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Effect of Biochar on Available Phosphorus Status in Alfisols Derived From Charnockite In Ekiti State, Nigeria

Ilori, A. O. A., Shittu, O. S., Ayodele, O. J., Awe, G.O., and Oso, A. O.

Department of Soil Resources and Environmental Management, Ekiti State University, Ado-Ekiti, Ekiti State

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Corresponding Author's E-mail Address:

iloriaugustus@gmail.com .

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ABSTRACT

Biochar, a carbon-rich product of pyrolyzed biomass, has been used as an amendment to improve the properties of marginal highly-weathered soils in the tropics characterized by widespread phosphorus (P) deficiency. Alfisols derived from charnockite in Ekiti State are typically deficient in available phosphorus. Two alfisols from Ire-Ekiti and Ijan-Ekiti were amended with 0 (P-only), 5, 10 and 20% (*w/w*) biochars from maize stover (mB) and sawmill waste (sB) and incubated for 56 days with the addition of 60 mg kg^{-1} P in solution and a control without biochar and P-solution. Incubated soils were sampled fortnightly and analyzed for available P using Mehlich III extractant, pH, and electrical conductivity (*EC*) in water (1:2 *w/v*). Results show that biochar increased the soil pH by 1-2 units and EC from the native 0.02 to 8.37 *d*S m^{-1} with mB at 10 and 20%, causing soil salinity (EC > four *d*S m^{-1}). Biochar increased available P to values ranging from 9.96 to 376.22 mg kg^{-1} compared to 2.93 to 7.64 mg kg^{-1} in control and 5.42 to 40.13 mg kg^{-1} in P-only treatments. The available P increased with days of incubation up to day 42 and followed by a slight decline, but the P in biochar-treated soils was significantly higher than other treatments. The mB significantly improved soil properties (soil pH, EC, and available P status), particularly at higher rates more than sB. The 5% mB in which the problem of salinity problem associated with higher rates is avoided should be recommended.

1.0. Introduction

Highly weathered soils of the humid tropical zones where low agricultural productivity due to loose, structurally unstable, low moisture and nutrient retainability, and pronounced available P deficiency needs to be improved to reduce poverty (Barrett and Bevis 2015; Folberth *et al*. 2016) Alfisols derived from charnockite rock in Ekiti State are typical example of such weathered soils deficient in available phosphorus (Shittu, 2008; Ilori and Shittu, 2015). The application of inorganic P-fertilizers to such soils is not usually enough for sustainable crop production due to several adverse fates of the applied phosphorus. The applied P may be fixed to the voids in the soils' mineral lattice or adsorbed to the surface of the soil colloids particu-

larly in soils with high activities clay minerals, and could also be washed off in weak structural sandy soils to the extent of causing eutrophication of nearby surface water body. This makes the application of inorganic P-fertilizers along with a medium that would sustain P-availability in the soil for the entire life-cycle of the crop an interest, mainly arable crops.

Biochar is a product of pyrolyzed agricultural biomass in which the available nutrient elements that could have been mineralized and possibly wasted during the natural decomposition of the biomass are preserved and also mitigates environmental hazards associated with the carbon dioxide (CO_2) released during decomposition. Biochar-soil amendments directly or indirectly improve soil and environmental qualities and reduce heavy metal toxicity (Ndor *et al.*, 2015; Eduah *et al.*, 2017; Shi *et al*., 2018; Yuan *et al.*, 2018). Simon *et al*. (2017) reported that biochar boosts soil fertility and crop yields in the tropics than in the temperate regions of the world. Research on the potentials of biochar as a soil amendment or conditioner is gaining momentum. However, alfisols that developed on charnockite in Ekiti State have not been amended to assess and ensure a sustainable soil P-availability, mainly using biochar. The objectives of this study are to evaluate the effects of biochar on phosphorus availability in soils from charnockite in Ekiti State and to establish the potential of biochar to enhance phosphorus availability in soils, sustainably.

