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Full Length Article

Biochar and Biochar-Based Nitrogenous Fertilizers: Short-Term Effects on Chemical Properties of Soils

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Abstract

Because of its large surface area and rich functional groups, biochar has been used as an inhibitor to regulate the release of nitrogen from inorganic nitrogenous fertilizers. The experimental treatments included a control condition (CK; no nitrogen and no biochar), ammonium nitrate and no biochar (AN), biochar and no nitrogen (BC), blending-processed biochar-based nitrogenous fertilizer (BP-BNF), adsorption-processed BNF (AP-BNF), and reaction-processed BNF (RP-BNF). The properties of biochar and BNFs and their effects on chemical properties of soils, winter wheat growth, and grain yield were investigated. The order of the nutrient-loading capabilities and quantities and retention intensities of BNFs compared to AN was RP- >AP- >BP-BNF. Biochar and BNFs had no significant effects on the soil nutrient indexes; however, the productive tiller, 1000 grain weight, and biomass and grain yield of winter wheat increased by 5.50, 8.46, 23.85 and 23.42%, respectively, owing to the addition of BNFs. Additionally, the quantity of nitrogen in grain increased significantly with BNF treatments. By quantifying nitrogen utilization, a conclusion was drawn that the RP-BNF treatment was the most effective of the three kinds of BNFs. © 2018 Friends Science Publishers

Keywords: Biochar; Biochar-based nitrogenous fertilizer; Winter wheat; Fertilizer effects

Introduction

In the last decade, biochar has captivated scientists. Biochar was defined by Lehmann and Joseph (2009) as a carbon-rich product derived from the pyrolysis of biomass at high temperatures (400–1300°C) in the absence of oxygen. Biochar production and its use in agriculture play a key role in climate change mitigation (Cayuela *et al.*, 2014) and improve the management of waste biomass generated by agriculture and forestry (Cantrell *et al.*, 2007).

Previous studies have focused mainly on biochar application in agriculture, such as the impact of biochar on crop yields or the effects of biochar on soil amelioration (Glaser *et al.*, 2002; Asai *et al.*, 2009). As reported, biochar can improve soil health by improving nutrient retention (Gao *et al.*, 2016) and serve as a source of nutrients (Beesley *et al.*, 2011); the porous structure is beneficial for the protection of soil microorganisms, thereby improving the microbial activity of the rhizosphere (Jindo *et al.*, 2012; Nielsen *et al.*, 2014). In addition, researches shown that most biochar has very high porosity and large specific surface area, resulting in strong cation exchange capacities, which favor the retention of nutrients, thereby preventing nutrient loss (Liang *et al.*, 2006; Novak *et al.*, 2009; Zwieten *et al.*, 2010). Although the physical properties of biochar were well known by people, the use of biochar as a nutrient carrier, e.g., in controlled-release fertilizer research, is still rare.

Internationally, the efficiency of nitrogen utilization is only approximately 33% (Cassman *et al.*, 2002), where excess nitrogenous fertilizer application and loss from soils have been closely linked to extreme levels of environmental pollution on an ecosystem-level in past decades (Dzikiewicz, 2000; Jenkinson, 2001). Therefore, an improvement in the efficiency of nitrogen use is of great environmental importance. In recent years, many synthetic controlled-release fertilizers, made by coating/encapsulating substrates (Mulder *et al.*, 2011; Ni *et al.*, 2011) or by adding inhibitors (Byrnes and Freney, 1995), have extended the availability of fertilizer to boost agricultural production. Although these fertilizers are quite useful, the materials used for coating (e.g., resin) are slow to degrade, whereas the preparation of inhibitors is a time-consuming and costly affair. The negative aspects of these commercial products have necessitated a search for an alternative substrate to regulate the release of nitrogen from inorganic nitrogenous fertilizers. Biochar, as an environmental protection material, can be used as a nutrient carrier to delay the release of

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fertilizer into soil (Cai *et al.*, 2016), reduce nutrient leaching, and improve the nutrient utilization efficiency of fertilizer (Manikandan and Subramanian, 2013; Oh *et al.*, 2014). In addition, after the release of nutrients, biochar can still play further roles in soil improvement.

