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ADSORPTION AND RELEASE OF Cu(II), Co(II), Ni(II) AND Mn(II) ON TROPICAL PEATLANDS FOR AGRICULTURAL APPLICATIONS

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SUMMARY

Peat is used as adsorbents of metal species and organic fertilizers. The union of these applications makes the use of peat a possible alternative to improve agricultural productivity. This work aimed to evaluate the adsorption capacity of the micronutrients Cu(II), Co(II), Ni(II) and Mn(II) ions in tropical peatlands, and to evaluate the release of previously adsorbed micronutrients. The adsorption results showed the following order of affinity: Cu(II)>Ni(II)>Co(II)>Mn(II), where about 99, 80, 71 and 70% adsorbed micronutrients by the peat samples, respectively. Release experiments showed that the order of release was: Mn(II)>Co(II)>Ni(II)>Cu(II), where about 16, 14, 10 and 1% released micronutrients by peat sample, respectively.

KEY WORDS: peat, micronutrients, adsorption, release, agricultural.

INTRODUCTION

According to the Food and Agriculture Organization of the United Nations (FAO) it is expected that by the year of 2050 the world's population increases to about 9 billion people, and consequently food production will grow approximately 70% overall and 100% in developing countries (FAO, 2011). This fact causes the need to use a larger amount of fertilizers taking into account that the agricultural areas cannot be expanded because of the lower water and soil availability. In Brazil, IBGE (Brazilian Institute of Geography and Statistics) showed that the harvested area corresponds to only about 12.5% of the cultivated area. One possible explanation for this is the lower fertility of Brazilian soils (Figure 1). Thus the need to use fertilizer to increase the productivity of agricultural areas in Brazil is already inevitable.

Improvement in productivity is achieved with water availability and nutrients. Thus, it is high time to develop systems that enable maximum utilization of these nutrients in order to avoid the waste and environmental contamination.

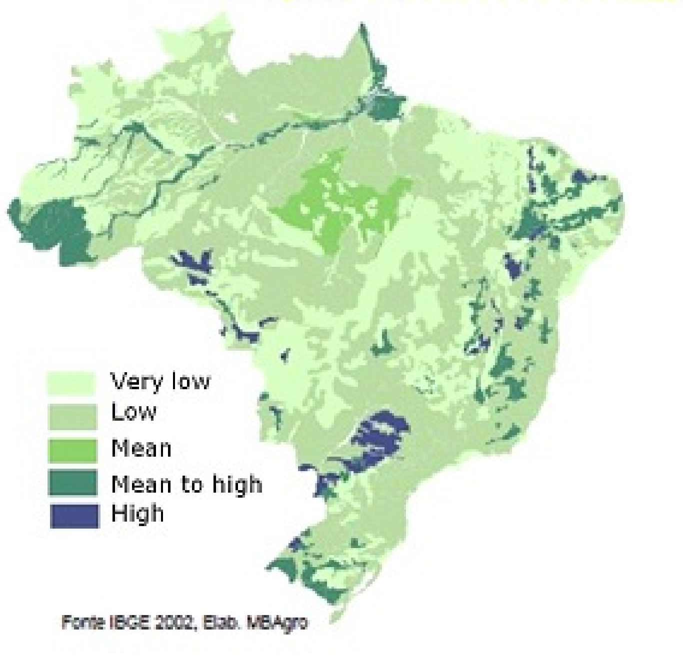

Figure 1. Map of Brazilian soil fertility.

The peat soil is rich in organic matter formed as a result of partial decomposition and humification of vegetable material by microbiological oxidation (Rocha *et al*, 2004). The constituents of peat are compounds of lignin, cellulose and humic substances. These compounds have polar functional groups in their chemical structure, for example, aldehydes, ketones, carboxylic acids and phenols which can be responsible for the binding interactions with metal species (Al-Faqih *et al*, 2008). This interaction depends on the chemical composition and structural characteristics of peat, which varies with the source of plant material as well as such factors as climate, topography and vegetation of the region. The high organic matter content (60-80%) and the binding interactions with metal species, for example, micronutrients, enable peats useful for improvement of agricultural productivity.

