Sorption studies of Cd and Cu on Brazilian alluvial soils

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ABSTRACT

The Local Production Arrangement, located in the Pernambuco’s Agreste state, has been significantly developing the region's economy. Despite its importance, industrial activity has caused relevant environmental concerns regarding the disposal of textile effluents, especially from industrial laundries. This waste is made up of many chemicals, and among them are various types of heavy metals. The evaluation of the sorption behavior of contaminant transport mechanisms such as heavy metals is essential to assess the risk of contamination of alluvial aquifers. This study evaluated the sorption of heavy metals (Cu and Cd) in an alluvial sediment deposit in the Capibaribe River. Kinetics and isotherm experiments allowed the analyses of Cu and Cd sorption. Kinetics sorption showed an equilibrium tendency after 16 h for Cu and 18 h for Cd and was better described by a pseudo-second order model. The isotherm data were adjusted to the Linear, Freundlich and Langmuir models. Both linear and Freundlich models satisfactorily described sorption isotherms for the two pollutants. The metals in the study represent a risk of contamination of the groundwater of alluvial aquifers, mainly due to physicochemical attributes of the soil, such as high sand content (85%), low MO (2.1 g kg-1) and alkaline pH (8.2). The environmental conditions decrease absorption and facilitate metal mobility, greatly increasing the environmental risks inherent in pollutant leaching. Cu showed a higher affinity with the soil studied in all assays performed compared with the results of the tests for Cd.

Keywords: heavy metals, isotherm, kinetics.

Estudo de sorção de Cd and Cu em solos aluviais Brasileiros

RESUMO

O Arranjo Produtivo Local localizado no Agreste de Pernambuco vem desenvolvendo significativamente a economia da região. Apesar da sua importância, a atividade industrial traz preocupações ambientais relevantes no que diz respeito à eliminação de efluentes têxteis,
principalmente das lavanderias industriais. Esses resíduos são compostos por diversos produtos químicos e, entre eles, vários tipos de metais pesados. A avaliação do comportamento de sorção de mecanismos de transporte de contaminantes como metais pesados é essencial para avaliar o risco de contaminação de aquíferos aluviais. Este estudo avaliou a sorção de metais pesados (Cu e Cd) em um depósito de sedimento aluvial no rio Capibaribe. Experimentos cinéticos e isotérmicos permitiram as análises de sorção de Cu e Cd. A cinética de sorção mostrou uma tendência de equilíbrio após 16h para Cu e 18h para Cd e foi melhor descrita por um modelo de pseudo-segunda ordem. Os dados de isoterma foram ajustados aos modelos Linear, Freundlich e Langmuir. Os modelos linear e de Freundlich descreveram satisfatoriamente as isotermas de sorção para os dois poluentes. Os metais em estudo representam risco de contaminação das águas subterrâneas de aquíferos aluviais, principalmente devido aos atributos físico-químicos do solo, como alto teor de areia (85%), baixa MO (2,1 g kg⁻¹) e pH alcalino (8,2 ). As condições ambientais diminuem a absorção e facilitam a mobilidade do metal, aumentando muito os riscos ambientais inerentes à lixiviação de poluentes. O Cu apresentou maior afinidade com o solo estudado em todos os ensaios realizados em comparação com os resultados dos ensaios para o Cd.

Palavras-chave: cinética, isoterma, metais pesados.

1. INTRODUCTION

Recently, heavy metal (HM) environmental contamination has become critical on a global scale. The deposition of HM in the soil has caused considerable concern about its environmental impacts and human health, especially regarding the consumption of contaminated water resources (Cerqueira et al., 2011; Shokr et al., 2016). Nowadays, the increasing pollution of water resources has been a major environmental problem. Potentially toxic metals may enter the environment from many sources, including metal enrichment, mining, automotive emissions, industrial emissions, fertilizers, pesticides, industrial effluent dyes, wastewater irrigation, and sewage sludge (Lu and Gibb, 2008; Tahervand and Jalali, 2017; Kanbar and Kaouk, 2019; Rechberger et al., 2019).

