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RESEARCH ARTICLE

EFFECTS OF POULTRY LITTER BIOCHAR ON ELECTROCHEMICAL PROPERTIES OF ELECTRONEGATIVES SOILS

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ABSTRACT

Biochar is an option in agriculture have been used with fertilizer and soil conditioner. Ultisol, Oxisol and Entisol with electronegative character were used for studies of electrochemical properties, before the addition of poultry litter biochars. Soil samples were incubated for 100 days with different treatments. After this period, the soil samples were dried, sieved, analyzed for pH_{H2O} and pH_{KCl}. With the values of pHs were calculated the values of the zero point of charge (ZPC) of electric charges and the surface electric potential (Ψ_0). The addition of biochar in soils increased pH, decreased the negative charge and the surface electric potential, increasing ZPC values. The values of ZPC correlated positively with the values of organic matter and biochar applied to all three soils and negatively with ΔpH and Ψ_0 values only in Oxisol and Ultisol.

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INTRODUCTION

The surfaces of the soil colloids are electrically charged, which means that these surfaces have excess or deficit of electrons (Uehara and Gillman, 1980). These charges are generated by adsorption and desorption potential determining ion (Schofield, 1949), particularly H^+ and OH^-, and hence the colloids are called per charge pH dependent (Zhang *et al*., 1991). The study of the electrical charges of the colloidal particles (organic and inorganic) is necessary for the understanding of different physical and chemical events that occur in the soil, because most electrochemical reactions influence fertility (Kononova, 1984) and plant nutrition interfering in phenomena related to its management and conservation that occur on the surface of these particles (Siqueira, 1985; Sposito, 1989; Fontes *et al*., 2001). Soils as the mineralogical composition may have both positive and negative electrical charges. The zero point of charge (ZPC) corresponds to the soil pH value in which the balance between positive and negative charges is zero. A comparison between the pH of the soil and ZPC defines the net surface charge of the particles, if it is negative (pH> ZPC), positive (pH < ZPC) or zero (pH= ZPC) (Appel *et al*., 2003). ZPC is, therefore, an electrochemical characteristic of great importance in soils with a predominance of pH dependent charges, affecting properties such as flocculation, dispersion, cation exchange and nutrient availability, among others (Fontes *et al*., 2001; Appel *et al*., 2003; Fontes and Alleoni, 2006). It is also possible, through the value of the ZPC; determine the potential of the electric double layer by the simplified equation of Nernst (Uehara and Gillman, 1980). The highly weathered soils, with a predominance of variable charge of minerals, constitute a group of different soils with similar electrochemical properties and whose cation exchange capacity depends mainly on soil organic matter. Therefore, the addition of organic matter to a system at equilibrium will promote changes in the soil pH and hence the charges due to direct or indirect factors. As an example, the adsorption of organic acids, which can increase the negative charge system, and thus a lowering of ZPC (Oades, 1984). Biochar, carbon-rich product produced by slow pyrolysis thermo-chemical biomass has been applied to the soil as a conditioner, improving its physical and chemical properties (Lehmann *et al*., 2006), and biological (Gundale and Deluca, 2006). Oguntunde *et al*. (2004) observed an increase in the pH level and the content of exchangeable cations in soil with the application of biochar, however, Topoliantz *et al*. (2005) noted a decrease in the pH level. The production of biochar from animal waste has higher nutritional value regarding the biochar produced from vegetable waste. Poultry litter is of special interest for the production of biochar in Brazil due to high production generated per year, which

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supposedly is about 6.8 million m^3 (Corrêa and Miele, 2011). According to Brazilian Poultry Union (2014), the poultry litter cannot be used for animal feed and then the excess of this waste, has been used as a source of organic matter in agricultural soils. Biochar obtained by pyrolysis of poultry litter is another option in agriculture can be effectively used as a fertilizer and soil conditioner (Sanvong and Suppadit, 2013) as noted by Andrade *et al*. (2015). Thus, considering the above and the fact that there is little information in this regard, the objective of this study was to evaluate the ZPC, electric charges and the surface potential of some Paraiba State soils by applying biochar from chicken manure.

