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RESEARCH ARTICLE

INFLUENCE OF AGROSILICON AND MB-4 ON THE ELECTROCHEMICAL ATTRIBUTES OF BRAZILIAN TROPICAL SOILS

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ABSTRACT

AgroSilicon (siderurgy slag) and MB-4 (rock powder) are materials of different compositions and when applied to the soil influence the properties thereof. This study was conducted in order to determine by potentiometric titration various electrochemical attributes of three soils of State Paraiba enriched with AgroSilicon and MB-4. For this, the soils were incubated for 100 days with different amounts of these conditioners. After this period the soils samples were air dried and subjected to potentiometric titration curves. The intersection of these curves determined the pH of the zero point of charge (ZPC), which reflects the equal condition of ion adsorption H^+ and OH^-. Based on pH and ZPC they were calculated ΔpH and surface electrical potential (Ψ_0). The soils presented electric charges variables and predominantly negative sign. Soil conditioners, AgroSilicon and MB-4, increased generally all electrochemical properties of soils.

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INTRODUCTION

In acid soils resulting from the weathering process and leaching of exchangeable bases, the toxicity of aluminum and / or manganese and low levels of calcium and magnesium, are limiting factors in the development of the cultures (Paiva *et al.*, 1996; Ernani *et al.* 2000). Liming is traditionally made using limestone, however, many industrial wastes by having in its composition such elements that can replace limestone, are being screened for the feasibility of their use in agriculture. Among these wastes, it has the siderurgy slag (AgroSilicon - calcium silicate and magnesium) and rock rock powder (MB-4). The slag is chemically composed of oxides and silicates of calcium and magnesium, iron and manganese oxides, metallic iron and other elements in smaller proportions. The composition is influenced by several factors, such as the steel production technique, the type of steel to be produced, the quality of the raw material used and the type of refractory used in the furnace walls (Prado *et al.*, 2001). The rock powder is produced by grinding magmatic rocks (basalt, granite) and is being used as a soil conditioner. It consists of various silicates, among them especially the magnesium, calcium and iron, which are present together with phosphorus, potassium and sulfur and several micronutrients, such as copper, zinc, manganese, cobalt, and others. Some surveys of these residues have demonstrated the power of them to increase the calcium and magnesium soil and, sometimes, neutralize the acidity of the soil, or to raise the pH. The increase in pH, consequently, increases the negative charges of the exchange complex, increasing, therefore, the retention of cations. The variation of soil pH influences both the magnitude and sign of the electrical charges on the colloids. A positive or negative surface charge is due to the adsorption or desorption of a proton, respectively. The point of zero charge (ZPC) corresponds to the pH value of the soil in which the balance between positive and negative charges is zero.

The comparison between soil pH and ZPC allows to define if the net surface charge of colloids is negative (pH> ZPC), positive (pH < ZPC) or zero (pH = ZPC).Therefore, the ZPC is an important parameter for the description of electrochemical phenomena of variable charge soils, affecting properties such as cation exchange and nutrient availability. Similarly, with the ZPC it is possible to determine the potential of the electric double layer by the simplified equation of Nernst (Uehara and Gillman, 1980).

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The electric charge and ZPC are dependent on the proportion of mineral and organic soil constituents, being influenced by chemical management employed in these soils. The application of calcium silicate and magnesium (AgroSilicon) and rock dust (MB-4) as a soil conditioner probably influence the electrochemical reactions occurring on the surface of soil colloids. Considering the above and the fact that the information in this regard it is scarce, the objective with this research to determine the electrochemical attributes of some Paraiba State soils with use of AgroSilicon and MB-4.

MATERIALS AND METHODS

The experiment was carried in Irrigation and Salinity Laboratory of the Department of Agricultural Engineering, Federal University of Campina Grande. To evaluate the behavior of AgroSilicon (calcium and magnesium silicate) and rock rock powder (MB-4), as soil conditioners in the electrochemical properties of the soil, samples of Ultisol, Oxisol and Entisol were collected in the municipalities Campina Grande, Areia and Lagoa Seca, respectively, in Paraiba State, Brazil, whose chemical characteristics according to the methodology of Embrapa (1997) are in Table 1.

