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Adsorption of heavy metals in Andisols, Vertisols and Humic Acids

Adsorción de metales pesados en Andisoles, Vertisoles y Ácidos Húmicos

Luis Enrique Cortés Páez[1], Isabel del Socorro Bravo Realpe[2], Francisco José Martín Peinado[3] and Juan Carlos Menjivar Flores[4]*

[1]Universidad Nacional de Colombia, Department of Basic Sciences. Palmira, Colombia. [2]Universidad del Cauca, Department of Chemistry. Popayán, Colombia. [3]Universidad de Granada, Department of Edaphology and Agricultural Chemistry. Granada, España. [4]Universidad Nacional de Colombia, Faculty of Agricultural Sciences. Palmira, Colombia. *Corresponding author: lecortesp@unal.edu.co

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Abstract

This research studied the adsorption of five heavy metals (Cd, Cu, Ni, Pb and Zn) in three adsorbents, two Colombian agricultural soils (Typic Melanudand and fine clay 1% isohyperthermic–Ustic Epiaquert) and Humic Acids (HA) extracted from leonardite samples of Spain. In both, HA and soils, the chemical properties determined were: pH, cation exchange capacity (CEC), organic carbon (% OC), exchangeable bases and total content of metals. The chemical composition of HA was determined using spectrometric techniques as ICP_MS, FTIR, UV–Vis, and CPMAS ^{13}C NMR and Py–GC/MS–THMA. The results from the adsorption of metals in the three adsorbents were adjusted to Freundlich model, and these show a different behavior of the absorbers relative to the metals studied, in the same way the maximum adsorption capacity (*K*) and the retention strength (*n*) of metals is significantly different ($p < 0.05$). According to *K* and *n* of each adsorbent, the adsorption selectivity sequences of the metals has the following order of preference for *K*: In Humic Acids: Cd> Pb> Cu> Ni> Zn, Andisol: Pb> Cu> Cd> Zn> Ni, and Vertisol: Cd> Pb> Cu> Ni> Zn. For *n*, Humic Acids: Pb> Zn> Cd> Cu> Ni, Andisol: Cu> Ni> Zn> Pb> Cd, and Vertisol: Zn> Ni> Cu> Pb> Cd.

Key words: Soils, humic acids, adsorption, sorption isotherms, heavy metals.

Resumen

Se estudió la adsorción de los metales pesados cadmio (Cd), cobre (Cu), níquel (Ni), plomo (Pb) y zinc (Zn) en Andisoles (Typic Melanudand) y Vertisoles (Epiaquert ústico arcilloso fino isohipertérmico 1%) de Colombia y en ácidos húmicos (AH) extraídos de muestras de leonardita tomadas en España. En todos los casos se determinaron las propiedades químicas y físicas: pH, capacidad de intercambio catiónico (CIC), carbono orgánico (%CO), bases intercambiables y contenido total de metales. La composición química de los AH se determinó empleando técnicas espectrométricas como ICP_MS, FTIR, UV–Vis, CPMAS ^{13}C NMR y Py–GC/MS–THMA. Los resultados de adsorción de los metales ajustados al modelo de Freundlich mostraron un comportamiento diferente de los adsorbentes en relación con los metales estudiados, siendo la máxima capacidad de adsorción (*K*) y la fuerza de retención (*n*) de los metales diferente ($P < 0.05$). Según estos parámetros, las secuencias de selectividad de adsorción de los metales presenta el siguiente orden de preferencia, para *K* en ácidos húmicos: Cd > Pb > Cu > Ni > Zn; en Andisol: Pb > Cu > Cd > Zn > Ni; y en Vertisol: Cd > Pb > Cu > Ni > Z. Para *n* en ácidos húmicos: Pb > Zn > Cd > Cu > Ni; en Andisol: Cu > Ni > Zn > Pb > Cd, y en Vertisol: Zn > Ni > Cu > Pb > Cd.

Palabras clave: Suelos, ácidos húmicos, adsorción, isotermas de adsorción, metales pesados.