2.0. Materials and Methods

2.1. Soil Description, Sample Preparation, and Biochars

Two locations where charnockite rocks exist in Ekiti State, Nigeria, were selected for the study. The locations are from Ire-Ekiti (latitude 7° 45' N and longitude 5° 23' E) in Oye Local Government Area, characterized by average annual temperature of 24.3 °C and annual rainfall of 1323 mm; and Ijan-Ekiti (latitude 7° 37' N and longitude 5° 24' E) in Gbonyin Local Government Area having mean annual temperature of 25.3 °C and mean annual rainfall of 1311 mm. Ire-Ekiti and Ijan-Ekiti belong to tropical savannah (Aw), according to Koppen-Geiger climate classification (2019). The soils have been classified as Grossarenic Plinthic Kandiudalf and Plinthic Kandiudalf, respectively (Shittu, 2008).

Composite soil samples were taken to 0-20 cm from each location, crushed and sieved through 2 mm sieve. The soils were analyzed for selected properties using the standard laboratory procedures described in Udo *et al.* (2009). Soil pH and electrical conductivity were determined in H_2O (1:2 *w/v*) using digital pH meter and conductivity meter, particle size distribution by hydrometer method; organic carbon by the Walkey and Black dichromate wet oxidation method; total nitrogen by macro-Kjeldahl method, and available phosphorus with Mehlich III extractant.

Biochars were produced in the Department of Soil Resources and Environmental Management, Ekiti State University, Nigeria, by slow pyrolysis of two feedstocks: maize stover and sawmill waste using a fabricated Top-Lit Up Draft (TLUD) carbonized at an average temperature of 460 °C and total residence time of 60 minutes. The biochars were characterized by Hong Kong Baptist University (Ho Sin Hang Campus) using the standard procedures recommended by the International Biochar Initiative (2012).

2.2. Phosphorus Incubation Study

The incubation study to evaluate the phosphorus availability in biochar amended soils was conducted in the Soil Laboratory, Ekiti State University, for 56 days. For each soil, the treatments include: three levels of each biochar type (mB_5, mB_{10}, mB_{20}, sB_5, sB_{10} and sB_{20}), a sample without biochar amendment (P-only) and control (0 mg kg^{-1} P and 0 % Biochar), in three replicates. For each treatment, 150 g portion of air-dried soil was placed in a plastic cup and amended with 7.5, 15, and 30 g biochars equivalent to 5, 10, and 20% (*w/w*) and addition of 60 mg kg^{-1} using potassium dihydrogen phosphate (KH_2PO_4) solution except the control. The biochar and soils were homogenized before adding the P-solution and watered with deionized water to field capacity. All cups were covered, with a small hole to allow gaseous exchange and minimize moisture loss. The incubation was at ambient room temperature for 56 days, and every seven days, deionized water supplied. At every fortnight, 20 g of soils were scooped from each incubation cup to determine pH, electrical conductivity, and available P. Data obtained were subjected to analysis of variance (ANOVA) and means separated by least significant difference (LSD) using SAS 2018 package.

3.0. Results and Discussion

3.1.1. Properties of Alfisols Developed from Charnockite in Ire-Ekiti and Ijan-Ekiti

Some properties of the soils used for these studies are presented in Table 1. The soil pH was moderately acidic at Ire -Ekiti (pH = 5.6) and slightly acid at Ijan-Ekiti (pH = 6.3). The average electrical conductivity (EC) for the two soils was low (EC = 0.024 *d*S m^{-1}), which implies a little amount of soluble inorganic salts. The mean available P in the soils was 6.81 mg kg^{-1}, which is higher than the Bray P -1 values of 1.11 and 1.36 mg kg^{-1} P reported for the surface soils of Ire-Ekiti and Ijan-Ekiti, respectively (Ilori and Shittu, 2015). The higher available P values could be due to the Mehlich III method used in this study for extracting available P compared to the Bray P-1 method previously used, in addition to the current fallow the farmlands are subjected to. The higher mean available P values recorded affirmed the aggressiveness of Mehlich III than other methods (Nathan *et al*., 2005; Ketterings and Barney, 2010) in evaluating soil available P, which has been reported to be of high significant correlation with plant P-uptake (Hamilton, 2014). However, the higher Mehlich III available P values were rated low being below the 8 mg kg^{-1} Bray P-1 critical level (Esu, 1999; Adepetu and Barber, 1979).

