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Ammoniacal and Nitrate Nitrogen Release Pattern from Biochar and Biochar Blended urea Fertilizers in Laterite Soil

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ABSTRACT: Recognition of biochar as a potential nutrient carrier to delay the release of nutrients in soils by blending with fertilizers is growing. However, the rate of release of mineralizable nitrogen from the biochar blended fertilizers in different soils is poorly understood. Hence a laboratory incubation study was conducted for 12 months with paddy husk biochar, biochar-bentonite (1:1), urea, biochar blended with urea fertilizer in different ratios (1:0.5, 1:1, 1:2) and biochar bentonite (1:1) blended with urea fertilizer in different ratios (1:0.5, 1:1, 1:2) including an absolute control to elucidate the ammoniacal and nitrate nitrogen release pattern in laterite soil. Paddy husk biochar was produced by the method of slow pyrolysis and biochar blended urea fertilizers by the adsorbent process. Bentonite clay, was also mixed with biochar in 1:1 ratio and blended with urea fertilizer to evaluate its influence on the nitrogen release pattern. Release of ammoniacal nitrogen from soil added with urea fertilizer was fast with maximum release at 30 days (199.73 mg kg^{-1}), followed by a sharp decline and maintaining a low value till the end of incubation, whereas the increase in ammoniacal nitrogen release was gradual and sustained reaching a maximum at 180 days (209.07 mg kg^{-1}) for soil + biochar: urea in 1:1. Nitrate nitrogen also followed the same trend with the maximum release observed for biochar: urea in 1:1 on the 180th day (225.9 mg kg^{-1}). Nitrate nitrogen release showed higher values compared to ammoniacal nitrogen throughout the incubation period for all the treatments. Blending of urea with biochar/ biochar-bentonite prolonged the period for maximum nutrient release. Among the blended fertilizers, the content of both ammoniacal and nitrate nitrogen were comparatively less for biochar –bentonite blended urea fertilizers.

Keywords: Biochar blended fertilizers, Ammoniacal and Nitrate Nitrogen, Laterite soil.

INTRODUCTION

Nitrogen is a limiting nutrient for crop growth, being adsorbed from soil in large quantities necessitating the application of nitrogenous fertilizers in large quantities. The use efficiency of nitrogenous fertilizers is very less (30-40%) being exposed to ammonia volatilization, nitrate nitrogen leaching and nitrous oxide releases which also result in serious pollution of surface waters, groundwater and the atmosphere. The primary goal of nutrient utilization is to improve crop performance by supplying adequate nutrition while limiting nutrient losses from the soil and promoting sustainability by enhancing soil quality components. Slow release fertilizers potentially extend nutrient availability to the plant over a longer period of time compared to conventional fertilizers thereby increase nutrient use efficiency by delaying the availability of nutrients after application and reducing leaching losses. Biochar prepared from agricultural waste may be utilized as a suitable matrix for blending with nitrogen fertilizers can act as a potential slow release fertilizer (Singh *et al.*, 2020).

Biochar is a stable carbon compound obtained by the thermal decomposition of organic materials under little or no oxygen and at relatively low temperatures (<700 ^{o}C), by the process of pyrolysis (Lehmann *et al.*, 2006). The nutrients in inorganic fertilizers can be efficiently loaded into biochar through intimate contact between them. The loading of fertilizer nutrients is made easier by the porous structure, large surface area, diverse functional groups, and a wide range of mineral components in biochar (Dong *et al.*, 2019). Various nutrient ions such as NH_4^+, NO_3^- and K^+ in fertilizers can be strongly adsorbed by the surface functional groups of biochar (Kimetu and Lehmann 2010) which facilitates the production of biochar blended fertilizers for slow nutrient release and reduced losses. The urea blended biochar has significantly higher apparent nitrogen utilization efficiency (Zhang *et al*., 2018) and relatively slow release pattern of nitrogen (Taghizadeh-Toosi *et al.*, 2012).

Thus, biochar blended fertilizers can enhance the nutrient use efficiency and potentially reduce the use of conventional fertilizers. Hence, the effect of biochar blended with urea fertilizer in different ratios on the rate and release pattern of ammoniacal and nitrate nitrogen and the role of bentonite clay on the retention of nitrogen were investigated through a laboratory incubation study.