Part of the northeast region of Brazil stands out as the second largest textile-manufacturing hub in the country (Alexandre et al., 2020). Pernambuco’s Agreste (Brazil) has an important local production arrangement of clothing factories, conferring over 1200 production units in more than 10 municipalities (Sebrae, 2013). This region has also historically suffered from prolonged droughts and low rainwater storage capacity (Montenegro and Ragab, 2012). Thus, one of the main alternatives for water supply is the exploitation of intermittent dry-bed alluvial aquifers (Usman et al., 2015). Besides being a source of water supply, alluvial aquifers are also used for the indiscriminate disposal of wastewater without treatment by industrial laundries and dry cleaners. This can create a considerable environmental problem, as the release of textile effluents is pointed to be one of the main ways of heavy metal entry such as Cd and Cu into the environment. (Ali et al., 2009; Shehzadi et al., 2014).

Regarding the toxicity in human health, Cd and Cu are among the most problematic HMs, making it important to study the fate of these HMs in fundamental alluvial formations for the preservation of water resources and public health. The consumption of water contaminated with Cu can lead to problems such as liver cirrhosis, kidney damage and intoxication. Cd poisoning can lead to kidney failure and chronic anemia (NRC, 2000; Genchi et al., 2020). The World Health Organization (WHO) has recommended a maximum acceptable Cu concentration of 0.05 mg L⁻¹ and Cd of 0.005 mg L⁻¹ in drinking water. However, a small dose from them may have negative effects (Abdellaoui et al., 2019).

The fate of HMs in the environment is related to their mobility in soil. Mobilization or
leaching potential, in turn, occurs as a function of the complex interactions (for example sorption and desorption) between HMs and the environmental matrix. These interactions depend on the chemical state of the metal and the physicochemical properties of the soil, such as pH, redox potential, soil colloids, mineralogy, cation exchange capacity, ionic strength, particle size, and organic matter content (Du et al., 2018; Shaheen et al., 2018; Fariña et al., 2018; Kanbar and Kaouk, 2019).

The use of sorption isotherm to describe sorption phenomena is essential for the correlation between its parameters and the physicochemical attributes of the soil (Covelo et al., 2007). Generally, HM sorption can minimize mobility in soil, but with the saturation of sorption sites, it can decrease the binding energy, facilitating mobility and increasing the risk of contamination (Cerqueira et al., 2011). The soil-water partition coefficient (KD) represents the mobility of solute; this parameter represents the distribution of the chemical between the liquid phase and the solid surface, being a reference parameter in sorption, becoming a prerequisite important for risk assessment of water-table contamination (Plavolic et al., 2018).

This work therefore evaluates the mobility of the heavy metals Cu and Cd in an alluvial deposit typical of the High Capibaribe, in Pernambuco’s Agreste. This work also assessed the sorption dynamics of these pollutants using kinetic and isotherm sorption experiments.

2. MATERIALS AND METHODS

2.1. Study area

The soil used in this research belongs to the most superficial layer of an alluvial sediment deposit of the Capibaribe Basin. The collection site of the study is located in the macrozone of Alto Capibaribe, in the division between the Pernambuco municipalities of Santa Cruz do Capibaribe and Brejo da Madre de Deus (Figure 1), with the geographic coordinates 7º56’57,6” S e 36º17’57,2” W. The Capibaribe riverbed at the collection site is dry during dry seasons. In contrast, the alluvial aquifer is widely exploited as a source of groundwater resources. The region has an average rainfall of 600 mm/year and a potential evapotranspiration of 1900 mm/year. The climatic conditions are semiarid and the native vegetation cover is Caatinga (Braga et al., 2015). Geologically the study area is located over the Borborema Province with crystalline rocky features and fissural domain hydrogeology (Beltrão et al., 2005).

Figure 1. Study area sites. 
Source: Rabelo et al. (2021)
2.2. Soil Physical-Chemical Characteristics

The physicochemical attributes of the soil are presented in Table 1. The Zero Charge Point (ZPC) was obtained by Alexandre et al. (2020) and others presented in the Table 1 were determined by Rabelo et al. (2021).

Table 1. Physicochemical attributes of the soil.

