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Copper and zinc adsorption in tropical soils

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A B S TR A C T

Copper and zinc are essential elements acting in the biochemical processes of plants and animals, however, the knowledge of the mobility and retention of these ions at the presence of other competitive metals, in different soils, is essential to predict their fate in the soil system and evaluate a possible contamination of surface and groundwater. Thus, the objective of this study was to evaluate the adsorption isotherms of copper and zinc in mono- and multi-component systems, for the tropical soils Oxisol, Inceptisol and Entisol Quartzipsamment. The evaluated isotherm models were Langmuir, Freündlich, multi-component Langmuir and multi-component Freündlich. The initial concentrations of the evaluated and accompanying ions were 10, 15, 30, 40 and 50 mg L^{-1}, and the Gibbs free energy and separation factor were determined. Copper was the most adsorbed ion by the porous medium in a mono-component system and the least adsorbed was the zinc in a multi-component system. The best-fit isotherm model was Freündlich for mono-component systems and Langmuir for multi-component systems. The Incentisol showed higher adsorption capacity, favoring the reduction of ion leaching, which leads to the attenuation of groundwater contamination, which may allow the application of copper and zinc-based wastewater or fertilizers to be a viable alternative for this soil. On the other hand, Entisol Quartzipsamment showed lower ion adsorption capacity and consequently greater ion leaching potential.

Keywords: Sorption isotherms; Competitive adsorption; Freündlich and Langmuir models; Leaching; Groundwater contamination.

Adsorção de cobre e zinco em solos tropicais

R E S U M O

O cobre e o zinco são elementos essenciais que atuam nos processos bioquímicos das plantas e animais, no entanto, o conhecimento da mobilidade e da retenção destes íons na presença de outros metais competitivos, em diferentes solos, é essencial para prever o destino e avaliar uma possível contaminação das águas superficiais e subterrâneas. Assim, objetivou-se avaliar as isotermas de adsorção de cobre e zinco em sistemas mono e multicomponentes nos solos tropicais: Latossolo Vermelho, Cambissolo Háplico, e Neossolo Quartzarênico. Os modelos de isotermas utilizados foram de Langmuir, Freündlich, Langmuir multicomponente e Freündlich multicomponente. As concentrações iniciais do íon avaliado e acompanhante foram de 10, 15, 30, 40 e 50 mg L^{-1}, além de determinada a energia livre de Gibbs e o fator de separação. O cobre foi o íon mais adsorvido pelo meio poroso em um sistema monocomponente e o menos adsorvido foi o zinco em um sistema multicomponente. O modelo de isoterma com melhor ajuste foi o de Freündlich para os sistemas monocomponentes e Langmuir para os multicomponentes. O Cambissolo apresentou maior capacidade de adsorção, favorecendo a redução da lixiviação de íons, o que leva à atenuação da contaminação das águas subterrâneas. Isto pode permitir que a aplicação de águas residuárias ou fertilizantes à base de cobre e zinco seja uma alternativa viável para este solo. Já o Neossolo apresentou menor capacidade de adsorção de íons e consequentemente maior potencialidade de lixiviação de íons.

Palavras-chave: Isotermas de adsorção; Adsorção competitiva; Modelos de Freündlich e Langmuir; Lixiviação; Contaminação de águas subterrâneas.

Introduction

Copper and zinc are essential elements for both animals and plants, as they act in their biochemical processes (Paulino et al., 2006). Their origin can be natural or anthropic, in which the concentration varies according to the source material of the soil, and the presence of organic or chemical fertilizers. In addition, these ions can be found in pig wastewater, which can be used to meet crops water and nutritional demand (Jensen et al., 2016; Zeng et al., 2021).

Knowledge about the characteristics related to the mobility and retention of these metal cations in the soil is especially relevant, as they can be toxic to crops and humans (Alloway, 2013; Hodson, 2013). From these studies, it is possible to carry out soil management in an appropriate way to ensure its fertility, yield, and quality of crops, in addition to enabling the recovery of polluted soils (Brand, 2004; Zhu et al., 2012; Huang, et al., 2014). There is also a possible impact on the quality of surface and groundwater when the maximum adsorption capacity of the porous medium is exceeded by the concentration of metals in the soil (Gonçalves, 2013).

In this context, one of the main processes responsible for the fate of metals in the soil is adsorption and desorption, since the mobility of metal ions is directly related to their partition between the solid phase and the soil solution (Burakov et al., 2018; Padilla et al., 2023). The metals adsorption capacity by porous media depends on the properties and characteristics of the soil, such as the presence of adsorption sites on the solid surface of the clay colloid, cation exchange capacity, pH of the soil solution, redox potential, organic matter content, carbonates, metal phosphates, silicates and metal oxides and hydroxides (Renu and Singh, 2017).

