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Effect of pH on boron adsorption in selected Indian soils

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ABSTRACT

The adsorption of B by soil is the main phenomenon that affects its availability to plants. This study aimed to evaluate the effect of pH on B adsorption in soils in south Indian samples (Andhra Pradesh). Samples from the 0-20 cm layer, from four soils (acidic alfisol (AA), neutral red alfisol (NRA), alkaline black vertisol (ABV) and coal fly ash (CFA)) were used. The soils were incubated with increasing doses of calcium carbonate until a constant pH. To determine the amount of B adsorbed, soil samples were kept in contact, by stirring for 24 h, with 0.01 mol /L NaCl solutions containing 0.1; 0.2; 0.4; 0.8; 1.2; 1.6; 2.0; and 4.0 mg /L of B. The adjustment of the experimental results was performed by the non-linear form of the Langmuir isotherm. The adsorption of B was dependent on the pH of the soil, having increased as a function of the pH in the range between 4.6 and 7.4. The highest capacity for maximum B adsorption was found in the soil Acidic alfisol (49.8 mg /kg), followed by Neutral red alfisol(22.5 mg /kg), Alkaline black vertisol (17.4 mg /kg)) and Coal fly ash (7.0 mg /kg).

Keywords: Langmuir isotherm, maximum boron adsorption capacity, Soil samples from Guntur District.

INTRODUCTION

Boron (B) deficiency in the soil constitutes a serious limitation for the development of several crops of economic interest, due to the low natural fertility of some soils, the removal by crops and the inadequate and / or excessive application of acidity correctives, that contribute to its insolubilization. It should also be noted that the adequate management of B in the soil-plant system is usually difficult, due to the fact that the concentration interval between deficiency and toxicity is the smallest, when compared to that of other nutrients. Becoming of great relevance the knowledge of the chemical behavior of B in the soil from the agronomic and environmental points of view. The availability of B in the soil depends on the adsorption-desorption processes, which are influenced by the physical-chemical characteristics soil [1]. The amount of B that a soil can adsorb depends on the pH of the soil solution, the mineral composition of the soil and the texture. Of these, pH has been related as the main factor affecting the adsorption of B in the soil [2], mainly because it influences the control of the predominant species of B in the solution and in attributes related to its adsorption, like the load balance on the colloid surface. Other factors, such as clay content, Fe and Al (hydr) oxides, soil organic matter also affect the adsorption of B in agricultural soils [3].

The adsorption of B increases with increasing pH and reaches a maximum around pH pH 9, and decreases thereafter, as the maximum development of B adsorption sites occurs at a pH equivalent to constant of dissociation (pKa) of boric acid, approximately 9.2. The increase in B adsorption occurs due to the

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increase in the proportion of borate anions [B $(OH)^-$], which accompanies the increase in pH and can form both internal and external sphere complexes with mineral surfaces [4] .

Studies carried out on India soils have shown significant increases in the amount of B adsorbed with increasing pH [5]. This effect may be even greater in soils cultivated under no-tillage systems, where the surface application of the correctives without further incorporation promotes an increase in the pH in the topsoil. This study aimed to evaluate the effect of pH on B adsorption in some soils in Andhra Pradesh, Guntur District.

MATERIAL AND METHODS

Samples collected in the superficial layer, 0-20 cm, from four classes of soils in the western region of the State of Andhra Pradesh, Guntur District were used. The soils sampled were a Red Latosol (AA), a Red Nitosol (NRA), a Red-Yellow Argisol (ABV) and a Coal fly ash (CFA), all with negative load balance. The samples were air dried, ground and passed through a 2 mm mesh sieve, and characterized physically and chemically, and some characteristics are shown in Table 1.