In the present study, three types of biochar-based nitrogen fertilizers (BNFs) were produced using environmentally friendly biochar as a sustained-release carrier. To determine the effects of biochar and BNFs on the chemical properties of soils, crop biomass and grain yield, as well as the differences among the three types of BNFs, the properties of the BNFs were characterized and the BNFs were subsequently applied to field soils. We hope that this study will serve as a reference, not only for further investigations, but also in the production and utilization of environmentally friendly, slow-release fertilizers.

Materials and Methods

Materials

Biochar and fertilizer: Biochar made by residual wood was produced by pyrolysis of agricultural waste biomass provided by Shaanxi Yi-xin Bioenergy Technology Development Co., Ltd (Yangling, Shaanxi, China). The reactor was maintained at the desired temperature (450°C) in the absence of oxygen for 4 h and then cooled. The basic properties of biochar are shown in Table 1. The granule size of biochar particles was less than 2 mm.

Analytical-grade ammonium nitrate (particle size < 1 mm), 15% aqueous ammonia, and 30% nitric acid solution were used to prepare the BNFs.

Test crop and experimental soils: Field trials were conducted on soils at an experimental station at the Northwest Agriculture and Forestry University (NWAFU) in Yangling, Shaanxi, China (34°15'N, 108°4'E). The basic properties of the soil used in the experiment were shown in Table 2. Winter wheat was sown on October 18, 2011, at the recommended seed rate of 150 kg·ha^{-1}. The wheat variety Xiaoyan 22 was selected by NWAFU.

Experimental Design

Preparation of BNFs: In this study, three types of BNF were prepared using the following techniques:

1) BNF prepared via the blending process (BP-BNF): Solid ammonium nitrate was added to biochar at a ratio of 35 to 65. The two components were mixed by stirring. The resulting nitrogen content of BP-BNF was 12%.

2) BNF prepared via the adsorbent process (AP-BNF): First, 35 kg of ammonium nitrate was dissolved in 100 kg of water. Subsequently, 65 kg of biochar was added to the above solution, stirred for 30 min, and allowed to sit for 24 h at room temperature. Finally, the mixture was dried in an oven at 60°C. The resulting nitrogen content of the AP-BNF was 12%.

3) BNF prepared via the reactive process (RP-BNF): In this process, the RP-BNF was prepared in a specific reactor using the stirring function. First, 6.5 kg of biochar was added to 9.5 kg of 15% aqueous ammonia in the reaction kettle, and stirred continuously for 15 min. Then, 7 kg of 30% nitric acid solution was added to the aforementioned mixture and stirred continuously for 30 min. Feedstock was added via the feed inlet, the feed inlet was closed, and the reactor was allowed to sit for 24 h. After 24 h, the feed outlet was opened, and the reactive product was collected. Finally, 15% aqueous ammonia was used to adjust the pH of the reactive product to 7, and the BNFs were heated and dried in an oven at 60°C. The resulting nitrogen content of RP-BNF was approximately 12%.

Field trials: A single-factor, randomized block experiment with four replications was performed to explore the influence of the three types of BNFs on soil and winter wheat. The treatments were as follows: CK (no nitrogen and no biochar), BC (biochar and no nitrogen), AN (ammonium nitrate and no biochar), BP-, AP-, and RP-BNF. Phosphorous (P) and potash (K) were applied at 150 and 180 kg ha^{-1}, respectively, as basal applications during sowing in all treatments, whereas 220 kg ha^{-1} nitrogen (N) was applied to the AN and BNF treatments. The applied dosage of BC was the same as the content in BNFs. Study plots had an area of 3 m × 4 m. During the growth period, a unified management strategy was adopted for wheat.

Soil and Plant Sampling and Analysis

Sampling: Soil samples were collected at the seedling, wintering, jointing, heading, and mature stages and analyzed for mineral N (NH_4^+-N, NO_3^--N, and NO_2^--N). Soils were collected before and after the experiment to analyze their basic chemical properties. At the mature stage, plant samples were collected to measure the nitrogen content of the wheat grain and straw as well as the grain yield, biomass, and yield components.