In this process, conditions such as metal concentration, contact time between adsorbate and adsorbent and ionic potential can influence the adsorption behavior of metals (Strawn, 2021), and metals of lower ionic potential, adsorbed at the soil surface electrical charges, can be displaced by metals of higher ionic potential (Kummer et al., 2018).

From this perspective, research on the adsorption of metal ions has been carried out, using equilibrium-based models, with Freündlich and Langmuir isotherms frequently being used (Arias et al., 2005; Abat et al., 2012; Huang et al., 2014; Lima, 2013; Lemke de Castro et al., 2015; Moreira and Alleoni, 2010; Paulino et al., 2006; Zhu et al., 2012).

However, many evaluations of ion adsorption in solution have been conducted focusing on the study of a single target metal. This is a relevant consideration due to the soil solution being made up of ions that compete for adsorption sites, increasing their mobility (Padilla et al., 2023). Thus, the understanding of the competitive adsorption of metal ions is essential, since the overall research developed, in most cases, has not focused on the discussion about the mechanisms of interaction of multi-component adsorption processes (Cherono et al., 2021).

Therefore, the objective of this study was to evaluate the adsorption isotherms of copper and zinc in mono and multi-component systems, in three tropical soils with distinct physical, chemical, and mineralogical characteristics.

Materials and methods

The analyses were carried out at the Universidade Federal de Lavras, in the Water Analysis Laboratory of the Department of Water Resources. For the determination of adsorption isotherms, Oxisol (O), Inceptisol (I) and Entisol Quartzipsamment (E) based on soil taxonomy were used at a depth of 0 to 40 cm. Those soils are not submitted to agricultural activities. In the Table 1, Table 2 and Figure 1 are the physical, chemical, and mineralogical analyses.

Table1. Soil types used in the sorption tests and their respective textures and locations.

Soil type	Location (City and Coordinates)	Textural classification	Texture (%)		
			Sand	Silt	Clay
Oxisol	Lavras – MG - Brazil (21° 13.9' S 44° 57.9' O)	Very clayey	13	26	61
Inceptisol	Lavras – MG - Brazil (21° 13.8' S 44° 59.2' O)	Clayey	37	30	33
Entisol Quartzipsamment	Itumirim – MG - Brazil (21° 21.7' S 44° 52.4' O)	Sandy	78	9	13

Source: Terra Planta Ltda – Soil analysis laboratory (2020).

Table 2. Chemical analysis of the soils used in the adsorption tests.

Variable	Oxisol	Inceptisol	Entisol Quartzipsamment
P	0.48	1.56	1.76
K	58.00	26.00	20.00
Ca	0.89	3.44	0.26
Mg	0.24	0.37	0.07
Al	0.33	0.00	0.50
H+Al	4.41	2.50	2.61
$CEC_{pH=7}$	5.68	6.37	2.99
T	9.31	19.30	23.00
SB	1.27	3.88	0.38
t	1.60	3.88	0.88
m	20.61	0.00	56.50
v	22.37	60.81	12.87
OM	2.90	1.57	0.72
Cu	3.10	0.10	1.10
Zn	0.90	2.80	3.50

P, K: Mehlich extractor (mg/dm³); Ca, Mg, Al: Extrator KCl IN ($cmol_c/dm^3$); H + Al: SMP Extrator ($cmol_c/dm^3$); CEC at pH 7.0: (Sb + H + Al) (cmolc/dm³); T: clay activity ($cmol_c/kg$); Sb: Sum of Exchangeable Bases (Ca + Mg + K), ($cmol_c/dm^3$); t: effective CEC ($cmol_c/dm^3$); m: aluminum saturation (%); v: bases saturation of CEC at 7.0 pH (100.S/T) (%); OM: organic matter by oxidation with sodium bichromate + sulfuric acid (dag/kg); Cu, Zn: Mehlich extractor (mg/dm³).
Source: Terra Planta Ltda – Soil analysis laboratory (2020)

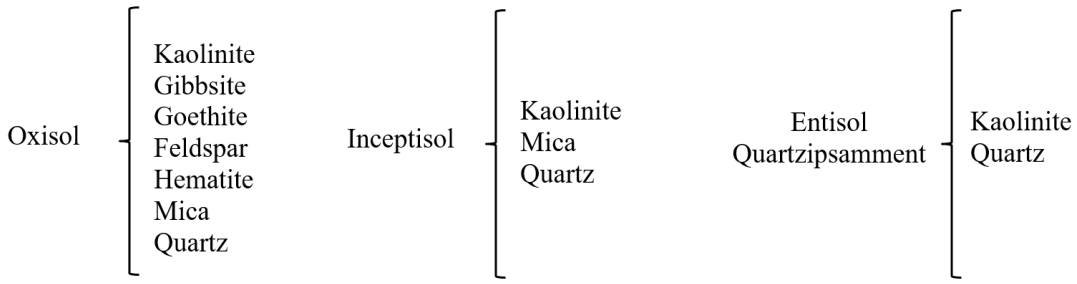

Figure 1. Minerals present in the clay fraction of the soils used in the sorption tests.