<table>
<thead>
<tr>
<th>Soil classif.</th>
<th>SS</th>
<th>pH in water</th>
<th>ZPC</th>
<th>BS</th>
<th>CEC</th>
<th>OM</th>
<th>OC</th>
<th>V2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loamy sand</td>
<td>3.75</td>
<td>8.26</td>
<td>5.02</td>
<td>7</td>
<td>7.4</td>
<td>2.17</td>
<td>1.26</td>
<td>94</td>
</tr>
</tbody>
</table>

Oxides

<table>
<thead>
<tr>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Sr</th>
<th>Ti</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>V</th>
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<tbody>
<tr>
<td>231</td>
<td>13897</td>
<td>9</td>
<td>25</td>
<td>32</td>
<td>409</td>
<td>2356</td>
<td>7112</td>
<td>64760</td>
<td>384913</td>
<td>28185</td>
<td>7367</td>
<td>66</td>
</tr>
<tr>
<td>±</td>
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<tr>
<td>29</td>
<td>445</td>
<td>4.9</td>
<td>7</td>
<td>12</td>
<td>6</td>
<td>93</td>
<td>981</td>
<td>1852</td>
<td>11468</td>
<td>633</td>
<td>927</td>
<td>12</td>
</tr>
</tbody>
</table>

SS: Specific Surface; ZPC: Zero Charge Point; BS: Sum of Bases; CEC: Cation Exchange Capacity; OM: organic matter; OC: organic carbon; V2: Base saturation, calculated as the ratio between effective CEC and total CEC.

The studied soil is 82% sand and 11% clay, respectively. Despite the low percentage of clay (7%) and OM (2.17 g kg\(^{-1}\)), the soil presented average values of cation exchange capacity (7.0 cmol\(_e\) dm\(^{-3}\)). Soil CEC values indicate average cation retention (Kalubi et al., 2017). The soil presents pH in water (8.26) greater than ZPC (5.02). The ZPC represents the pH value of the environment when the matrix shows zero surface charge. The low OM, clay and moderately alkaline pH values (8.26) favor the low sorption of cations increasing the risk of groundwater contamination.

2.3. Sorption Kinetics

The sorption kinetics assay consisted of stirring mixtures between the soil and the solutions with the studied solutes. In each flask (amber type), 5 g of soil and 50 mL of the contaminant solution (soil:solution ratio of 1:10 m/v) were added (Elbana et al., 2018). This solution was prepared with a CaCl\(_2\) (purity ≥ 99%) support electrolyte at a concentration of 0.01 mol L\(^{-1}\), aiming to avoid the precipitation of metals in the solutions. The concentration for Cd (Cadmium Nitrate - Cd(NO\(_3\))\(_2\).4H\(_2\)O) was 60 mg L\(^{-1}\) (Linhares et al., 2009) and for the Cu (Copper Nitrate - Cu(NO\(_3\))\(_2\).3H\(_2\)O) was 100 mg L\(^{-1}\) (Linhares et al., 2010; Xing et al., 2018). Other studies with a similar theme also used heavy metals in the form of nitrate (Yang et al., 2017).

The flasks were stirred on a shaker test table at 200 rpm, as per Freitas et al. (2017), at the following time intervals: 0 h (solutions were manually shaken to ensure the interaction between sediment and solution), 1 h, 2 h, 4 h, 8 h, 10 h, 12 h, 16 h, 24 h, 36 h and 48 h. To read Cu and Cd concentration in the samples, the Agilent Atomic Absorption Spectrometry (AAS) apparatus was used, following the manufacturer's recommendations for wavelength and calibration curve (Agilent, 2017). In order to ensure the accuracy of the results, three parallel experiments were conducted for each stirring time.

Two kinetic models were used to adjust the experimental data, the pseudo-first order models and the pseudo-second order model (Ho e Mckay, 1999). The pseudo-first order model assumes that the sorption rate is directly proportional to the difference between equilibrium concentration and solid-phase concentration over time (Equation 1), whereas the pseudo-second
order model assumes that the adsorption indices are proportional to the square of this difference (Equation 2). This difference is called the driving force of adsorption (Febrianto et al., 2009).