Introduction

The presence of heavy metals in soil is due to natural and anthropogenic causes. For the study of edaphic adsorption of these metals some models are used, among which stand out the sorption isotherms (Langmuir, Scatchard and Freundlich). The use of these isotherms to predict the mobility of heavy metals in different environments is based on the fact that it takes into account the ionic and bonding strengths, pH, redox potential, cationic exchange capacity, organic matter, clay content and the reaction mechanisms on the internal and external spheres of the soil colloids (Bradl, 2004; Calace *et al.*, 2009; Cerqueira *et al.*, 2011).

Studies by Calace *et al.* (2009) for Ni and Cd adsorption by humic acid addition to a sandy clay loam soil, poor in organic matter, showed that the Ni is adjusted to the Freundlich model, while the Cd is adjusted to the Langmuir model. Cerqueira *et al.* (2011), studied the Cu and Cd adsorption in Humic Umbrisol, Umbric Cambisol, Endoleptic Luvisol and Humic Cambisol soils and did not find adjustment to the Freundlich and Langmuir models; to the opposite, Fontes and Gomes (2003) observed that the adsorption of heavy metals such as Cr, Ni, Cu, Zn, Cd and Pb in Oxisol, Ultisol and Alfisol soils was adjusted to the Langmuir model. In Colombia, the studies on adsorption and heavy metals contamination in agricultural soils is scarce (Bonilla *et al.*, 1991; Insuasty *et al.*, 2006; Arboleda, 2013); for this reason in this study the adsorption and retention of Cd, Cu, Ni, Pb and Zn in Humic Acids (HA) and in Andisols and Vertisols, which act as adsorbents of these metals were evaluated.

Materials and methods

The research was performed in the Edaphology and Agricultural Chemistry Lab and in the Center for Scientific Instrumentation of the University of Granada, Spain, using andisol and vertisol soils from the agricultural zones of Colombia and humic acids from leonardite. The soil samples were taken till 20 cm of depth, air dried and sieved through a No. 10 mesh to determine: texture by the Robinson pipette method (Loveland and Whalley, 1991), clay mineralogy (Martín, 2004), pH (USDA, 1999), organic carbon (IGAC, 2006), interchangeable bases and CEC (ammonium acetate 1N at pH 7) and total content of Ni, Cu, Zn, Cd and Pb (EPA, 1999).

Humic acids characterization

The humic acids (HA) were extracted from 200 g of leonardite collected in Spain, following the methodology of Mosquera *et al.* (2007) by using extracting solutions of $Na_2B_4O_7$ 0.1 N pH 9.3, $Na_4P_2O_7$ 0.1 N pH 10.2 and NaOH 0.1 N pH 12.1, till obtaining a clear supernatant. The humic acids were separated from the fulvic ones by precipitation with H_2SO_4 till pH < 2; then, were purified with 1% HCl–HF and ultra-centrifuged followed by dialysis on 12000 Da membrane; later they were lyophilized on a FLEXI–DRY–μP equipment and were characterized by pH determination (1:2.5), the cationic exchange capacity (CEC) and interchangeable bases with ammonium acetate 1N pH 7, determined by atomic absorption spectrometry in a Varian Spectra–220Z equipment, organic carbon (OC%) by Walkley and Black (IGAC, 2006). The chemical composition of the HA was determined by using different spectroscopy techniques such as ICP_ MS spectroscopy, Fourier transformed infrared spectroscopy, FTIR, UV–Vis, CPMAS ^{13}C NMR spectroscopy, Py–GC/MS–THMA.

Evaluation of the metal adsorption process in humic acids and soils

For this evaluation a complete randomized design with 60 treatments and three replicates for each one was used, the treatments resulted from the combination of three adsorbents (HA, Andisol and Vertisol), five metals (Ni, Cu, Zn, Cd and Pb) and, four concentrations per metal selected according to the Environmental Counselor of Andalucia (CMAJA, 1999).

Samples of each absorbent were taken and suspended in 0.03 M NaCl solutions, 1:10 ratio, with four concentrations (mg/l) for each material (Ni^{+2}: 40, 100, 300, 400; Cu^{+2}: 50, 100, 300, 700; Zn^{+2}: 200, 500, 1000, 1300; Cd^{+2}: 2, 5, 10, 30: Pb^{+2}: 100, 200, 400, 700) which were continuously shaked for 6 h at 160 rpm on a lineal shaker JP Selecta rotaterm, till the equilibrium point; later, each metal concentration was quantified in a ICP–MS NEXION 300D. The adsorption was quantified by the difference between the administered metal (mg/kg) and the one in the equilibrium solution. In the last one the desorption by the determination of each metal with IPC-MS, obtained by the extraction of the residue with 0.5 M citric acid, dried at 60 °C for 24 h and agitation for 2 h was established. The net (real) adsorption corresponds to the difference between the amount of adsorbed and desorbed metal.

