COPPER AND CADMIUM BIOAVAILABILITY IN SOILS OF BAIXADA MARANHENSE

BIODISPONIBILIDADE DE COBRE E CÁDMIO EM SOLOS DA BAIXADA MARANHENSE

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ABSTRACT
The Maranhão lowlands present a diversified amount of wild animals, insects, and plants. The population has a food source based mostly on fishing, family farming, cattle, and buffalo farming. In this context, it is essential to investigate the anthropic impacts present in this environment. This work aims to verify the bioavailability in the adsorption of the potentially toxic metals Cu²⁺ and Cd²⁺ in natural and anthropized soils of the Maranhão lowlands. Soil samples were collected from two phytogeographic zones in Maranhão, the Cajari, and Viana municipalities. Determinations of organic matter, organic carbon, pH, PCZ, and quantification of the adsorbed metals in soil samples were carried out. The results showed that the pH and zero charge point (ZPC) parameters produced effects on the studied metal ions' adsorption capacity. The elements Cu²⁺ and Cd²⁺ described the adsorption favorably, with Cu²⁺ having greater adsorption capacity and bioavailability.

KEYWORDS: Metals; Physicochemical Parameters; Adsorption; Anthropic Impacts.

RESUMO
A baixada maranhense apresenta quantidade diversificada de animais silvestres, insetos e plantas. A população tem como fonte de alimentos, alericada em grande parte, pela pesca, agricultura familiar, criação de gados e bubalinos. Nesse contexto, é fundamental investigar os impactos antrópicos presentes nesse ambiente. O objetivo deste trabalho é verificar a biodisponibilidade na adsorção dos metais potencialmente tóxicos Cu²⁺ e Cd²⁺ em solos naturais e antropizados da baixada maranhense. Foram coletadas amostras de solos proveniente de duas zonas fitogeográficas do estado do Maranhão, os municípios Cajari e Viana. Foram realizadas determinações de matéria orgânica, carbono orgânico, pH, PCZ e a quantificação dos metais adsorvidos nas amostras de solo. Os resultados mostraram que os parâmetros de pH e ponto de carga zero (PCZ) produziram efeitos na capacidade de adsorção dos íons metálicos estudados. Os elementos Cu²⁺ e Cd²⁺ descreveram favoravelmente a adsorção, sendo o Cu²⁺ com maior capacidade de adsorção e biodisponibilidade.

PALAVRAS-CHAVE: Metais; Parâmetros Físico-químicos; Adsorção; Impactos Antrópicos.

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INTRODUCTION

Soils contaminated by potentially toxic metals (MPT) are among the main challenges for humanity. These toxic elements are linked to weathering processes, volcanism, soil formation or are deposited in the environment through anthropic actions such as mining activities, improper deposition of waste, or uncontrolled waste distribution. Related to this, On the planet, for every four people, there is one death from contaminated environments associated with air pollution, soil, and water contamination, resulting in approximately 12.6 million deaths. In this context, children and the elderly are the most affected individuals with values between 1.7 and 4.9 million deaths, respectively (LI et al., 2017; CUI et al., 2018).

Zhao (2020) describes that in situ, remediation activities can provide better quality to cadmium-contaminated soils. However, to obtain these results, the verification of the capacity of adsorption of metal ions, mobility, and bioavailability are critical factors for understanding the interaction between soil, metals, and plants. Copper also has a relevant function in nature, considering that it is an essential micronutrient for plants. However, if available in quantities above average, it can be an element with a high toxicity level.

The interpretation of bioavailability is a fundamental mechanism to analyze the effects of toxicity of toxic elements. Biological, physical chemical factors, compounds, and ions are among the main parameters that influence bioavailability. These conditions depend on the atomic structure of the metallic elements, systematically described by the periodic table. (IUPAC, 2002).

Among the factors that influence bioavailability, organic matter is composed of properties basically of humic substances originated through chemical, enzymatic degradation, and synthetic action of microorganisms, which assist in the adsorption and complexation of metal ions, also establish in changes in their chemical properties caused by immobilization and reduction phenomena, that is, organic matter influences adsorption due to the formation of complex, soluble and insoluble substances, between humic substances and the element (SOUSA et al., 2015).