The mean total N at 0.87 g kg^{-1} is below the critical range of 1.5-2.0 g kg^{-1} (Udo *et al.,* 2009). Even though the Ire-Ekiti soil exhibits a medium nitrogen content with its value of 1.07 g kg^{-1}. Soils around the study areas have been reported to be deficient in N and P (Shittu, 2008; Aruleba *et al*., 2009). The TOC contents of the soils are very low, with a mean value of 12.45 g $kg^{-1,}$ which is below 20 g kg^{-1} crit-

ical level established for soils in Nigeria (Udo *et al*., 2009). Whereas Ilori and Shittu (2015), reported higher TOC mean values for similar surface soils. The lower values reported in this study an indication that the organic matter contents of these soils have been depleted over the years, which could be attributed to intensive cultivation, leaching and erosion effects, total crop harvesting and low lignified vegetation that has replaced the native woody plants. Thus, there is a need for practices that would increase and sustained the OM level.

3.1.2. Properties of the Maize stover (mB) and Sawmill waste (sB) biochars

Some of the properties the biochars were presented in Table 2 and Figure 1. The maize stover biochar (mB) generally had higher values compared to the sawmill waste biochar (sB) in some selected properties except in ash and volatile matter contents, which could be due to the nature of the feedstocks. The SEM imagery of the biochars (Fig. 1) showed many porous structures having different sizes and shapes on their surface, which according to Jiang *et al*. (2012), are an indication of potentially different capabilities for reactivity.

3.2. Effects of Biochar on Soil pH

The pH of soils amended with biochar is shown in Table 3. The pH decreased with an increase in the days of incubation in the control and P-only treatments in the two soils.

Table 1. Some properties of soils used in the incubation studies

Soil	pH	EC	Avail. P	Total N	TOC	Clay	Silt	Sand	Textural class
		(dS m^{-1})	(mg kg^{-1})		(g kg^{-1})		(g kg^{-1})		
Ire-Ekiti	5.6	0.023	6.19	1.07	12.69	62.4	66.4	871.2	LS
Ijan-Ekiti	6.3	0.024	7.42	0.66	12.21	42.4	56.4	901.2	S

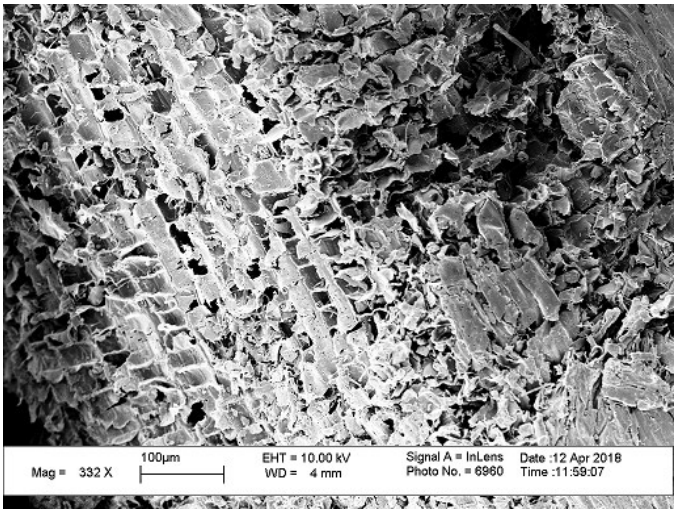
EC = electrical conductivity, CEC = cation exchange capacity, LS = loamy sand, S = sand

Table 2. Some properties of biochars used in the incubation studies

Biochar	pH	EC	Avail. P	Total N	TOC	Ash	Volatile
		(dS m^{-1})	(mg kg^{-1})		(g kg^{-1})	(%)	matter
Maize Stover, mB	10.41	3.64	184.12	12.70	6.34	2.06	50.0
Sawmill waste, sB	9.92	0.24	114.85	8.70	4.94	2.67	64.2

EC = electrical conductivity, TOC = total organic carbon

a.)



b.)

