

Nickel adsorption and desorption in an acric oxisol as a function of pH, ionic strength and incubation time

Adsorção/dessorção de níquel em solo ácido em função do pH, da força iônica e tempo de incubação

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ABSTRACT

Although nickel (Ni) has both important potential benefits and toxic effects in the environment, its behavior in tropical soils has not been well studied. Nickel adsorption-desorption in topsoil and subsoil samples of an acric Oxisol was studied at three pH values (from 3.0 to 8.0). Adsorption-desorption isotherms were elaborated from experiments with increasing Ni concentration (5 to 100 mg L⁻¹), during 0, 4, and 12 weeks, using CaCl₂ 0.01 and 0.1 M as electrolytic support in order to also verify the effect of Ni-soil time contact and of ionic strength on the reaction. Experimental results of Ni adsorption fitted Langmuir model, which indicated that maximum Ni adsorption (71,440 mg kg⁻¹) occurred at subsoil, after 12 weeks. Nickel affinity (K_L) was also greater at subsoil (1.0 L kg⁻¹). The Ni adsorption in the topsoil samples was higher, due to its lower point of zero salt effect (PZSE) and higher organic matter content. The increase in soil pH resulted in the increase of Ni adsorption. Nickel desorbed less from soil samples incubated for 4 or 12 weeks, suggesting that Ni interactions with colloidal particles increase over time. The amount of Ni desorbed increased with increasing ionic strength in both the topsoil and subsoil soil samples. Finally, adsorption-desorption hysteresis was clearly observed. Soil pH, ionic strength of soil solution and the Ni-soil contact time should be considered as criteria for selecting the areas for disposal of residues containing Ni or to compose remediation strategies for acric soils contaminated with Ni.

Index terms: Sorption; bioavailability; soil pollution; heavy metal.

RESUMO

Apesar de o níquel (Ni) ser um elemento importante no ambiente, tanto pelo seu potencial benéfico, como tóxico, informações sobre o seu comportamento em solos tropicais são escassas. Reações de adsorção-dessorção de Ni em amostras superficiais e subsuperficiais de um Latossolo ácido foram estudadas em três valores de pH do solo, variando de 3,0 a 8,0. Isotermas de adsorção-dessorção foram elaboradas a partir de experimentos com concentrações crescentes de Ni (5 a 100 mg L⁻¹), durante 0, 4 e 12 semanas, usando CaCl₂ 0,01 e 0,1 M como eletrólito suporte para verificar o efeito do tempo de contato e da força iônica sobre a reação. Resultados experimentais foram adequadamente ajustados pelo modelo de Langmuir, o qual apontou que a máxima adsorção de Ni (71.440 mg kg⁻¹) ocorreu após 12 semanas de contato do Ni com amostras do subsolo. A afinidade do Ni também foi maior pelas amostras de subsolo (1,0 L kg⁻¹). A adsorção de Ni foi maior nas amostras superficiais, devido ao menor ponto de efeito salino nulo e ao maior teor de matéria orgânica. A elevação do pH do solo aumentou a adsorção de Ni. Houve menos dessorção de Ni das amostras de solo incubadas por 4 e 12 semanas, sugerindo que as interações entre o Ni e as partículas do solo aumentam ao longo do tempo. A quantidade de Ni dessorvido aumentou com o aumento da força iônica, independentemente da profundidade de amostragem do solo. Finalmente, a histerese da reação de adsorção-dessorção de Ni foi claramente observada. O pH do solo, a força iônica da solução e o tempo de contato do Ni com o solo devem ser considerados critérios para a seleção de áreas para a disposição de resíduos contendo Ni e para compor estratégias de remediação para solos ácidos contaminados por Ni.

Termos para indexação: Sorção; biodisponibilidade; poluição do solo; metal pesado.

INTRODUCTION

The bioavailability of nickel (Ni) depends on its concentration and on how readily it desorbs from colloidal soil particle surfaces into the soil solution. Understanding this desorption process in soil is as important as understanding the corresponding adsorption process (Bolt et al., 1986). However, metal desorption from soil particles has not

been as widely studied as its adsorption, partly because of methodological difficulties (Zhu; Alva, 1993). Although many studies on metal adsorption in tropical soils have appeared in the literature, few researchers have examined the corresponding desorption processes (Hoog et al., 1993).