The results of the metal adsorption in the three adsorbents were subjected to analysis of sorption isotherms by Freundlich, Scathchard and Langmuir, finding that the best adjustment was the Freundlich model, which lineal regressions give the maximum adsorption capacity (K) and the retention strength (n).

Results and discussion

Characterization of the adsorbents

The soils showed contrasting properties in the organic matter content (OM), texture, clay mineralogy, bulk density, pH and CEC. Andisol is rich in allophones or Al-humus complexes, its taxonomical classification correspond to a Typic Melanudand (IGAC, 2009) with silt loam texture, a moderate acid pH due to dolomitic lime use, high levels of OC, K and CEC, middle levels of Ca and Mg, and normal of Na. Vertisol (Epiaquert ustico fine clay isohyperthermic 1%) (Roveiro *et al.*, 1997), had a clay loam texture and it is characterized by expandable clays (2:1 type), neutral pH and low CEC with high levels of Ca and Mg and normal of Na. the humic acids showed an extremely acid pH, high CEC and high OC and, low levels for basis, except for Na (Table 1).

In the HA prevails the carbon (C) (57.74%), followed by oxygen (O) (36.81%), with low level of nitrogen (N) (1.44%) and

Table 1. Characterization of the adsorbents (Andisol, Vertisol and humic acids) for heavy metals.

Adsorbent	pH	OC	CEC	Ca	Mg	Na	K	Cl	L	S
		(%)	(cmolc/kg)					(%)		
Andisol	5.56	9.76	54.98	5.36	1.53	0.05	0.36	13.74	50.06	36.20
Vertisol	7.15	0.71	21.20	11.16	6.59	0.25	0.29	32.02	31.20	36.77
HA	3.42	57.18	326.09	0.63	1.04	30	Bdl	n.a	n.a	n.a

OC: organic carbon; CEC: cationic exchange capacity; Ca: calcium; Mg: Manganese; Na: Sodium; K: Potassium; Cl: clay; L: lime; S: sand; bdl: below detection limit; n.a: does not apply.

sulfur (S) (0.01%) and predominant aromatic compounds of highly condensate structures, lateral chains with low oxidation levels, high stability and maturity reflected on the values of the C/O (2.10), C/H (1.20) and E_4/E_6 (4.88) ratios, OR indexes (R1 = 0.69 and R2 = 0.57), aromaticity factor (72.27%) and hydrophobicity index (3.22). In relation to the molecular composition, the higher fraction corresponds to fat acids (62.6%), followed by aromatics (23.7%), N and S compounds (11.6%) and terpene compounds (2.1%), without presence of polysaccharides, therefore they associate with plant origin molecules.

Metal adsorption

Adsorption of metals presented a lineal behavior in function to the administered doses (Figure 1 and Table 2). The analysis of vari