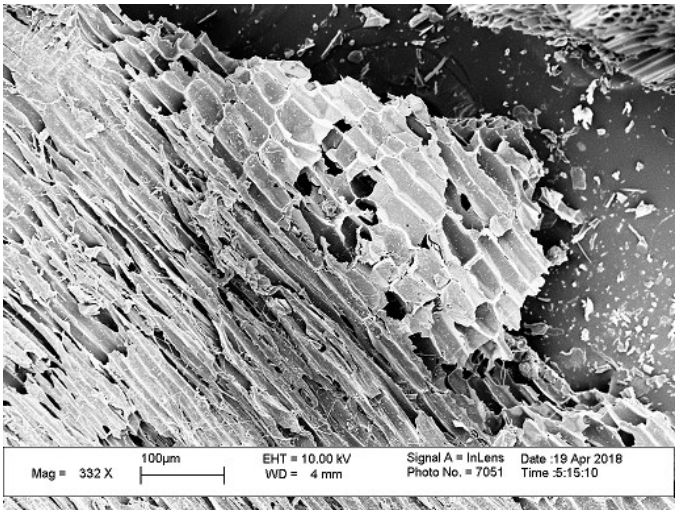


Figure 1. SEM imagery of (a). Maize stover biochar (mB) and (b). Sawmill waste biochar (mB)

This could be attributed to the dissociation effects of the added P source (KH2PO4), resulting in more H+ ions in the soil solution. This change in soil pH towards a more acidic nature, in addition to a possible reduction in microbial activities, tends to make most soil nutrients, particularly P, to be unavailable to the plants. The soil from Ire-Ekiti amended with biochar showed increasing pH with days of incubation up to day 42 and generally declined by less than 0.5 pH unit at day 56. Ijan-Ekiti soils also exhibited a similar trend in pH increment as influenced by different rates of biochar amendment. Generally, the r2 ranged from 0.8034 – 0.9996 (Fig. 2a and b) in biochar amended treatments of both soils, indicating a near-perfect relationship between the soil pH and days of incubation as influenced by the added biochars. In addition to enhancement of availability of essential plant nutrient elements in soil, biochar also increase soil pH (Edmunds, 2012; 2013; Zhai et al., 2014; Mohamed et al., 2017) and would reduce toxic effects of the nutrient elements (Brady and Weil, 2008; Bashir et al., 2018). Similarly, Knox et al. (2015)

reported soil pH to be increased from 5.9 to 7.3 by the addition of biochar even though the intending clubroot disease of Chinese cabbage SB1 Kilo's control was not achieved.

Generally, the soil pH significantly increased with the biochar rates except in the case of sB where amendment at 5% biochar non-significantly outperformed the 10% biochar rate in both alfisols. The results also showed that mB enhanced soil alkalinity better than the sB, particularly at higher biochar rates in both soils. Similarly, the biochar amended soils recorded higher pH values than the other treatments without the biochar amendment. It shows that biochar would be a good substitute for liming materials, especially when they are not accessible.

Comparing the biochars based on amendment rates, there was no significant difference in their performance at a 5% rate; whereas, higher amendment rates showed that mB increases soil pH significantly better than the sB. The increment in soil pH could be attributed to the alkaline nature of the biochars (Table 2), which contributes to their ability to counteract soil acidity (Blanco-Canqui, 2017; Jha et al., 2016; Shi et al., 2018).

