Effects of Poultry Biochar on Electrochemical Properties of an Alfisol and Vertisol of Northern Nigeria

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Abstract: This study was aimed to know the effects of biochar on charge properties of an Alfisol and Vertisol of semi-arid soils of Northern Nigeria. A laboratory experiment was conducted to determine the effects of biochar on point zero charge of soils. An experiment was laid out in a complete randomized design and consisted of two factors; 2 soil types and biochar at 4 levels giving a total of 8 treatment combinations with 3 replications each. The results obtained from the study showed that the pH in KCl of the incubated soils ranged from 7.3 to 7.4 and 7.6 to 7.9 for the Alfisol and Vertisol; 7.5 to 7.7 and 7.9 to 8.3 pH in H2O, was obtained for the Alfisol and Vertisol respectively. Electrical conductivity obtained ranged from 3.22 to 4.72 and 2.88 to 4.21 dS m⁻¹ for Alfisol and Vertisol respectively. Electrical potentials ranged from -19.70 to -35 and -31.45 to -63.04 for the Alfisol and Vertisol respectively. The Point Zero Charge of soils correlated positively with the properties of the soils and the biochar rates. The addition of biochar to soils modified the PZC, increased the pH, electrical conductivity (ECe), and cation exchange capacity (CEC) of the soils.

Introduction

Retention and availability of plant nutrients are some major problems in agricultural soils of the semi-arid regions of northern Nigeria, due to high temperature, leaching, loss of surface soil due to erosion, wide range of pH variations, and low organic matter content. This inadvertently affects the nature and composition of the soil colloids (Ibrahim et al., 2014). The surfaces of soil colloids are largely dominated by negative charges which aid in the attraction and retention of cations in the soils. The predominance of these charges largely influences the cation exchange capacity of soils. These charges are generated by the adsorption and desorption potential of the ions, particularly H⁺ and OH⁻ hence the colloids are called per charge pH-dependent (Zhang et al., 1991). The study of the electrical charges of colloidal particles (organic and inorganic) is necessary for the understanding of different physical and chemical reactions that occur in the soil because most electrochemical reactions influence fertility and plant nutrition (Fontes et al., 2001; Kononova, 2006).

Point of Zero Charge (PZC) is an electrochemical characteristic of great importance in soils with a predominance of pH-dependent charges, affecting soil properties such as flocculation, dispersion, cation exchange, and nutrient availability, among others (Fontes et al., 2001; Appel et al., 2003; Fontes and Alleoni, 2006). "The point of Zero Charge (PZC) is corresponding to the soil pH value in which the balance between the positive and negative charges is zero. i.e., if it is negative, pH>PZC, and positive, if pH<PZC or zero, if pH=PZC (Appel et al., 2003)."

Biochar affects crop yield indirectly by improving soil physical properties (bulk density, water holding capacity, soil aggregation and...
permeability, saturated hydraulic conductivity, etc), chemical properties (e.g. nutrient retention and availability), and biological properties (Glaser et al. 2002; Lehmann and Rondon, 2006; Yamato et al. 2006; Chan et al. 2007, Asai et al. 2009). Therefore, this study was carried out to determine the effects of poultry biochar on electric potential and Point Zero Charge of two benchmark soils (Vertisols and Alfisols) of Jama’are (Bauchi State) and Dutse (Jigawa states) both of the Sudan savanna agro-ecological zones of Nigeria.

METHODS
Description of Study Area
The two Semi-arid soils used for this study are classified as Alfisol and Vertisol (Voncir et al., 2008). The Alfisol for this study was collected from the Teaching and Research Farm of Federal University Dutse, (Lat 11°46’39” N and Long 9°20’3” E) Jigawa State, Nigeria while the Vertisol was sampled from Jama’are in Jama’are Local Government area (Lat 11°06’6’’ N and Long 9°54’7’’ E) of Bauchi State, Nigeria. Both study areas are semi-arid in nature and fall within the Sudan savannah agro-ecological zone of Northern Nigeria. The study areas are fertile arable land, which most tropical cereal crops can adapt. The Sudan savannah vegetation zone is also made up of vast grazing lands suitable for livestock production. The soil samples were air-dried, crushed, sieved, and stored in clean polythene bags and labeled. The soil samples were analyzed for their physiochemical parameters using standard analytical procedures.

