

Original Research Article

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Characterization of Biochar and Humic Acid and their Effect on Soil Properties in Maize

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ABSTRACT

Keywords

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A field study was carried out at college farm, College of Agriculture, Rajendranagar, Hyderabad, Andhra Pradesh during *Kharif* 2013 on an Alfisol to characterize the biochar and humic acid and their effect on soil properties along with application of fertilizers in maize crop. Soil had a pH of 7.72, EC of 0.217 dS m⁻¹ and low organic carbon (0.49%). The experiment was laid out in a Randomized Block Design and replicated thrice with three factors comprised of factor-I (fertilizers- 100 % RDF and 75 % RDF), Factor-II (biochar levels- 0, 5 and 7.5 t ha⁻¹) and Factor-III (humic acid levels of 0 and 30 kg ha⁻¹). Biochar application showed a non-significant increase in soil pH. Significantly higher EC was shown when 100% NPK was integrated with biochar @ 7.5 t ha⁻¹. Soil CEC was significantly higher when 100% NPK was applied in combination with biochar @ 7.5 t ha⁻¹ and humic acid. Such increase at later stages was not significant. Biochar elucidated a significant increase in organic carbon from 0.51 to 0.62 per cent at 30 DAS when applied at 7.5 t ha⁻¹.

Introduction

Maize (*Zea mays* L.) is an important food and feed crop which ranks third among cereals after wheat and rice in the world. It is a multipurpose crop that provides food for humans, feed for animals (especially poultry and livestock) and raw material for the industries.

This crop has much higher grain protein content than our staple food rice. Maize is a heavy feeder of nutrients hence it is a very efficient converter of solar energy into dry matter. India is the fifth largest producer of maize in the world contributing 3 per cent of the global production (Arif *et al.*, 2012).

Climate change and global warming have worldwide adverse consequences. Biochar production and its use in agriculture can play a key role in climate change mitigation and help improve the quality and management of waste materials coming from agriculture and forestry. Biochar is a carbonaceous material obtained from thermal decomposition of residual biomass at relatively varying temperatures and under oxygen limited conditions (pyrolysis). Biochar is currently a subject of active research worldwide because it can constitute a viable option for sustainable agriculture due to its potential as a long term sink for carbon in soil and benefits

for crops (Alburquerque *et al.*, 2013). The application of biochar to agricultural land is receiving increasing attention as an intervention strategy for the sequestration of carbon and as a means of improving soil quality and nutrient cycling thereby aiming at reduced fertilizer use (Richard *et al.*, 2012). Studies suggest that biochar sequesters approximately 50% of the carbon available within the biomass feedstock being pyrolyzed (Kelsi Bracmort, 2010).

Humic acid are mainly produced from nitrogenous compounds containing decomposed amino acids and aromatic complexes (Andriessse, 1988). Those organic complexes can improve physical properties of soils due to carboxyl (-COOH) and phenolic (-OH) groups (Lee and Bartlette, 1976).

This present investigation is planned to characterize the biochar and humic acid and their effect on soil properties along with application of fertilizers in maize crop.

Material and Methods

This experiment was conducted during *kharij*, 2013 at the College Farm, Acharya N.G Ranga Agricultural University, Rajendranagar, Hyderabad comes under the Southern Telangana agro-climatic zone of Andhra Pradesh. The details of the material used and the methods adopted during the course of the present investigation are given below.

The pH and Electrical conductivity of the soil samples were determined in soil: water (1:2) suspension using a glass electrode pH meter and conductivity meter respectively (Jackson, 1973). Organic carbon percentage in soil sample was determined by wet digestion method (Walkley and Black, 1934). Cation exchange capacity of soil, biochar and humic acid was determined by neutral normal ammonium acetate method.

