional groups of organic matter, including the carboxylic and phenolic groups, which are strong Lewis bases. Pb, in addition to being a strong Lewis acid, has a higher electronegativity (2.33, 2.00, and 1.65 for Pb, Cu, and Zn, respectively), and lower pKH (negative log of the first hydrolysis constant: 7.71, 8.00, and 9.00 for Pb, Cu, and Zn, respectively) [26]. As a result, Pb has preference for sorption/complexation reactions, with formation of internal sphere complexes when compared to the others [3,30]. Usually, Pb presents internal sphere bonds with ferrol and aluminol groups of the clay fraction minerals [34]. It should be also noted that if the ability of the metal to be retained was based only on electrostatic bonds, the strongest bonds would be those formed between the metals with the highest charge: ionic radius. However, it should be noted that the metallic bonds are not entirely electrostatic [26,35]. Among the evaluated metals, the hydrated ionic radius follows the following decreasing sequence: Zn (0.430 nm), Cu (0.419 nm), Pb (0.401 nm). Thus, as the hydrated radius of Pb^{2+} is lower than that of the other elements, the coulombian interactions of Pb with the exchange sites are favoured.

In relation to Cu, the main attributes for this retention are the clay, CEC and organic carbon contents, since this metal has great affinity to form complexes with organic matter, mainly due to the presence of humic and fulvic acids [2,25,36]. The carboxylic and phenolic groups of the organic matter have strong affinity for the Cu and form complexes of low solubility [6]. The higher the degree of humification and the higher the pH, the higher is the Cu binding strength, making it more unavailable to the environment [37]. The soil sample B presented lower MAC due to the fact that it had lower clay content, lower OM content and, consequently, lower CEC (Table 1), which means lower number of negative charges in its colloids in which metals could be adsorbed.

In the case of soil A, in the SNC, the Langmuir model underestimated the adsorption capacity of Cu and Pb (Fig. 3). For these two metals, the Freündlich isotherm was closer to the values found experimentally. Araújo and Amaral Sobrinho [36] emphasised that Cu adsorption is best represented by the Freündlich equation due to the heterogeneity of the adsorption surface. Similar results were found in the studies carried out by Sodré et al. [6], Silveira and Alleoni [25], and Chaves et al. [2], who also found a better fit of the Freündlich model to Cu adsorption.

In soil B, in SNC, the only metal that had its behaviour appropriate to the Langmuir and Freündlich isotherms models was Pb (Fig.3). For this metal, the maximum adsorption capacity was 1.00 mg g^{-1}. Due to the lack of adjustment of the Langmuir isotherm to the Cu and Zn data, it was not possible to compare the MAC values of these metals with Pb.

The adsorption of Zn in soil A (SNC) was well represented by both models tested (Fig. 3). Zn was the metal that had the lowest adsorption capacity when compared to the others. The MAC obtained by the Langmuir isotherm was 0.63 mg g^{-1}. Linhares et al. [28], when comparing the adsorption of Zn and Cu to different types of highly weathered soils, also found that Zn was the element with the lowest adsorption capacity (Zn - 0.25 and Cu - 0.63 mg g^{-1}). Chaves et al. [38] analysed the adsorption of Zn in Argisols of the state of Paraíba (BR) and found MAC values ranging from 0.11 to 0.78 mg g^{-1}. The highest values were attributed to soils that presented the highest values of negative electrical potential and not to soils with the highest clay content. In the present study, due to the great textural difference of the soils (Table 1), the clay fraction mineralogy was less important to define the CEC of the soils. Comparing only the quality of the clay fraction, soil A would have lower CEC because it is a more oxidic system (higher Fe_2O_3DCB contents and expressive hematite peaks by XRD - Table 2 and Fig. 3). Fe oxides present a pHzgp (zero charge point) around 8-9 and for pH values below this limit, AEC will predominate on the surface of the particles [19]. In the clay fraction of soil B, kaolinite, due to its low value of pHzgp (around 3.5), and esmectite, because it presents high permanent negative charge density (isomorphic substitution of Si^{4+} for Al^{3+}), present higher density of surface negative charges. However, as a final result, the amount of clay was more expressive than its quality and soil A presented higher adsorption capacity for metals. The higher organic matter content was also important to increase soil CEC.

In the clayey soil, in SC, Pb was the element that had the highest values of K_F, followed by Cu and Zn (Table 3). When the three metals are together competing for the same active sites, the tendency is for the Pb to be retained with greater force. The K_L (Langmuir K) parameter also had this same sequence. In the case of sandy soil, also in SC, the element with higher K_F was Cu, followed by Pb (Zn was not determined due to the lack of adjustment to the Freündlich model). In this case, because to the sandy soil contained little clay, the factor that most influenced the adsorption probably was the organic matter content, which, although was also small, guarantees strong adsorption with Cu [3].

Considering the aspects of metal availability to the plants and environmental contamination, the sandy soil sample (soil B), in its original pH, because of its lower binding energy and lower adsorption capacity, would be the one in which the element present in the soil would be more available, both to be absorbed by the plants and to be leached, and could contaminate the water table.

In summary, the studied soils, cause they were derived from materials of different origins, presented different chemical, physical and mineralogical characterisation. In both soils, mainly kaolinite and oxides of iron and aluminium are present, predominantly those with higher crystallinity; Pb is the metal with the highest adsorption capacity when compared to Cu and Zn, both in clayey soil and in sandy soil, even in a competitive system or not; In the clayey soil, the physical-chemical models proposed by Langmuir and Freündlich were adequate to represent the adsorption behaviour of Cu, Pb and Zn in a multimetal system; The Langmuir model underestimated the maximum adsorption capacity of Cu and Pb in the clayey soil in a monometallic system; The competition between the metals affected the adsorption magnitude of all metals, with the lowest variation for Cu; The distinct behaviour of metals in both evaluated systems showed that competitive adsorption should be considered to evaluate more realistically the bioavailability, toxicity and leaching potential of heavy metals in soils; In the case of simultaneous soil contamination with the three metals, Zn is the one with the greatest potential to cause damage to the environment, especially to plants and groundwater, since it has the lowest potential of binding to the fractions less available of soil.

4. CONCLUSION

The studied soils presented different chemical, physical and mineralogical characterisation. In both soils, mainly kaolinite and oxides of iron and aluminium are present, predominantly those with higher crystallinity; Pb is the metal with the highest adsorption capacity when compared to Cu and Zn, both in clayey soil and in sandy soil, even in a competitive system or not; In the clayey soil, the physical-chemical models proposed by Langmuir and Freündlich were adequate to represent the adsorption behaviour of Cu, Pb and Zn in a multimetal system; The Langmuir model underestimated the maximum adsorption capacity of Cu and Pb in the clayey soil in a monometallic system; The competition between the metals affected the adsorption magnitude of all metals, with the lowest variation for Cu; The distinct behaviour of metals in both evaluated systems showed that competitive adsorption should be considered to evaluate more realistically the bioavailability, toxicity and leaching potential of heavy metals in soils; In the case of simultaneous soil contamination with the three metals, Zn is the one with the greatest potential to cause damage to the environment, especially to plants and groundwater, since it has the lowest potential of binding to the fractions less available of soil.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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