Biochar Production
Biochar used in this study was produced from poultry droppings using an electric muffle furnace (SX-4-10) at a constant temperature of 400°C for 30 minutes. The pH of the biochar was determined in water and in 0.01 M KCl solution using a 1: 2.5 biochar: water ratio as described by Gee and Bauder (1986) on two-way equilibration with a buffer solution at pH 4.0, 7.0 and 10.0.

Incubation Study
The experiment was laid out in a complete randomized design (CRD). Fifty grams of soil was incubated with 50, 60, 70, and 80 grams of biochar on a weight per weight basis. The soils and biochar doses combinations were made on weight by weight bases. Eight treatments were obtained from soils (Alfisol and Vertisol) and biochar combinations. The treatments were replicated 3 times and incubated for one month. Under incubation, each treatment was watered to soil water holding capacity using deionized water once in a week. Constant stirring of soil and the biochar materials was carried to get a uniform composition.

Point of Zero Charge Determination
The point zero charge (PZC) of the soil biochar treatment combinations was estimated by the equation outlined by Keng and Uehara (1974) and adopted by Chaves et al., (2016) in the estimation of PZC and surface electrical potential: 

\[ \Delta pH = pH_{KCl} - pH_{H_2O} \]  

With pH values obtained, \( \Delta pH \) of the treatments were also calculated using the formula: 

\[ \Delta pH = pH_{KCl} - pH_{H_2O} \]  

The value of the surface electrical potential (\( \Psi_0 \)) expressed in mV was calculated using the Nernst equation, simplified by Chaves et al., (2016) as follows:

\[ \Psi_0 = 59.1 \left( PZC - pH_{H_2O} \right) \]

Soil Analysis
Particle size analysis was determined using Bouyoucos hydrometer method as described by Jaiswal (2003). pH determination was carried out according to the procedure outlined by Agbenin (1995). Electrical conductivity was measured in a 1:2.5 fresh soil-water suspension with a glass electrode meter according to the procedure described by Jackson (1962). Total Nitrogen was determined using the Kjeldhal procedure as described by Bremner (1996). The exchangeable bases were determined according to the ammonium acetate procedure described by Anderson and Ingram (1993). Cations exchange capacity (C.E.C) was determined by the summation method as outlined by Anderson and Ingram (1993). Organic matter content was determined using the Walkley-Black procedures (FAO, 1974). Available phosphorus was determined colorimetrically by the ammonium molybdate blue method using ascorbic acid as a reducing agent (Reeuwijk, 1993).

Statistical Analysis
The data obtained were subjected to descriptive statistics and one-way analysis of variance (ANOVA). Mean separation was carried out using the least significant difference (LSD) as
Pearson correlation analysis was used to determine the relationships between the electrochemical properties of the biochar-incubated soils and the measured PZC. All statistical analysis was carried out using SAS software package version 9.1.

RESULTS AND DISCUSSION

Soil physical and chemical parameters

Table 1 shows the properties of the soils used for the study. The soil texture is sandy clay loam for Dutse and clay loam for Jama’are. The soil reaction in Table 1 ranged from 4.9–5 in Dutse and 4.4–4.8 in Jama’are, indicating slight acidity to neutrality. Electrical conductivity (ECe) values of 1.08 and 1.06 dSm⁻¹ were obtained for Dutse and Jama’are. Organic matter contents of the soils, Dutse (1.034 g kg⁻¹) and Jama’are (2.68 g kg⁻¹) were below the critical level of 20 g kg⁻¹ hence low. Total N contents of 0.6 and 0.8 g kg⁻¹ of the soils obtained from Dutse and Jama’are were low as the values were below the critical level of 1.5 g kg⁻¹ and hence crop responses to fertilizer applications are likely. Available P values of 11.02 and 27.9 mg kg⁻¹ for Dutse and Jama’are soils respectively. The cation exchange capacity of Dutse soil was low (3.53 C mol (+) kg⁻¹) while the value of 6.47 C mol (+) kg⁻¹ was medium for Jama’are as against the critical values of < 6 (low), 6–12 (medium) and > 12 (high). Exchangeable bases Ca²⁺ was 1.82 and 4.01 C mol (+) kg⁻¹; Mg²⁺ 0.92 and 1.44 C mol (+) kg⁻¹; K⁺, 0.18 and 0.42 C mol (+) kg⁻¹ and Na⁺, 0.58 and 0.60 C mol (+) kg⁻¹ for Dutse and Jama’are soils, respectively.