The total acidity of biochar and humic acid was determined by Baryta absorption method Calcium acetate method was used for determining - COOH groups in both biochar and humic acid by calcium acetate method (Schnitzer, 1972). Biochar suspensions containing a normalized quantity of C (0.25 g) were placed in 25 mL of sodium hydroxide (0.1 M) and were stirred in a closed vessel for 20 to 24 hr. A 10 mL filtered aliquot was added to 15 mL of standard HCl (0.1 M) solution. The HCl neutralized the unreacted base and prevented further reaction between atmospheric CO₂ and the base. The solution was then back titrated with standard NaOH (0.1 M) solution. The volume of NaOH required to neutralize the sample was converted to titratable negative surface charge. The total negative surface charge was expressed as mmol H⁺ eq/g C (Boehm, 1994).

Results and Discussion

Characterization of biochar and humic acid

Biochar and humic acid pH (8.20 and 4.87), electrical conductivity (1.28 and 0.034 dS m⁻¹), cation exchange capacity (49 and 86 c mol (p⁺) kg⁻¹), total negative charges (2.60 and 2.98 m mol H⁺ eq g⁻¹), total acidity (2.5 and 3.25 me g⁻¹) and carboxyl groups (0.2 and 3.11 me g⁻¹) were given in table 1.

Effect of combined application of biochars, humic acid and fertilizers on some soil properties

Soil pH

Soil pH was not influenced significantly by either individual or integrated application of fertilisers, biochar and humic acid at any stage of crop growth. However, a non-significant increase was observed with the application of biochar. The alkaline nature of the biochar exchanges H⁺ with the

surrounding soil, causing a rise in soil pH. Streubel *et al.*, (2011) elucidated a significant increase in soil pH by biochar application (Tables 2, 3, 4).

Electrical conductivity

Electrical conductivity of the soil shown differently at different stages of the crop. Electrical conductivity of the soil was not influenced by either individual and integrated application of fertilisers, biochar or humic acid at 30 DAS (Tables 5, 6, 7).

Whereas at 60 DAS a significant influence was exerted by individual application of fertilisers and humic acid and interaction between biochar and humic acid. Mean electrical conductivity of the soil was 0.140 dS m⁻¹ with recommended NPK as against 0.123 with reduced NPK. However, both are having normal conductivity values only. Application humic acid @ 30 kg ha⁻¹ decreased the mean electrical conductivity of the soil significantly from 0.137 to 0.125 dS m⁻¹. Interaction between biochar and humic acid resulted in a significant increase in electrical conductivity of the soil to 0.152 without biochar and humic acid as against 0.116 dS m⁻¹ with humic acid. Fertilisers and biochar leave salts in the soil thus increasing EC. Similar increase in EC with biochar application was elucidated by Alburquerque *et al.*, (2013).

The electrical conductivity of the soil at harvest was influenced only by the interaction between biochar and humic acid, fertilisers with biochar and humic acid. These results are in line with the findings of Kareer *et al.*, (2013) and Alburquerque (2013) and Nigussie *et al.*, (2012). Interaction between biochar and humic acid resulted in a significant increase in EC from 0.239 dS m⁻¹ without biochar to 0.292 dS m⁻¹ with humic acid (Table 7). The interaction of fertilisers with biochar and humic acid resulted in significant increase in

EC. Reduced NPK alone resulted in significantly lower EC of 0.227 dS m⁻¹ as against recommended NPK alone was significantly gave higher EC of 0.358 dS m⁻¹. Between 300 to 600° C organic acids and phenolic substances are created and alkali salts are formed that raise the pH of the biochar (Shinogi and Kanri, 2003).

Cation exchange capacity (CEC)

Significantly higher mean CEC of 17.11 c mol (p⁺) kg⁻¹ was obtained with the application of recommended NPK as against 15.56 c mol (p⁺) kg⁻¹ with 75% NPK. Application of biochar brought about significant increase in the mean CEC from 15.61 c mol (p⁺) kg⁻¹ to 17.40 c mol (p⁺) kg⁻¹ with biochar @ 7.5 t ha⁻¹. However, the CEC registered in the treatments receiving 5 and 7.5 t ha⁻¹ of biochar were at a par. The results corroborate the findings of Cornelissen *et al.*, (2013) and Major *et al.*, (2010) and Brodowski *et al.*, (2005). Application of humic acid @ 30 kg ha⁻¹ increased the mean CEC significantly from 15.91 to 16.74 c mol (p⁺) kg⁻¹. Similar results were obtained by Khattak *et al.*, (2013) and Ebtisam *et al.*, (2012).