Effects of Biochar on Soil Electrical Conductivity (dS m-1)

The EC is an indirect indication of the extent of soluble salt content in soil solution and directly measured the salinity level. The higher the measured EC of a soil solution, possibly the more the amount of dissolved elemental ions in the soil solution, and it is a function that determines/ influences the nutrient availability in soils. Table 4 presented the electrical conductivity (EC) of the incubated alfisols has influenced by biochar amendments. In the control and P-only treatments, EC increases with the days of incubation in the alfisols. Generally, values recorded in the untreated soils were not significantly lower than EC values recorded in sB treated soils with few exceptions at day 14 of incubated soils. The EC ranged from 1.61 – 8.37 dS m-1 in mB amended soils, respectively, at day 28 and 42 in mB amended Ire-Ekiti soil. The 5% amendment rate increased the soil EC with increased incubation days, particularly in Ire-Ekiti soil, whereas, the trends were not consistent in Ijan-Ekiti soil. Other amendment rates caused the EC to

Table 3. Effect of biochar addition on soil pH during the incubation period

		----------Incubation time, days----------							
	Biochar	14	28	42	56	14	28	42	56
Treatment	rate, %	Ire soil				Ijan soil			
Control	-	7.15^{c}	6.77^{d}	6.59^{d}	6.37^{d}	7.85^{d}	7.46^{e}	6.99^{e}	7.11^{d}
P-only	-	6.67^{d}	6.26^{e}	6.63^{d}	6.41^{d}	7.04^{f}	6.91^{f}	6.80^{e}	6.81^{e}
mB	5	7.40^{cA}	7.77^{cA}	8.05^{cA}	7.72^{cA}	8.22^{cA}	8.80^{cA}	8.66^{bA}	8.70^{bA}
	10	8.30^{bA}	9.09^{aA}	9.16^{aA}	9.10^{aA}	8.81^{bA}	9.31^{bA}	9.24^{aA}	9.28^{aA}
	20	8.90^{aA}	9.36^{aA}	9.49^{aA}	9.45^{aA}	9.10^{aA}	9.54^{aA}	9.44^{aA}	9.34^{aA}
sB	5	7.31^{cA}	7.67^{cA}	8.20^{bA}	7.94^{cA}	7.55^{eA}	8.15^{dA}	8.33^{cdA}	8.23^{cA}
	10	7.04^{cB}	7.91^{bB}	8.05^{cB}	7.87^{cB}	7.27^{fB}	8.14^{dB}	8.21^{dB}	8.12^{cB}
	20	7.31^{cB}	8.21^{bB}	8.46^{bB}	8.44^{bB}	7.61^{deB}	8.22^{dB}	8.50^{cB}	8.55^{bB}

mB = maize stover biochar, sB = sawmill waste biochar

Means with different superscript lowercase letters in each column are significantly different at P > 0.05 for all treatments comparison

Means with a different superscript uppercase letter in each column are significantly different at P > 0.05 for biochar comparison

Table 4. Effect of biochar addition on soil EC (dS m-1) during the incubation period

		----------Incubation time, days----------							
	Biochar	14	28	42	56	14	28	42	56
Treatment	rate, %	Ire soil				Ijan soil			
Control	-	0.05^{e}	0.05^{d}	0.15^{d}	0.22^{c}	0.05^{f}	0.05^{d}	0.13^{d}	0.16^{e}
P-only	-	0.07^{e}	0.07^{d}	0.16^{d}	0.12^{c}	0.08^{f}	0.07^{d}	0.09^{d}	0.11^{e}
mB	5	1.86^{cA}	1.61^{cA}	1.96^{cA}	3.22^{bA}	2.01^{cA}	2.55^{cA}	2.83^{cA}	2.07^{cA}
	10	3.55^{aA}	3.74^{bA}	4.05^{bA}	3.47^{bA}	3.85^{bA}	4.38^{bA}	4.60^{bA}	4.02^{bA}
	20	5.02^{aA}	4.86^{aA}	8.37^{aA}	6.85^{bA}	5.95^{aA}	5.40^{aA}	7.42^{aA}	5.01^{aA}
sB	5	0.35^{dB}	0.19^{dB}	0.22^{dA}	0.32^{cB}	0.32^{eB}	0.28^{dB}	0.31^{dB}	0.26^{dB}
	10	0.53^{dB}	0.41^{dB}	0.49^{dB}	0.40^{cB}	0.59^{dB}	0.43^{dB}	0.41^{dB}	$0.41e^{dB}$
	20	0.74^{dB}	0.51^{dB}	0.75^{dB}	0.56^{cB}	0.72^{dB}	0.55^{dB}	0.56^{dB}	0.53^{dB}