According to Costa-Neto (2001), the Baixada Maranhense fields, located in the state of Maranhão, serve as grazing areas for cattle and buffalo from July to December, a period of less frequent rains in the country. The Baixada Maranhense expresses ecological, economic, and social values because of the significant number of active citizens economically focused on exploiting resources associated mainly with flooded fields (FILHO, 2006). Therefore, this work aims to evaluate Copper and Cadmium's bioavailability in representative soils of Baixada Maranhense.

MATERIALS AND METHODS

The soils collected for analysis come from two phytogeographic regions belonging to Maranhão, located in the Cajari and Viana Municipalities. The samples were collected and stored in the laboratory according to methods addressed by Camargo et al. (2009). The replicas are the 12 areas, each of which represents the sampling unit. There are 6 areas for each municipality, 3 of them in areas with a good state of conservation and 3 in areas with visible anthropic impacts, including erosive currents caused by water and wind (the consequence of the suppression of vegetation cover), inadequate garbage deposition, domestic effluents and disposal of materials composed of toxic elements and pasture plantation for cattle and buffalo breeding. The distance between the investigated areas corresponds to approximately 2 km. They have chosen anthropized areas according to anthropic impacts resulting from the examples mentioned above.
The soil samples were transferred to a tray and subsequently air-dried. After this process, followed by decompression and crushing of this material, they were fractionated with 0.35 mm sieves and subdivided into a polyethylene flask. In the metals analysis, the samples were dried in an oven at 60°±1°C within 24 hours. Weighed the soil samples on a digital analytical scale after preparation and treatment. Then, we made pH determinations in H₂O and KCl with pH meter, percentage of organic matter, organic carbon, and zero charge point. The analyzes were performed in triplicate.

The method for determining the Zero Charge Point (ZCP) was carried out according to Regalbuto (2004). The procedure consisted of the composition of 50 mg of biomass with 50 ml of the aqueous solution under different conditions of initial pH (1, 2, 3, 4, 5, 6, 8, 9, 10, 11, and 12) followed by the determination of pH after 24 hours of equilibrium. In the acidic and basic range of pH solutions, dilutions of HCl 1 mol L⁻¹ and NaOH 1 mol L⁻¹ were used, respectively.

Standard solutions of increasing concentrations of CdCl₂ and a standard solution of CaCl₂ 0.01 mol L⁻¹ were prepared. The metallic species' standard solutions were prepared to obtain a soil ratio: 1:30 solution. The initial concentrations of the respective metallic species in the equilibration solution were 2.5; 5; 10; 14; 22; 30; 40 mg L⁻¹. Aliquots of 1,000 g of soil were weighed and sieved at 2 mm in conical flasks, then added 20 mL of the 0.01 mol L⁻¹ CaCl₂ solution.

All samples were subjected to constant stirring at 200 rpm for 24 hours. After this interval, 10 mL of the metal's standard solutions under analysis were added to the samples. The samples were subjected to constant agitation on an orbital shaker, model TE-140, at 200 rpm for the next 24 hours. After the stirring time, the filtered supernatant was filtered through a 0.45 mm filter membrane; the filtrate was packed in a dark-colored plastic bottle and kept under refrigeration until the moment of quantification of the metallic species. The quantification in the metal in the filtered solution was made using the Atomic Absorption Spectrometer by flame atomization (FAAS), brand VARIAN-model Spectra AA / 55 the wavelength of the specific metal. All samples were taken in triplicate.

Statistical treatments

The data obtained for the adsorption capacity were subjected to the statistical analysis of variance as a function of the solutions' concentrations. The averages of the adsorption capacities obtained in the different concentrations of the metallic species were compared by the Tukey test at 5% probability using software version 7.7 Beta 2015, as instructed by Silva; Azevedo (2002) and Viana et al. (2012).

RESULTS AND DISCUSSION

Physicochemical analysis

The data presented in Tables 1 and 2 are the values for organic carbon, organic material, pH in H₂O, and KCl and ΔpH for the municipalities of Cajari and Viana, respectively. Table 1 shows that the levels of organic carbon and organic matter in soils from natural areas were higher in Viana's municipality. In contrast, higher concentrations of organic carbon stock and organic material in anthropized environments were identified in the municipality of Cajari. Comparing the natural and anthropized areas, it is observed that the levels of organic carbon and organic matter were higher in areas with soil in a natural environment. The soil of the municipality of Cajari showed a percentage of 5.41 % higher organic carbon in a natural environment compared
to the anthropized environment. For Viana's municipality, the difference was even more significant, with 124.39 % higher organic carbon in a natural environment than the anthropized environment.