Table 1. Chemical characterization of soil samples used for the tests

Attributes Chemical	Ultisol	Oxisol	Entisol
Calcium ($cmol_c$ kg^{-1})	2.02	2.09	0.78
Magnesium ($cmol_c$ kg^{-1})	1.46	1.60	1.19
Sodium ($cmol_c$ kg^{-1})	0.09	0.09	0.08
Potassium ($cmol_c$ kg^{-1})	0.14	0.07	0.14
Sum of bases ($cmol_c$ kg^{-1})	3.71	3.85	2.19
Hydrogen ($cmol_c$ kg^{-1})	6.36	11.97	2.72
Aluminium ($cmol_c$ kg^{-1})	0.40	0.40	0.20
CTC ($cmol_c$ kg^{-1}) [1]	10.07	16.22	5.11
Organic Matter (g kg^{-1})	11.90	31.50	9.60
Comparable phosphorus (mg kg^{-1})	3.20	2.60	11.40
pH H_2O (1:2.5)	5.12	5.14	5.30
V (%)[2]	36.84	23.74	42.85
Sand (g kg^{-1})	730	588	832
Silt (g kg^{-1})	142	101	141
Clay (g kg^{-1})	128	311	27

[1]= cátion Exchange capacity; [2]= percentage of base saturation

The corrective agents to be tested were produced by AgroSilicon Hascos Minerals with 35% of Calcium; 6% of Magnesium; 10.535% of silicon and 64.6% PRNT named in this research as silicate. The rock dust, known as MB-4 to be tested in soil, was produced by MIBASA (2016) with the following composition 39.7% of SiO_2; 7.1% of Al_2O_3; 6.9% of Fe_2O_3; 5.9% of CaO; 17.8% of MgO; 1.5% of Na2O; 0.8% of K_2O; 0.075% of P_2O_5; 0.2% of S. To increase the bases saturation of soils, around 80%, the silicate doses calculated from your PRNT corresponded to 5.99; 2.26 and 0.97 g of silicate / kg of Oxisol, Ultisol and Entisol, respectively. Since it is not known PRNT of MB-4, doses were corresponding to twice the quantities necessary to increase the bases saturation of soils with calcium carbonate (PRNT 100%), ie, 7.73; 2.92 and 1.26 g of MB-4 / kg Oxisol, Ultisol and Entisol, respectively. Incubation of these samples was done by placing in plastic pots (experimental units) three hundred grams of each soil sample mixed with the quantities of the conditioners mentioned above and wetted with deionized water at about 60% of field capacity during 100 days. After this period, the soil samples were air dried and subjected to potentiometric titration curves. For each soil sample were obtained two potentiometric titration curves, one prepared in suspension of $CaCl_2$ 0.1M, and another for water. To this were placed 4 g of ground 13 cups of 100 ml. Then it was added in 7 cups 0.5 ml of 0.1M $CaCl_2$ solution and HC1 0.1 M solution from 0 to 3 mL (0.5 in 0.5 ml); in the other 6 cups 0.1M HC1 was added from 0,5 to 3 mL (0.5 in 0.5 ml); in all cups was added distilled water to make 20 ml of solution. The pH was determined after 72 hours of contact, at which the suspensions were shaken occasionally. The each soil sample pH values were plotted graphically as a function of the amounts of hydrogen (HCl) expressed in meq / 100 g soil originating two curves titration. The intersection of these curves determined the pH of the zero point of charge (ZPC), which reflects the equal condition of ion adsorption H^+ and OH^-. Based on pH and ZPC they were calculated ΔpH and surface electrical potential (Ψ_0) according the equation Ψ_0 = 59,1 (ZPC – pH) in mV (Raij and Peech, 1972).

RESULTS AND DISCUSSION

The incubation of the soil samples with silicate and MB-4 led to an increase the pH neutralizing, partly, the acidity of soils (Table 2). The amount of silicate used was sufficient to achieve the saturation by soil base (80%), however, the amount used of MB-4 (twice the amount of calcium carbonate required to achieve 80% saturation by soil base) was not sufficient to reach this saturation (Mendes *et al*., 2015). The recommendation of calcium carbonate in Ultisol, Oxisol and Entisol to reach 80% of base saturation was 4.32; 9.12 and 1.9 t / ha, respectively. However, as noted above, it was used twice greater than these amounts, ie, much higher than the recommended dosage of fertilizing plants by the manufacturer, 2 t / ha (MIBASA, 2016). Thus, under the conditions of this work, the MB-4 application left to be desired. The ΔpH is indicative of the predominance of charges net of the soil, ie, whether they are negative or positive.