Analysis: A Hitachi S-3400N scanning electron microscope (Hitachi High Technologies, Tokyo, Japan) and Fourier transform infrared spectrometer (Nicolet NEXUS 470-type, Thermo Nicolet, American) were used to acquire the microstructure and infrared spectra of biochar and BNFs, respectively. FTIR spectra were recorded in transmission mode between 4000 and 500 cm^{-1} for all samples.

A portion of each sample was sieved through a 2 mm sieve and the pH was determined using a water-to-soil ratio of 2.5:1. This soil was then used to measure available nitrogen using a continuous flow analyzer (AA3 HR Auto Analyzer, Germany). Mineral N is the sum of NH_4^+-N, NO_3^--N, and NO_2^--N contents. The remaining soil was air-dried and then ground to pass through a 1 mm sieve to analyze the following indexes: total nitrogen content using the Kjeldahl method, phosphorus using the Olsen method, potassium using a flame photometer, and organic carbon using the $K_2Cr_2O_7$-titrimetric method (Lu, 2000).

Finally, nitrogen use efficiency was calculated. Nitrogen apparent utilization efficiency (NAU) refers to the percentage of N uptake by the above-ground plant (i.e., winter wheat) relative to the amount of applied nitrogen, which can reflect the quality or performance of a fertilizer to some extent. Nitrogen harvest index (NHI) is the portion of total nitrogen partitioned to the grain, and it represents the transfer efficiency of nitrogen to the grain. Nitrogen agronomic efficiency (NAE) is the grain yield increase per unit of applied nitrogen, which reflects the yield effect of a nitrogenous fertilizer. The formulas used are as follows:

NAU (%) = ((N uptake of N treatment - N uptake of N0 treatment)/amount of N applied) ×100

NHI (%) = (N uptake of grain/N uptake of plant) ×100

NAE ($kg \cdot kg^{-1}$) = (yield of N treatment - yield of N0 treatment)/amount of N applied

Statistical Analyses

Statistical analyses were performed with one-way and two-way analyses of variance (ANOVA) using SPSS 18.0 (SPSS Inc., Chicago, 600 IL, USA). The level of significance was set at 0.05. Origin Pro 9.0 (Origin Lab, Inc., Northampton, MA, USA) and Microsoft Office Excel 2013 were used to plot infrared spectroscopy and data consolidation, respectively. All data are presented as the mean ±SE of at least three replications.

Results

Properties of Biochar and Biochar-based Nitrogenous Fertilizers

SEM micrographs of biochar and BNFs showed that biochar had a high quantity of internal pores, which varied in size and shape, and that the surface of pore walls was smooth (Fig. 1). The surface morphology of biochar was altered following the loading of ammonium nitrate via the different processing strategies. Fig. 1B shows that, in a few cases, some granular substances appeared on the surface of the porous biochar walls, which may be attributed to absorbed ammonium nitrate particles in the process of blending. The quantity of ammonium nitrate absorbed by the biochar in AP-BNF (Fig. 1C) was much higher than that of the biochar in BP-BNF (Fig. 1B), with a higher incidence of crystals and flaky substances on the broken walls of biochar particles in AP-BNF. A similar phenomenon also occurred for RP-BNF, which adsorbed such a high quantity of salt particles on the pore walls and pores that the surface microstructure was blurred (Fig. 1D). The highest adsorption capacity of biochar for ammonium nitrate was observed in the RP-BNF treatment, followed by AP and BP-BNF in sequence.