Table 1. Chemical and physical attributes of soil samples collected in the western region of the State of Andhra Pradesh, Guntur District in the 0-20 cm depth layer

Soil	pH	Δ pH	MO	Al	CTCe	Bsol.	Clay	SiO2	Fe2O3	Al2O3	Ki
g dm^{-3}				mmolc dm^{-3}		mg dm^{-3}	----------------- g /kg -----------------				
acidic alfisol	4.6	-0.4	22.8	2	78	0.16	580	209	169	179	1.98
neutral red alfisol	4.7	-0.6	32.6	3	130	0.35	740	234	198	223	1.79
alkaline black vertisol	4.9	-0.8	10.9	2.5	98	0.4	720	206	162	197	1.78
coal fly ash	5.1	-1.9	12.5	0	129	0.54	490	261	196	153	2.86

pH in water in the soil: water ratio of 1: 2.5; Δ pH: delta pH used to estimate the load balance; MO: organic matter; CTCe: effective cation exchange capacity; Bsol .: B soluble in hot water. SiO_2, Fe_2O_3 and Al_2O_3: oxides of silicon, iron and aluminum extracted by sulfuric attack. Ki: weathering index: SiO2 / Al_2O_3.

To evaluate the effect of pH on the adsorption of B in the soil, sub-samples of soil were incubated until constant pH (about 40 days), after receiving 0, 1, 2, 4 and 8 Mg/ha of $CaCO_3$. After this period, the samples were air dried and passed through a 2 mm mesh sieve. The pH values in water ranged from 4.6 to 6.8 in the AA soil; from 4.7 to 7.3 on the NRA soil; from 4.8 to 6.5 on the ABV soil; and, from 5.9 to 7.4 on CFA soil.

For the study of B adsorption, samples of 2.0 g of soil were placed in polyethylene tubes and added with 20 mL of 0.01 mol /L NaCl equilibrium solution, which contained 0.0; 0.1; 0.2; 0.4; 0.8; 1.2; 1.6; 2.0; and 4.0 mg /L of B in the form of boric acid. The tubes were kept in slow agitation for 24 h, in a vertical shaker at 24 ± 2 ºC. Then, the suspension was filtered on Whatman type 42 filter paper, and a 5 mL aliquot of the supernatant was taken for the determination of B by the colorimetric method of Azomethine-H at 420 nm [6].

The amount of B adsorbed (Bads) and the percentage of adsorption (% Bads) were calculated by the following ratios, respectively:

$B_{ads} = [(C_0 - C_{eq}) V] / m$ Eq ..1

$\% B_{ads} = [C_0 - C_{eq}) / C_0] x 100$ Eq ..2

where, B_{ads} is the amount of B adsorbed after equilibrium (g /kg); C_0 and C_{eq}, the initial added and equilibrium concentration (mg /L), respectively; V, the volume of solution (mL); and m, the mass of soil sample

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(g). The amount of B originally present in the samples (Table 1), although small, was discounted in the calculation of the amount of B adsorbed.

Adsorption isotherms (Bads vs. Ceq) were built from the experimental results, and the adsorption of B was compared with that estimated by the nonlinear form of the Langmuir isotherm:

$B_{ads} = (K_L C_{eq} Ads_{max})/(1 + KLC_{eq})$ [3]

Where K_L is the parameter related to soil affinity for B (L/mg) and Ads_{max} is the maximum adsorption capacity of B (mg /kg). The Langmuir isotherm was adjusted to the results of B adsorption by the Fit fun programs, using the non-linear regression technique. The method of least squares for curve adjustment has been recommended in recent years, because it does not require the linearization of the isotherm, which avoids both the introduction of changes in the distribution of errors and the acquisition of parameters.

RESULTS AND DISCUSSION

The Langmuir model adjusted well to the values of B adsorbed by soils, over the entire concentration and pH range studied (Figure 1), as it has high determination coefficients (R2 ≥ 0.96). These results were expected, because there are no records of deviations from the Langmuir equation at concentrations below 30 mg /L of B [6].

