

Analysis of sorption/desorption of cadmium and lead in the legal amazon soils

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Technical Note

Keywords

Heavy metals
Sorption
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Abstract

Sorption and desorption tests were carried out for competitive and non-competitive systems with isotherms to verify the presence of Cd and Pb in soils. The soils investigated were: (i) with natural content of organic matter and (ii) with residual content of organic matter. Hydrated nitrate salts of Cd and Pb diluted in 0.01 M calcium nitrate solution in six concentrations were used for the Cd solutions and, for the solutions of Pb, five concentrations. For multi-element solutions, mixtures of the simple Cd and Pb solutions in a 1:1 ratio were used. The results of the first stage tests (i) showed good adjustments of the experimental data to the isotherms of Langmuir, Freundlich and Linear, which did not occur for the tests in stage (ii). According to the tests (i), the organic matter was the soil attribute of dominant influence in the sorting mechanisms. The parameters Q_0 and K_d were adequate to evaluate the adsorption of the studied metals, especially Cd. In step (ii), there was a significant increase in metal retention, especially for element Pb in the samples of Haplic Cambisol (AM) and Red-Yellow Latosol¹ (RO), justified by the combined action of (1) increasing the surface area of the mineral fraction, previously covered by organic matter; and (2) increase in soil pH . The Cd element was more bioavailable in relation to the Pb. This was confirmed by the high desorption values observed for Cd. The samples of Haplic Cambisol and Red-Yellow Latosol demonstrated greater capacity to retain Cd and Pb.

1. Introduction

The soil acts as a natural support for engineering works, as well as for plants and agricultural production, functioning as a means of regulating chemical, physical and biological processes, as well as a “filter” for the removal of contaminants.

Soil contamination is the main cause of damage to groundwater, the result of several factors ranging from fertilizers, pesticides, sewage treatment sludge, manure, automobile and industrial gases, coal combustion, waste burning and disposal.

Since it is a compartment of the environment with the capacity to accumulate many contaminants, the soil is vulnerable to contamination because, if its buffer power is exceeded, the environmental matrices that integrate this system will begin to present serious risks due to the transport of these pollutants through the profile of the soil (Amaral Sobrinho, 2009).

Among the pollutants, we highlight the heavy metals that are quite stable in nature, likely to accumulate in the soil and in the biological system of living beings, in addition to being a potential risk of contamination for groundwater.

In this context, the study of the interaction mechanisms between the soil and its chemical constituents assumes a fundamental role for the control and evaluation of potential environmental impacts, since understanding its dynamics is a tool in the prediction of bioavailability and mobility of heavy metals in the soil. Sorption isotherms are the mathematical models used to represent the mobility mechanisms of certain elements in the soil.

Its quantitative modeling is made possible due to the existence of parameters that function as environmental indicators, which are related, to a lesser or greater capacity, to retain elements by the solid constituents of the soil. Its estimation is possible through the adjustment between experimental data and the tested isothermal curve.

The bioavailability of metals to a greater or lesser degree is the result of a combination of factors: the chemical species present in the soil and its chemical, physical and mineralogical attributes, with emphasis on the surface charge of the solid particle, the levels of iron oxides, aluminum, clay silicate minerals, cation exchange capacity (CTC), organic matter and hydrogen potential (pH) (Shaheen, 2009, Antoniadis & Golia, 2015, Shaheen et al., 2013). These characteristics vary according to the type of soil and, therefore, its sorting capacity also varies.

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This research included the analysis of the sorting and desorptive behavior of metals Cd and Pb in soil samples from the Legal Amazon, using sorption isotherms for both competitive and non-competitive systems.

2. Materials and methods

2.1 Characterization of the physical and chemical attributes of the samples

After collecting the material, the samples were dried in the open air and subjected to analysis of the physical and chemical soil attributes according to the methodology recommended by EMBRAPA (1997).

2.2 Removal of organic matter

Seeking to check the interference of the organic matter attribute in the assortment and desorption mechanisms in the soil-solution system, tests were carried out using two types of soil: (i) soils with natural content of organic matter (untreated soils) and (ii) soils with residual organic matter content (treated soils).

The organic material was totally or partially removed by oxidative routes, with the application of hydrogen peroxide (H_2O_2) 30% in gradual doses on the soil samples until no foam was observed in the supernatant.