mB = maize stover biochar, sB = sawmill waste biochar

Means with different superscript lowercase letters in each column are significantly different at *P* > 0.05 for all treatments comparison

Means with a different superscript uppercase letter in each column are significantly different at *P* > 0.05 for biochar comparison

oscillate with incubation days asides in Ijan-Ekiti soil in which 20% sB lowers the EC as incubation days increases. The effect of mB biochar in increasing soil EC was significantly higher than other treatments in both soils and increased with amendment rates, but the effects of sB were not significantly different from amendment rates, even though the soils EC increased with amendment rates. Zhai et al. (2014) found that maize straw biochar significantly ($P<0.05$) increased the EC of two typical Chinese arable soils, and the EC values increased by increasing amounts of biochar addition after 42 days of incubation. Conversely, Kloss et al. (2014), reported that following three years of amendment of Planosol at 3% biochar rate, woodchip biochar increased soil EC higher than straw biochar. The high EC exhibited in mB treated soil was due to the higher EC value of the mB (3.64 $dS\ m^{-1}$) compared to that of sB (0.24 $dS\ m^{-1}$) (Table 2). The properties of biochar, including EC, depends on the feedstock materials and method used for z pyrolyzing.

Furthermore, biochars served as dopants or impurities in the soil, which generates either negative or positive charges due to the difference in the charges between the biochar particles and the soil minerals. However, mB amendment higher than 5% rate increased soil salinity beyond the critical limit of 4.0 $dS\ m^{-1}$ which will subsequently have undesirable effects on plant growth grown on such amended soil.

Al-Wabel *et al.* (2013) reported these effects of high salinity on plant development. Hence, this study indicates that sB at 20% will be more appropriate in amending alfisols that developed over charnockite to avoid soil salinization and ensure P-availability.

3.3. Phosphorus Availability Status in Biochar Amended Alfisols

The mean content of Mehlich 3-P in the biochar amended incubated soils were presented in Table 5. Generally, the available P increases with days of incubation but starts declining after day 42 with a few exceptions. Both soils showed a similar response to the biochar amendment in terms of P-availability, and there were also perfect relationships ($r^2 = 1$) between the available phosphorus and days of incubation (Fig. 3a and b). The mean available P ranged from 2.93 mg kg^{-1} at day 28 of incubation in control soil of Ire-Ekiti to 376.22 mg kg^{-1} at day 42 in Ijan-Ekiti soil amended with mB20. The control soils without biochar and P-solution showed an increase in available P with incubation days, but these values were below the Bray P1 critical level of 8 mg kg^{-1} P recommended for soils in Nigeria (Udo *et al.*, 2009) except in Ijan-Ekiti soil at 42 days of incubation (12.15 mg kg^{-1} P) and beyond.

Ire soil incubated with only 60 mg kg^{-1} P without biochars showed a wavy trend of soil available P content which drastically below the critical P-level at day 56 of incubation. Whereas, its counterpart soil (Ijan-Ekiti) exhibited a consistently increasing trend of P-availability with days of incubation. However, the available P in the P-only incubated soils were below the added 60 mg kg-1 P, the deficit of which could have been adsorbed or fixed by the organic matter and clay minerals present in the soils. In mB amended soils at all studied rates, a notable increase in available P were recorded in both soils up to day 42 of incubation with a slight dive at day 56 except for a 5% mB rate that continuously increases the available P contents of the soils studied.