The integrated pseudo-first order model is represented by applying the limits t=0 to t=t and \( S_t = S_0 \) to \( S_t = S_t \), by Equation 2 (Ho and Mckay, 1999; Yaneva and Koumanova, 2006):

\[
\frac{dS_t}{dt} = k_1(S_{e1} - S_t) \tag{1}
\]

\[
\log(S_{e1} - S_t) = \log S_{e1} - \frac{k_1}{2.303} t \tag{2}
\]

Where in, \( S_{e1} \) and \( S_t \) represent the equilibrium sorption capacities in time, represented by t, for the first-order model and \( k_1 \) is the constant first-order sorption rate.

For the pseudo-second order model, applying the same limits for integration, we have the Equations 3 and 4 (Ho and Mckay, 1999; Yaneva and Koumanova, 2006):

\[
\frac{dS_t}{dt} = k_2(S_{e2} - S_t)^2 \tag{3}
\]

\[
\frac{1}{S_{e2} - S_t} = \frac{1}{S_{e2}} + k_2 t \tag{4}
\]

Where in, \( S_{e2} \) and \( S_t \) represent the equilibrium sorption capacities in time, represented by t and \( k_2 \) is the constant second-order sorption rate.

After adjusting for these two models, a statistical analysis was performed to determine which of these models best fit the data. This analysis was based on four statistical criteria: Mean Square Error (MSE), Deviation Ratio (DR), Modeling Efficiency (ME), and Residual Mass Coefficient (RMC). Besides these, the determination factor (R²) will also be analyzed. The equations of these parameters are shown below (Equations 5, 6, 7 and 8):

\[
MSE = \left( \frac{\sum_{i=1}^{N} (T_i - M_i)^2}{N} \right) \frac{1}{M} \cdot 100 \tag{5}
\]

\[
DR = \frac{\sum_{i=1}^{N} (M_i - \bar{M})^2}{\sum_{i=1}^{N} (T_i - M_i)^2} \tag{6}
\]

\[
ME = \frac{\sum_{i=1}^{N} (M_i - \bar{M}) - \sum_{i=1}^{N} (T_i - M_i)^2}{\sum_{i=1}^{N} (M_i - M)^2} \tag{7}
\]

\[
RMC = \frac{\sum_{i=1}^{N} M_i - \sum_{i=1}^{N} T_i}{\sum_{i=1}^{N} M_i} \tag{8}
\]

Where in, \( T_i \) is the values calculated by the model, \( M_i \) is the experimental values, \( M \) is the average of the experimental values and \( N \) is the number of determinations.

The DR describes the dispersion ratio of the values calculated by the theoretical model, and it tends to one. In the absence of systematic deviations between the theoretical and experimental values, the RMC tends to zero. It indicates whether the model tends to overestimate or underestimate, with negative or positive RMC values, respectively. The MSE indicates the deviation degree between the experimental determinations and the values calculated by the theoretical model. Its expected value tends to zero. The ME indicates whether the theoretical model provides a better estimation of the experimental determinations than the mean value of these determinations, and its value tends to one (Rabelo et al., 2021).
2.4. Sorption Isotherms

The concentrations chosen for this part of the study were: 0; 10; 20; 40; 60; 80; 100; 120 mg L\(^{-1}\) for the Cu (Copper Nitrate - Cu(NO\(_3\))\(_2\).3H\(_2\)O) and 0; 10; 20; 30; 40; 50; 60; 80 mg L\(^{-1}\) for the Cd (Cadmium Nitrate - Cd(NO\(_3\))\(_2\).4H\(_2\)O). The sediment-solution ratio was 1:10, i.e., 5 g of sediment and 50 mL and was prepared in triplicate to ensure accuracy of the results.

The solutions were transferred through a graduated burette pellet to 50 mL amber glasses sealed with black phenolic screw caps with a PTFE-faced rubber liner. The samples were shaken at 200 rpm on a shaker table for 24 h, which corresponds to the equilibration time established by sorption kinetics for the two pollutants. After stirring, 1 mL aliquots of the supernatant were collected in triplicate for each of the three parallel experiments of the sediment sample. In order to read Cu and Cd concentration in the samples, the Agilent Atomic Absorption Spectrometry (AAS) apparatus was used, following the manufacturer’s recommendations for wavelength and calibration curve (Agilent, 2017).