In this experiment, the solutions of Copper Sulfate Pentahydrate P.A. A.C.S. ($CuSO_4.5H_20$), Zinc Sulfate Heptahydrate for analysis P.A. A.C.S. ($ZnSO_4.7H_2O$), and mixed solution of these were used. For the latter, the same concentration for both ions in the equilibrium adsorption essays were added. Moreover, Batch method was used, and all experimental procedures were conducted at a constant temperature of 20 °C.

The models used for the estimation of the mono- and multi-component adsorption equilibrium were Freündlich and Langmuir. The Freündlich isotherm for the evaluation of a single ion in solution are shown in Equation 1.

$$S = K_f . C_{eq}^N \quad (1)$$

In which S is the mass of sorbed solute per unit mass of the solid phase of the adsorbing soil (mg kg^{-1}), C_{eq} is the equilibrium concentration of the adsorbate in the soil solution (mg L^{-1}), K_f is the Freündlich partition coefficient (L kg^{-1}), which is related to the capacity that the soil has to adsorb the solute, and N is the Freündlich exponential coefficient (dimensionless), equivalent to the inverse of the Freündlich constant, i.e., to 1/n.

The Langmuir isotherm mathematical model for systems containing only one ion can be calculated by Equation 2.

$$S = \frac{K_L . b . C_{eq}}{1 + K_L . C_{eq}} \quad (2)$$

The sorbed mass of solute per unit mass of the adsorbent solid phase (mg kg^{-1}) is given by S. K_L is the affinity constant between adsorbate and adsorbent (L mg^{-1}), b is the maximum adsorption capacity (mg kg^{-1}), and C_{eq} is the equilibrium concentration of the solute in the soil solution (mg L^{-1}). The separation factor R_L for classifying the type of the isotherms was determined using the Equation 3.

$$R_L = \frac{1}{1 + K_L . C_0} \quad (3)$$

In which K_L is the Langmuir coefficient (L mg^{-1}), and C_0 is the initial concentration (mg L^{-1}). For the standard Gibbs free energy of adsorption (ΔG^0_{ad} in kJ.mol^{-1}), from the Langmuir constant (K_L in L mol^{-1}), can be calculated by the Equation 4.

$$\Delta G^0_{ad} = -R . T . \ln K_L \quad (4)$$

R is the universal gas constant ($8.314.10^{-3}$ kJ K^{-1} mol^{-1}), and T is the temperature (293 K). The Freündlich isotherm for ion evaluation in a multi-component system is shown in Equation 5.

$$S_1 = K_{F1} . C_{eq1} \left(C_{eq1} + a_{1,2} . C_{eq2}\right)^{N_1 - 1} \quad (5)$$

In which S_1 is the mass of the sorbed target metal per unit mass of the solid phase of the adsorbing soil (mg kg^{-1}), K_{F1} is the Freündlich partition coefficient of the target metal (L kg^{-1}), C_{eq1} and C_{eq2} are the equilibrium concentrations of the target metal and the competitive metal (mg L^{-1}), n is the Freündlich adsorption capacity constant (dimensionless) and $a_{1,2}$ is a competition coefficient between the evaluated ions. This coefficient can be determined, according to Vidal et al. (2009), by Equations 6 and 7.

$$\beta_1 = \left(\frac{K_{F1} . C_{eq1}}{S_1}\right)^{\frac{1}{1 - N_1}} \quad (6)$$

$$C_{eq1} = -a_{1,2} . C_{eq2} + \beta_1 \quad (7)$$

For these calculations it was initially used the K_F and n values estimated for the mono-component system. Then, these were recalculated for the Freündlich equation for multi-component system applying a regression tool. The competitive multi-component Langmuir isotherm as shown in Equation 8 (Markham and Benton, 1931).

$$S_1 = \frac{K_{L1} . b_1 . C_{eq1}}{1 + K_{L1} . C_{eq1} + K_{L2} . C_{eq2}} \quad (8)$$

In which S is the sorbed mass of solute per unit mass of the adsorbent solid phase (mg kg^{-1}) of the target ion, K_{L1} and K_{L2} are the Langmuir constant for the target and competitive metal (L mg^{-1}), b_1 is the maximum adsorption capacity of the target metal (mg kg^{-1}) and C_{eq1} and C_{eq2} are the equilibrium concentration of the solute in the soil solution (mg L^{-1}) of the target and competitive metal, respectively. The variables were obtained by the mono-component Langmuir model.