Samples from horizon A (0-20 cm) from six (06) States in the Legal Amazon region were used for sorption and desorption tests: Red-Yellow Latosol (LVA¹) - Rondônia, Red-Yellow Latosol (LVA) - Tocantins, Haplic Planosol (SX) - Roraima, Ortio Quartzene Neosol (RQ) - Mato Grosso, Plintossolo (P) - Amapá and Cambisol Haplic Cambisol (CX) - Amazonas.

The experiments were carried out using the batch method, a procedure widely adopted in the assortment and desorption studies of soils.

2.3 Sorption and desorption tests

It should be noted that, although there is an expressive scientific volume of Brazilian studies in this area, the absence of a standard methodology is evident. In this work, intermediate conditions were adopted to those employed in other studies of sorption and desorption in Brazilian soils.

Initially, 2 g of TFSA (air-dried fine earth) from each sample was stored in falcon-type tubes (50 mL). Then, 40 mL of solution was added in increasing concentrations of Cd and Pb, both in the form of hydrated nitrate salts (soil/solution ratio: 1/20). The initial concentrations (C_o) adopted for the simple solutions (monometal solution) were 0, 50, 100, 200, 400 and 600 mg / L for the Cd element and 0, 200, 400, 800 and 1200 mg / L for the element Pb.

The multi-element solutions (bimetal solution) were prepared by mixing the simple solutions of Cd and Pb in a 1:1 ratio.

The electrolyte support solution used in the dilution of the metals was $Ca(NO_3)_2$ 0.01M, with *pH* adjusted to 5.5. According to Pierangeli et al. (2007), the choice of this value is justified because it is suitable for the development of plants in tropical conditions, in addition to being a figure in which the possibility of precipitation of cationic metals is limited, either in the form of oxides or in the form of metal carbonate.

The soil-solution systems were then sent to the horizontal shaker for 72 hours (alternating 12 h of shaking and 12 h at rest at 150 rpm). After this period, the suspensions were centrifuged for 15 minutes at 3000 rpm aiming to separate the solid material and the supernatant.

Clear aliquots were removed from the supernatant and diluted in a 25% nitric acid (HNO_3) solution for the sorption tests and 12.5% for the desorption tests.

After diluting the aliquots, they were collected to determine the concentrations of metals in the equilibrium solution (C_{eq}) by optical emission spectrometry with induced plasma - ICP OES (Optical Emission Spectrometry with Induced Plasma).

The amount of metal (Cd and Pb) absorbed by the soils was calculated according to the equation:

$$qe = \frac{[Vol_{sol}(C_o - C_{eq})]}{M_{soil}} \quad (1)$$

2.4 Obtaining sorption isotherms

The sorption isotherms were constructed using IsoFit software (Isotherm Fitting Tool), a program that adjusts the isothermal parameters of the mathematical models to the experimental data produced in the laboratory. This adjustment is made by minimizing the weighted sum of the quadratic error of the objective function and, according to Matott & Rabideau (2008), supports 10 (ten) sorption isotherms: (i) Brunauer-Emmett-Teller (BET); (ii) Freundlich; (iii) Freundlich with linear partitioning; (iv) generalized Freundlich-Langmuir; (v) Langmuir; (vi) Langmuir with linear partitioning; (vii) Linear; (viii) Polanyi; (ix) Polanyi with linear partitioning; and (x) Toth.

Thus, after the insertion of the of qe and C_{eq} values, the program provided the isotherm model with the best adjustment to the experimental data, as well as the estimation of their respective parameters, such as Q_o (maximum sorption capacity - Langmuir model) and K_d (distribution coefficient - linearized form of the Freundlich model).

3. Analysis and results

3.1 Physical and chemical characteristics of soils

Tables 1 and 2 show the results obtained from the analysis of the chemical and physical constituents of the studied soils.

The data revealed the LVA¹ (RO) and CX (AM) samples had the highest values for all the attributes analyzed, with exception of *pH*.

The granulometric composition of the soils indicates that the LVA¹ (RO) sample showed a high clay texture, with 447 g / kg, surpassing the CX, with 368 g / kg by 79 units. Therefore, both soils have a higher clay content compared to the others.

The CX (AM) showed a high *CTC* value, with 34.4 cmolc / kg. The second highest value was for the LVA (TO), 29 units below the previous one. The assortment complex for CX (AM) (sum) was higher than the value recorded for LVA¹ (RO), both with the highest values.

CX (AM) was the soil with the highest residual carbon content, justified by its high value before the treatment stage. For the same reason, the LVA¹ (RO) soil had the second highest residual carbon value.