According to Gao et al. (2003), metal desorption depends on the free element content in the soil solution, the soil pH, the temperature, the amount of metal added and

the contact time between the soil and solution. The amount of organic matter present and the pH have the strongest direct and/or indirect effects on the bioavailability of heavy metals (Rodríguez-Rubio et al., 2003). Camargo, Rovers and Valadares (1989) studied Ni adsorption in a calcium-saturated oxisol topsoil and found that the specific adsorption was low and that the preferential adsorption of Ni over calcium was nearly non-existent. The maximum amount of Ni adsorbed was less than 40% of the cation exchange capacity (CEC) at pH 7.0 and was found to depend on the pH and organic carbon content. According to a literature review by Barrow, Gerth and Brummer (1989), the electrolyte concentration affects metal adsorption, but the nature of the effect depends on the pH. If the metal adsorbs at low pH, the amount adsorbed increases with increasing electrolyte concentration, whereas the amount adsorbed decreases with increasing electrolyte concentration at high pH.

In reversible exchange studies, it is assumed that cation exchange occurs via identical ion adsorption and desorption mechanisms. However, the desorption process might be affected by hysteresis (Evangelou, 1998). Metals associated with organic matter are rapidly adsorbed, but their desorption is slow. Thus, their adsorption-desorption isotherms exhibit hysteresis because their release tends to be slow and/or incomplete due to the high activation energy required for the inner-sphere complex to desorb (McBride, 1989). The magnitude of the hysteresis effect is affected by the length of the equilibration period (Evangelou, 1998). Thus, the magnitude of the hysteresis effect tends to decrease (the hysteresis increases) as the contact time between the soil and the metal increases (Padmanabham, 1983; Barrow, 1985).

Few studies have examined the behavior of heavy metals in acric soils (Iglesias; Casagrande; Alleoni, 2007). These soils cover approximately 170,000 ha of São Paulo State, Brazil, and consist of mostly iron (Fe) and aluminum (Al) oxides and kaolinite, which results from high silica loss. In the subsoil layers, the point of zero salt effect (PZSE), which is the pH at which the surface electric potential of a reversible system is unaffected by the ion concentration of the liquid, is lower. Under these conditions, the PZSE is higher than it is at the original pH, resulting in a positive charge balance, especially at depths greater than 0.5 m, where organic matter (OM) does not influence (Soares et al., 2008).

This study aims to investigate the effects of the pH and electrolyte ionic strength on Ni adsorption and desorption in acric soil and to evaluate the Ni adsorption-desorption hysteresis for incubation periods of 0, 4 and 12 weeks.

MATERIAL AND METHODS

Soil characterization

Topsoil (0–0.2 m) and subsoil (at the greatest expression of the Bw horizon expression, 1.0–1.3 m) samples of an acric, medium-texture Anionic “Xanthic” Acrudox (XA), were collected in Guaira (20°19’S, 48°18’W), São Paulo State, Brazil.

The samples were passed through a 2-mm mesh sieve after drying in an oven at 105° for 72 hours and subsequently subjected to chemical analysis using the methods of Camargo et al. (1986). In particular, the organic carbon content was quantified by oxidation with potassium dichromate in the presence of sulfuric acid, followed by titration with ammonium iron(II) sulfate. The pH was determined by potentiometry in H₂O and in 1 M KCl suspensions with 1:2.5 soil:solution ratio, and the difference $\Delta\text{pH} = \text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$ was used as estimate of the net charge balance (Mekaru; Uehara, 1972). The total oxide content was measured by reaction with sulfuric acid. The free iron and aluminum were reduced by dithionite and complexed with sodium citrate, whereas the amorphous iron and aluminum were dissolved in an ammonium oxalic acid solution. The clay content was determined by the pipette method.

The effective cation exchange capacity (ECEC) was estimated by $\text{ECEC} = \text{SB} + \text{Al}$. Sum of bases (SB = Ca + Mg + K + Na) were calculated after extraction by ionic exchange resins. Calcium and Mg were determined by atomic absorption spectroscopy, and Na and K by flame photometry. The exchangeable aluminum (Al³⁺) was extracted by a M KCl solution and determined by titration with ammonium hydroxide (0.025 M). The specific surface area (SSA) was determined based on the retention of ethylene glycol monoethyl ether (EMEG) (Chiacek; Bremner, 1979). The point of zero salt effect (PZSE) was measured by titration with H⁺ and hydroxide (OH⁻) ions at three different potassium chloride (KCl) concentrations. The PZSE is the pH at which the titration curves intersect. The permanent (σ_p) and variable (σ_H) charges were measured following the method of Anderson and Sposito (1991), which is based on the fact that Cs⁺ adsorption in the siloxane cavities of clay minerals is twice as favorable as that on ionizable surfaces.