For the Coal fly ash (CFA) the isotherms exhibited the classic "L" type behavior (Langmuir), particularly at the lower pH values (Figure 1), with less adsorption energy, characterized by a decrease in adsorption as the surface of the adsorbent is becoming saturated. From the slope of the adsorption isotherms, an increase in the adsorption of B at lower concentrations is observed. With the increase in the concentration of B in solution, more sites were occupied and the reaction was more difficult to occur, causing a decrease in the inclination of the isotherm. For the other soils studied, the apparent constant slope (Figure 1) is inherent to type "C" isotherms, which indicates high adsorption affinity. In this type of curve, the number and energy of the sites available for adsorption remain constant over the entire range of concentration and the expansion of the available surface may occur in proportion to the amount adsorbed, until all the adsorption sites are occupied . This was due to the low initial concentrations of B (C_0) used in the study.

The adsorption of B was dependent on the pH of the solution, having increased due to the increase in pH in the range between 4.6 and 7.4 (Figure 1 and Table 2). Several studies have shown that pH is one of the main factors that affects the availability of B in soils [7]. The two species of B present in the soil [8]. [B (OH) $^-$ and B (OH)] have different affinities for colloids and appear in varying proportions in the equilibrium solution in response to changes in pH. At pH below 7.0, the species B (OH) 3 predominates and, since the affinity of clay minerals for boric acid is low, the amount of B adsorbed tends to be small.

With an increase in pH to close to 9.0, the proportion of B (OH) - increases rapidly, but it is still small to exercise effective competition with borate anions. From that value, followed by increases in pH, resulting in an increase in the concentration of OH- in relation to that of B (OH) -, and the adsorption of B decreases due to competition with OH adsorption [6].

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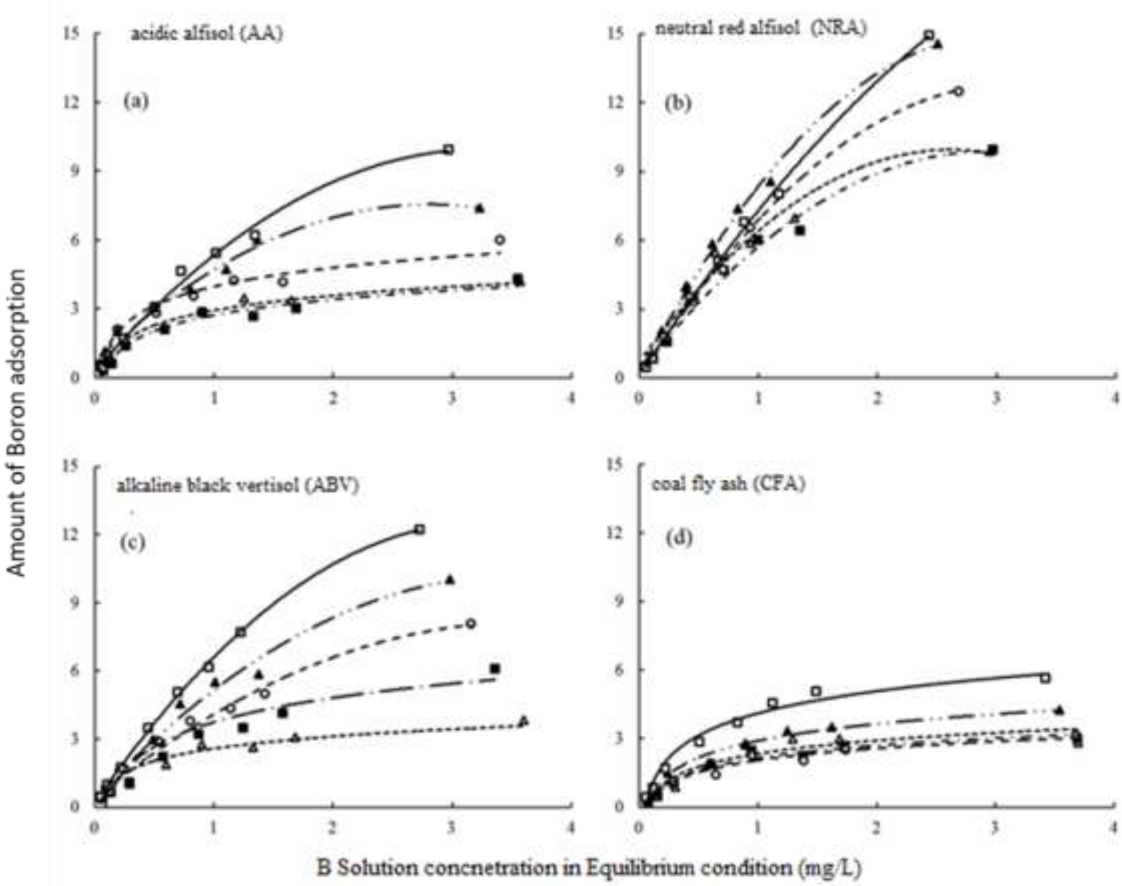