Table 1. Physical and Chemical Properties of the Study Soils

| Soil Properties                  | Alfisol | Vertisol |
|---------------------------------|---------|----------|
| Particle Size Distribution      | Clay (%)| 22       |
| Silt (%)                        | 14      | 30       |
| Sand (%)                        | 64      | Sandy clay loam |
| Textural Class                  | Clay loam| 38       |
| pH (H₂O)                        | 5       | 4.8      |
| pH (KCl₂)                       | 4.9     | 4.4      |
| EC (dS m⁻¹)                     | 1.06    | 1.08     |
| Organic Carbon (g kg⁻¹)         | 4.9     | 5.95     |
| Organic Matter (g kg⁻¹)         | 1.03    | 2.68     |
| Total Nitrogen (g kg⁻¹)         | 0.6     | 0.8      |
| Available P (mg kg⁻¹)           | 11.02   | 27.9     |
| Exchangeable Ca (C mol (+) kg⁻¹)| 1.82    | 4.01     |
| Exchangeable Mg (C mol (+) kg⁻¹)| 0.92    | 1.44     |
| Exchangeable K (C mol (+) kg⁻¹) | 0.18    | 0.42     |
| Exchangeable Na (C mol (+) kg⁻¹)| 0.58    | 0.60     |
| SEB (Cmol (+) kg⁻¹)             | 3.53    | 6.47     |

SEB: Sum of Exchangeable Bases

Chemical Properties of Biochar

The chemical properties of the biochars are presented in Table 2. The pH of the biochar was slightly alkaline (pH= 8). Mineral analysis showed that the biochar has various amounts of inorganic elements. The amounts of the mineral elements contained in the biochar (Table 2) were higher than the amounts of elements contained in the soil samples (Table 1) used for the laboratory study thereby signifying their potential as alternative sources to fertilizers.
The nitrogen content of the biochar was 31.01 g kg⁻¹. Total P was 52.02 g kg⁻¹ respectively for poultry biochar. The P content obtained from the biochar was high when compared to soil P. Lower K value of 25.46 cmol (+) kg⁻¹ was reported for the biochar. Calcium (59.75 cmol (+) kg⁻¹) in the biochar was higher than the Ca in soils as shown in Table 1.

**Effect of Poultry Biochar on Properties of Dutse and Jama'are Soils**

Table 3 shows the effect of biochar on charge properties of the soils. Electrical conductivities of the soils increased with increasing rates of biochar. Significant (p<0.05) differences were observed among the ECₑ means obtained from the soils. The ECₑ values of the biochar infused soil samples as shown in Table 3 were significantly (p<0.05) different. Treatments with 80 g infused biochar from both soils had the highest EC values of 4.21 and 4.72. Wide variation in ECₑ was also observed as the values vary from 0.39 - 4.18 dSm⁻¹.

| Factors | Alfisol | Vertisol | Significance level |
|---------|---------|----------|--------------------|
| ECE     | -0.13   | 0.62     | *                  |
| pH      | 0.91    | 0.84     | ***                |
| Ψ₀      | 0.91    | 0.81     | **                 |

*, **, *** are significance level of < 0.05, < 0.01 and < 0.001, respectively; NS: not statistically significant.
Correlation Coefficient between PZC and Some Selected Properties of Biochar Incubated Soils

The result of the estimated relationship between PZC and electrochemical properties of the soils are shown in Table 4. The result showed that the pH and Ψ0 had a strong correlation with the PZC of the Alfisol and Vertisol under the experimental conditions. The r value of 0.91 showed that 91% change in PZC in the Alfisol was influenced by ΔpH and Ψ0. For the Vertisol, Pearson r value of 0.62, 0.84 and 0.81 revealed that PZC strongly correlated with ECe, pH and Ψ0. This showed that variations in the PZC of the Vertisol were highly influenced by the three parameters mentioned above. Electrical conductivity (ECe) had no effects on the PZC of the Alfisol as shown in Table 4. This was contrary to the results obtained from the Vertisol, which showed a significant correlation between the ECe and the Vertisol.