Ni adsorption-desorption

Soil samples were previously prepared to study the effects of pH and contact time on Ni adsorption-desorption reactions. Three topsoil samples and three subsoil samples had the pH adjusted with calcium carbonate or

hydrochloric acid to 4.7, 6.0 and 7.4, and 3.9, 5.6 and 7.7, respectively. The selected range between about 4.0 and 8.0 can be justified by the range of interest for the evaluation of adsorption - desorption process according to Barrow (1983, 1984) and to Casagrande and Camargo (1997). The samples were incubated with 25% water to promote chemical reactions between calcium carbonate and hydrochloric acid and to equilibrate the pH, which required 45 days after the calcium carbonate and hydrochloric acid were added. In order to evaluate three contact times of soil-Ni for either 0, 4 and 12 weeks, Ni was added as NiCl₂ in increasing concentrations (0, 5, 10, 20, 30, 40, 60, 80 and 100 mg L⁻¹) to the untreated topsoil and subsoil samples, i.e. at natural soil pH (Table 1), with moisture content kept at 25% (soil field capacity).

To determine the effect of soil pH, Ni adsorption isotherms were elaborated for all soil samples. To quantify the amount of Ni adsorbed, 2.0 g of the air-dried of each

soil sample and 20 mL of a CaCl₂ background solution with increasing Ni concentration (0, 5, 10, 20, 30, 40, 60, 80 and 100 mg L⁻¹), maintaining the 1:10 soil:solution ratio. The set was placed in a polyethylene tube and agitated for 24 hours. For the simultaneous verification of the pH and ionic strength effects on the Ni adsorption reaction, the CaCl₂ background electrolyte solution was used at 0.1 and 0.01 M. After the system was equilibrated, the suspension was centrifuged twice at 2500×g, and the Ni concentration of the supernatant was then determined by atomic absorption spectrometry. All determinations were made in triplicate. The quantity of adsorbed Ni was calculated by the ratio $Ni_{ads} = ((Ni_0 - Ni_{eq}) V)/M$, where Ni_{ads} was the quantity of Ni adsorbed after equilibrium (mg kg⁻¹); Ni₀ and Ni_{eq} were the added initial and equilibrium concentration (mg L⁻¹), respectively; V = solution volume (mL); and M = mass of the soil sample (g). The Ni quantities originally present in the soil samples were subtracted from the quantity of Ni adsorbed.

Table 1: Chemical, physical and mineralogical properties of the acric oxisol studied in this study.

Soil attributes	Sampling depth	
	m	
	0.0-0.2	1.0-1.3
pH H ₂ O	4.60	5.10
PZSE	3.40	6.00
ECEC (mmolc kg ⁻¹)	13.0	3.0
σ _v (mmolc kg ⁻¹)	32.3	8.4
σ _H (mmolc kg ⁻¹)	18.4	1.3
ΔpH	-0.60	0.60
SSA (m ² g ⁻¹)	65.0	53.0
Ki	0.98	0.97
OC (%)	1.60	0.60
Clay (g kg ⁻¹)	350	450
Fe ₂ O _{3,total} (%)	7.00	7.00
Fe _{Free} (%)	4.00	4.00
Fe _{Amorphous} (%)	0.20	0.20
Al ₂ O _{3,total} (%)	9.00	13.0
Al _{Free} (%)	2.20	3.10
Al _{Amorphous} (%)	0.60	0.80
Kaolinite (%)	24.0	37.0
Gibbsite (%)	25.0	32.0

PZSE = point of zero salt effect; ECEC = effective cation exchange capacity; σ_v = variable charge; σ_H = permanent charge; ΔpH = pH_{KCl} - pH_{H₂O}; SSA = specific surface area; Ki = weathering index = SiO₂/Al₂O₃; OC = organic carbon; Fe_{Free} and Al_{Free} = iron and aluminum extracted by sodium citrate-bicarbonate-ditionite (Na-CBD); Fe_{Amorphous} and Al_{Amorphous} = iron and aluminum extracted by Tamm's solution [(COOH)₂·2H₂O+(NH₄)₂C₂O₄·H₂O]; Fe_{total} and Al_{total} = iron and aluminum extracted by H₂SO₄ 9 M.

The measure amount of Ni adsorbed was compared to that estimated by the nonlinear Langmuir isotherm: $Ads_{eq} = K_L C_{eq} Ads_{max} / (1 + K_L C_{eq})$, where K_L is the parameter related to maximum Ni adsorption capacity ($mg\ kg^{-1}$) (Soares; Casagrande; Mouta, 2011). The Langmuir isotherm was fitted to the Ni adsorption results by CurveExpert 1.4.