The functional groups identified from the FTIR spectra of biochar, ammonium nitrate, and BNF samples are shown in Fig. 2. The main absorption peaks of biochar appear near 3450, 1940, and 1430 cm^{-1}, and these peaks are attributed to -OH stretching vibration, C=O antisymmetric stretching vibration, and C-O characteristic absorption peaks, respectively. The FTIR spectrum of RP-BNF showed two distinct absorption peaks (3425 and 3130 cm^{-1}) in the long-wave infrared (IR) region. The peak at 3425 cm^{-1} (hydroxyl, -OH) was clearly different from the peak at 3130 cm^{-1} (N-H), where the latter also corresponded to the peaks of other BNFs. The spectrum at 1380 cm^{-1} contains the characteristic absorption peaks of NO_3^- from RP-BNF. Moreover, the absorption peak of the three types of BNFs at 820 cm^{-1} was characteristic of ammonium nitrate, indicating the presence of ammonium nitrate crystals in the BNFs.

Effects on Soil Nutrient Index and Crop

Dynamic changes of soil available nitrogen in wheat at different growth stages: Nitrogen treatments (i.e., AN, BP-, AP- and RP-BNF) significantly increased the content of NO_3^--N and available nitrogen in soils, where all nitrogen forms displayed the trend of first increasing and then decreasing in synchrony with the phenology of the plants (Fig. 3).

The NO_3^--N content of soils in response to nitrogen treatments during the seedling stage and wintering stage remained steady, reaching its highest level at the jointing stage. However, nitrate content decreased at the heading stage because of the increased uptake by wheat and leaching as a result of irrigation. The NO_3^--N content of soil in response to the different nitrogen treatments did not differ significantly. As shown in Fig. 3B and C the highest content of NH_4^+-N occurred at the wintering stage, whereas the peak content of nitrate occurred during the heading stage. With the exception of the BP- and RP-BNF treatments, the release of NH_4^+-N exhibits a "sigmoidal" pattern, significantly differing from the other treatments in that respect.

Soil nutrient content after winter wheat harvest: In contrast to the original soil (14.69 g/kg), with the exception of the BP- and AP-BNF treatments, organic matter content decreased in the control as well as in other treatments. The total nitrogen contents in the BC, AN, BP- and AP-BNF treatments were higher in comparison to pre-planting; however, there were no significant differences between these treatments. For the total P content in soils during the trial, however, total potassium and available potassium both displayed declining trends.

The changes in pH in the present study show that the pH values of the BC and BNF treatments were higher than those of the control treatment (Table 3), suggesting that the biochar increased the pH of the test soils. Of all the treatments, BC displayed the highest increase in pH, as the pH of the biochar in the BNFs was affected by the addition of nitrate salt. During the wheat growing season, the pH values of the soils were 7.51–7.77, which was suitable for crop growing.

Table 1: Properties of biochar tested in experiments

Surface area ($m^2 \cdot g^{-1}$)	Ash content %	Specific gravity ($g \cdot cm^{-3}$)	pH	Organic carbon (%)	Nitrogen (%)
86.70	13.98±0.23	1.11±0.02	9.99 ± 0.06	72.38±1.34	1.18±0.05

The data are based on the mean ± SE of three repeats

Table 2: Basic properties of experimental soil

Bulk density ($g \cdot cm^{-3}$)	O.M. ($g \cdot kg^{-1}$)	CEC ($cmol \cdot kg^{-1}$)	TN ($g \cdot kg^{-1}$)	TP ($g \cdot kg^{-1}$)	TK ($g \cdot kg^{-1}$)	AP ($mg \cdot kg^{-1}$)	AK ($mg \cdot kg^{-1}$)
1.31±0.02	14.69±0.15	7.60±0.03	0.83±0.02	1.01±0.05	21.23±0.66	24.50±0.20	211.03±16.12

O.M.: organic matter, TN: total nitrogen, TP: total phosphorus, TK: total potassium, AP: available phosphorus, AK: available potassium. The data are based on the mean±SE of four repeats