About organic material, the natural environment of Cajari obtained 5.51 % higher than the levels of organic matter in the anthropized environment. For Viana, the organic material content was 127.14 % higher in the natural environment. The higher percentages of organic matter in natural environments indicate a greater tendency for copper and cadmium complexation than anthropized environments. A set of physicochemical phenomena influences metals' adsorption; therefore, analyzing only the content of organic carbon and organic material is not sure about the adsorption of metal ions, being essential to a more significant number of works that can contribute to this line research.

Gastalho et al. (2009) state that pH values between 3.5 to 5.0 are considered very acid, and values between 5.0 to 6.5 give the soil an acid character. The anthropized soil showed values close to natural soil results in pH both in H2O and KCl. ΔpH is a chemical analysis parameter used to determine the predominance of negative or positive soil charges. In electropositive soils, there is a predominance of positive charges over negative ones; otherwise, there is a predominance of negative charges. The results in Table 2 related to the municipality of Cajari in an anthropized environment, and the values in table 1 for both Cajari and Viana in a natural environment under pH showed that all values were higher than the values obtained for pH. This can be attributed to the fact that when the pH value is not always measured in water, it can only have total acidity, due to the protons and aluminum forms attached to the exchange complex.

Generally, the interchangeable acidity resulting from fixed protons in ion-exchange complexes is likely to move after the exchange of neutral salts (KCl). The buffering capacity limits the pH variations by the continuous exchange between the soil and the soil solution, thus obtaining the pH. These measurements usually give pH values lower than the pH measurements. The pH overestimates the sample, and the pH underestimates it, which, in this case, for the city of Viana in an anthropized area, the pH value in KCl was slightly higher than the pH value in water. All ΔpH values are found according to the relationship ΔpH = pH - pH.

The difference (ΔpH) can be more significant than one pH unit. The ΔpH values are used to obtain an estimate of the net soil load. Except for Viana's municipality, ΔpH showed positive values (pH < pH), indicating a predominance of positive charge on the soil surface and adsorb more anions than cations; on the other hand, Viana soil demonstrated the ability to attract cations.

Starting from the principle of Kiekens (1983), there is less solubility of metals in the pH range between 4 and 6 due to the formation of insoluble and sulfide complexes. In comparison to the results obtained, the pH range described in Tables 1 and 2 indicate that the metals studied showed low solubility; in addition, the values also show that the metals Cu and Cd did not have high mobility, as the increase in pH reduces the mobility of potentially toxic elements (SOUZA et al., 2015).

<table>
<thead>
<tr>
<th>Municipios</th>
<th>C.O (g/dm³)</th>
<th>M.O (g/dm³)</th>
<th>pH H2O</th>
<th>pH KCl</th>
<th>ΔpH</th>
</tr>
</thead>
</table>


<table>
<thead>
<tr>
<th>Municípios</th>
<th>C.O (g/dm$^3$)</th>
<th>M.O (g/dm$^3$)</th>
<th>pH$_{H_2O}$</th>
<th>pH$_{KCl}$</th>
<th>ΔpH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAJARI</td>
<td>77,90</td>
<td>134,40</td>
<td>5,41</td>
<td>5,39</td>
<td>0,02</td>
</tr>
<tr>
<td>VIANA</td>
<td>92,40</td>
<td>159,40</td>
<td>5,99</td>
<td>5,98</td>
<td>0,01</td>
</tr>
</tbody>
</table>

Table 1. Physical-chemical characterization of natural soil.

C.O = Organic carbon; M.O = Organic matter; pH$_{H_2O}$ = pH in water; pH$_{KCl}$ = pH in Potassium Chloride; ΔpH = pH$_{H_2O}$ − pH$_{KCl}$ = variation between pH in water and pH in Potassium Chloride.

Table 2. Physicochemical characterization of anthropized soil

<table>
<thead>
<tr>
<th>Municípios</th>
<th>C.O (g/dm$^3$)</th>
<th>M.O (g/dm$^3$)</th>
<th>pH$_{H_2O}$</th>
<th>pH$_{KCl}$</th>
<th>ΔpH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAJARI</td>
<td>73,50</td>
<td>127,00</td>
<td>5,52</td>
<td>5,29</td>
<td>0,23</td>
</tr>
<tr>
<td>VIANA</td>
<td>40,72</td>
<td>70,30</td>
<td>5,74</td>
<td>5,75</td>
<td>-0,01</td>
</tr>
</tbody>
</table>

C.O = Organic carbon; M.O = Organic matter; pH$_{H_2O}$ = pH in water; pH$_{KCl}$ = pH in Potassium Chloride; ΔpH = pH$_{H_2O}$ − pH$_{KCl}$ = variation between pH in water and pH in Potassium Chloride.