Nickel was desorbed from all samples according procedures used by Casagrande et al. (2004). After determining the amount of Ni adsorbed, three 2h-periods of desorption were performed by adding 20 mL of a $CaCl_2$ electrolyte solution (0.1 and 0.01 M) to each 2.0 g of the soil used for the Ni adsorption experiments. After centrifugation at 4,000 rpm, the amount of desorbed Ni in the supernatant was determined by atomic absorption spectrometry. The soil was resuspended in fresh electrolyte solution, and the desorption process was repeated twice. The total Ni desorbed was the sum of the Ni concentration obtained at each desorption period. Desorption process was performed for both the topsoil and subsoil samples at each Ni concentration and pH studied to examine the hysteresis of the adsorption-desorption isotherms. Hysteresis is any phenomenon in which the variation in one physical quantity depends on whether a second physical quantity is increasing or decreasing. In this study, the adsorption and desorption isotherms of each soil sample were compared.

RESULTS AND DISCUSSION

Chemical, physical and mineralogical characteristics of the acric oxisol samples studied are presented in Table 1. The net charge (ΔpH) was negative at the topsoil, most likely due to the presence of organic matter. However, in the subsoil sample, the surface charge balance was positive, as reflected by the ΔDpH values and the net charge. It should be noted that the change in the charge balance at the subsoil horizon, which is characteristic of acric soils, usually occurs at depths greater than 0.5 m, where the effect of organic matter is less pronounced (Uehara, 1988). As expected for Oxisols, the Ki index at the depth of diagnostic horizon (Bw – 1.0-1.3 m) was low. According to the criteria of Resende and Santana (1988), acric oxisols are classified as kaolinite sesquioxides ($Ki > 0.75$ and $Kr \leq 0.75$). On average, the free iron oxide content was 50% of the total iron oxide content of the soil. However, the free aluminum oxide content averaged only 25% of the total aluminum oxide content.

The PZSE of the topsoil horizon (3.4) was lower than the pH range studied (4.0 to 8.0), whereas the PZSE of the subsoil sample was in the middle of this range (6.0). These values are consistent with those of highly weathered soils

reported in the literature (Alleoni; Camargo, 1994; Guilherme; Anderson, 1998). The subsoil horizon had a higher PZSE value than the topsoil horizon because it contained less organic matter and was predominantly aluminum and iron oxides, which have PZSE values near 8.0 (Sparks, 1995).

The Ni adsorption isotherms fit the Langmuir adsorption model well at all studied pH values and incubation times. The parameters obtained from the model fittings are given in Tables 2 and 3. The maximum amount of Ni adsorbed was higher in the topsoil layer than in the subsoil. The maximum adsorption of Ni calculated using the Langmuir equation increased with increasing pH and incubation time and appeared to be independent of the ionic strength.

The maximum amount of Ni adsorbed was higher for samples with high pH values and for those incubated for 12 weeks, demonstrating that both the pH and contact time affect the Ni adsorption capacity of the soil.

For the topsoil samples, 52% and 75% of the Ni were adsorbed at pH 4.7 and 6.0, respectively, whereas 21% and 42% were adsorbed at pH 3.9 and 5.6, respectively, for the subsoil (Figure 1), demonstrating the influence of both the pH and depth of the soil layer on the amount of Ni adsorbed.

The large difference between the Ni adsorption capacities of the topsoil and subsoil samples might be explained by the difference between their PZSE (3.4 and 6.0, respectively). In other words, at the topsoil, the net surface charges are negative when the pH is greater than 3.4, facilitating higher Ni adsorption. In the subsoil region, the net surface charges become negative when the pH exceeds 6.0. Moreira et al. (2008) studied Ni adsorption by oxidic soils from São Paulo State, Brazil, using adsorption envelopes (fixed metal doses applied over a wide range of pH values), and obtained similar results. They also found that the amount of Ni adsorbed by topsoil samples was higher than that adsorbed by subsoil samples. In addition, the difference between the PZSE values of the soil samples studied by Moreira et al. (2008) was similar to that observed in this study, supporting the above hypothesis. According to the results of Silveira and Alleoni (2003), Casagrande, Soares and Mouta (2008), Mouta, Soares and Casagrande (2008), and Soares, Casagrande and Mouta (2009), the higher amounts of metals adsorbed in topsoil horizons are correlated to the organic matter content. Soil organic matter may be responsible for 50 to 95% of the cation exchange capacity (CEC) in Brazilian Oxisols, whose inorganic fraction is predominantly composed by low reactive minerals (Soares; Alleoni, 2008). This probably favors the adsorption of a greater quantity of Ni, mainly by outer-sphere complex formation with colloid surface (Soares; Casagrande; Mouta, 2011).