Readings were also taken by atomic absorption spectrometry. Thus, it was possible to determine the concentration sorbed by the soil through Equation 9 below.

\[
S = (C_o - C_e) \cdot FD
\]

Where in, \(S\) is the concentration sorbed by the soil, \(C_o\) is the initial concentration of the contaminant placed in contact with the soil, \(C_e\) is the concentration of the contaminant after equilibrium and FD is the soil-solution ratio.

After this step, the values of the sorbed concentrations were adjusted by the Freundlich and Langmuir linear model, using the computer software SigmaPlot Version 11.

Langmuir's model is based on the hypothesis that the interaction forces between the adsorbed molecules are negligible and that each void site can be occupied by only one molecule. Freundlich’s model considers heterogeneous solid and exponential distribution to characterize the various types of adsorption sites, in which one has different adsorptive energies (Xiang et al., 2018). The expressions of these models are represented in Equations 10, 11 and 12 below.

**Linear:**
\[
S = K_D C_e
\]

**Langmuir:**
\[
S = \frac{K_L q_m C_e}{1 + K_L C_e}
\]

**Freundlich:**
\[
S = K_F C_e^{1/n}
\]

Where in, \(S\) is the amount of metal adsorbed in mg kg\(^{-1}\) from the soil, \(K_D\) is the soil-solution partition coefficient, \(C_e\) is the concentration of metal in the equilibrium solution in mg L\(^{-1}\), \(q_m\) is the maximum adsorption capacity in mg kg\(^{-1}\), \(K_L\) is the constant related to the binding energy in mg L\(^{-1}\) from the metal in the soil, \(K_F\) is the Freundlich adsorption coefficient in mg kg\(^{-1}\) and \(n\) is a dimensionless parameter (indicates the affinity of the soil for the solute) (Sodrê et al., 2001; Linhares et al., 2010).

3. RESULTS AND DISCUSSION

3.1. Sorption Kinetics

At all stages of testing, the pH of the solutions was kept between 5.0 and 6.0. The sorption kinetics of Cu and Cd, as well as the respective adjusted curves of the pseudo-first order and pseudo-second order models, are represented in Figure 2. The parameters concerning the adjustments of pseudo-first order and pseudo-second order models are displayed in Table 2.
Sorption studies of Cd and Cu on…

Figure 2. The sorption kinetics for the Cu (A) and Cd (B).

Table 2. Equilibrium sorption capacity values and Statistical Parameters for pseudo-first and pseudo-second orders fitted models.

<table>
<thead>
<tr>
<th>Model</th>
<th>$S_e$ (mg kg$^{-1}$)</th>
<th>$k_1$ (h$^{-1}$)</th>
<th>$k_2$ (kg kg$^{-1}$h$^{-1}$)</th>
<th>$R^2$</th>
<th>MSE</th>
<th>DR</th>
<th>ME</th>
<th>RMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Pseudo-first order</td>
<td>86.56</td>
<td>0.738</td>
<td>0.970</td>
<td>6.319</td>
<td>0.836</td>
<td>0.977</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second order</td>
<td>86.96</td>
<td>0.008</td>
<td>0.996</td>
<td>10.837</td>
<td>1.124</td>
<td>0.934</td>
<td>-0.013</td>
</tr>
<tr>
<td>Cd</td>
<td>Pseudo-first order</td>
<td>10.92</td>
<td>0.233</td>
<td>0.991</td>
<td>3.299</td>
<td>1.099</td>
<td>0.991</td>
<td>-0.002</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second order</td>
<td>14.99</td>
<td>0.049</td>
<td>0.999</td>
<td>9.061</td>
<td>0.844</td>
<td>0.935</td>
<td>-0.003</td>
</tr>
</tbody>
</table>