The interaction between fertilisers and biochar was found significant. CEC significantly increased from 16.84 c mol (p⁺) kg⁻¹ obtained with recommended NPK along with biochar @ 5 t ha⁻¹ to 18.67 c mol (p⁺) kg⁻¹ was obtained with recommended NPK with biochar @ 7.5 t ha⁻¹ as against 15.84 with recommended NPK alone. While when there was no integration, both the fertiliser levels were at a par with regard to CEC with the corresponding values of 15.84 and 15.39 c mol (p⁺) kg⁻¹ and at 7.5 t ha⁻¹ level there was significant difference among the two levels. The interaction between fertilisers and humic acid, biochar and humic acid and fertilisers with biochar and humic acid did not influence the CEC of the soil at 30 DAS.

Table.1 Characterization of biochar and humic acid

Particulars	Value	Method of analysis
A. Biochar		
pH	8.20	Glass Electrode pH meter, model: Elico LI 120 (Jackson, 1973)
Electrical conductivity (dS m ⁻¹)	1.28	Conductivity bridge method, model: Elico CM 180 (Jackson, 1973)
Cation exchange capacity (c mol (p) kg ⁻¹)	49	Neutral normal ammonium acetate method (Jackson, 1973)
Total negative charges (m mol H ⁺ eq g ⁻¹)	2.60	Boehm method (Boehm, 1994)
Total acidity (me g ⁻¹)	2.5	Baryta absorption method (Schnitzer, 1972)
Carboxyl groups (me g ⁻¹)	0.2	Calcium acetate method (Schnitzer, 1972)
B. Humic acid		
pH	4.87	Glass Electrode pH meter, model: Elico LI 120 (Jackson, 1973)
Electrical conductivity (dS m ⁻¹)	0.034	Conductivity bridge method, model: Elico CM 180 (Jackson, 1973)
Cation exchange capacity (c mol (p ⁺) kg ⁻¹)	86	Neutral normal ammonium acetate method (Jackson, 1973)
Total negative charges (m mol H ⁺ eq g ⁻¹)	2.98	Boehm method (Boehm, 1994)
Total acidity (me g ⁻¹)	3.25	Baryta absorption method (Schnitzer, 1972)
Carboxyl groups (me g ⁻¹)	3.11	Calcium acetate method (Schnitzer, 1972)
Phenolic group (me g ⁻¹)	2.02	Acetylation with acetic anhydride method (Stevenson, 1982)
E4/E6	4.86	Absorption method (Kononova, 1966)

Table.2 Soil pH at 30 DAS of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser
Fertiliser levels	HA ₁	HA ₂	Mean	HA ₁	HA ₂	Mean	HA ₁	HA ₂	Mean	Mean
100% NPK	7.20	7.26	7.23	7.14	7.30	7.22	7.26	7.52	7.39	7.28
75% NPK	7.15	7.28	7.22	7.13	7.02	7.08	7.02	7.18	7.10	7.13
Mean	7.18	7.27	7.22	7.14	7.16	7.15	7.14	7.35	7.25	7.20
CV (%)	3.15									
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S						

Table.3 Soil pH at 60 DAS of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser Mean
	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean	
100% NPK	7.10	7.04	7.07	7.15	7.04	7.10	7.03	7.11	7.07	7.08
75% NPK	7.08	7.21	7.15	6.98	7.09	7.04	7.07	7.23	7.15	7.11
Mean	7.09	7.13	7.11	7.06	7.06	7.07	7.05	7.17	7.11	7.09
CV (%)	2.81									
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S						