Table 2: Langmuir model parameters for Ni adsorption at different ionic strengths and soil pH values.

Sampling depth m	Ionic strength mol L ⁻¹	pH	Langmuir equation	Ads _{max} mg kg ⁻¹	K _L L kg ⁻¹
0-0.2	0.01	4.7	$y=453+0.063*x/(1+0.063*x)$	453	0.063
		6.0	$y=657+0.243*x/(1+0.243*x)$	657	0.243
		7.4	$y=1390+0.591*x/(1+0.591*x)$	1390	0.591
	0.1	4.7	$y=445+0.064*x/(1+0.064*x)$	445	0.064
		6.0	$y=702+0.161*x/(1+0.161*x)$	702	0.161
		7.4	$y=1270+0.604*x/(1+0.604*x)$	1270	0.604
1.0-1.3	0.01	3.9	$y=5580+0.001*x/(1+0.001*x)$	5580	0.001
		5.6	$y=319+0.066*x/(1+0.066*x)$	319	0.066
		7.7	$y=759+1.0*x/(1+1.0*x)$	759	1.000
	0.1	3.9	$y=4490+0.001*x/(1+0.001*x)$	4490	0.001
		5.6	$y=345+0.051*x/(1+0.051*x)$	345	0.051
		7.7	$y=738+0.888*x/(1+0.888*x)$	738	0.888

Ads_{max} = maximum adsorption; K_L = affinity constant.

Table 3: Langmuir model parameters for Ni adsorption at different ionic strengths and Ni-soil contact times.

Sampling depth m	Ionic strength mol L ⁻¹	Incubation time	Langmuir equation	Ads _{max} mg kg ⁻¹	K _L L kg ⁻¹
0-0.2	0.01	No incubation	$y=437+0.076*x/(1+0.076*x)$	437	0.076
		4 weeks	$y=1140+0.143*x/(1+0.143*x)$	1140	0.143
		12 weeks	$y=1190+0.124*x/(1+0.1244*x)$	1190	0.124
	0.1	No incubation	$y=445+0.064*x/(1+0.064*x)$	445	0.064
		4 weeks	$y=1140+0.063*x/(1+0.063*x)$	1140	0.063
		12 weeks	$y=1130+0.302*x/(1+0.302*x)$	1130	0.320
1.0-1.3	0.01	No incubation	$y=319+0.065*x/(1+0.065*x)$	319	0.065
		4 weeks	$y=1670+0.547*x/(1+0.547*x)$	1670	0.547
		12 weeks	$y=41800+0.111*x/(1+0.111*x)$	41800	0.111
	0.1	No incubation	$y=344+0.051*x/(1+0.051*x)$	344	0.051
		4 weeks	$y=1250+1.0*x/(1+1.0*x)$	1250	1.000
		12 weeks	$y=71440+0.232*x/(1+0.232*x)$	71440	0.232

Ads_{max} = maximum adsorption; K_L = affinity constant.

The Ni adsorption-desorption isotherms measured after different incubation times are shown in Figure 2. The amounts of Ni adsorbed by the samples incubated for 4 and 12 weeks were similar and significantly higher than those adsorbed by the unincubated samples at both ionic strengths for both the topsoil samples (at pH 5.4) and the subsoil samples (at pH 5.9). The percent of total Ni

adsorbed by the topsoil samples at a pH of approximately 5.0 ranged from 51.5%, for the unincubated sample, to nearly 100% for the samples incubated for 4 and 12 weeks. A similar trend was also observed for the subsoil samples. Bruemmer, Gerth and Tiller (1988) determined that the percent of total Ni adsorbed by goethite, an iron oxide with frequent and abundant occurrence in yellow

Oxisols, was 12% after 12 days of incubation and 70% after 42 days of incubation.

In most studies of heavy metal adsorption on soil components, such as iron oxides, the reaction times were relatively short, i.e., only a few hours (Forbes; Posner; Quirk, 1976; Benjamin; Leckie, 1981). The results of this study agree with the observations of Bruemmer, Gerth and Tiller (1988) that the amount of metal adsorbed can increase even after several weeks of reaction. Therefore, a larger amount of metal becomes immobilized over time due to aging or crystallization of the reaction products (Mckenzie, 1980; Kuo; Mikkelsen, 1980).