The available P in mB amended soils were generally higher than the critical P-level (8 mg kg-1 P, Udo et al., 2009) and ranged from 9.96 mg kg-1 P at day 14, 5% mB to 376.22 mg kg-1 P at day 42, 20% mB, both in Ijan-Ekiti soil. The higher available P values in Ijan-Ekiti soil compared to Ire-Ekiti soil could be attributed to the lower clay content (42.4 g kg-1, Table 1) and near neutrality nature of Ijan-Ekiti soil in addition to biochars' contribution to the soil alkalinity. Sawmill waste biochar (sB) amended soils commonly exhibited an increased soil available P with days of incubation. Although, values recorded were higher than the critical P-level but were basically below the 60 mg kg-1 P added except in Ijan-Ekiti soil at 42 days of incubation and beyond. Biochar amended soils broadly

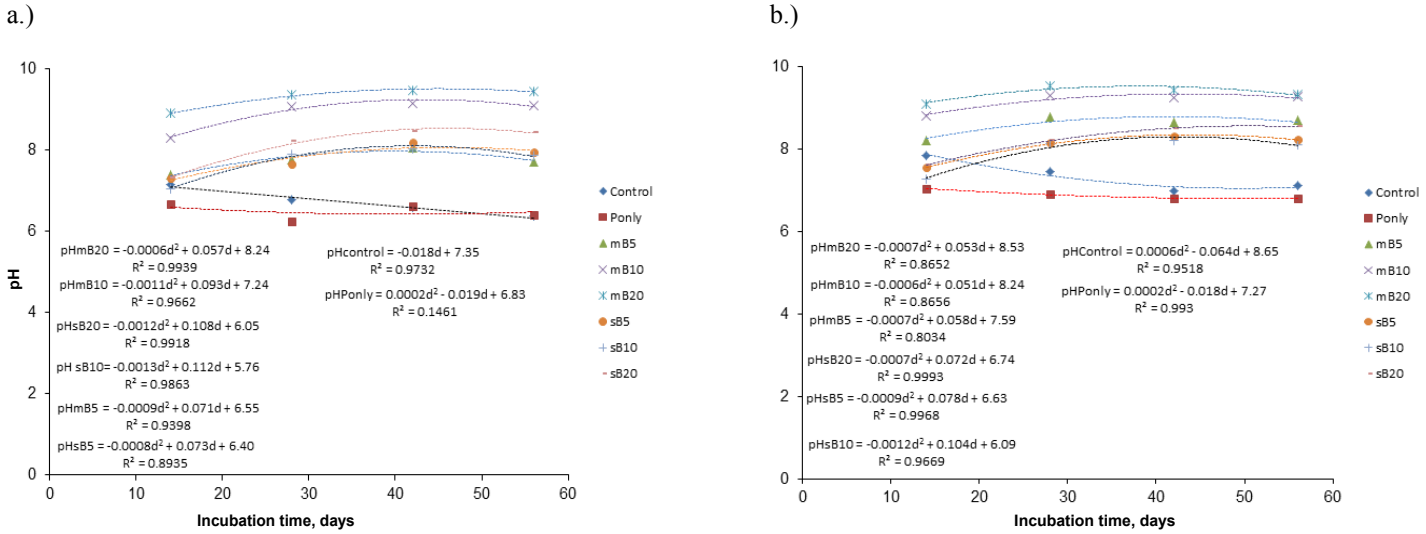
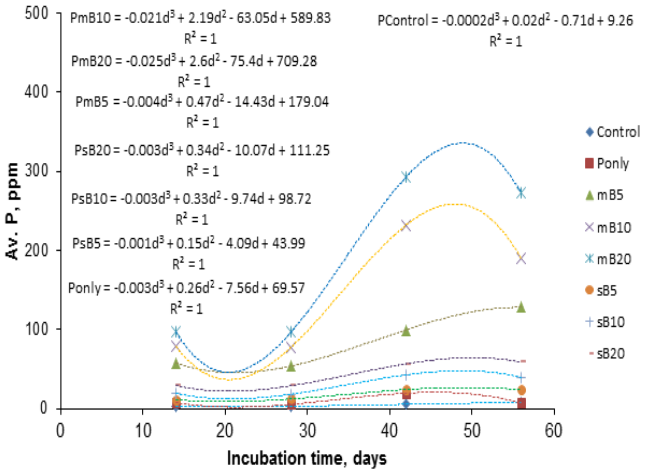