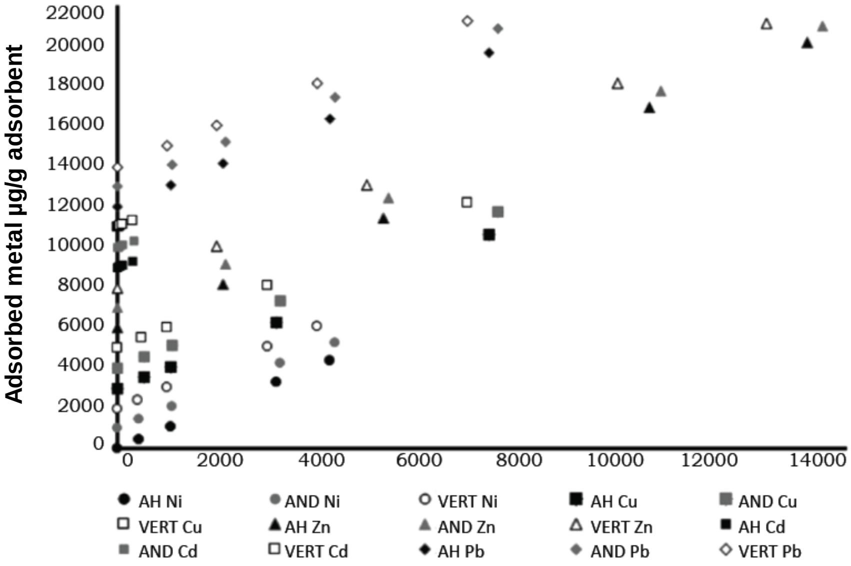

Figure 1. Metal adsorption trend in humic acids and in Andisols and Vertisols. The Y values were displaced from the coordinate origin in order to show the metal adsorption trend: AND Ni (+1000), VERT Ni (+2000), AH Cu (+3000), AND Cu (+4000), VERT Cu (+5000), AH Zn (+6000), AND Zn (+7000), VERT Zn (+8000), AH Cd (+9000), AND Cd (+10000), VERT Cd (+11000), AH Pb (+12000), AND Pb (+13000), VERT Pb (+14000).

Table 2. Metal adsorption trend in humic acids and soils.

Adsorbent	Metal	Equation	R^2
HA (humic acid)	Ni	Y = 0.9983x - 0.1801	$R^2 = 1$
	Cu	Y = 0.9986x - 0.0704	$R^2 = 1$
	Zn	Y = 0.9976x + 0.3254	$R^2 = 1$
	Cd	Y = 0.9992x - 0.0149	$R^2 = 1$
	Pb	Y = 0.9992x + 0.2521	$R^2 = 1$
Andisol	Ni	Y = 0.9605x + 14.587	$R^2 = 1$
	Cu	Y = 0.9907x + 8.7211	$R^2 = 1$
	Zn	Y = 0.9591x + 34.545	$R^2 = 1$
	Cd	Y = 0.9977x - 0.1973	$R^2 = 1$
	Pb	Y = 0.9996x + 0.0416	$R^2 = 1$
Vertisol	Ni	Y = 0.9921x + 1.748	$R^2 = 1$
	Cu	Y = 0.9994x + 0.2273	$R^2 = 1$
	Zn	Y = 0.9821x + 16.77	$R^2 = 1$
	Cd	Y = 0.9905x + 0.0344	$R^2 = 1$
	Pb	Y = 0.9997x + 0.0494	$R^2 = 1$

ance showed that there were not differences (P > 0.05) for the adsorption by the effect of the adsorbents (Table 3). However, there were differences (P > 0.05) by the effect of the administered doses and by the interaction adsorbent x dose (Table 4). The Tukey´s mean comparison test (P < 0.05) (Table 5) showed a significant increase in the retention of each metal as the administered dose was increased as well, a similar behavior to the one reported by Fontes and Gomes (2003) in Brazil soils.

In the Table 6 is observed a high positive correlation between CEC and the different metals and, between these and the OC. The negative values between the metal adsorption and the contents of calcium (Ca), potassium (K) and sodium (Na), indicate that as the exchangeable base concentration is reduced the easier is the release of interchangeable places in the CEC, which are occupied by the metals when displacing these elements. The K^+ higher values showed weak retention strength of this element because it is monovalent (Okada *et al.*, 2005); it is not the same for Ca^{2+}, which

Table 3. Kruskal Wallis test for metal adsorption (P < 0.05) in function to the adsorbents (humic acid, Andisols, Vertisols).

Statistical	Metals				
	Ni	Cu	Zn	Cd	Pb
Chi-square	1.95	1.95	1.95	1.95	1.95
Gl.	2.00	2.00	2.00	2.00	2.00
Sig. asymptotic	0.38	0.38	0.38	0.38	0.38

Table 4. Inter-subject effects test for adsorption (P < 0.05) of heavy metals in humic acids, Andisols and Vertisols.