Table.4 Soil pH at harvest of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser Mean
	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean	
100% NPK	7.04	7	7.02	7.21	6.69	6.95	7.17	6.85	7.01	6.99
75% NPK	7.03	7.02	7.03	6.96	6.85	6.91	7.21	7.08	7.15	7.03
Mean	7.04	7.01	7.02	7.09	6.77	6.93	7.19	6.96	7.08	7.01
CV (%)	4.37									
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S						

Table.5 Soil EC (dS m⁻¹) at 30 DAS of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser Mean
	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean	
100% NPK	0.209	0.199	0.204	0.203	0.175	0.189	0.185	0.19	0.187	0.193
75% NPK	0.192	0.183	0.187	0.173	0.184	0.178	0.162	0.189	0.175	0.180
Mean	0.200	0.191	0.195	0.188	0.179	0.183	0.173	0.189	0.181	0.186
CV (%)	14.03									
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S						

Table.6 Soil EC (dS m⁻¹) at 60 DAS of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser Mean
	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean	
100% NPK	0.150	0.122	0.136	0.120	0.126	0.123	0.151	0.170	0.161	0.140
75% NPK	0.154	0.119	0.137	0.155	0.107	0.131	0.091	0.110	0.101	0.123
Mean	0.152	0.120	0.136	0.137	0.116	0.127	0.121	0.140	0.131	0.131
CV (%)	13.73									
CD at 5% level	Fert. = 0.012 Biochar = N.S Humic acid = 0.012			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = 0.022 Fert. x biochar x humic x acid = N.S						

Table.7 Soil EC (dS m⁻¹) at harvest of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser
Fertiliser levels	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean	Mean
100% NPK	0.358	0.204	0.281	0.270	0.283	0.276	0.255	0.307	0.281	0.280
75% NPK	0.227	0.275	0.251	0.288	0.281	0.284	0.290	0.257	0.274	0.270
Mean	0.292	0.239	0.266	0.279	0.282	0.280	0.273	0.282	0.277	0.274
CV (%)	11.283									
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = 0.037 Fert. x biochar x humic x acid = 0.052						

Table.8 Cation exchange capacity of soil (c mol (p) kg⁻¹) at 30 DAS of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser
Fertiliser levels	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean	Mean
100% NPK	15.13	16.54	15.84	16.58	17.10	16.84	18.32	19.01	18.66	17.11
75% NPK	15.20	15.58	15.39	14.23	16.09	15.16	15.95	16.33	16.10	15.56
Mean	15.16	16.06	15.61	15.40	16.59	16.00	17.13	17.67	17.40	16.33
CV (%)	4.62									
CD at 5% level	Fert. = 0.52 Biochar = 0.64 Humic acid = 0.52			Fert. x biochar = 0.90 Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S						

Table.9 Cation exchange capacity of soil (c mol (p) kg⁻¹) at 60 DAS of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser
Fertiliser levels	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean	Mean
100% NPK	15.76	15.39	15.58	14.86	15.51	15.19	16.11	15.99	16.05	15.60
75% NPK	15.09	15.36	15.23	15.01	14.91	14.96	15.1	15.64	15.37	15.18
Mean	15.42	15.37	15.40	14.93	15.21	15.07	15.60	15.81	15.71	15.39
CV (%)	5.28									
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S						

Table.10 Cation exchange capacity (c mol (p) kg⁻¹) of soil at harvest of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹			Fertiliser
Fertiliser levels	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean	Mean
100% NPK	15.27	15.05	15.16	15.5	15.14	15.32	15.01	15.17	15.08	15.18
75% NPK	15.23	15.15	15.19	15.14	15.04	15.09	15.22	15.08	15.15	15.14
Mean	15.25	15.10	15.18	15.32	15.09	15.21	15.11	15.12	15.12	15.15
CV (%)	4.36									
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S						