However, the weaknesses in studies that assess the ability of tropical peat to adsorb nutrients under different experimental conditions and subsequently evaluate the release of these nutrients is still a limiting factor for its use in agriculture. In this context, the objective of the present work was to investigate the mechanisms that influence the capacity of tropical peats to adsorb the micronutrients copper, cobalt, manganese and nickel and evaluate the release of these nutrients by peat under different conditions of pH.

MATERIAL AND METHODS

Sampling

The samples were collected from a peatland at Santo Amaro das Brotas in Sergipe State, Brazil, (36º58'52”W; 10º49'3”S) (Figure 2). Integrated samples (n = 5) were collected at a depth of 0-20cm from the surface. The samples were stored in polyethylene bags after being air-dried, grinded and homogenized in a porcelain mortar, and sieved through a 2mm mesh sieve.

Figure 2. Sampling site at Santo Amaro das Brotas, Sergipe, Brazil.

Characterization of the peat sample

The pH of samples was determined in water and in the presence of $CaCl_2$. The organic matter content was measured by gravimetry. Granulometry was performed according to the pipette technique. The concentrations of the micronutrients copper, cobalt, manganese and nickel were determined by atomic emission spectroscopy, using an Agilent 700 ICP-OES instrument. The sample was characterized by ^{13}C nuclear magnetic resonance (^{13}C NMR) and element analysis (CHN).

Adsorption of micronutrients by the peats: influence of pH

The batch adsorption experiments employed 2.0g of peat sample, which was transferred to a beaker together with 300 ml of deionized water. The micronutrients (copper, cobalt, manganese and nickel) were added to the solution to give concentrations of 10 mg l^{-1}. The pH was adjusted to different values (3.0, 4.5, and 6.0) using solutions of 1.0 mol l^{-1} HCl or 1.0 mol l^{-1} NaOH, and 5 ml aliquots were withdrawn for analysis at predetermined time intervals (0, 10, 30, 60, 120, 240, 1440, 2880, and 4380 minutes). The aliquots were centrifuged at 3500 rpm, and the concentrations of micronutrients in the supernatants were determined by ICP-OES. The concentrations of the adsorbed micronutrients were then calculated as the difference between the initial concentration and the concentration measured in the supernatant.

Release of micronutrients by the peats

The release experiments were performed using two different values of pH 4.5 and 6.0. 1 mL aliquots were withdrawn for analysis at predetermined time intervals (0, 30, 60, 120, 240 minutes e 1, 2, 3, 4 and 5 days). The concentrations of micronutrients copper, cobalt, manganese and nickel were determined by ICP-OES.

RESULTS

Characterization of the peat sample

The results of physic-chemical characterization of peat sample are shown in Table 1. The organic matter (OM) content of samples exceeded 80%, indicating a high degree of chemical and biological activity in the peatland. This level of organic matter is higher than values reported in the literature for peats from both Brazil and temperate regions (Tipping *et al.*, 2003; Romao *et al.*, 2007), and is in agreement with measured pH values, since greater decomposition of organic matter reduces pH due to conversion of plant materials to carboxylic acids, esters, ketones, and alcohols. The granulometric measurements showed high clay content in samples. The micronutrient contents of the peats were low, which could be due to both geological factors and an absence of anthropogenic activity in the region (Kyzoil, 2002;Al-Faiqh *et al.*, 2008).

Table 1. Physico-chemical characteristics of peat samples.

	OM[1] (%)	**pH (H_2O)**	**pH ($CaCl_2$)**	**Granulometry (%)**			**Metals (μg g^{-1})**			
				sand	**silt**	**Clay**	**Cu**	**Co**	**Mn**	**Ni**
TSA	83.1	3.8	2.9	56.3	1.2	42.6	15.0	LD	181.7	17.5

DL = 2.24 μg g^{-1}; [1]OM: organic matter;

The elemental compositions, atomic ratios and relative percentages of different carbon-containing groups obtained by ^{13}C NMR of the peat sample are provided in Table 2. Lower H/C and O/C ratios were obtained for samples. The results therefore show that samples wer more aromatic, in agreement with their higher organic matter content. The percentages obtained show that aromatic, phenolic and carboxylic carbons were favoured.

Table 2. Elemental composition (%) and atomic ratios, and percentages assigned to different carbon groups in peat samples.