The sorption equilibrium time was determined by sorption kinetics assays. This time was approximately 16 h for Cu and 18 h for Cd. In the first case, the value adsorbed by the soil was of the order of 83 mg kg$^{-1}$ and 14 mg kg$^{-1}$ in the second case. Regarding the equilibrium time, the results are in accordance with those presented by Mellis and Rodella (2008), in a study that included an adsorption of metals Cu and Cd in an untreated Latosol treated with sewage sludge, in which the authors concluded that the stirring time of 24 h is the most appropriate time to obtain the real adsorption of the metal for both cases. Other studies also used this value (Mattos et al., 2016; Fangjie et al., 2017). These results indicate that Cu has a greater potential to be absorbed, that is, less mobility than Cd. Cu, on the other hand, has a high capacity to interact chemically with the organic and mineral components of the soil (Linhares et al., 2010). Several studies confirm a higher sorption of Cu metal than Cd metal in different soils by the method of Batch and column study (Fonseca et al., 2011; Mouni et al., 2017; Kim and Hyun, 2017; Elbana et al., 2018; Lin and Xu, 2020). The aspects related to the interactions of both metals with the soil are better understood from the isothermal study.

From the statistical data shown in Table 2, the two models showed good adjustments to the experimental data for both pollutants. $R^2$ values for all cases were close to the unit, with the pseudo-second order model being higher. The values of the MSE parameters indicate a better fit of the model when they tend to zero, this trend was observed for the pseudo-first order model for both pollutants. Yet the values of ME and DR indicate better adjustment when they tend to be close to unity; considering the ME, this trend was observed for both pollutants. Considering the DR, for copper the best model was the second order, for Cd the best model was first order. Analyzing the RMC results, the pseudo-second order model overestimated in both pollutants and the pseudo-first order model overestimated only in the case of Cd.

The values of the equilibrium sorption capacities reaffirm the higher affinity of Cu sorption with the studied soil type, since for the two adjusted models the values of $S_{e1}$ and $S_{e2}$ were higher. The difference in soil sorption capacity between Cu and Cd is explained by the presence of organic matter in the study soil layer. Cerqueira et al. (2011) evaluated, in a study with different soils, that organic matter is the main component of the soil that retains Cu. Elbana et al. (2018) also demonstrated, in a study with varied soils, that Cu is more strongly retained by...
factors such as CEC and organic matter compared to Cd.

Bogusz et al. (2019), in a study to evaluate the effect of biochar on soil adsorption capacity, confirmed that the pseudo-second order model best describes the kinetic behavior of these contaminants, obtaining a coefficient of determination of 1.000 for Cu and of 0.998 for Cd. Other studies also report a good fit of the pseudo-second order model to the experimental data of metal adsorption kinetics in soils (Mishra et al., 2017; Umeh et al., 2021). Hence, on the basis of better fitting of experimental data in the pseudo-second order kinetic model, the main adsorption mechanism is probably a chemisorption reaction that may be the rate-limiting step (Kumar et al., 2010; Mishra et al., 2017; Abdus-salam and Adekola, 2018).

Thus, the time chosen for the isotherm agitation was 24 hours.

3.2. Sorption Isotherms

In Figure 3 are displayed the Cu and Cd sorption isotherms and their adjustments for the linear, Freundlich and Langmuir models. The parameter values found in the adjustments made are shown in Table 3.

![Figure 3. Adjustments for the Linear Model, of Langmuir and Freundlich for Cu (A) and Cd (B) sorption isotherms.](image)

**Table 3.** Sorption parameters adjusted for sorption isotherms.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Cu</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>K_D (L kg^{-1})</td>
<td>0.8593</td>
<td>0.7674</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.988</td>
<td>0.932</td>
</tr>
<tr>
<td>Freundlich</td>
<td>K_F (kg^{-1} mg^{1-1/n} L^{1/n})</td>
<td>1.45</td>
<td>1.356</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.991</td>
<td>0.987</td>
</tr>
<tr>
<td>Langmuir</td>
<td>K_L (L mg^{-1})</td>
<td>0.0027</td>
<td>0.0236</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.987</td>
<td>0.979</td>
</tr>
</tbody>
</table>