For the isotherm essay, 2 g of air-dried sieved soil (2 mm mesh) and 20 mL of the ion solutions were placed in a refrigerated incubator shaker for a contact time of 24 hours, with initial concentrations of 10, 15, 30, 40 and 50 mg L^{-1}. The samples were homogenized, acidified with 1% nitric acid (volume/volume), stirred at a constant temperature of 20 °C, and centrifuged.

Then, the samples were filtered and the ions in the solution were quantified using an Atomic Absorption Spectrophotometer (AAS), according to the Standard Methods for the Examination of Water and Wastewater 3111 B - direct air-acetylene flame method (APHA, 2017). The concentration of the solute adsorbed by the porous media was determined by Equation 9.

$$S = \left(C_o - C_{eq}\right) . \frac{V}{m} \quad (9)$$

In which S is the solute concentration adsorbed to the porous media (mg kg^{-1}), C_0 is the initial solute concentration in the solution (mg L^{-1}), C_{eq} is the equilibrium concentration (mg L^{-1}), V is the volume of solution used (L), and m is the mass of soil (kg).

The adsorption isotherms experiment was conducted in an entirely randomized design in a 3 x 4 factorial scheme, the variation sources being soil (three levels: Inceptisol, Oxisol and Entisol Quartzipsamment) and adsorbate (Cu in mono-component solution, Zn in mono-component solution, Cu in multi-component solution with Zn,

and Zn in multi-component solution with Cu), with three repetitions.

For adjustment of the models to the observed data, the Solver package of Microsoft Excel 365® was used, by the method of minimizing the sum of the square of the deviations between the observed and simulated data for adsorbed solute through the GRG Nonlinear Solving method. The statistical indicators: root mean square error - RMSE (Equation 10), residual mass coefficient - RMC (Equation 11) and the coefficient of determination (R^2) were also calculated, in addition to the F-test (Equation 12), from which the best fit was observed.

$$\mathrm{RMSE} = \left[\frac{1}{\mathrm{N}}.\sum_{\mathrm{i=1}}^{\mathrm{N}}\left(\mathrm{S_{obs,i}} - \mathrm{S_{est,i}}\right)^2\right]^{\frac{1}{2}} \quad (10)$$

$$\mathrm{RMC} = \frac{\sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{S_{obs,i}} - \sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{S_{est,i}}}{\sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{S_{obs,i}}} \quad (11)$$

$$\mathrm{F\ test} = \frac{\sum \bar{\mathrm{S}}_{\mathrm{aj,i}}{}^2}{\sum \bar{\mathrm{S}}_{\mathrm{residual,i}}{}^2} \quad (12)$$

Where N is the number of observations of the experiments, S_{obs} is the adsorption obtained experimentally, S_{est} is the adsorption fitted by the model, and $S_{residual}$ is the residual adsorption, that is, the difference of S_{obs} and S_{est}, and $\bar{S}_{est}$ and $\bar{S}_{residual}$ are the averages of the model-fitted and residual adsorptions, in this order.

Results

Adsorption isotherms

The mathematical isotherm model that fitted the observed data of copper and zinc adsorption in a mono-component system for all soils was the Freündlich model. In addition, the values found for the Gibbs free energy (average for Cu = -5.98 kJ mol^{-1} and for Zn = -9.19 kJ mol^{-1}) indicated the occurrence of a spontaneous and favorable adsorption process.

From Table 3, the Freündlich model in a copper mono-component system, in O and I soil, showed an overestimation of the adsorption in relation to the observed data (RMC = -0.0003 and -0.0074, in this order). For E soil, an underestimation was detected (RMC = 0.0001). In both cases, the small RMC values corroborate the accuracy of the fitted model. As for the RMSE values, these represent an error of 11.8% for O soil, 18.7% for I soil, and 8.6% for E soil relative to the average amount of adsorbed solute.

However, the Freündlich model in a zinc mono-component system was underestimated when simulating the adsorption observed in the O and I soil porous media and overestimated for E soil (Table 3). The calculated RMSE relative to the average observed adsorption ranged from 8.4% for I soil to 15.5% for E soil.