MATERIALS AND METHODS

A. Production of biochar and biochar blended fertilizers

The method of slow pyrolysis was used for the production of biochar from paddy husk. The process of slow pyrolysis at a temperature around 300 -350 °C continued upto 1.5 to 2 h to obtain the final biochar product, with recovery percentage nearly 50 per cent.

The produced biochar was blended with urea through the adsorbent process in three ratios *viz*., biochar: fertilizer in 1:0.5, 1: 1, and 1:2, by adding urea solution to biochar in the prescribed ratios, stirring for 30 minutes and allowing to cure for 24 h followed by shade drying to produce biochar blended nitrogen fertilizers (Zhang *et al.,* 2018). Biochar-bentonite blended fertilizers were also produced by blending urea in the prescribed ratios with a mixture of biochar and bentonite in a ratio of 1:1. Thus six biochar- urea fertilizer blend combinations were produced *viz*., Biochar- Urea 1:0.5 (B:U= 1:0.5),Biochar- Urea 1:1 (B:U= 1:1), Biochar-Urea 1:2 (B:U= 1:2), Biochar-Bentonite: Urea1:0.5 (Bio-Ben: U= 1:0.5), Biochar-Bentonite: Urea 1:1 (Bio-Ben: U= 1:1) and Biochar-Bentonite: Urea 1:2 (Bio-Ben: U= 1:2) and the total nitrogen content of the produced biochar/biochar-bentonite blended fertilizers were 18.48, 25.81, 33.04, 17.78, 20.74 and 31.13 percentages respectively. The powdered and 2 mm sieved biochar samples were digested and subjected to micro kjeldahl distillation to determine the ammoniacal and nitrate nitrogen content.

B. Ammoniacal and nitrate nitrogen release

Release of mineralizable nitrogen from the biochar and biochar- blended fertilizers in laterite soil was determined through a laboratory incubation study conducted at the Department of Soil Science & Agricultural Chemistry, College of Agriculture, Vellayani, Thiruvananthapuram. The surface soils (0-15 cm) for the incubation study was collected from College of Agriculture, Vellayani, Thiruvananthapuram situated at 8.50° North latitude and 76.90° East longitude at an altitude of 29m above MSL. The soil was acidic in reaction (pH 5.04), low in available nitrogen (204.88 kg ha^{-1}), high in available soil phosphors (66.03 kg ha^{-1}) and low in available potassium (63.46 kg ha^{-1}). The treatments included an absolute control -5 kg soil alone (T_1), soil 5 kg + biochar (paddy husk) @ 20 t ha^{-1} (T_2), soil 5 kg + biochar- bentonite @ 20 t ha^{-1} (T_3), soil 5 kg + biochar-urea - 1:0.5, 1:1, 1:2 (T_4-T_6), soil 5 kg + biochar-bentonite: urea -1:0.5, 1:1, 1:2 (T_7-T_9), soil 5 kg + urea (T_{10}). Five kilograms of air dried and 2 mm sieved soil was placed in plastic containers and mixed thoroughly after the treatments were imposed. Blended fertilizers were characterized for nutrient content and added to the soil so as to supply nitrogen at the rate of 75 kg ha^{-1}. Soil samples after imposing the treatments were arranged in a completely randomized design in triplicate and incubated separately for 360 days. Distilled water was added to maintain the soil at field capacity during the incubation period. Periodic sampling and chemical analysis of samples were done at 0, 15, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 360 days of incubation. The ammoniacal and nitrate nitrogen were analysed using the steam distillation method (Mulvaney, 1996). Analysis of variance was used to test for treatment effects and treatment significance was tested using F test in ANOVA using GRAPES- General Rshiny Based Analysis Platform Empowered by Statistics software with the level of significance set at 0.05.