Figure 2. Relationship between soil pH and incubation time under different types and levels of biochar addition at a) Ire-Ekiti and b) Ijan-Ekiti

a.)



b.)

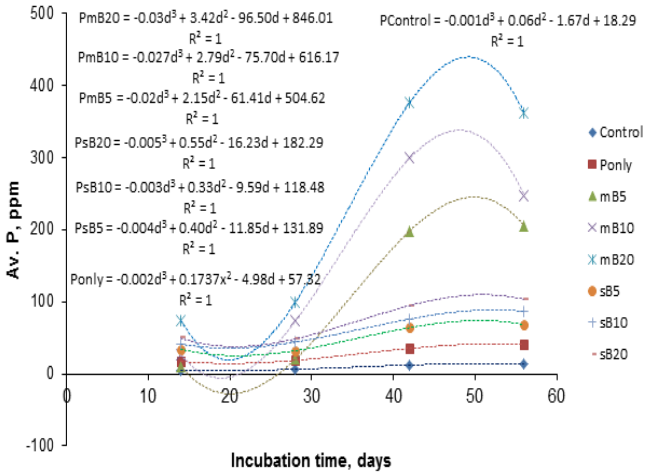


Figure 3. Relationship between available phosphorus (ppm) and incubation time under different types and levels of biochar addition at a) Ire-Ekiti and b) Ijan-Ekiti

showed a significantly high available P contents than the non-biochar amended soils. Biochar can significantly change soil pH, mostly by increasing the pH in highly weathered acidic soils (Biederman and Harpole, 2013), which would influenced P availability (De Luca et al., 2015). An implication that biochar is an unavoidable enhancer for sustainable phosphorus availability in soils that developed on charnockite.

The P-availability in the incubated soils increases with increasing rate of biochar amendment and mB performed better than the sB in ameliorating the P-deficiency in the studied alfisols has mB at various amendment rates significantly differs from sB apart from at day 14 of incubating Ijan-Ekiti soil where sB significantly performed better than mB at 5 and 10% amendment rates. The improvement effect of biochars on the availability of soil phosphorus could be attributed to the basic properties of the biochars. The biochar act as dopant generates charges that makes phosphorus ions to be more readily available in the soil solution rather than being fixed and adsorbed by the organic matter and clay minerals constituents of the soils. The significantly better performance of mB in enhancing the soil phosphorus availability could be attributed to the higher available P content in the mB (184.12 g kg-1).

4.0. Conclusion

The incubation study established the potential of biochar as a soil amendment in ensuring sustainable P availability in alfisols derived from charnockite in Ekiti State. Increasing the biochar application rate significantly increased the soil pH, EC, and available phosphorus, particularly the maize stover biochar (mB). Biochar increased soil pH by 1 -2 units creating more favourable soil conditions for soil microorganisms and plant nutrients such as phosphorus availability. In this study, 5% mB is recommended as higher rates are associated with salinity problems. Likewise, 20% of sB could also be used in amending the charnockitic alfisols for optimum phosphorus availability without encountering salinity problems. However, field studies should be done to ascertain the biochar's potentials for sustainable soil fertility improvement for optimum crop production.

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