In the multi-component systems, the multi-component Freündlich isotherm was not fitted for Cu and Zn (Table 3). For multi-component Langmuir model, with Cu as target ion, only in I soil the isotherm was not significant at 5% statistical probability by the F-test. For the Zn as target ion, on the other hand, the isotherms were significant at 5% statistical probability by the F-test. All models, except for E soil with Zn as target ion, underestimated the observed data.

Through the analysis of the graphs in Figure 2, it is observed that the isotherms can be classified, according to Giles (1960), as L-shaped, except for zinc in multi-component system in E soil, which demonstrated H-shaped behavior. The first class has a reduction of the slope of the curve due to the filling of the adsorption sites and, consequently, a greater difficulty to find vacant sites (Giles et al., 1960). For the H-shaped adsorption, that is, of high affinity, there was an initial adsorption with high binding energy even though the soil presented low adsorption (Linhares et al., 2009).

Table 3. Coefficient of determination, root mean square error, residual mass coefficient and F-test for the mono- and multi-component isotherm models.

Ion	Model	Soil	R^2	RMSE (mg kg^{-1})	RMC	F-test
Copper	Freündlich	O	0.97	18.93	-0.0003	99.40*
		I	0.92	39.13	-0.0074	40.10*
		E	0.97	8.31	0.0001	167.60*
	Langmuir	O	0.96	20.34	0.0058	85.94*
		I	0.94	33.65	-0.0073	54.64*
		E	0.96	9.85	0.0013	118.92*
Zinc	Freündlich	O	0.98	13.42	0.0022	186.80*
		I	0.98	15.07	0.0002	207.30*
		E	0.83	21.06	-0.0005	26.10*
	Langmuir	O	0.93	25.37	0.0180	51.51*
		I	0.94	27.85	0.0192	59.98*
		E	0.83	20.80	0.0018	26.76*
Cu multi-component	Freündlich	O	-	-	-	-
		I	-	-	-	-
		E	-	-	-	-
	Langmuir	O	0.96	18.03	0.0035	85.59*
		I	0.83	80.55	0.2262	7.30^{NF}
		E	0.94	11.29	0.0027	71.67*
Zn multi-component	Freündlich	O	-	-	-	-
		I	-	-	-	-
		E	-	-	-	-
	Langmuir	O	0.72	32.67	0.007	12.60*
		I	0.90	22.74	0.007	38.50*
		E	0.70	10.17	$-6.29E^{-5}$	14.076*

Cu: copper in mono-component solution; Zn: zinc in mono-component solution; Cu multi-component: copper in multi-component solution; Zn multi-component: zinc in multi-component solution. * Significant at 5% statistical probability by F-test; NS Not significant at 5% statistical probability by F-test.

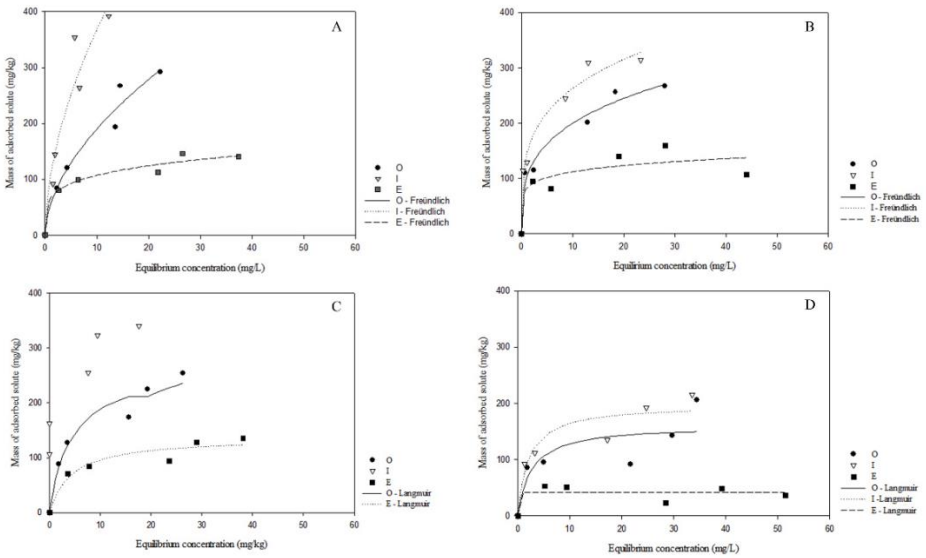

Figure 2. The adsorption isotherm models for copper and zinc in mono- (A and B) and multi-component (C and D) systems with the best fits to the observed data.

It can also be observed that for the lowest initial concentration used (10 mg L^{-1}), there was high adsorption in all soils, which led to a small equilibrium concentration. In the sequence, however, a reduction in the slope of the curve was observed.