For the unincubated topsoil samples at pH 4.7 (Figure 1), the percent of Ni desorbed ranged from 57%, at the ionic strength of 0.01 M CaCl_2 , to 67%, at the ionic strength of 0.1 M CaCl_2 when the initial Ni dose was 60 mg dm^{-3} . The percent of Ni desorbed from the subsoil samples at pH 3.9 was 28-38% (Figure 1). These percentages show

that more Ni desorbed from the topsoil samples, which also adsorbed more Ni, than from the subsoil samples. This enhanced Ni desorption observed for the topsoil samples was due to the facilitated adsorption of this metal by organic material. Mellis et al. (2004) found that eliminating the Ni adsorption by organic material in the same oxisol resulted in a 15% decrease in the Ni adsorption relative to that of the unaltered soil.

Organic matter provides sites for cation exchange, but it exhibits a strong affinity for metals because the ligands or functional groups in organic matter form complexes or chelates with metals (Stevenson, 1991). McBride (1989) determined that the affinity of organic matter for metals decreases as follows: $\text{Cu} \gg \text{Ni} \gg \text{Pb} \gg \text{Co} \gg \text{Ca} \gg \text{Zn} \gg \text{Mn} \gg \text{Mg}$. Ni and other heavy metals form complexes with various organic soil constituents. However, the degree of complexation increases as the percentages of humic and fulvic acids, which are present in organic matter in large