Table 2. Electrochemical properties of soils incubated with silicate and MB-4

Attributes		**Ultisol**	
	Natural soil	Silicate 2.26 g /kg	MB-4 2.92 g/kg
pH H_2O	4.9	5.9	5.6
ΔpH	-1.04	-1.32	-1.29
PCZ	2.45	3.15	2.79
Ψ_0, mV	-144.79	-162.52	-166.07
V,%	31.4	73.0	57.6
		Oxisol	
	0 g/kg	5.99 g/kg	7.73 g/kg
pH H_2O	4.8	6.0	5.8
ΔpH	-0.96	-0.93	-1.30
PCZ	3.05	4,65	4.15
Ψ_0, mV	-103.42	- 79.78	-97.51
V,%	20.9	100	55.6
		Entisol	
	0 g/kg	0.97 g/kg	1.26 g/kg
pH H_2O	4.9	6.0	5.7
ΔpH	-1.03	-1.22	-1.18
PCZ	2.65	2.00	2.25
Ψ_0, mV	-132.97	-236.40	-203.89
V,%	40.5	100	60.1

In the laboratory it is possible to obtain the ΔpH value of the difference of pH in water values and pH in $CaCl_2$ or in pH KCl, and when it approaches zero, indicates that the soil is close to PCZ. As data presented in Table 2, the ΔpH increased due to the application of conditioners in soils except silicate in the Oxisol, i.e., in this situation, there was a decrease, although small, in the difference between negative and positive charges (charges net). However, all ZPC values remained below pH values in water, indicating the predominance of negative charges in the soil samples and the surface charge density with a negative sign. In this case, the cation exchange capacity of the soil continues to exceed the anion exchange capacity in natural pH conditions and to the extent to which increases the pH of the soil above the ZPC, increase the negative charge density and consequently the cation exchange capacity.

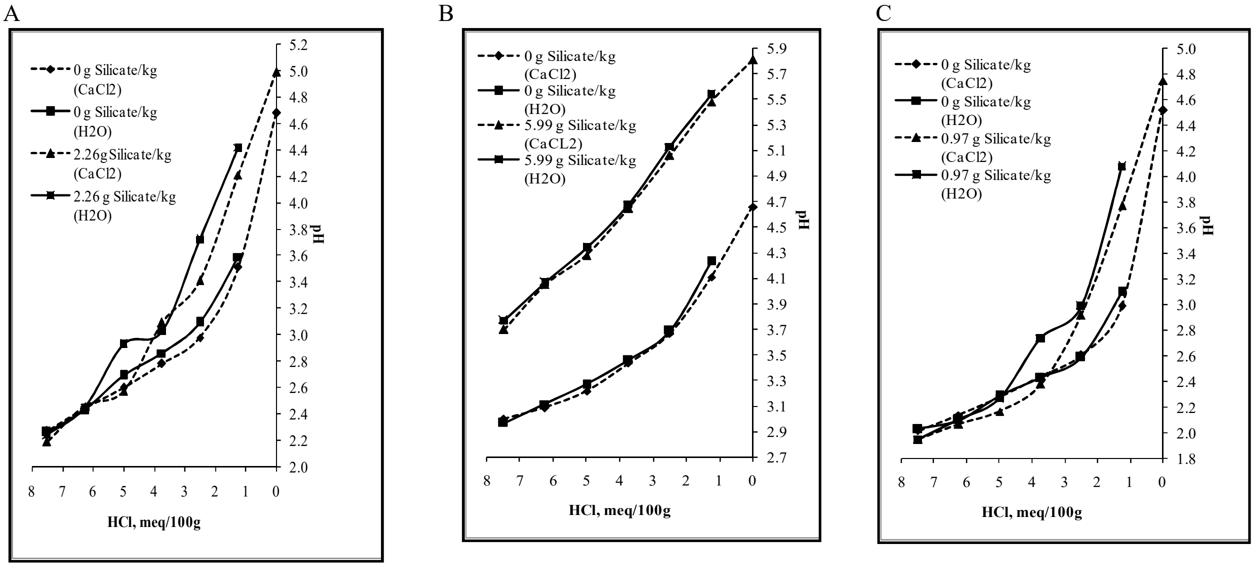

Figure 1. Potentiometric titration curves in $CaCl_2$ and in water of the soil samples Ultisol (A) Oxisol (B) and Entisol (C) incubated with and without silicate, used to determine the ZPC