Zero Load Potential (ZPC)

The soil may contain a balance of positive, negative, or zero electrical charges. When the balance is null, it is called Zero Charge Point (ZPC). Parks and Bruyn (1962) define ZPC as a pH value that integrates a reversible double layer zero systems established by a value resulting from the potential determining ions in the solid phase. At this point, the values of positive and negative charges are equal. Several factors can influence the results of a ZPC analysis, such as organic matter, organic carbon, iron oxide, and soil pH. Figures 1 and 2 shows the ZPC values of anthropic and natural areas in Cajari and Viana's municipalities. Nascimento et al. (2014) describe that the adsorbent in aqueous solution can adsorb OH$^-$ or H$^+$ ions, considering that each particle's surface charge depends on the pH of the solution. Comparing the values of each area under study and taking into account that Cu and Cd are cations, the adsorption will be favorable when the solution's pH is greater than the zero charge potential.

The results for the anthropic and natural areas studied indicate a pH$_{KCl}$ below the soil pH indicated in Figures 1 and 2. This shows a soil with a predominance of positive charges, making it possible to say that such areas have anion retention capacity. However, this phenomenon differs from the others when related to soil samples collected in Viana, in which the natural area (Figure 2) obtained a zero charge point equal to 6.1 with a predominance of negative charges that point to a greater cation exchange capacity; this result shows that the investigated metals are in exchangeable form. The remaining values assume a range of 4.3 to 4.8, which makes it possible to distinguish a range, where below these values, we have positive charges, and above them, we will have negative charges.
The statistical comparisons are shown in Tables 3 and 4 shows the concentrations of metal ions in soil samples for each added dose of the adsorbate. According to table 3, in the soil samples collected in the municipality of Cajari, there were no significant differences between the areas in Cu concentrations, except in dosages 14 and 30. In Cd concentrations, there were substantial differences in all dosages added. In Table 4, in the city of Viana, in both natural and human-made environments, there were no differences in low concentrations of dosages from 2.5 to 10. However, in dosage 14 of Table 4, there were significant differences between areas and metallic species studied. Therefore, it is inferred that in the evaluated environments, the soil has adsorption capacity influenced by the physical-chemical characteristics, mainly related to pH and...
the potential of zero charges in the interaction of surface charges in natural environments and environments with anthropic influence. These factors contribute to the mobility of, Cu²⁺ and, Cd²⁺ in SBM, which can be accelerated in field conditions by the preferential flow of the solution in the profile and the formation of complexes of organic metal binders that are easily transported in the environment. Under very acidic conditions, the concentration of copper and cadmium ions in soluble form can be extremely toxic to fish and plants. By absorption by plants, metallic species can acquire levels harmful to human and animal health through their consumption. It is noteworthy that these elements are bioaccumulative; that is, they accumulate in living organisms present in flooded fields and can reach irreversible toxic levels.

**Table 3.** Statistical comparison of the Cu (II) and Cd (II) adsorption capacity of the Cajari soil in natural and anthropized areas at different dosages

<table>
<thead>
<tr>
<th>Area</th>
<th>Dosage added (mg L⁻¹)</th>
<th>2,5</th>
<th>5</th>
<th>10</th>
<th>14</th>
<th>22</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>Cu</td>
<td>0,74 aG</td>
<td>1,47 aF</td>
<td>2,95 aE</td>
<td>4,11 aD</td>
<td>6,46 aC</td>
<td>7,55 bB</td>
<td>10,25 aA</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0,45 cG</td>
<td>1,41 bF</td>
<td>2,94 aE</td>
<td>3,20 dD</td>
<td>5,41 cC</td>
<td>5,72 dB</td>
<td>8,91 cA</td>
</tr>
<tr>
<td>Anthropized</td>
<td>Cu</td>
<td>0,73 aG</td>
<td>1,47 aF</td>
<td>2,97 aE</td>
<td>3,79 bD</td>
<td>6,48 aC</td>
<td>7,76 aB</td>
<td>10,23aA</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0,60 bG</td>
<td>1,14 cF</td>
<td>2,72 bE</td>
<td>3,39 cD</td>
<td>6,10 bC</td>
<td>6,91 cB</td>
<td>9,35 bA</td>
</tr>
</tbody>
</table>

The averages followed by the same lowercase letter in the column and uppercase in the row do not differ statistically. The Tukey test was applied at the level of 5% probability.