MATERIALS AND METHODS

The experiment was carried in Irrigation and Salinity Laboratory of the Department of Agricultural Engineering, Federal University of Campina Grande, from biochar samples incubated with soil. Soil samples of 0.00 to 0.20 m layer were obtained from areas with Ultisol, Oxisol and Entisol classified as Typic Hapludult, Typic Hapludox and Typic Udorthent (Soil Survey Staff, 2014), 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
CEC ($cmol_c\ kg^{-1}$) [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
V (%)[2]	Biochar amount (g) incorporated to the soil (kg)		
50	0.890	3.600	0.240
60	1.563	4.967	0.583
70	2.240	6.367	0.920
80	2.917	7.733	1.257

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

Biochar is produced by slow pyrolysis of chicken manure, by the company SPPT Research Technology Ltd, with the following composition: pH (H_2O) = 10.1; N = 42.31 g kg^{-1}; P = 32.56 g kg^{-1}; K^+ = 48.56 g kg^{-1}; Ca^{2+} = 57.75 g kg^{-1}; Mg^{2+} = 12.40 g kg^{-1}; Na = 14.37 g kg^{-1}; Fe = 137 g kg^{-1}; Cu = 812 g kg^{-1}; Zn = 700 g kg^{-1}; Mn = 862 g kg^{-1}. Treatments for Ultisol, Oxisol and Entisol consisted of four increasing doses of this biochar corresponding to twice the amount needed to raise the saturation soil bases around 50; 60; 70 to 80%, calculated on the basis of calcium carbonate (Relative Power of Total Neutralization, RPTN, 100%). This was done because it is not known biochar RPTN (Table 1). We used a completely randomized design with two replications. For the incubation of these soils with biochar, each mixed soil sample with biochar, in accordance with the treatments, it was placed in plastic pots (experimental units) and wetted with deionized water in about 60% of field capacity, maintained at a temperature of 28 °C, and weighed every five days to maintain a constant humidity. After 100 days of incubation, the soil samples were air dried, sieved 2 mm mesh and subjected to pH analysis in H_2O (1:2.5) and KCl (1:2.5). From these values, it was estimated the zero point of charge (ZPC), as the equation proposed by Keng and Uehara (1974):

$$ZPC = (2 \times pH_{KCl}) - pH_{H2O}$$

With pH values were also calculated the ΔpH values using the formula:

$$\Delta pH = pH_{KCl} - pH_{H2O}$$

The value of the surface electrical potential (Ψ_0) expressed in mV was calculated using the Nernst equation, simplified by and Raij and Peech (1972) as follows:

$$\Psi_0 = 59.1\ (ZPC - pH_{H2O})$$

The results were statistically analyzed with ANOVA and subsequent application of the Tukey test at 5% probability (biochar) and regression (doses).

RESULTS AND DISCUSSION

Adding biochar to soils caused linear increase of pH performed in water (H_2O) and potassium chloride (KCl), corroborating Andrade *et al*. (2015). Similarly, the values corresponding to ZPC also increased with the increasing doses of biochar (Figure 1) disagreeing with Benites and Mendonca (1998) who observed a decrease of the point of effect salt null on a Oxisol using organic fertilizers.