Effects of Biochar on Electrochemical Properties of Soils

The application of poultry biochar to the soils increased the PZC of the soils. The PZC of both soils was within the same range. Higher pH values were obtained from the biochar treated soils concerning the native pH values of the soils though there was no corresponding increase in pH values with increase biochar rates. The high pH values obtained from the biochar were similar to the range of pH values of biochars obtained by Chan and Xu (2009). This tends to be in contrast with the result obtained by Lehmann (2007) which stated that the pH of soils increased with an increase in biochar rates and Chaves et al. (2016) who also obtained a similar linear increase in pH with an increase in biochar rates in Ultisol, Oxisol, Entisols.

The increase in pH values of the biochar-incubated soils could be linked to the dissociation reactions of functional groups containing oxygen on the surfaces of the biochar and these are consistent with the findings by Marta et al., (2019). Also, the liming effects of biochar could have played a role in an increase in soil pH, which could reduce cationic attraction and mobility due to reduced competition between the H+/metal cations for the exchange sites on the biochar and soil surfaces (Beesley et al., 2011).

Similarly, negative electric potential (Ψ0) values as shown in this study were due to the increase in pH of the biochar incubated soils as well as the low PZC values (Table 3). Higher negative charges were obtained from the Vertisol after incubation. The number of surface charges could be directly linked to the clay mineral contents of the soils. Charges have been known to vary from positive under acidic conditions to negative under strongly alkaline conditions. With the effects of the biochar on the pH of the soils as observed from the study, it is logical to assume that the negative potential values obtained from the study were directly influenced by the modification of the soils’ pH by the biochar. This corresponds with the observation made by Chaves et al. (2006) who stated that “this negative sign and magnitude of Ψ0 were directly influenced by the related magnitude of the ΔpH”. The increase in negative charges could be directly linked to the aging of the biochar as well as the dissociation of functional groups and activity of PDI (potential determining ions, e.g., H+ and OH) during the incubation period. This is similar to the findings of Cheng et al. (2006) that 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 negative charge consequently leading to an increase in the CEC.

The negative ΔpH values indicated a predominance of negative charges in the two soils samples. In this case, the cation exchange capacity (CEC) of these soils exceeded the anion exchange capacity (AEC) of the incubated soils in the modified pH conditions. However, the magnitude of ΔpH decreased with increasing biochar rates and as well, showed a reduction of CEC. The cation exchange capacity increase is primarily attributed to the negative charge on the outer surface of the biochar, which arises from the dissociation of functional groups (Cheng et al. 2006). Anegbe et al. (2015) also demonstrated that cation exchange capacity increased with the increased doses of biochar and lapse of time from the application of material into the soil. On the other hand, Kuzyakov et al. (2009) reported that biochar introduced into the soil undergoes an aging process in the presence of air, water, and microorganism activity, which in turn leads to the formation of stable complexes of trace element and biochar.
Strong positive correlations were identified for the ECe (Vertisol), pH and \( \Psi_0 \). This indicated that increased variations in PZC were strongly influenced by change in ECe, pH (\( \Delta \text{pH} \)) and surface electrical potential (\( \Psi_0 \)). A high pH in biochar can be linked to the high content of alkaline minerals contained in the biochar. The charge development in the soils could as well be linked to the dissociation of the functional groups contained in the biochar. This also largely depends on the pH of the biochar, as dissociation of different functional groups varies with the pH of the biochar material.

**CONCLUSION**

This study showed that the properties of the semi-arid soils were influenced by the addition of the biochar. The chemical properties of Alfisol and Vertisol obtained from Dutse and Jama’are were enhanced by the application of poultry waste biochar. The addition of biochar to the soils modified and decreased the values of the \( \Delta \text{pH} \), \( \Psi_0 \), CEC but raised the PZC of the soils. This study has also revealed the importance of the role played by biochar due to the increase in negative charges that will help in plant nutrients (cations) adsorption and retention thereby increasing the fertility status of the soil. Therefore the addition of biochar to soils will lead to positive responses by plants due to improved fertility of the soils. Hence knowledge of the effects of biochar on pH and electric charges of soils will contribute immensely to understanding its impact on soil fertility and plant nutrient retentions in soils, especially when used as soil amendments. It is therefore recommended that biochar amendments applied to the soil should be allowed to decay over some time before cultivating such soil as this helps to lower the PZC of the soil thereby improving soil fertility.

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