Metal	Origen	Sum od squares type III	FD	Cuadratic mean	F	Sig.
Nickel	Model	249726347.60[b]	12	20810528.97	231699.945	0.00
	dosissum	80850054.29	3	26950018.10	300055.69	0.00
	adsorbent x dosissum	180824.68	6	30137.45	335.54	0.00
	Error	2155.60	24	89.82		
Copper	Model	572407781.06[b]	12	47700648.42	41546.53	0.00
	dosissum	249731837.16	3	83243945.72	72504.20	0.00
	adsorbent x dosissum	812389.64	6	135398.27	117.93	0.00
	Error	27555.02	24	1148.13		
Zinc	Model	2730719252.53[b]	12	227559937.71	63695.72	0.00
	dosissum	665586850.86	3	221862283.62	62100.90	0.00
	adsorbent x dosissum	1820647.26	6	303441.21	84.94	0.00
	Error	85742.63	24	3572.61		
Cadmium	Modelo	976178.14[b]	12	81348.18	173907.60	0.00
	dosissum	450391.08	3	150130.36	320951.38	0.00
	adsorbent x dosissum	1141.77	6	190.30	406.82	0.00
	Error	11.23	24	0.47		
Lead	Modelo	695436210.33[b]	12	57953017.53	461654.05	0.00
	dosissum	206767142.68	3	68922380.89	549036.05	0.00
	adsorbent x dosissum	497564.57	6	82927.43	660.60	0.00
	Error	3012.80	24	125.53		

Table 5. Adsorption of heavy metals in function of adsorbent type and dose.

Adsorbent	**Dose (mg/l)**	**Retained amount (adsorbed metal (µg/g of soil))**				
		Ni	**Cu**	**Zn**	**Cd**	**Pb**
Humic acid	1	435.40^{a}	546.05^{a}	2168.94^{a}	21.76^{a}	1093.85^{a}
	2	1090.28^{b}	1091.24^{b}	5387.37^{b}	54.53^{b}	2185.45^{b}
	3	3269.81^{c}	3280.12^{c}	10756.52^{c}	109.07^{c}	4374.00^{c}
	4	4351.18^{d}	7647.41^{d}	13956.34^{d}	327.00^{d}	7633.60^{d}
Andisol	1	418.17^{a}	540.75^{a}	2010.31^{a}	20.56^{a}	1085.70^{a}
	2	1044.42^{b}	1076.66^{b}	4991.76^{b}	51.72^{b}	2157.27^{b}
	3	3098.84^{c}	3193.69^{c}	10021.22^{c}	102.91^{c}	4307.63^{c}
	4	4096.10^{d}	7328.80^{d}	13055.06^{d}	306.34^{d}	7526.41^{d}
Vertisol	1	387.29^{a}	494.64^{a}	1904.67^{a}	19.02^{a}	996.28^{a}
	2	971.97^{b}	978.91^{b}	4743.83^{b}	48.08^{b}	1984.49^{b}
	3	2898.70^{c}	2974.99^{c}	9433.73^{c}	96.78^{c}	3957.83^{c}
	4	3885.32^{d}	6682.47^{d}	12291.63^{d}	289.04^{d}	6841.44^{d}

* values on the same column followed by different letters statistically differ ($P < 0.05$), according to Tukey´s test.

Table 6. Summary of the correlations between metal adsorption and adsorbents properties.

Properties	**Adsorption (%)**				
	Ni	**Cu**	**Zn**	**Cd**	**Pb**
CEC	0.938**	0.886**	0.926**	0.949**	0.964**
OC	0.921**	0.883**	0.907**	0.934**	0.963**
Ca	-0.688*	-0.763**	-0.651*	-0.709**	-0.855**
K	-0.987**	-0.886**	-0.960**	-0.974**	-0.958**
Na	0.994**	0.886**	0.960**	0.974**	0.958**

** Highly significant at 0.01 level (bilateral). * Significant at 0.05 (bilateral).

is divalent (Bradl, 2004; Komy *et al.*, 2014; Sparks, 2003).