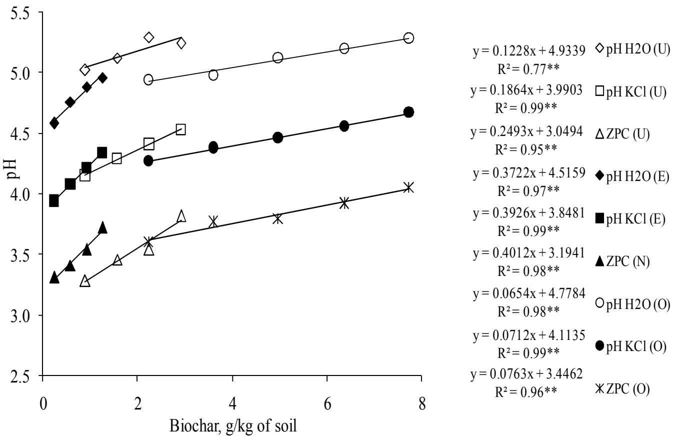

Figure 1. pH values determined in water, potassium chloride (KCl) and corresponding to zero point of charge (ZPC) in Ultisol (U), Entisol (E) and Oxisol (O) depending on biochar dose. ** Significant at 1% probability

The pH values of soil samples incubated with biochar and the calculation results of the electrochemical properties are presented in Table 2. In all soil samples, ZPC values were lower than the pH_{H2O} (Table 2) resulting in negative values of electrical potential (Ψ_0). The negative sign and magnitude of Ψ_0 are related to the sign and magnitude of the ΔpH being the behavior of these attributes according of increasing biochar doses was similar and significantly according to the equations presented on Figure 2 (A and B).

Table 2. Electrochemical properties of soils incubated with biochar doses applied to the soil to achieve different percentages of base saturation

Electrochemical properties	Percentage of base saturation (V%)			
	50	60	70	80
	Oxisol			
pH $_{H2O}$	4.99	5.13	5.21	5.29
pH $_{KCl}$	4.38	4.46	4.57	4.67
ΔpH	-0.61	-0.67	-0.64	-0.62
ZPC	3.77	3.79	3.92	4.05
Ψ_0 (mV)	-71.51	-78.60	-75.65	-72.69
	Ultisol			
pH $_{H2O}$	5.02	5.12	5.29	5.25
pH $_{KCl}$	4.15	4.29	4.42	4.53
ΔpH	-0.87	-0.83	-0.88	-0.72
ZPC	3.28	3.46	3.54	3.81
Ψ_0 (mV)	-102.83	-98.11	-103.42	-84.51
	Entisol			
pH $_{H2O}$	4.58	4.76	4.89	4.96
pH $_{KCl}$	3.95	4.09	4.22	4.34
ΔpH	-0.64	-0.68	-0.67	-0.62
ZPC	3.31	3.41	3.54	3.72
Ψ_0 (mV)	-75.06	-79.78	-79.19	-73.28

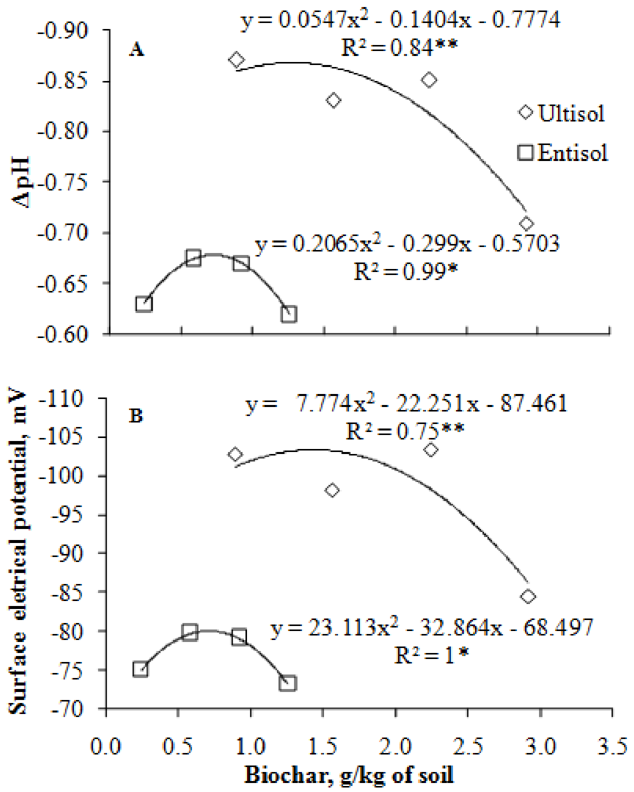

Figure 2. Delta pH (ΔpH) (A) and surface electric potential, mV (B) according to the biochar doses in Ultisol and Entisol. *, ** Significant at 5 and 1%, respectively