Table.11 Soil OC (%) at 30 DAS of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹		
	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean
100% NPK	0.48	0.56	0.52	0.59	0.61	0.60	0.61	0.60	0.61
75% NPK	0.47	0.51	0.49	0.58	0.60	0.59	0.62	0.63	0.63
Mean	0.48	0.54	0.51	0.59	0.61	0.60	0.62	0.62	0.62
CV (%)	16.87								
CD at 5% level	Fert. = N.S Biochar = 0.05 Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S					

Table.12 Soil OC (%) at 60 DAS of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹		
	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean
100% NPK	0.53	0.57	0.55	0.6	0.66	0.63	0.64	0.65	0.65
75% NPK	0.59	0.66	0.63	0.69	0.63	0.66	0.69	0.68	0.69
Mean	0.56	0.62	0.59	0.64	0.65	0.65	0.66	0.67	0.67
CV (%)	8.62								
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S					

Table.13 Soil OC (%) at harvest of maize as influenced by fertiliser, biochar and humic acid levels and their interaction

Treatments	BC @ 0 t ha ⁻¹			BC @ 5.0 t ha ⁻¹			BC @ 7.5 t ha ⁻¹		
	HA ₁	HA ₂	Mean	HA ¹	HA ₂	Mean	HA ₁	HA ₂	Mean
100% NPK	0.59	0.59	0.59	0.6	0.63	0.62	0.68	0.67	0.68
75% NPK	0.54	0.57	0.56	0.65	0.63	0.64	0.66	0.68	0.67
Mean	0.57	0.58	0.57	0.63	0.63	0.63	0.67	0.67586	0.67
CV (%)	12.58								
CD at 5% level	Fert. = N.S Biochar = N.S Humic acid = N.S			Fert. x biochar = N.S Fert. x humic acid = N.S Biochar x humic acid = N.S Fert. x biochar x humic x acid = N.S					

100 % NPK: 180-60-50 N-P₂O₅-K₂O kg ha⁻¹

75 % NPK: 135-45-37.5 N-P₂O₅-K₂O kg ha⁻¹

HA₁: 0 kg ha⁻¹

HA₂: 30 kg ha⁻¹

Beneficial characteristics of biochar as a soil amendment are its high cation exchange capacity (CEC of 40 to 80 me per 100 g), high surface area (51 to 900 m² g⁻¹), which leads to increased soil pH and water holding capacity, and affinity for micro and macro plant nutrients (Lehmann, 2007; Laird *et al.*, 2009; Novak *et al.*, 2010). When soil was amended with charcoal, annual crop yields increased by

100% or more (Steiner *et al.*, 2007). Cation exchange capacity was not influenced significantly by either individual or integrated application of fertilisers, biochar or humic acid at 60 DAS and at harvest (Tables 8, 9, 10). When biochar is added to the soil, due to its alkaline nature and high CEC it increases the CEC of the soil instantly. However, with passage of time, soil buffering capacity will

again lower the pH bringing the CEC to equilibrium state (Yamato *et al.*, 2006).

Organic carbon (%)

Individual application of fertiliser and humic acid levels did not influence significantly the organic carbon content of the soil whereas biochar application brought about significant increase in the mean OC from 0.51 to 0.62 %. Biochar since is a carbonaceous material having wide C: N ratio adds organic carbon to the soil (Widowati, 2012). Interaction between fertilisers and biochar, fertilisers and humic acid, biochar and humic acid, fertilisers with biochar and humic acid were found non-significant. There was no significant influence of either individual and integrated application of fertilisers, biochar or humic acid on OC of the soil at 60 DAS and also at harvest (Tables 11, 12, 13).

Soil pH was not influenced significantly by either individual or integrated application of fertilisers, biochar and humic acid at any stage of crop growth. However, a non-significant increase was observed with the application of biochar. Recommended NPK and biochar at 7.5 t ha⁻¹ brought about a significant increase in EC of the soil during the initial stages. Cation exchange capacity of the soil was significantly increased by humic acid @ 30 kg ha⁻¹ and biochar at 7.5 t ha⁻¹ at all the stages of growth, however, the effect was significant 30 DAS. Biochar application brought about significant increase in the mean OC from 0.51 to 0.62 %.

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