Sorption isotherms

The metal adsorption was adjusted to the Freunlich model, with high correlation coefficients (Figure 2 and Table 7). The HA had a superior affinity (*n*) to metals in comparison to other adsorbents (Table 8) which is attributed to, both the higher OC and high CEC (Mas and Azcue, 1993). Additionally, they have in their structure high contents of carboxylic, phenolic, alcoholic and carbonyl groups, which allow the formation of more stable complexes in the exterior sphere by the electrostatic interactions and with an inner sphere to retain and immobilized the metals (Bradl, 2004; Calace *et al.*, 2009). The K values in the adsorbents (Table 8) were higher than the ones found for high Andean Andisoles (Arboleda, 2013), indicating the high retention capacity and metal immobilization. The statistical differences of the *K* and *n* values of the metals in each adsorbent (Table 9) are probably associated with differences on the composition of the soil solutions, the superficial net charges of the ions that form complexes at the inner and outer spheres and, the ionic cloud of the double diffuse layer (Spósito, 2008). Also, they associate with the content of carboxylic (ACOOH), hydroxylic (AOH) and phenolic (aromatic ring–OH) functional groups present in the humic acids (Pérez–Esteban *et al.*, 2014).

Even though the Vertisol had a lower OC content and lower CEC, its maximum

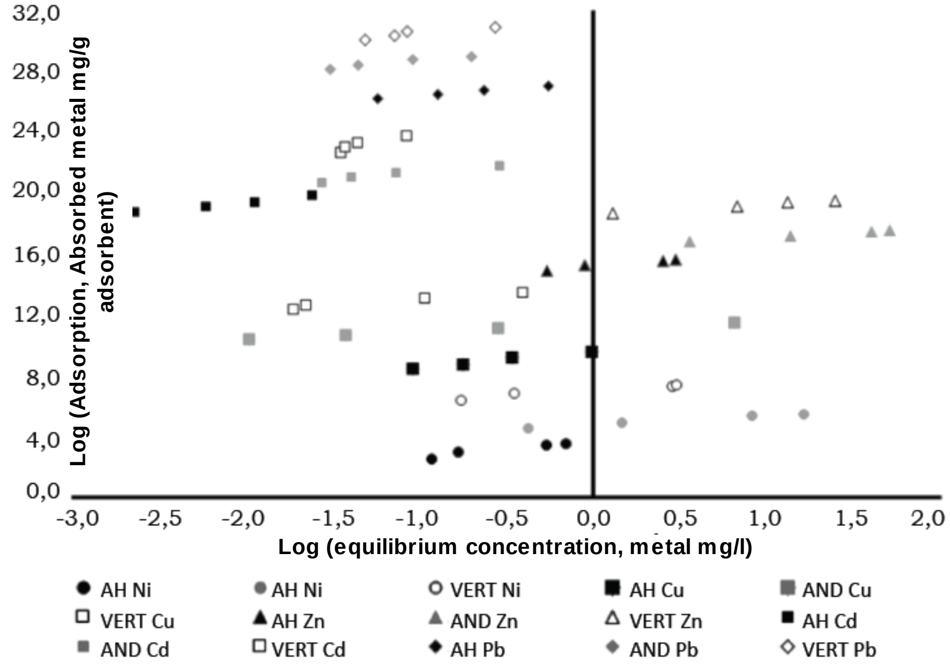

Figure 2. Freundlich isotherms for each metal under study.

The Y values were displaced from the coordinate origin in order to show the metal adsorption trend: AND Ni (+2), VERT Ni (+4), AH Cu (+6), AND Cu (+8), VERT Cu (+10), AH Zn (+12), AND Zn (+14), VERT Zn (+16), AH Cd (+18), AND Cd (+20), VERT Cd (+22), AH Pb (+24), AND Pb (+26), VERT Pb (+28).

Table 7. Freundlich isotherms for the metals under study in humic acids, Andisols and Vertisols.

Adsorbent	Metal	Lineal equation	R^2
Humic acid	Ni	$Y = 1.1921x + 3.839$	0.9628
	Cu	$Y = 1.1476x + 3.9407$	0.9779
	Zn	$Y = 1.001x + 3.6748$	0.9540
	Cd	$Y = 1.1408x + 4.3073$	0.9900
	Pb	$Y = 1.1992x + 2.8141$	0.9991
Andisol	Ni	$Y = 0.6285x + 2.904$	0.9935
	Cu	$Y = 0.4092x + 3.6237$	0.9682
	Zn	$Y = 0.6822x + 2.9624$	0.9971
	Cd	$Y = 1.0869x + 3.1696$	0.9450
	Pb	$Y = 1.3662x + 3.4836$	0.9761
Vertisol	Ni	$Y = 0.7126x + 3.2283$	0.9646
	Cu	$Y = 0.7982x + 4.2111$	0.9584
	Zn	$Y = 0.6513x + 3.2242$	0.9821
	Cd	$Y = 2.651x + 5.3865$	0.8504
	Pb	$Y = 1.0459x + 4.5169$	0.8300