The data of Table 3 infers that the linear isotherm adjustment was satisfactory for Cu (R^2 = 0.9882), but it was not satisfactory for Cd (R^2 = 0.9321). The values of K_D were 0.8593 L kg^{-1} for Cu and 0.7674 L kg^{-1} for Cd. The Langmuir model presented a good adjustment (R^2 = 0.987 for Cu and R^2 = 0.979 for Cd) and the values of K_L were close to zero (K_L = 0.0027 L mg^{-1} for Cu and K_L = 0.0236 L mg^{-1} for Cd). Bogusz et al. (2019) performed adjustments according to the Langmuir and Freundlich models for Cu and Cd isotherms and observed, for the Langmuir model, K_L = 0.0103 L mg^{-1} (R^2 = 0.977) for Cu and K_L = 0.0036 L mg^{-1} (R^2 = 0.564) for Cd. Finally, Freundlich model best adjusts the experimental data for both Cu (R^2 = 0.991) and Cd (R^2 = 0.987). By the distribution of the experimental points obtained for the two cases (Figure 3), it is noted that there was no
equilibrium of the sorption sites, only a trend in the highest concentration points, especially in the Cd isotherm.

The absence of a level in the isotherms indicates, for the analyzed concentration range, that the saturation of the surface has not been reached (Linhares et al., 2008). It is important to highlight that, even with the satisfactory performance of the Freundlich and Langmuir models to describe the experimental isotherms ($R^2 > 0.95$), both models suffered considerable deviations to higher concentrations, especially in Cd isotherms.

By the distribution of the experimental points obtained for the two cases, it is noted that there was no equilibrium of the sorption sites, only a trend in the highest concentration points, especially in the Cd isotherm. This fact indicates that isotherms are adjusted in the Freundlich model better, as this model considers that sorption sites have not yet been fully depleted. This result is in accord with the results found by Pierangeli et al. (2009) for Cd. It may also be said that Freundlich's model adjusts better for Cu than Cd data.

Waleeittikul et al. (2019), in the investigation of the effect of salinity levels in the Cd sorption in sandy loam soils, observed that, for all salinity levels, the sorption was well explained by the Freundlich isotherm. Similarly, this isothermal model fit the adsorption characteristics for Zn, Cd, Cu and Pb, alone or as a mixture, in different soils classified as loam, clay, silty clay and clay (Mouni et al., 2017). From the validation of this model to describe the sorption isotherms of both metals in the soil, considerations can be made. First, the Freundlich isotherm is a function of two parameters, $K_F$ and exponent $1/n$. $K_F$ is positively related to the metal sorption capacity of soils (Elbana et al., 2018; Lin and Xu, 2020). The values found for the parameter were $1.45$ kg-1 mg-1−1/n L1/n and $1.356$ kg-1 mg-1-1/n L1/n, respectively for Cu and Cd, and indicate that Cu has a higher retention potential in this soil than Cd. The values obtained for $n$ were $1.135$ for Cu and $1.253$ for Cd. The value obtained for Cu is closer to the unit, indicating an approximation for a linear-type isotherm.

The data of Table 3, is inferred that the Langmuir model graphically presented a good adjustment ($R^2 = 0.987$ for Cu and $R^2 = 0.979$ for Cd). The values of $K_L$ were close to zero ($K_L = 0.0027$ L mg-1 for Cu and $K_L = 0.0236$ L mg-1 for Cd). Values of the same order of magnitude were also found by Linhares et al. (2008), that found a value of 0.0053 L mg-1. Values close to zero indicate that the model does not apply to the measured data or has no physical significance. The adsorption behavior of the tested systems does not follow the assumption on which Langmuir's approach is based (Kiurski et al., 2011). Other papers also found values of the same order of magnitude for the Langmuir model adjustments (Kiurski et al., 2012; Amosa et al., 2016; Potgieter et al., 2018).

Bogusz et al. (2019) performed adjustments according to the Langmuir and Freundlich models for Cu and Cd isotherms. Observing the Langmuir values, the authors obtained a $K_L = 0.01$ L mg-1 for Cu and $K_L = 0.0036$ L mg-1 for Cd, which indicates that the binding energy between sandy soils and these metals is low, that is, sorption is not difficult to reverse.