Figure 1. B adsorption isotherms obtained from adjustment by the Langmuir equation in four soils in the State of Andhra Pradesh, Guntur District with different pH values. ** p <0.01.

Table 2. Maximum B adsorption (Ads_{max}), affinity constant (K_L) and percentage of B adsorption (% B_{Ads}) after the addition of 2.0 mg /L of B in four soils in the State of Andhra Pradesh, Guntur District with different values of pH

Soil	pH	Langmuir Constant Adsmax mg /kg	Langmuir Constant KL L mg^{-1}	%BAds
acidic alfisol (AA)	4.6	4.9	1.6	28
	4.9	5.4	1	36
	5.2	6.8	1.6	41
	5.7	8.9	1.4	52
	6.8	17.4	0.4	63
neutral red alfisol (NRA)	4.7	12.7	1	34
	5.4	16.1	0.5	41
	6.1	26.3	0.3	53
	6.7	33	0.3	58
	7.4	49.8	0.2	62

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alkaline black vertisol (ABV)	4.9	4.4	1.6	36
	5.4	9	0.6	41
	6	13.3	0.5	51
	6.7	16.5	0.5	64
	7.3	22.5	0.4	78
coal fly ash (CFA)	5.1	3.5	1.7	26
	5.5	3.8	1.2	33
	6.1	4	1	34
	6.5	5.5	1	39
	7	7	1.4	43

The values of the Langmuir constants (Table 2) were similar to those found in studies that used a similar range for the concentration of B added to the soils. The K_L affinity constant ranged from 0.17 to 1.67 L/mg, while the maximum adsorption (Ads_{max}) oscillated between 3.54 and 49.75 g /kg. The great variation of these parameters can be attributed to the differences in the chemical, physical and mineralogical attributes of the soils, in addition to the effect of the pH variation.

The highest values of Ads_{max} were found in soil NRA, followed by ABV and AA. The CFA soil had the lowest Ads_{max} values (Table 2). The lower B adsorption capacity obtained for the CFA soil can be explained by the fact that this soil is little evolved in terms of the weathering degree, evidenced by the weathering index Ki above 2.46 (Table 1), in addition to presenting a higher proportion of loads negative (Δ pH of -1.90) in relation to the other soils (Table 1).

The percentage of B adsorption (Table 2) increased with increasing pH. In the AA, the increase in pH from 4.6 to 6.8 resulted in an increase of 35%. For NRA, the increase in pH from 5.9 to 7.3 resulted in an increase of 27%. In the ABV and CFA, the pH increase from 4.8 to 6.5 and from 6.0 to 7.4 increased the adsorption of B by 43% and 16%, respectively. This increase in maximum adsorption with an increase in pH can be explained by the increase in the number of active adsorption sites and the greater proportion of the borate ion [B (OH)-] in relation to boric acid [B(OH)].

CONCLUSIONS

The amount of B adsorbed by soils increased with increasing concentration of this element. B adsorption increased with increasing soil pH. Binding energy decreased with pH in most soils, which indicates that at higher pH values, B is more poorly adsorbed. The greater capacity for maximum B adsorption in Acidic alfisol is due to the higher content of clay and organic matter in this soil.

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