By Figure 2D it is also possible to realize that there was adsorption and desorption for zinc in multi-component system that resulted in an observed mean adsorption approximately 60% lower than that of copper in multi-component system for E soil.

The Freündlich isotherms for copper and zinc in a mono-component system indicated favorable sorption ($0 < N < 1$) (Table 4). In such cases, there is a high amount of solute adsorbed by the porous media for a low equilibrium concentration.

Table 4. Freündlich partition coefficient (K_F), Freündlich constant (n) and Freündlich exponential coefficient (N) for mono-component system.

Ion	Model	Soil	K_F (L kg^{-1})	n	N
Cu	Freündlich	O	53.35	1.81	0.55
		I	104.15	1.82	0.55
		E	65.43	4.68	0.21
Zn		O	101.31	3.40	0.29
		I	143.58	3.81	0.26
		E	81.30	7.22	0.14

The higher partition coefficients for I soil in Table 4 (KF = 104.15 L g^{-1} for Cu and 143.58 L g^{-1} for Zn) indicate higher adsorption capacity of this soil. However, the higher binding energy between the porous media and the ion, evidenced by the Freündlich constant (n), demonstrates affinity between E soil and mono-component ions. It is also worth mentioning that this soil has the highest clay activity among the others, which can be classified as medium activity (Santos et al., 2018), besides E soil having the highest content of the metal originally retained.

Furthermore, although copper is retained in larger quantities by the I soil in comparison with the E soil, the latter presents a higher affinity for the ions evaluated, resulting in greater fixation of these ions by the porous media. This fact is inversely related to the mobility of ions in the soil and groundwater contamination.

From Table 5 it is possible to verify that the binding energy of zinc as competitive ion for E soil and copper as competitive ion for O and I soil were null, demonstrating that the model disregarded the performance of these in the adsorption of the target ion. For the multi-component zinc in E soil, on the other hand, showed high binding energy of both ions with the soil, reinforcing the affinities between the soil and the ions. The binding energy was higher for all soils containing zinc as a target ion, but the maximum adsorption capacity of these soils was lower than for copper.

Table 5. Langmuir partition coefficient (K_L) for the target and competitive ion and the maximum adsorption capacity (b) for multi-component system.

Ion	Model	Soil	$K_{L\ target}$ (L mg^{-1})	$K_{L\ competitive}$ (L mg^{-1})	b (mg kg^{-1})
Cu multi-component	Langmuir	O	0.14	0.07	463.11
		E	0.24	1.00E-04	136.98
Zn multi-component		O	0.39	1.00E-04	160.64
		I	0.49	1.00E-04	197.37
		E	498328.05	12710.89	42.63

Cu multi-component: copper in multi-component solution; Zn multi-component: zinc in multi-component solution.

The ANOVA for the sources of variation, adsorbates, and soils, for the mono- and multi-component systems in relation to the observed average adsorption showed that there is significance by the F-test between the evaluated porous media, the solutions, and their interaction (Table 5).

Comparing the graphs of isotherms (Figure 2) and Table 6 it is possible to identify that the copper ion was, on average, adsorbed in larger amounts in mono-component systems, and preferentially adsorbed in the multi-component systems.

Table 6. Mean adsorption values in different soils, for the copper and zinc mono and multi-component systems.

Absorbate	Observed Mean Adsorption (mg kg^{-1})
Cu	154.51 a
Zn	146. 84 b
Cu multi-component	142.63 c
Zn multi-component	87.47 d

Cu: copper in mono-component solution; Zn: zinc in mono-component solution; Cu multi-component: copper in multi-component solution; Zn multi-component: zinc in multi-component solution. Means followed by the same letter do not differ at 5% statistical probability by Scott-Knott test.

For all the systems, the I soil was the porous media that adsorbed the most ions, which indicates a high affinity between the soil and the adsorbate (Table 7). This soil presents, in comparison to the other studied, higher effective cation exchange capacity (t) and base saturation at pH 7 (v), besides average clay activity, as presented in Table 2. In addition, this soil has clay minerals of 2:1 type, such as mica and kaolinite (Figure 1), whose surface is negatively charged and acts favorably in the retention of ions (Ronquim, 2010). Due to this mineralogical composition, the I soil has the highest cation exchange capacity (CEC) among the studied ones (Table 2).

Table 7. Mean adsorption values for the equilibrium tests performed with Cu and Zn solutions in mono- and multi-component systems.

Soil	Observed Mean Adsorption (mg kg^{-1})
I	178.80 a
O	141.38 b
E	78.40 c

Means followed by the same letter do not differ at 5% statistical probability by the Scott-Knott test.