adsorption capacity (*K*) is higher ($P < 0.05$) than all the metals in the Andisol and HA, between which there are no differences ($P > 0.05$) (Table 9). This is due, probably, to its high content of 2:1 clay type that with high specific surface have high CEC and, as result, the interchangeable bases are displaced by the metals with higher ionic radius and valence (Bradl, 2004) and, therefore, those metals can be absorbed in the clay sheet increasing its retention capacity (Spósito, 2008).

The Andisol had the maximum adsorption capacity (*K*), similar to the HA and, its retention strength (*n*) is significantly higher than the HA and Vertisol. Between the latest ones, there were no differences ($P > 0.05$), possibly by the type and composition of the OM, which humic substances are younger and reactive (Mosquera *et al.*, 2007; Martínez *et al.*, 2014).

The inverse relation between *K* and *n* in the adsorbents, is confirmed by the negative and highly significant correlations (Table 10). This indicates that the metal retention on the outer sphere of the OM is easy to be displaced by the soil solution because it has lower retention strength; at the same time the mobilization of adsorbed metals in the inner sphere is impeded by the formation of highly stable bonds (Hizac and Apak, 2006a and 2006b). The HA of the leonardite showed a low capacity and retention strength, since in their molecular composition aromatic compounds prevail which are condensed structures of high stability and maturity but, with low oxidative levels on the lateral chains (Ding *et al.*, 2002).

The lower affinity (*K*) and higher retention strength (*n*) of the adsorbents was observed in Ni, Cu and Zn, probably, because of the smaller ionic radius (0.69°A, 0.73°A and 0.74°A, respectively). The higher ionic radius for Pb and Cd (0.95°A and 1.40°A, respectively) gives them higher adsorption capacity (*K*) but, less retention strength (*n*); despite that, the lower retention capacity of the Pb in respect to Cd and the absence of significant differences (Table 9) are attributed to the differences in the used doses, the generation of a smaller electric field, a labile electronic configuration and a higher trend to be polarized by functional groups in the colloids (organic matter and clay) (Spósito, 2008).

The Ni and Zn *K* is positively and significantly correlated with the CEC, OC and the Na^+, due to its higher retention by the electrostatic strengths and by the ionic interchange with the Na^+. Its negative correlation with pH, Ca^{2+} and K^+ indicates that the increase in bases can substitute the hydrogen of the charges that depend on pH increasing the cationic exchange. At the same time, the acidity increase in the soils can reduce the CEC by blocking the active

Table 8. Parameters of adsorption of the Freundlich isotherms for heavy metals in humic acids (HA), Andisols and Vertisols.

Metal	**Strength (*n*)**			**Capacity (*k*)**		
	HA	**Andisol**	**Vertisol**	**HA**	**Andisol**	**Vertisol**
Ni	0.84^{b}	1.59^{e}	1.40^{e}	6902.40^{c}	801.31^{b}	1692.00^{c}
Cu	0.87^{c}	2.44^{a}	1.25^{d}	8723.69^{d}	4199.52^{e}	16356.86^{d}
Zn	1.00^{e}	1.47^{d}	1.54^{a}	4729.33^{b}	917.06^{c}	1676.10^{b}
Cd	0.88^{d}	0.91^{b}	0.38^{b}	20290.80^{a}	1492.79^{d}	246320.18^{a}
Pb	1.14^{a}	0.99^{c}	0.95^{c}	13835.66^{e}	43742.14^{a}	32885.16^{e}

* values on the same column followed by different letters statistically differ ($P < 0.05$), according to Tukey´s test.

Table 9. Mean values of the maximum adsorption capacity (*K*) and adsorbent strength (*n*) by heavy metals in humic acids, Andisols and Vertisols.