**Table 4.** Statistical comparison of the adsorption capacity (Qe) of Cu (II) and Cd (II) of Viana soil in a natural and anthropized area at different dosages.

<table>
<thead>
<tr>
<th>Area</th>
<th>Dosage added (mg L⁻¹)</th>
<th>2,5</th>
<th>5</th>
<th>10</th>
<th>14</th>
<th>22</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>Cu</td>
<td>0,74 aG</td>
<td>1,48 fA</td>
<td>2,98 aD</td>
<td>2,73 dE</td>
<td>6,29 aC</td>
<td>7,63 bB</td>
<td>11,19 bA</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0,60 bF</td>
<td>1,16 bE</td>
<td>2,90 cD</td>
<td>3,61 bC</td>
<td>6,12 bB</td>
<td>6,11 bD</td>
<td>9,17 dA</td>
</tr>
<tr>
<td>Anthropized</td>
<td>Cu</td>
<td>0,75 aG</td>
<td>1,50 fA</td>
<td>2,93 bE</td>
<td>4,19 aD</td>
<td>6,11 bC</td>
<td>8,42 bA</td>
<td>11,77 aA</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0,59 bG</td>
<td>1,16 bF</td>
<td>2,72 dE</td>
<td>3,48 cD</td>
<td>6,11 bC</td>
<td>6,91 bC</td>
<td>9,42 cA</td>
</tr>
</tbody>
</table>

The averages followed by the same lowercase letter in the column and uppercase in the row do not differ statistically. The Tukey test was applied at the level of 5% probability.

**Adsorption study**

The graphical relationship between the concentration of ions adsorbed by the solid phase and cadmium and copper concentration in the Ce equilibrium solution is called the adsorption isotherm. The shape of the isotherms, especially their initial inclination, is convenient to describe the chemical speciation behavior, as well as MINTEQA2 (ALLISON et al., 1990). The experimental results are linked to the adjustment of models that present information related to...
the ability to retain the element and the force in which the metal is retained in the soil. The retention of molecules identified on the surface of the material as well as the degree to which these molecules are accentuated and characterized in the study of adsorption generally occurs at the analyte interfaces (QFL 0406 IQ-USP).

The verification of Cu (II) and Cd (II) adsorption can be observed according to the isotherms in the investigated soils' competitive system. Figures 3 and 4 shows the adsorption isotherms in soils obtained from Cajari and Viana in natural and anthropized environments. According to Souza and collaborators (2015), among the characteristics that indicate the bioavailability of metals in the environment, these elements are adsorption to the material represented by fine particles.

In most curves, a lower level of inclination was observed, particularly in the initial part of the isotherms. All dosages of adsorbed copper and cadmium increased due to the increase in the doses that were added. Also, the competitiveness between the metals under study exerted a more significant effect on the ionic composition in the adsorption of ions in the material's particles.

The values indicated in the graphs below show that in this competitive system between the adsorption of metals in the soil. However, the two elements showed an increase in adsorption; copper is considered a favorable element for adsorption than cadmium; this means that copper is a metal with better performance related to bioavailability specifically in this system. Identified this observation in all areas studied in the two municipalities of Baixada Maranhense.

Figure 3. Cu (II) and Cd (II) adsorption isotherm in the competitive system for Cajari soil in a natural and anthropized environment
**Figure 4.** Cu (II) and Cd (II) adsorption isotherm in the competitive system for Viana soil in a natural and anthropized environment

**CONCLUSIONS**

The results obtained showed that the physical-chemical parameters influenced the adsorption of the studied metals. The zero charge potential proved to be an essential parameter for understanding the adsorption process of metallic species, since the investigated soil presented a predominance of positive charges, indicating that the areas have anion retention capacity. The elements Cu and Cd were favorable to adsorption and showed high bioavailability in natural and anthropized environments. However, between the two metallic species under study, it was found that Cu + described adsorption better and consequently obtained a higher bioavailability index.

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