On the other hand, the O soil, due to its advanced stage of weathering and, consequently, the loss of silica from clay minerals, has iron and aluminum oxides in its mineralogical constitution, whose ion retention capacity and clay activity is lower, and inferior compared to the I soil (Table 2).

Among the soils, E soil had the highest clay activity and the highest original zinc concentration (Table 2). However, despite having kaolinite in its mineral composition, this soil has the lowest proportion of clay and a low sum of exchangeable bases (Sb), which results in a lower ion adsorption capacity (Table 2).

From the Table 8 it is possible to see that there was a statistically significant difference between the solutions for I soil, with copper being the most adsorbed ion. On the other hand, for the O and E soil, the adsorption of copper and zinc in mono-component system were not statistically different. For the multi-component adsorptions, however, the observed mean adsorption was different among the solutions and soils. Copper in the multi-component system was 9.3 and 12.1% less adsorbed to O and E soil, in this order, when compared to the mono-component system and, for zinc, the reduction was of the order of 34.8 and 63.8%, respectively.

Table 8. Observed mean adsorption for the interaction between mono- and multi-component solutions of copper and zinc and soils in the adsorption equilibrium test.

Adsorbate	Observed Mean Adsorption (mg kg^{-1})		
	I	O	E
Cu	207.69 aA	159.51 aB	97.11 aC
Zn	197.96 bA	158.23 aB	96.32 aC
Cu multi-component	185.18 cA	144.61 bB	85.32 bC
Zn multi-component	124.37 dA	103.19 cB	34.84 cC

Cu: copper in mono-component solution; Zn: zinc in mono-component solution; Cu multi-component: copper in multi-component solution; Zn multi-component: zinc in multi-component solution. Means followed by the same lower case vertical letter and the same upper case horizontal letter do not differ at 5% statistical probability by Scott-Knott test.

Discussion

Adsorption isotherms

According to Wang et al. (2016) there is occurrence of physisorption when the Gibbs free energy is between -20 and 0 kJ mol^{-1} and chemisorption for $-80 > \Delta G°_{ads} > -400$ kJ mol^{-1} (Table 3). Therefore, the occurrence of physisorption with low energy released by the system was verified.

This adsorption type is non-specific and not localized, i.e., all ions present in the soil solution are able to bind to the active sites, which are arranged all over the surface of the porous media (Nascimento et al., 2014), and there may be the formation of multilayers. Such considerations agree with the Freündlich model behavior, which assumes numerous adsorption sites and does not predict their saturation (Boniolo et al., 2010; Franguelli, 2018).

Gonçalves and Figueiredo (2020) also point out that physisorption is a weak interaction due to the occurrence of van der Waals forces and reversible, with no sharing of electrons. Kummer et al. (2018) and Gonçalves (2013), who studied copper adsorption isotherms in a Oxisol dystrophic, also reported a reduction in the slope of the curve, as seen in Figure 2.

Dias et al. (2001) explain that this phenomenon indicates that for a low solute concentration, there is a high affinity between the ion and the adsorption sites available in the soil, and this affinity is reduced for higher concentrations. Furthermore, Nascimento et al. (2014) point out that metallic ions, such as copper and zinc, present similar adsorption behavior for the Freündlich and Langmuir models when their concentration is low; information that supports the similarity of the values found for the statistical indicators and the good fittings observed for both models.

Gonçalves (2013) also emphasize that the intensity of adsorption reduces with increasing concentration of ions in the soil solution due to the saturation of the exchange sites. Nascimento et al. (2014) also explain that, empirically, the reduction in adsorption energy with increasing ions bound to the adsorbent surface is caused by the heterogeneity of the porous media.

It is worth mentioning that of the adsorption reduction can also occur due to the ionic radius of the ion and its hydrolysis constant. Thus, when the ion is hydrated, there is a contact reduction with the adsorption site, causing the interaction to be inversely proportional to the ion's hydration radius (Nascimento et al., 2014). In this case, the Zn^{2+} hydration radius is larger than that of Cu^{2+}, resulting in a higher copper adsorption although zinc has a greater affinity for the adsorption sites.

Regarding the hydrolysis constant, the formation of a thermodynamically more stable complex results in a greater ease of adsorption when compared to a metal in its free form (Futalan et al., 2019; James and Healy, 1972). Thus, copper, which has a lower hydrolysis constant, has a higher affinity with soil adsorption sites.

The adsorption and desorption for zinc in mono-component system may have occurred due to the adsorbent limitation of the porous media, i.e., the rapid saturation of the exchange sites, even with the low ion concentration of the adsorbates. Linhares et al. (2010) verified that the K_F values and the adsorption energy sites were higher for zinc in mono-component system for the same Brazilian soils, corroborating with the presented.