RESULTS AND DISCUSSIONS

A. Release pattern of ammoniacal nitrogen

The release of ammoniacal nitrogen in laterite soil treated with paddy husk biochar blended fertilizers at different periods of incubation is depicted in Table 1. During the initial days of incubation (upto 30th day) the ammoniacal nitrogen content was significantly higher than all other treatments in soil treated with urea alone (199.73 mg kg^{-1}), thereafter showing a gradual decrease from the 60th day (162.4 mg kg^{-1}) to the end of the incubation (89.60 mg kg^{-1}). Among the blended fertilizers, NH_4-N content was more in soil treated with biochar blended with urea in 1:2 ratio (B:U=1:2), showing an increase from 91.47 mg kg^{-1} on the 0th day to 201.60 mg kg^{-1} at 90 days after incubation and which was significantly higher than all other treatments at 60 and 90 days of incubation, thereafter showing a gradual decrease. In soils blended with biochar: urea in 1:1 ratio the increasing trend in ammoniacal nitrogen release was prolonged upto the 180th day, reaching a maximum of 209.07 mg kg^{-1}, thereafter showing a decline (Fig. 1). From 150 to 210 days after incubation, the ammoniacal nitrogen content was significantly higher for biochar: urea in 1:1 compared to all other treatments. Jabin and Rani (2020) also noticed the slow release pattern of ammoniacal nitrogen from paddy husk biochar treated laterite soils and the sustainability was prolonged to 150 days of incubation compared to absolute control. Since biochar can assist with the mineralization of nitrogen from applied fertilizer, the amount of ammoniacal nitrogen in soil treated with biochar could be higher than that of untreated soils (Widowati *et al.*, 2011). Biochar can have cationic sorption sites, making it able to adsorb NH_4^+ and reduce rapid release of NH_4^+ from soils (Mandal *et al.*, 2018). Initial adsorption of urea in the micropores of biochar and its complete reaction with the amino and carbonyl groups on the surface of biochar may be the cause of prolonged and sustained release of nitrogen from the biochar/ biochar-bentonite blended fertilizers (Xiang *et al*., 2020). Shi *et al*. (2020) noticed that interactions between organic matter and mineral additives in biochar blended fertilizers protect urea from rapid hydrolysis, thereby retarding the rate of nitrogen release.

The biochar-bentonite blended urea fertilizer showed gradual and sustainable increase in the release of ammoniacal nitrogen upto 240 and 270 days of incubation respectively for blending ratios 1:0.5 (171.73 mg kg^{-1}) and 1:1 (188.53), whereas in 1:2, the maximum release was at the 150th day (166.13 mg kg^{-1}) thereafter declining gradually. From 270 to 360 days of incubation, the ammoniacal nitrogen content was significantly higher for biochar-bentonite: urea 1:1 followed by biochar: urea 1:1. The sustainability of biochar-bentonite blended fertilizers was comparatively more than biochar blended fertilizers even though the value was lower for biochar-bentonite blended fertilizers during the initial days (Fig. 2). According to Lu *et al*. (2019), the controlled and sustained release of nitrogen from biochar-bentonite blended fertilizers might be due to its adsorption to bentonite, hydrogen bonding, and electrostatic interactions of the N–C=O and oxygen-containing functional groups.

Ammoniacal nitrogen release from biochar: urea at 1:1 ratio in laterite soil showed a maximum increase of approximately 93.1% compared to absolute control at 180 days of incubation and that of biochar-bentonite: urea in 1:1 showed maximum increase of 102% at the 270th day of incubation. On the 0th day, the percentage increase in NH_4-N release from soils treated with biochar blended urea fertilizer ranged from 7-11% for different ratios, biochar-bentonite blended urea fertilizers ranged from 5-7 % while the soil treated with urea alone showed a 23% increase compared to control. Thus, the rate of release of nitrogen from biochar blended fertilizers could be reduced as compared to that of urea alone (Chen *et al.*, 2018) and the slow release properties was greater for biochar blended fertilizers (Wen *et al*., 2017).

Biochar molecules have the ability to adsorb NH_4^+-N followed by its slow mineralization from organic to inorganic form over time. This leads to a gradual and sustained release of NH_4^+-N during the incubation period. During the initial period of incubation, a smaller amount of NH_4^+-N was released upon the combination of biochar and biochar bentonite treatments compared to urea fertilizer alone. This might be due to the retention of ammonium ions to the negatively charged surface functional (CO-stretch) groups through hydrogen bonding and electrostatic interaction (Wen *et al*., 2017; Lee *et al.*, 2017).

Table 1: Effect of treatments on ammoniacal nitrogen content at different periods of incubation in laterite soil, mg kg^{-1}.