Parameter	**Adsorbent**			**Metal**				
	Ha	**Andisol**	**Vertisol**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
K	10896.38^{b}	10230.56^{b}	59786.06^{a}	3131.90^{b}	9760.02^{b}	2440.83^{b}	89367.92^{a}	30154.32^{a}
n	0.95^{b}	1.48^{a}	1.10^{b}	1.28^{b}	1.52^{a}	1.34^{b}	0.72^{c}	1.03^{c}

* values on the same column followed by different letters statistically differ ($P < 0.05$), according to Tukey´s test. .

groups with H^+ and by the obstruction of the permanent and dependent charges done by the Al, Fe and Mn polymers, reducing the maximum adsorption capacity (*K*) and increasing the retention capacity (*n*) as is confirmed by a negative and highly significant correlation (Table 10) (Juárez *et al.*, 2006).

The Cb and Pb *K* had a positive and highly significant correlation with pH and Ca^{2+}, whereas the *n* showed a negative correlation with this two parameters, showing that the retention of these two metals can happen by cationic interchange with the Ca^{2+}; while its positive correlation with the OC indicates that the complexes formed with OM are highly stable, making difficult its displacement towards the soil solution (Tai *et al.*, 2013, Li *et al.*, 2013). The negative correlation of the Pb *K* with CEC and OC was due to its low adsorption in the HA and higher affinity for the electrostatic bonds of the clays, hydroxides and Fe and Al oxides (Kabata–Pendias, 2011; Janoš *et al.*, 2010).

The positive and significant correlation of the Cu *K* with the Ca^{2+} and Mg^{2+} bases indicated that the CEC is increased first with the displacement of such bases; however, the negative and highly significant correlation of the Cu *n* with CEC showed that this metal retention happens mainly by the formation of OM complexes, together with the iron, aluminum and manganese oxides (Vega *et al.*, 2008; Gomes *et al.*, 2001).

Table 10. Correlations among adsorption capacity (***K***), retention strenght (***n***) and the adsorbent properties.

Adsorbent properties	Metals				
	Ni	**Cu**	**Zn**	**Cd**	**Pb**
			Capacity (*K*)		
CEC	0.972**	-0.245	0.958**	-0.528	-0.892**
CO	0.960**	-0.292	0.943**	-0.568	-0.870**
pH	-0.840**	0.552	-0.809**	0.779**	0.693*
Ca	-0.753**	0.666*	-0.717**	0.861**	0.583*
Mg	-0.451	0.897**	-0.402	0.989**	0.234
Na	0.992**	-0.140	0.983**	-0.434	-0.936**
K	-0.999**	-0.038	-1.000**	0.267	0.983**
Strength	-0.994**	-0.618*	-0.953**	-1.000**	-0.843**
			Strength (*n*)		
CEC	-0.940**	-0.610*	-1.000**	0.543	0.995**
CO	-0.923**	-0.571	-1.000**	0.583*	0.999**
pH	0.775**	0.314	0.949**	-0.791**	-0.972**
Ca	0.676*	0.175	0.895**	-0.870**	-0.928**
Mg	0.350	-0.208	0.662*	-0.992**	-0.720**
Na	-0.971**	-0.691*	-0.992**	0.451	0.979**
K	0.998**	0.809**	0.954**	-0.285	-0.927**

** Highly significant at 0.01 level (bilateral). * Significant at 0.05 (bilateral).

Conclusions

- The Ni, Cu, Zn, Cd and Pb adsorption, both in Humic Acids and on Andisols and vertisols, showed a lineal behavior in function to the administered doses, showing a good adjustment to the Freundlich isotherms model.
- The adsorption selectivity by the metals based on *K* values, followed the preference order: for Humic Acids = Cd > Pb > Cu > Ni > Zn; for Andisols = Pb > Cu >

Cd > Zn > Ni; and for Vertisols = Cd > Pb > Cu > Ni > Zn. The retention strength (*n*) in Humic Acids was = Pb > Zn > Cd > Cu >Ni; in Andisols was = Cu > Ni > Zn > Pb > Cd; and in Vertisols was = Zn > Ni > Cu > Pb > Cd; behavior that determine a potential use of each adsorbent, to immobilize metals in contaminated soils.

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