3.2 Soil *pH* measurement

Table 3 shows the *pH* values (in water) of the soil before and after the oxidation of organic matter. With exception of SX (RR) soil, there was an increase in soil *pH*.

Although this verification for CX (AM) soil (*) was not possible for technical reasons – shown in the Table 3, it is believed there was an increase in the *pH* of the soil as observed for the others.

Weber et al. (2009), when studying the sorption of a certain insecticide in the organic and mineral fractions of a latosol, found that the removal of organic matter by 30% hydrogen peroxide raised the soil *pH* from 5.43 (natural soil) to 6.51 (soil after oxidation of organic matter).

Stevenson (1994) suggests that by oxidizing organic matter, acid groups complexed to it are eliminated, which causes an increase in soil *pH*, corroborating the results found in this study.

3.3 Sorption assays

The graphs shown in Figure 1 (a,b) correspond to the plot of the experimental data from the sorption tests. Seeking to facilitate the comparison of results, the tests carried out with soils with natural organic matter content are coded as (a), while the tests carried out with soils with residual organic matter content are marked as (b).

Table 1. Soil chemical attributes.

Soils	<i>pH</i> (water)	Sortiv Complex (cmolc/kg)	<i>CTC</i> (cmolc/kg)	Carbon Organic (g/kg)	
				Soil N-Treated	Soil Treated
LVA ¹	3.8	0.7	5.3	13.4	1.7
LVA	4.5	0.2	2.3	5.5	0.5
SX	5.1	0.1	1.8	2.9	0.6
RQ	4.0	0.3	5.7	9.9	0.6
P	4.8	0.3	2.6	6.9	0.4
CX	4.0	8.1	34.4	78.4	7.7

Legend: see List of symbols.

Table 2. Physical attributes of soils.

Soils	Granulometric Composition			
	Coarse Sand	Fine Sand	Silt	Clay(<0.002 mm)
LVA ¹	412	85	56	447
LVA	364	555	21	60
SX	485	363	92	60
RQ	428	482	30	60
P	100	458	382	60
CX	6	17	609	368

Table 3. Soil *pH* values measured before (initial *pH*) and after (final *pH*) the oxidation of organic matter.

Soils	<i>pH</i> (initial)	<i>pH</i> (final)
LVA ¹	3.8	5.2
LVA	4.5	5.7
SX	5.1	4.7
RQ	4.0	5.5
P	4.8	5.6
CX	4.0	(*)

(*)The final *pH* verification for soil type CX (AM) was not performed due to technical issues; however, it is believed that there was an increase in *pH*, as observed for the other soil types.