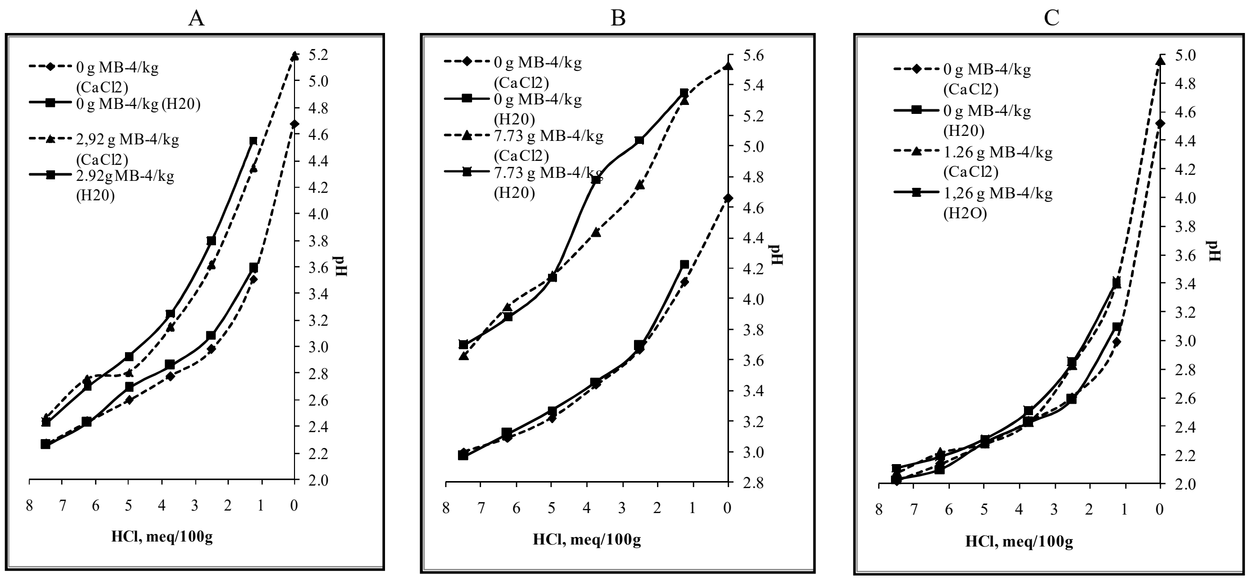

Figure 2. Potentiometric titration curves in $CaCl_2$ and in water of the soil samples Ultisol (A) Oxisol (B) and Entisol (C) incubated with and without MB-4, used to determine the ZPC

Figure 1 and 2 presents the soil titration curves with and without silicate and MB-4 and the corresponding points of zero charge, whose values are shown in Table 2. The application of these soils conditioners increased ZPC values, with except in Entisol, whose values were lower compared to the natural soil. This seems to be more coherent based on increased net negative charge, i.e., as it increases the ΔpH the ZPC decreases. The values of the ZPC Ultisol (2.45), Oxisol (3.05) and Entisol (2.65), without the application of conditioners were similar to those of Chaves and Trajano (1992), ie , 2.6 ; 3.4 and 2.5, respectively. According to various authors, the sign and magnitude of ΔpH are related to the signal and magnitude of the Ψ_0, ie, the variation values of Ψ_0 followed the variation of the ΔpH value and have become increasingly negative as the pH increased, confirming Albuquerque *et al.* (2000) and

Chaves and Trajano (2001). The variation of the results presented in Table 2 can be attributed the mineralogical diversity of soils once they present different source materials and physico-chemical characteristics (Table 1). The sandy soil, such as Entisol, probably had a minor buffering capacity, so had greater spacing between ZPC and pH (2.25; 4.0; 3.45, to natural soil, silicate e MB-4, respectively). Unlike the Oxisol, which has higher value of clay.

Conclusion

The soils presented electric charges variables and predominantly negative sign. Soil conditioners, silicate and MB-4, increased generally all electrochemical properties of soils.

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