Merlo et al. (2023) evaluated the adsorption kinetics of copper and zinc in single and multi-component systems in the same soils evaluated with this work. According to these same authors, for zinc in a mono-component system for the I soil, there was a rapid adsorption in the initial 2 minutes of contact, followed by desorption at 5 minutes, and then reaching maximum adsorption. Desorption can occur due to the small number of exchange sites in the soil, which can result in leaching of ions into the deeper layers of the soil, contaminating groundwater, and posing a health risk (Merlo et al., 2023) both to humans and other animals.

Merlo et al. (2023) also concluded that the highest adsorption of copper and zinc ions occurred at the initial contact times for the mono-component solution. For the multi-component solution, the lowest adsorptions were observed for the initial minutes of contact (up to 20 minutes), which increased and remained constant after this time (Merlo et al., 2023).

Regarding the binding energy and maximum adsorption capacity of soils, Linhares et al. (2009) point out that there is no direct relationship between them, that is, if a soil has high retention capacity and low binding energy, the metal can become available again in the soil and

move due to the lower affinity between the adsorption sites of the porous media and the ion.

Thus, even though zinc is retained in larger quantities by the I soil in comparison with the E soil, the latter presents a greater affinity for the ion, as indicated by the higher K_L value, resulting in greater fixation of the metal by the porous media. This fact is inversely related to the mobility of ions in the soil and groundwater contamination.

The larger amounts of copper adsorption in mono- and multi-component systems are related to the competition between the ions for adsorption sites and the higher electronegativity of this bivalent ion when compared to zinc. In a similar way, Merlo et al. (2023) also found that the most adsorbed ion in the mono- and multi-component systems was copper, and the least adsorbed ion in the multi-component system was zinc.

The behavior of ion retention for I soil favors the reduction of their mobility in the porous media and, consequently, contributes to the attenuation of contamination of the subsurface soil layers and groundwater.

Merlo et al. (2023) presented correlations between the physical and chemical properties of soils, adsorption of copper and zinc in mono and multi-component solutions, as well as the parameters of adsorption kinetics by Principal Component Analysis. The authors found that the first principal component was related to the adsorption phenomenon, but I and E soils had a behavior opposite to this component due to the low cation exchange capacity and sum of exchangeable bases of the soils. The second principal component, on the other hand, exhibited a relationship with copper and adsorbent surfaces, such as clay and organic matter, in addition to having the direct contribution of the O soil, which has a higher percentage of clay.

Lopes (2009) evaluated the mono- and multi-component adsorption of cadmium, nickel, copper, and zinc in several types of soils and, similarly to this study, soils with low values of CEC and organic matter were those that had the lowest adsorption, as occurred for E soil, which was the porous media with the lowest adsorption among the ions studied. The author also showed that copper was more adsorbed than zinc, which corroborates what was verified in this study.

Furthermore, the E soil was described as strongly to excessively acidic (Silva et al., 2005), resulting in a H^+ concentration rise in soil solution and, leading H^+ to compete with copper and zinc ions for the adsorption sites (García et al., 1978).

According to Sena (2018) the reduction of adsorption in soils when the ions are in a multi-component system is related to the adsorption sites that are common for both ions, thus there is competition between them.

Conclusions

The isotherm model with the best fit was Freündlich for the mono-component systems and Langmuir for the multi-component ones. The Gibbs free energy value indicated that the adsorption process was spontaneous and with a predominance of physisorption.

The largest ion adsorbed by the porous media was copper in a mono-component system and the least adsorbed was zinc in a multi-component system. The Inceptisol presented the highest adsorption capacity and the Entisol Quartzipsamment the least adsorbed ions.

The ion retention behavior of Inceptisol favors the reduction of ion leaching in this porous medium due to its higher retention capacity and, consequently, contributes to the attenuation of contamination of the subsurface layers of soil and groundwater. This can allow the application of wastewater or copper and zinc-based fertilizers to be a viable alternative, providing higher crop yields.

On the other hand, sandy soils, such as Entisol Quartzipsamment, have a greater tendency to ion leaching, due to their low adsorption capacity. Despite its high affinity for zinc in a mono-component system and having zinc originally retained, this soil may have few adsorption sites available.

Oxisol is characterized by its high soil saturated hydraulic conductivity and, even though it has an average ion adsorption capacity compared to other soils, it can behave like Entissol Quartzipsamment and allow the leaching of metal ions.

It is important to emphasize that even with the adsorptive property of soils, the increase in the concentration of the metal can result in the saturation of the adsorption sites and higher mobility of the ions

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