The analysis of soil characteristics to understand the aspects involved in the adsorption process is of fundamental importance. For example, Lin and Xu (2020) observed that loam with high OC and CEC exhibited strong sorption for Cd and Zn. Gonçalves et al. (2013), in a study of Cu adsorption in a Brazilian clay soil, point out that the high content of clay, organic matter and CEC in this soil were factors that favored the adsorption process. Elbana et al. (2018) found that soils with high organic matter and soils with high CEC and pH exhibited strong sorption for Pb, Cu, Cd, Zn and Ni, while sandy soils with low CEC showed the lowest sorption for all metals analyzed. Regarding organic content, Defo et al. (2016) found a strong influence of organic matter in the retention of Pb and Cd in soils in a tropical urban watershed. Considering characteristics such as low clay content (7%), low OM (2.17 gg-1) and median CEC value (7.4 cmolc.dm-3), it is possible to infer that the analyzed soil does not present favorable conditions for a considerable retention of both metals in the soil, being indicative of high mobility and low retention.
Mishra et al. (2017), studying Cu sorption isotherms, found, for a red soil with CEC conditions similar to the soil sample of this work, a value of $K_F$ equal to $1.71 \text{ L mg}^{-1}$, which resembles the value found of $1.45 \text{ kg L}^{-1} \text{ mg}^{-1}$ for adjusting the Freundlich model.

Oliveira et al. (2010), performing the linear adjustment for the Cd sorption isotherms, for a soil-like Eutroferric Red Nitosol of content such as studied in this paper (79% of sand) and with a CEC of 3.43, obtained values close to those shown in Table 3 ($K_D = 0.4304 \text{ L kg}^{-1}$ and $R^2 = 0.8566$). This difference may be explained by the high soil CEC studied in this work, which is a critical intervening factor for Cd adsorption, where Cerqueira et al. (2011) showed that the correlation between these parameters is 0.833, greater than the correlation with the particle-size content, which is 0.732.

Regarding the influence of the pH of the solution, Umeh et al. (2021) observed that the level of Cd$^{2+}$ removal increases with increase in pH. Rezaei et al. (2021) observed that soils with higher pH values showed greater Cd sorption capacity than acidic soils. Lin and Xu (2020) observed that sandy loam with high pH exhibited strong sorption for Cu. According to Yang et al. (2017), at higher pH more specific adsorption with strong selectivity and irreversibility may occur. Under acidic conditions, electrostatic repulsion occurs on the bonding location of the adsorbent site (Umeh et al., 2021) and, with the increase in pH, there is a decrease by competition between hydrogen and metal ions for the surface sites (Abdus-salam and Adekola, 2018). Additionally, for higher pH values more negatively charged surface becomes available (Abdus-salam and Adekola, 2018), a condition that favors the exchange of cationic compounds (Nomanbhay and Palanisamy, 2005), such as Cu and Cd. In this study, the pH value is moderately high (8.26) and higher than the ZPC (5.02), a condition for the occurrence of the negative surface load of the soil (Bachratá et al., 2013), being, therefore, a configuration that benefits the retention of the metals in the analyzed soil.

From the adjustments of the Freundlich and Langmuir models, it may be inferred that most models adjusted the experimental data for both Cu and Cd. All adjustments suffered considerable deviations to higher concentrations, especially in Cd isotherms.

### 4. CONCLUSION

This work evaluated the mobility of heavy metals Cu and Cd in an alluvial soil of the Capibaribe River, in northeastern Brazil. The study consisted of kinetic tests, with adjustments to the pseudo-first and pseudo-second order model, and sorption isotherms, with adjustments to the Linear, Freundlich and Langmuir models.

Although both models describe the sorption kinetics satisfactorily, the Cu and Cd sorption kinetics were best described by a pseudo-second order model, which indicates a slow sorption for the analyzed soil. On the other hand, both linear and Freundlich models satisfactorily described sorption isotherms for the two pollutants. The Langmuir model presented $K_l$ values close to zero, having no physical significance.

It is noted by the distribution of the experimental points of sorption isotherms, that there was no equilibrium of the sorption sites, only a trend in the highest concentration points, especially in the Cd isotherm, i.e., the saturation of the surface has not been reached.

The results indicated that Cu has more affinity with this type of soil. This fact represents that Cu was more retained by the soil, while Cd is more mobile.

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6. REFERENCES


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