Table 3. Correlation coefficients between ZPC and attributes of soils

Attributes	Oxisol	Ultisol	Entisol
	ZPC	ZPC	ZPC
ΔpH	-0.888*	-0.889*	-0.719ns
Ψ_0	-0.889*	-0.897*	-0.711ns
CEC	-0.373ns	-0.552ns	-0.329ns
OM	0.965**	0.978**	0.995**
Biochar	0.975**	0.979**	0.995**

. *; **; ns, significant at 5 and 1% probability and not significant, respectively

ΔpH and Ψ_0 values in the Oxisol samples were also negative and varied depending on the biochar doses (Table 3), however, they were not significant.

The negative signal of ΔpH indicates that there is a predominance of negative charges in the three soils samples. In this case, the cation exchange capacity (CEC) of these soils exceeds the anion exchange capacity (AEC) in natural pH conditions. However, the magnitude of ΔpH decreasing according of increasing biochar doses (Figure 2A) showed a reduction of CEC. Likewise, the magnitude of the surface electric potential, Ψ_0, also decreased as the application of biochar in the soil (Figure 2B), and thus the ZPC values increased (Table 2). This behavior was confirmed by the correlations between the values of the ZPC and those of ΔpH and Ψ_0, which varied inversely, significantly in Oxisol and Ultisol (Table 3). The correlation between ZPC and CEC values was not significant in the soils, but the negative sign, confirms the inverse variation between these values.

The ZPC values correlated positively to 1% probability with the organic matter (OM) and biochar values applied in all three soils. This behavior disagrees with the literature, which points out that the organic matter and, consequently, organic carbon, tends to decrease the ZPC value. According Raij and Peech (1972), the decrease in the ZPC value was attributed to adsorption of organic anions in the mineral matrix of the soil, which does not occur with the application of biochar in the soil. Probably does not occur in biochar reactive groups of organic matter, mainly carboxyl groups, which when dissociated, originate negative charges in the common pH range for soil (Schnitzer, 1986). The biochar applied to the soil, due to its alkalinity neutralizes the potential acidity (H + Al) of soils by increasing the pH of these and even increasing the levels of exchangeable cations, decreases the CEC due to decreased potential acidity (Table 4). However, according to Cheng *et al.* (2006) over time with aging biochar in the soil and the occurrence of abiotic oxidation reaction on its surface, especially for the formation of carboxyl groups tend to increase the CEC.

Table 4. Potential acidity and cation exchange capacity levels, in $cmol_c\ kg^{-1}$, corresponding to the soil without biochar and soil incubated with the highest biochar dose

Soil	Without Biochar		Higher biochar dose	
	potential acidity	CEC	potential acidity	CEC
Oxisol	13.58	17.49	8.19	15.43
Ultisol	7.14	10.78	4.13	8.48
Entisol	5.12	3.05	4.84	2.28

Pyrolysis of poultry litter changed the quality of the carbon compounds in biochar; also caused increased stability of carbon in this product decreasing the biochar mineralization rate when applied to soil and consequently less effective in the generation of charges in the soil, compared to the application of poultry litter. Probably for these reasons there was no increase in ΔpH and therefore did not decrease the ZPC value. According to Andrade *et al.* (2015), carbon from biochar is recalcitrant in the environment, so additional increments CEC should be expected over time, especially for reapplication of biochar in the same area.

Conclusion

The electrochemical properties of Ultisol, Oxisol and Entisol samples were affected by the application of biochar. The application of biochar in soils decreased values, in module, of the ΔpH and Ψ_0, of the CEC and has raised the ZPC.

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