Treatments	**0th**	**15th**	**30th**	**60th**	**90th**	**120th**	**150th**	**180th**	**210th**	**240th**	**270th**	**300th**	**330th**	360th
T_1- Absolute control	82.13	87.73	91.47	100.80	106.40	110.13	115.73	108.27	104.50	98.93	93.33	91.47	87.73	84.00
T_2- Soil + biochar	85.87	95.20	108.27	115.73	130.66	140.00	136.27	126.93	117.60	108.27	104.53	98.93	93.33	91.47
T_3-Soil + biochar-bentonite	84.00	93.33	106.40	112.00	128.80	138.13	141.87	145.60	140.00	136.27	128.80	117.60	110.13	106.40
T_4-Soil+ biochar-urea 1:0.5	87.73	100.80	119.47	132.53	153.10	171.73	181.07	175.47	166.13	158.67	149.33	140.00	130.67	121.33
T_5- Soil + biochar-urea 1:1	89.60	104.53	130.67	151.20	164.30	192.27	201.60	209.07	194.13	182.93	175.47	166.13	154.93	140.00
T_6-Soil +biochar-urea 1:2	91.47	121.33	143.73	177.33	201.60	194.13	186.67	171.73	162.40	156.80	145.60	138.13	125.07	115.73
T_7- Soil + biochar-bentonite: urea 1:0.5	85.87	97.07	112.00	134.40	140.00	149.33	154.93	160.53	166.13	171.73	154.93	147.47	136.27	130.67
T_8- Soil + biochar-bentonite: urea 1:1	87.73	98.93	117.60	138.13	143.73	151.20	158.67	164.27	171.70	181.07	188.53	177.33	162.40	151.20
T_9- Soil + biochar-bentonite: urea 1:2	87.73	102.67	119.47	141.87	147.50	154.93	166.13	160.53	153.10	149.33	143.73	130.67	121.33	112.00
T_{10}- Soil + urea	100.80	158.67	199.73	162.40	153.06	134.40	132.53	123.20	115.73	106.40	97.07	95.20	91.46	89.60
CD (0.05)	**6.966**	**6.516**	**4.607**	**5.776**	**4.266**	**4.607**	**5.224**	**6.516**	**8.707**	**5.776**	**4.925**	**5.507**	**6.032**	**9.215**

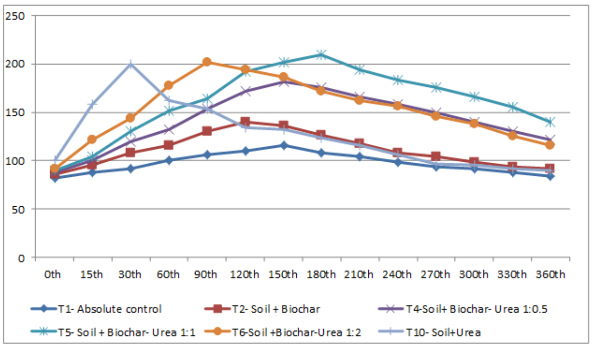

Fig. 1. NH_4-N release from biochar and biochar blended urea fertilizers in laterite soils.

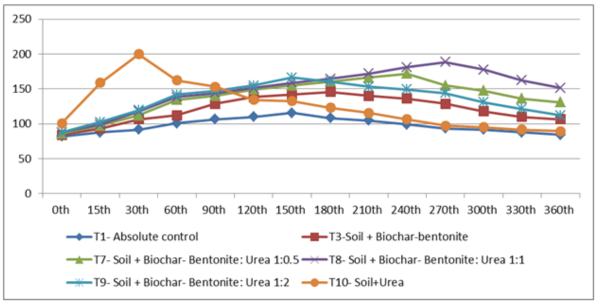

Fig. 2. NH_4-N release from biochar- bentonite blended urea fertilizers in laterite soils.