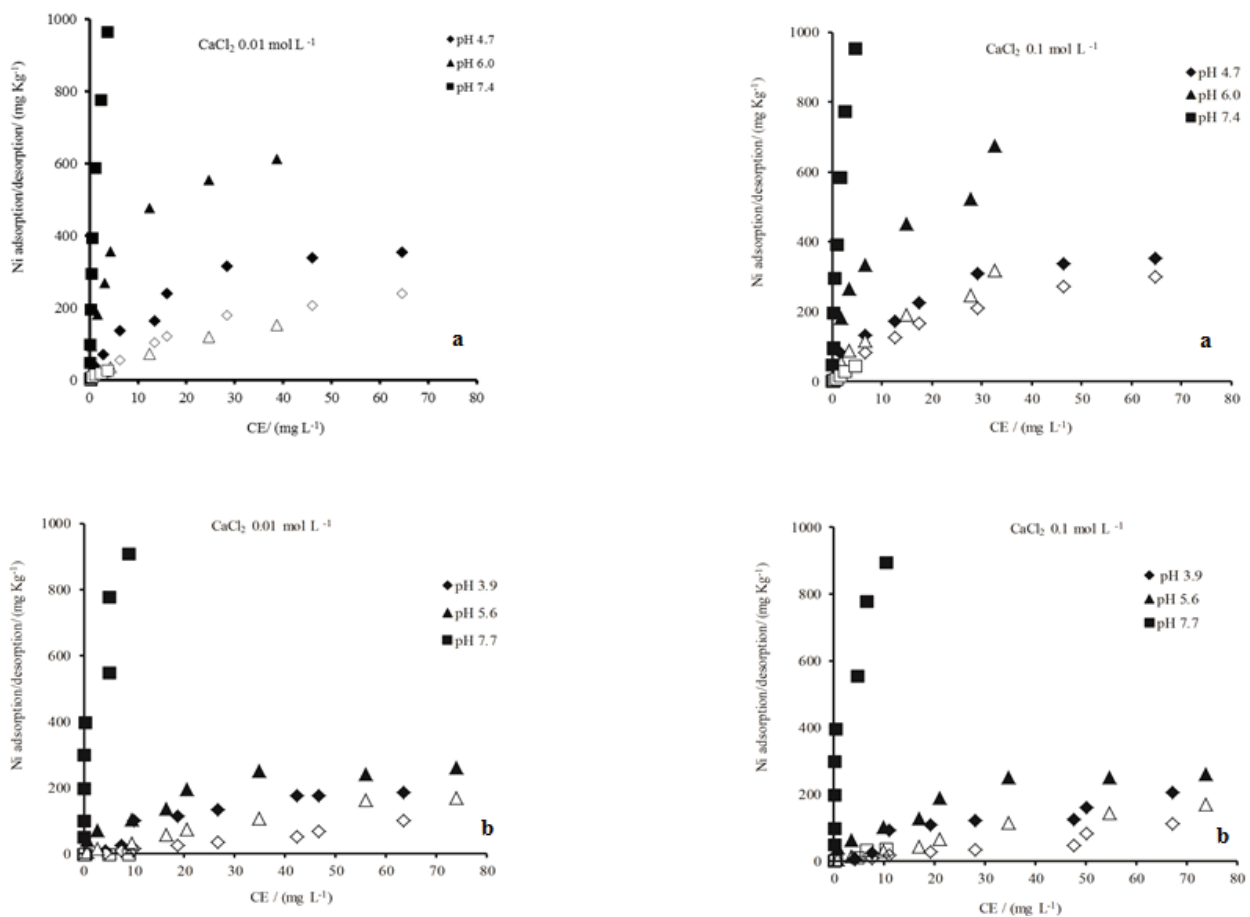


Figure 1: Nickel adsorption (filled symbols) and desorption (empty symbols) isotherms for the topsoil (0.0-0.2 m) (a) and subsoil (1.0-1.3 m) (b) acric oxisol samples with different pH values at two ionic strengths.

quantities, increase. Humic acid typically forms insoluble complexes, whereas fulvic acid complexes are generally soluble (Stevenson, 1991). Several studies have focused on the influence of the organic matter in different soil types, including acric oxisols, on heavy metal adsorption (Camargo; Rovers; Valadares, 1989; Barrow; Gerth; Brummer, 1989; Mellis et al., 2004).

The amount of Ni desorbed (Figure 1) was 10% higher for both the topsoil and subsoil samples when the ionic strength was increased. At pH values higher than 7.0, very little Ni desorption occurred at both electrolyte concentrations, probably because the pH-dependent negative charges on the organic matter interacted with

the dissociated hydrogen instead. According to Mellis et al. (2004), the effect of organic matter on Ni adsorption is weak at pH values higher than 6.0-6.5.

The amount of Ni desorbed from the Ni-dosed soils incubated for 4 and 12 weeks (Figure 2) was very low compared to that desorbed from the unincubated soils. For the topsoil samples (Figure 2), dosed with 40 mg dm⁻³ Ni, 73%, 3.2% and 1% of the Ni desorbed due to the CaCl₂ electrolyte (ionic strength of 0.1 M) after incubation times of 0, 4 and 12 weeks, respectively. When the ionic strength was lower (0.01 M CaCl₂) but the Ni dose was the same (40 mg dm⁻³), only 51%, 0.4% and 0% of the Ni desorbed after 0, 4 and 12 weeks,