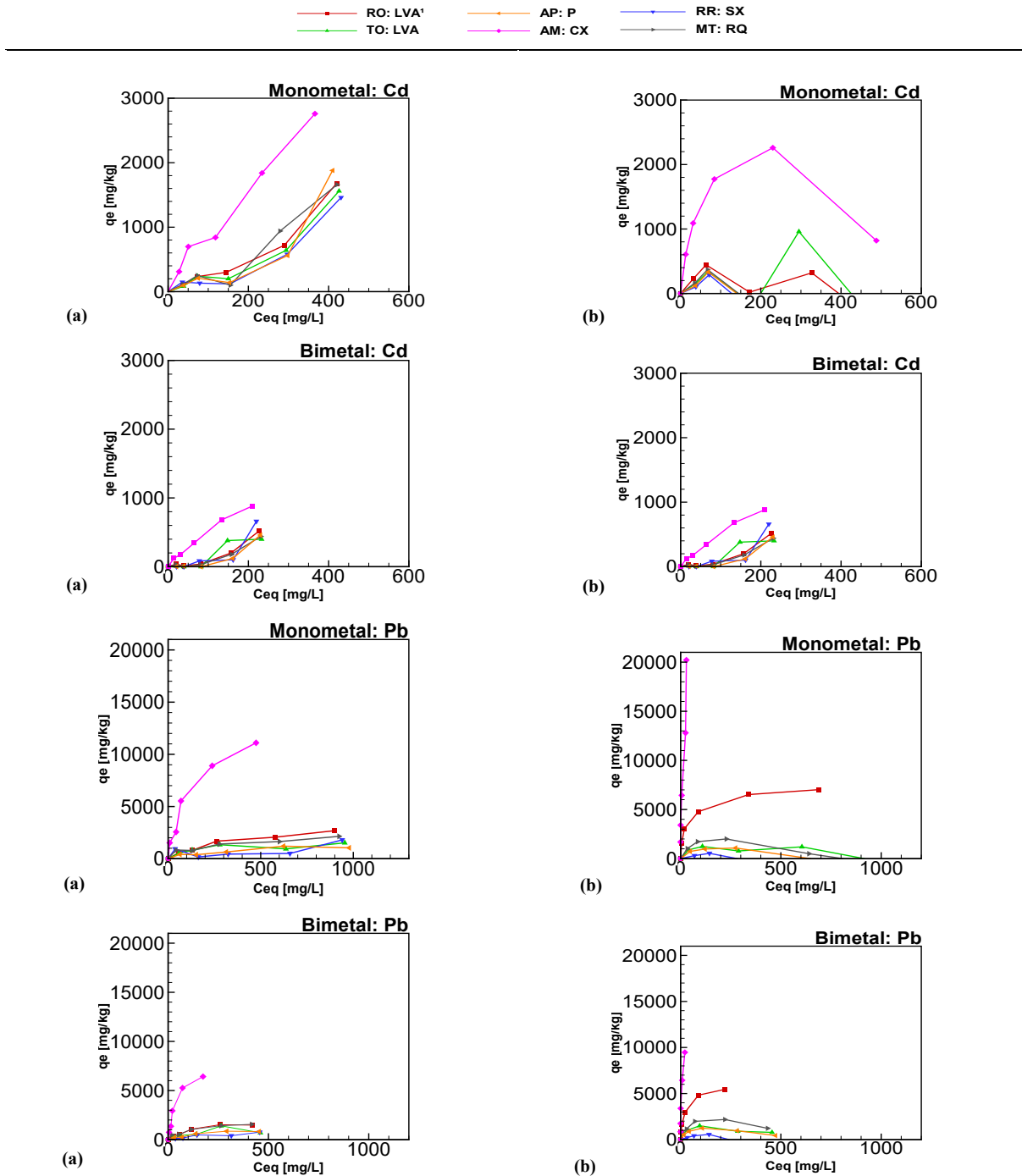


Figure 1. Sorption curves for Cd and Pb in monometal and bimetal Solutions for soils with natural organic matter content (a) and for soils with residual organic matter content (b).

The assorted curves found for the soils in tests (a) revealed that, although the solutions of Cd and Pb were applied in different concentrations, the sorption of Pb was superior to that of Cd in all soils, both for non-competitive systems (monometal) and competitive systems (bimetal).

Pierangeli et al. (2007), when studying the sorption of Pb and Cd in Red-Yellow Latosols in the state of Minas Gerais,

observed that in both types of soil, Cd was less absorbed than Pb, indicating that Pb has more affinity for colloids than soil in relation to Cd in mono and bimetal systems.

This fact can be attributed to the element Cd being retained, mainly, in the sites of cationic exchange of the soil, being readily exchangeable for elements with greater affinity for the soil matrix, as is the case of Pb (Pierangeli et al., 2007).

The lead (Pb) demonstrated to have more affinity for CX (AM) and LVA¹ (RO) in relation to other soils. This fact is attributed to the high content of organic matter in these soils, in particular the CX (AM), with 82.9% organic carbon, followed by 17% for the LVA¹ (RO) soil.

Croué et al. (2003) affirm that humic or wet substances have a significant influence on the complexation of nutrients and metals, since these substances generate a negative net electrical charge, originated from the dissociation of H⁺ ions from certain organic functional groups, such as carboxylics and phenolics. Campos (2010) states that this dissociation is favored under *pH* conditions above 6.

Regarding the assortment curves found for the soils of the tests (b), a significant increase in the sorption of the elements Cd and Pb was noted, this increase being more accentuated in the mono and bimetal solutions of Pb.

The sorption curve of the Cd mono and bimetal solution for CX (AM) showed a decrease in the last applied dosage, suggesting saturation of the sorption sites, causing a decrease in metal retention. Except for CX (AM), the other curves showed sorption values alternating between positive and negative values.

These negative values can be justified by analytical errors during the tests, although they show the same pattern of decline. Unlike what was observed for the tests (a), the absence of organic matter significantly increased the sorption of the metals Cd and Pb, mainly for the mono and bimetal solutions of Pb. Therefore, this change is attributed to the absence of organic matter. of behavior in the sorption curves.

Like the results found for this research, Weber et al. (2009) studied the sorption of a certain insecticide in the organic and mineral fractions of an Oxisol, verifying an increase in the sorption of the insecticide by the soil with residual content of organic matter compared to natural soil. They also verified an increase in the *pH* of the soil from 5.43 (natural soil) to 6.51 (soil with residual organic matter).