B. Release of nitrate nitrogen

The release pattern of nitrate nitrogen from laterite soil treated with biochar/biochar-bentonite blended urea fertilizer given in Table 2 shows that the content of nitrate nitrogen was higher in biochar/biochar bentonite blended fertilizers compared to control throughout the incubation period. Even though the release of nitrate nitrogen was more than that of ammoniacal nitrogen for all the treatments, the decreasing trend in release of nitrate nitrogen after attaining a maximum value was comparatively less than that of NH_4^+-N. Jabin and Rani (2020) also observed higher content of nitrate nitrogen in biochar treated soils than ammoniacal nitrogen. Similar to ammoniacal nitrogen, the nitrate nitrogen content was significantly superior for soils treated with urea alone upto 60 days of incubation, showing a maximum value at the 30th day (216.53 mg kg^{-1}), thereafter gradually declining throughout the incubation period (Fig. 3). Among the blended fertilizers, the nitrate nitrogen content increased upto 90 days of incubation for biochar: urea in 1: 2 (209.1 mg kg^{-1}), thereafter showing a decrease, whereas for biochar: urea in 1:0.5 and 1:1 ratio, the gradual increase was upto 180 days of incubation and that of biochar-bentonite: urea in 1:0.5 and 1:1 it was upto 240 days of incubation. From 120 days to 210 days of incubation the biochar: urea in 1:1 maintained its superiority over all other treatments with the maximum value noticed at the 180th day (225.9 mg kg^{-1}). The amount of nitrate nitrogen released from biochar- bentonite blended urea fertilizer was higher compared to biochar blended urea fertilizer during the last months of incubation (Fig. 4). The decrease in nitrate nitrogen after the peak release was comparatively less for biochar-bentonite blended fertilizers compared to biochar blended fertilizers. Among the biochar-bentonite blended fertilizers, the highest nitrate nitrogen content was for biochar-bentonite: urea in 1:1 from 240 days to till the end of the incubation.

Compared to absolute control, a maximum of approximately 78% increase in nitrate nitrogen release was noticed from biochar: urea in 1:1 ratio at 180th day of incubation. On the 0th day, the percentage increase in NO_3^--N release from the soil treated with biochar blended urea fertilizer and biochar-bentonite blended urea fertilizer ranged from 9-12% and 7-10% respectively, while that of soil treated with urea alone ranged from 24% compared to control. According to Jia *et al.* (2021) the nitrate release from biochar blended fertilizer was 25% lower than urea alone. Hagemann *et al.* (2017) reported that the release of nitrate nitrogen from biochar treated soil was about 58% and that from soil alone was 70%.

Nitrate nitrogen release from biochar- bentonite blended fertilizers, was gradual and sustained compared to biochar blended fertilizers though the content was lower than that of biochar blended fertilizers due to the strong binding activity of bentonite. Throughout the incubation period, the content of nitrate nitrogen was more than that of ammoniacal nitrogen. This might be due to the conversion of NH_4^+ to NO_3^- as a result of reaction with biochar matrix (Liao *et al.*, 2020). Similar release pattern was also reported by Gwenzi *et al.* (2017); Roy *et al.* (2021). It was also observed that the nitrogen release from urea was rapid and that from biochar blended fertilizers was lower than that of the urea alone treatment during the initial stages due to the generation of new organic complex molecules by the packing of urea particles in the inner pores and channels of biochar. The application of biochar blended fertilizers will also improve the soil microbial community, enzyme activities and increase nitrification, thus enhancing the nitrate release from soils compared to absolute control and urea alone treatment. The biochar blended fertilizer can also potentially retard the rate of denitrification by limiting the nitrite reductase enzyme and increase the nitrate concentration in the soil compared to urea and soil alone treatments.

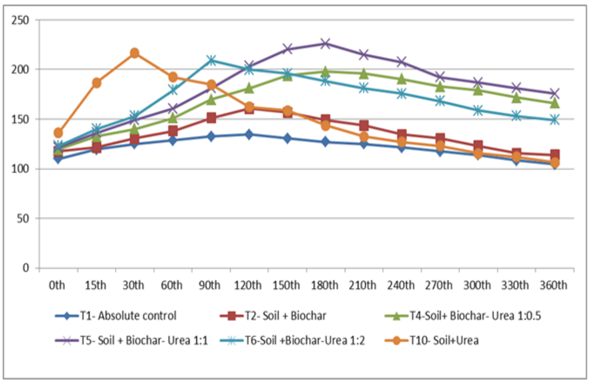

Fig. 3. NO_3^--N release from biochar and biochar blended urea fertilizers in laterite soil.