	Elemental analysis							**^{13}C NMR Chemical shift δ assignments (%)**						
	C	**H**	**O**	**N**	**H/C**	**O/C**	**C/N**	**C aliphatic (0-65)**	**Ethers, -OH, sugars (65-110)**	**C aromatic (110-140)**	**Phenols (140-160)**	**-COOH (160-190)**	**-CO (190-220)**
TSA	36.6	2.5	28.2	3.1	0.81	0.58	13.8	33.2	20.7	28.5	7.1	8.7	1.8

Influence of pH

It is recognized that pH influences metal adsorption, since it activates surface sites by either protonization or ionization. Determination of the optimum pH for micronutrient adsorption is particularly important in the case of peat, due to its high content of organic matter. The adsorption capacities of peat increased at higher pH (Figure 3), with greatest adsorption at pH 6.0. This behaviour reflected the ionization of acid groups capable of interacting with cationic species.

At all values of pH, preferential adsorption of the micronutrients followed the order: Cu(II) > Ni(II) > Co(II) > Mn(II) (Figure 3). This can be explained by different relative affinities for the metal cations, according to the hard-soft-acid-base principle. The Cu(II) cation is a soft acid, while Mn(II) is considered a hard acid. The cations have affinity for other compounds with similar characteristics; for example, soft acids have greater affinity for soft bases (Alloway, 1995). Since the composition of peat includes clay minerals, which are soft bases, there was preferential adsorption of the soft acid cation Cu(II), followed by the intermediate cations Co(II) and Ni(II) and finally the hard acid cation Mn(II).

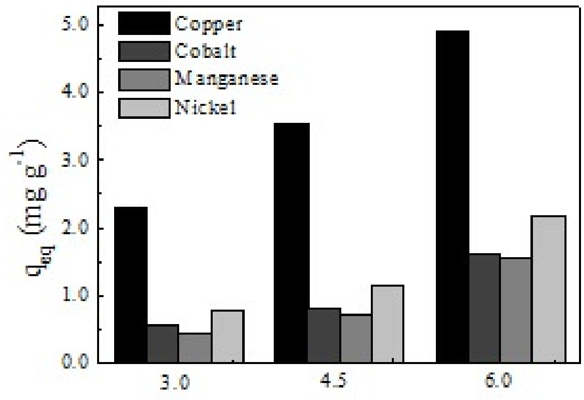

Figure 3. Adsorption capacities of the peat sample for the micronutrients Cu, Co, Mn and Ni at different pH values (3.0, 4.5, and 6.0).

Release experiments

The release experiments showed that after the third day of the experiment the concentration released does not change, it reaches an equilibrium for most micronutrients. Differences in releases evaluated with respect to pH, and the highest release was observed at pH 6.0. Table 3 was constructed for a better understanding of the adsorptive capacity of the peat samples by micronutrients, the concentration released in the two pH and the percentages of released observed at the two pH levels. The results confirm that release of micronutrients followed the order: Mn(II) > Co(II) > Ni(II) > Cu(II). What is seen is that the order of release is the opposite of the order of adsorption. The micronutrient Cu(II) was more adsorbed in peat samples and the micronutrient Mn(II) was the less adsorbed.

Table 3. Results of the adsorption experiments, of the release experiments and the percentage of micronutrient released as a function of the concentration initially adsorbed.

	Adsorbed mg g^{-1}	**Released µg g^{-1}**	**Released µg g^{-1}**	**% release**	**% release**
	pH 6.0	**pH 4.5**	**pH 6.0**	**pH 4.5**	**pH 6.0**
Copper	4.1	14.3	34.7	0.35	0.85
Cobalt	3.2	322.9	444.8	10.1	13.9
Manganese	2.9	356.5	459.1	12.3	15.8
Nickel	3.8	255.6	382.2	6.7	10.1

CONCLUSION

The results showed that tropical peat provides good adsorptive capacity for the micronutrients copper, cobalt, manganese and nickel. The order of adsorption was: Cu(II)>Ni(II)>Co(II)>Mn(II). The results of the release experiments showed a good percentage of release for the same micronutrients. The order of release was: Mn(II)>Co(II)>Ni(II)>Cu(II).

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