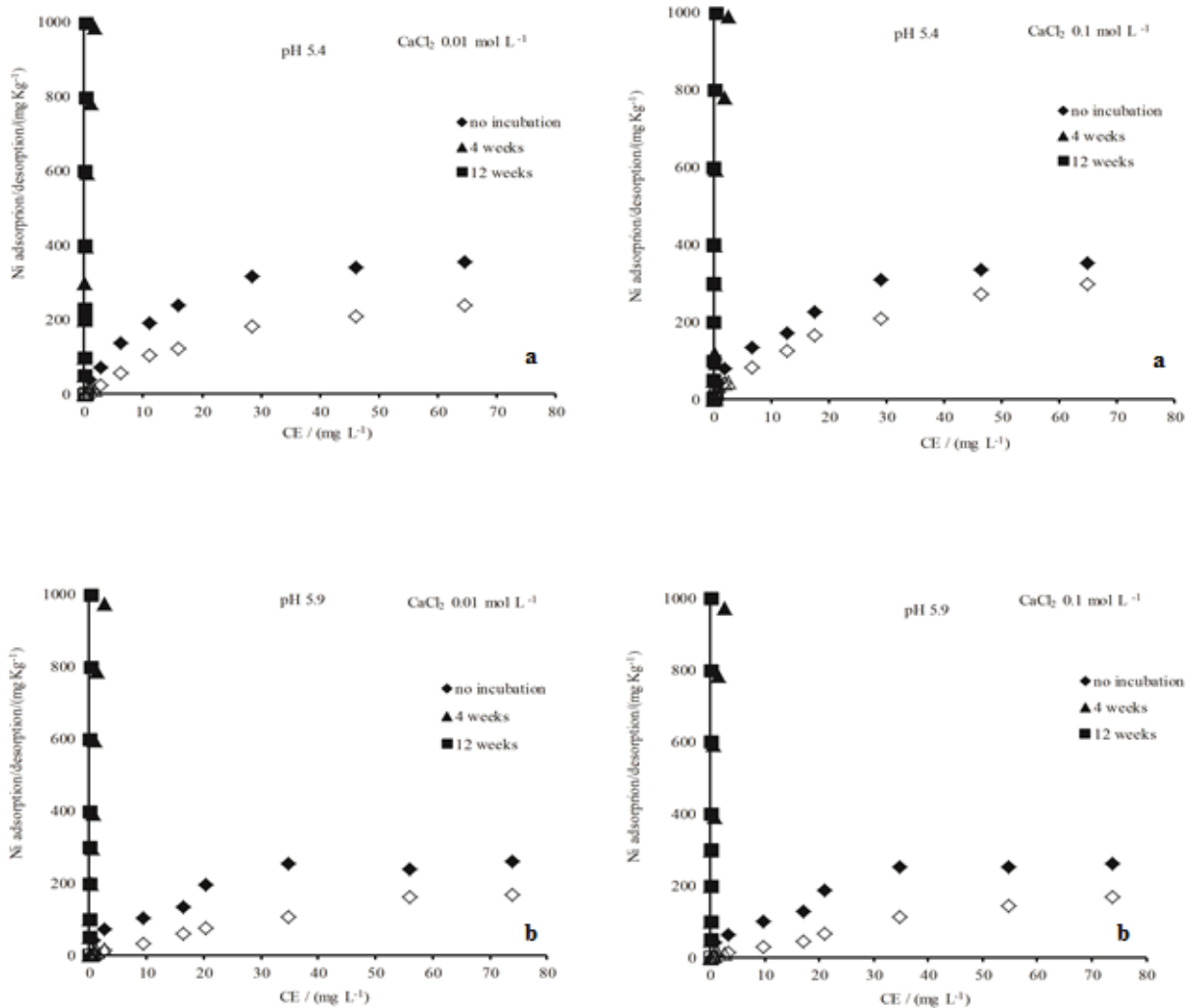


Figure 2: Nickel adsorption (filled symbols) and desorption (empty symbols) isotherms for the topsoil (0.0-0.2 m) (a) and subsoil (1.0-1.3 m) (b) acric oxisol samples incubated for different periods of time at two ionic strengths.

respectively. For the subsoil samples (Figure 2), the percentages of Ni desorbed at a given Ni dose were similar at both electrolyte concentrations. At a Ni dose of 40 mg dm⁻³, 38%, 1% and 0% of the Ni desorbed after 0, 4 and 12 weeks, respectively. These results demonstrate that Ni interacts strongly with colloidal soil particles over time. According to Mellis et al. (2012), the metal ions might serve as a bridge between humic substances and soil oxides. Varadachari, Chattopadhyay and Ghosh (1997) studied the complexation of synthesized iron and aluminum oxides by humic substances in the presence of mono-, di- and trivalent cations. The authors found that the amount of humic acids bound to goethite increased in the presence of di- and trivalent cations, whereas humic acid complexation to hematite did not depend on the cation valence state. Gibbsite was reduced by the presence of any ion. The authors concluded that humic acids bind to goethite and hematite indirectly via cations, whereas they directly bind to gibbsite.

According to Selim (2012), some authors have observed that goethite and gibbsite exhibit a strong affinity for Ni and that metals can diffuse through in goethite due to flaws or pores on the surface. A study of metal adsorption on synthesized mineral surfaces showed that these pores could be sealed by precipitating Fe³⁺, which further reduced the availability of the metal (Schwertman; Kampf, 1985). Accordingly, it is expected that the availability of metals decreases over time when they can form oxides, thereby leading to the enrichment of the soil in these minerals. Oxisols are good metal adsorbents as demonstrated by the lack of Ni desorption after 4 and 8 weeks of incubation (Figure 2).

As previously discussed, for both the topsoil and subsoil samples (Figure 1), Ni desorption was only observed at lower pH values (4.0 to 6.0) and was nearly nonexistent near pH 7.0. Moreover, only a small amount of Ni desorbed after 4 and 12 weeks of incubation (Figure 2), demonstrating that the strong interaction between Ni and the soil resulted in a pronounced adsorption-desorption hysteresis and suggesting that Ni probably diffused into the soil oxides.

CONCLUSIONS

The amount of Ni adsorbed by the acric oxisol was higher in the topsoil than in the subsoil layer. At pH values greater than 7.0, very little Ni desorbed from the soil particles. Nearly all the Ni remained adsorbed to the soil particles after 4 and 12 weeks of incubation. Hysteresis was observed in the Ni adsorption-desorption isotherms for the soil samples, but the amount of Ni desorbed increased with

increasing ionic strength for both the topsoil and subsoil samples. For practical implications, the use of fertilizers, the salinity of irrigation water and the saline potential of some wastes discharged in soil may be situations that increase the ionic strength of the soil solution and lead to higher desorption Ni, increasing the possibility of entering in food chain. The results of this study also suggest that liming, an usual practice in acid tropical soils, can be an efficient method to remediate soils contaminated with Ni.

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