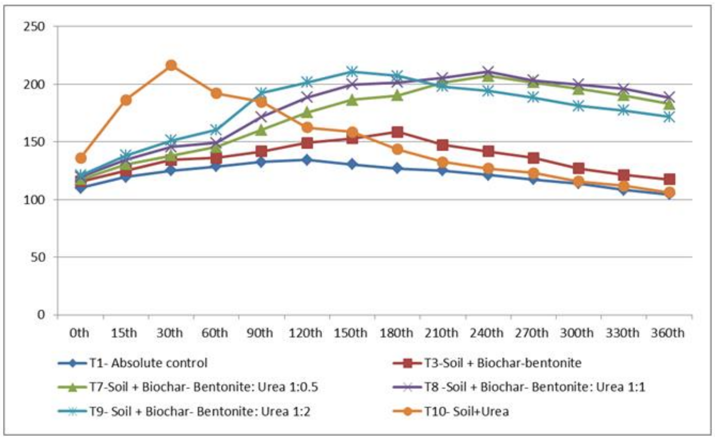

Fig. 4. NO_3^- -N release from biochar bentonite blended urea fertilizers in laterite soil.

Table 2: Effect of treatments on nitrate nitrogen content at different periods of incubation in laterite soil, mg kg^{-1}.

Treatments	0th	15th	30th	60th	90th	120th	150th	180th	210th	240th	270th	300th	330th	360th
T_1- Absolute control	110.1	119.5	125.1	128.8	132.5	134.4	130.6	126.9	125.1	121.3	117.6	113.9	108.3	104.5
T_2- Soil + biochar	117.6	121.3	130.6	138.1	151.2	160.5	156.8	149.3	143.7	134.4	130.7	123.2	115.7	113.9
T_3-Soil + biochar-bentonite	115.7	125.1	134.4	136.3	141.9	149.3	153.1	158.7	147.5	141.9	136.3	126.9	121.3	117.6
T_4-Soil + biochar-urea 1:0.5	119.5	132.5	140.0	151.2	169.9	181.1	194.1	197.9	196.0	190.4	182.9	179.2	171.7	166.1
T_5- Soil + biochar-urea 1:1	121.3	136.3	149.3	160.5	181.1	203.5	220.3	225.9	214.7	207.2	192.3	186.6	181.1	175.5
T_6-Soil + biochar-urea 1:2	123.2	140.0	153.1	179.2	209.1	199.7	196.0	188.5	181.1	175.5	168	158.7	153.1	149.3
T_7-Soil + biochar-bentonite: urea 1:0.5	117.6	130.6	138.1	145.6	160.5	175.5	186.6	190.4	201.6	207.2	201.6	196.0	190.4	182.9
T_8 -Soil + biochar-bentonite: urea 1:1	119.5	134.4	145.6	149.3	171.7	188.5	199.7	201.6	205.3	210.9	203.5	199.7	196.0	188.5
T_9- Soil + biochar-bentonite: urea 1:2	121.2	138.1	151.2	160.5	192.3	201.6	210.9	207.2	197.9	194.1	188.5	181.1	177.3	171.7
T_{10}- Soil + urea	136.2	186.6	216.5	192.3	184.8	162.4	158.6	143.7	132.5	126.9	123.2	115.7	112	106.4
CD (0.05)	**7.591**	**7.180**	**7.388**	**6.032**	**5.776**	**2.099**	**4.925**	**6.279**	**5.776**	**7.980**	**6.032**	**5.507**	**6.966**	**6.516**

CONCLUSIONS

A slow and steady release of nitrogen either as ammoniacal or nitrate was observed in laterite soil on blending biochar with urea compared to urea fertilizer alone. The rate of release of nitrate nitrogen was higher compared to ammoniacal nitrogen for all the treatments. Addition of bentonite to biochar resulted in slowing down of the release of both NH_4^+ -N and NO_3^-- N thus increasing the period of sustained release. The large surface area of biochar and abundant oxygen functional groups like carboxylic, hydroxyl and lactone groups on the surface of biochar- bentonite play a dominant role in adsorbing NH_4^+ and NO_3^-, ultimately reducing the N loss. Thus, biochar as a fertilizer carrier decelerates the release of nutrients into the soil and reduce fertilizer nutrient loss due to leaching, thereby increasing the efficiency of applied fertilizer.

FUTURE SCOPE

Future studies can be carried out to study the mechanism of slow release of nutrients from the biochar blended urea fertilizers and to study the effect of biochar blended fertilizers on soil properties and crop productivity.

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Conflict of Interest. None.

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