Stevenson (1994) justifies that this fact is due to the influence of the mineral fraction of the soil on the *pH*, as well as to the absence of acid groups of the organic matter, which was oxidized. As a result, there is no coverage of the mineral fraction exchange sites and, therefore, the exposure area of these sorted sites is increased, as also concluded by Weber et al. (2009).

Thus, it is believed that the increase in metal retention, especially for LVA¹ (RO) and CX (AM) soils in Pb mono and bimetal solutions, was the result of 2 (two) combined processes: (i) increase the surface area of the mineral fraction, previously covered by organic matter; and (ii) increase in soil *pH*.

3.4 Desorption tests

The desorption tests for soils with natural organic matter content revealed that, in general, there were higher percentages of desorption for the Cd element compared to

the percentages of desorption of the Pb element. Therefore, it is suggested the Cd absorbed to the colloids of the soil by means of external or non-specific sphere connections (less energetic connections) and, therefore, be more easily desorbed when compared to the element Pb.

Regarding the desorption tests for soils with residual organic matter content, a decrease was observed in the percentages desorbed from Cd and Pb, suggesting that the increase in soil *pH* combined with the increase in the available mineral fraction (previously covered by the matter organic) have retained the metal more strongly in the sorption stage, with more energetic bonds and, therefore, more difficult to be reversed, reducing its desorption.

3.5 Selection of sorption models

Regarding the tests for soils with natural organic matter content, for most cases, the Linear isotherm was the one that showed the best adjustment to the experimental data, for both systems (mono and bimetal). Regarding the tests for the Pb element, the Langmuir, Freundlich and Linear models obtained good adjustments, depending on the type of soil. The CX (AM) showed the highest *Q_o* value, confirming that this is the soil with the highest sorting capacity for both elements and systems. Regarding the tests for soils with residual organic matter content for the element Cd, it was not possible to adjust the experimental data to any of the studied isotherms. As for the Pb element, it was observed that the LVA¹ (RO) soil obtained a good fit for the Langmuir model, followed by the CX (AM) soil, with good adjustments to the Linear Model, showing a high value for *K_d*, confirming that this is the soil with greater sorting capacity.

4. Conclusions

For soils with a natural organic matter content, organic carbon was the attribute with the dominant influence on the assortment and desorption procedures.

For soils with residual organic matter content, the increase in the surface area of the mineral fraction was dominant in the metal retention process, mainly for Pb.

Greater Cd desorption was observed for soils with natural organic matter content and, therefore, greater mobility in soils and greater potential for environmental risk.

There was a sort of prevalent prevalence of the soil by the Pb element, both in competitive and non-competitive systems, indicating that this metal may have less potential for environmental contamination.

Langmuir, Freundlich and Linear isotherms were more suitable to evaluate the adsorption of Cd and Pb, especially Linear models.

The removal of organic material caused a significant increase in the retention of metals, showing a high affinity between Cd and Pb for the oxides present in the mineral

fraction of soils in the North of the country, especially in the Legal Amazon.

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Declaration of interest

The authors have no conflicts of interest to declare. All co-authors have observed and affirmed the contents of the paper and there is no financial interest to report.

Authors' contributions

Nicolay Silva Rocha: conceptualization, data curation, visualization, writing – original draft, review & editing, formal analysis, investigation, methodology, project administration, resources, software. Claudio Fernando Mahler: conceptualization, data curation, methodology, supervision, validation, funding acquisition, writing – review & editing.

Data availability

Data generated and analyzed during the current study are available in the M.Sc. Dissertation of Nicolay Silva Rocha, which has been published by the Civil Engineering Department, Federal University of Rio de Janeiro. All data produced or examined in the current study are included in this article.

List of symbols

pH	Hydrogen potential
q_e	Represents the amount of metal absorbed into the soil particles (mg / kg)
AP	Amapá State
AM	Amazonas State
BET	Brunauer-emmett-teller
C_o	Means the initial concentration of the metal (mg / L)
C_{eq}	Represents the concentration of metal in the equilibrium solution (mg / L)
CTC	Cation exchange capacity
K_d	Distribution coefficient
MT	Mato Grosso State
M_{soil}	Indicates the soil mass soil (kg)
Q_o	Maximum sorption capacity

RO	Rondônia State
RR	Roraima State
TFSA	Air-dried fine earth
TO	Tocantins State
$Volsol$	indicates the volume of the metal source solution (L)

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