Table 3: Nutrient content of soil after winter wheat harvest

Treatment	OM (g/kg)	TN (g/kg)	C/N	TP (g/kg)	TK (g/kg)	AP (mg/kg)	AK (mg/kg)	pH value	CEC (cmol/kg)
CK	13.18±0.45c	0.79±0.04a	9.71±0.29ab	1.02±0.002a	20.16±1.14a	34.0±0.35a	231.19±27.92a	7.51±0.15a	7.64±0.21a
BC	14.58±0.88ab	0.84±0.05a	10.12±0.58a	1.05±0.001a	20.11±1.19a	27.5±0.13a	219.82±37.47a	7.77±0.03a	7.71±0.12a
AN	14.18±1.09abc	0.87±0.07a	9.49±0.38b	0.95±0.001a	20.28±1.16a	33.0±0.19a	246.19±57.39a	7.67±0.09a	7.75±0.09a
BP-BNF	14.74±0.66a	0.86±0.07a	9.96±0.62ab	0.99±0.002a	20.13±0.95a	29.5±0.11a	229.64±25.61a	7.72±0.06a	7.69±0.13a
AP-BNF	14.71±1.05ab	0.86±0.06a	9.90±0.24ab	1.01±0.002a	19.76±0.93a	32.5±0.27a	222.93±29.75a	7.66±0.10a	7.83±0.07a
RP-BNF	13.52±0.48bc	0.82±0.03a	9.60±0.13ab	1.12±0.004a	19.63±1.10a	43.5±0.67a	207.93±14.96a	7.67±0.08a	7.87±0.05a

O.M.: organic matter, TN: total nitrogen, TP: total phosphorus, TK: total potassium, AP: available phosphorus, AK: available potassium. Lowercase letters represent significance differences at $P< 0.05$. The data are based on the mean ± SE of four repetitions

Table 4: Yield components, yield, and biomass of winter wheat

Treatment	Spikes (10^4 ha^{-1})	Increase compared to CK (%)	1000 -grain weight (g)	Increase compared to CK (%)	Grain Yield (kg ha^{-1})	Increase compared to CK (%)	Biomass ($kg \cdot ha^{-1}$)	Increase compared to CK (%)
CK	489.37± 6.57b	--	31.51± 0.47d	--	4535.87±299.97c	--	5604.19±415.29d	--
BC	496.25±10.51b	1.39	33.66±0.58bc	6.39	4868.00±194.57c	6.82	6329.75± 222.87c	11.46
AN	499.37± 3.75b	2.00	33.19± 0.50c	5.06	5418.54±349.03b	16.29	6024.69±294.98cd	6.98
BP-BNF	515.50±12.46a	5.07	34.00± 0.59b	7.32	5704.85±416.43ab	20.49	7165.62±66.17b	21.79
AP-BNF	516.87± 6.25a	5.32	34.17± 0.29b	7.78	5991.96±218.92a	24.30	7666.62±407.25a	26.90
RP-BNF	521.25± 8.54a	6.12	35.12± 0.34a	10.28	6086.48±262.70a	25.48	7264.37±214.29ab	22.85

Values are the mean ± SE (n = 4). Lowercase letters represent significance differences at $P< 0.05$

The values of cation exchange capacity (CEC) for all treatments were 7.64–7.87 cmol/kg, and there was no significant difference between any of the treatments (Table 3). The beneficial effects of biochar and BNFs on soil CEC should be further investigated under conditions of continual biochar and BNF application, along with the effects of biochar aging on soils.

Effects on plants: Wheat spikes, 1000-grain weight, yield and biomass with the various BNF treatments were significantly greater in comparison to that with the control CK (Table 4, $P<0.05$). Wheat spikes from the BP-, AP-, and RP-BNF treatments increased by 5.07%, 5.32% and 6.12%, respectively, in comparison to those observed for the control, and the wheat spikes from BP-, AP-, and RP-BNF were significantly higher than those from the BC and AN treatments. However, there were no significant differences between the BNF treatments. The 1000-grain weight with the three BNF treatments increased by 7.32–10.28% in comparison to that with CK, and that with RP-BNF was significantly higher than that with BP- and AP-BNF. There was no significant difference between BP- and AP-BNF.

The grain yields with AN and the BNF treatments significantly increased in comparison to those with the CK and BC treatments, which increased by 16.29–25.48% in comparison to those with the CK treatment; however, no significant differences in the grain yield was observed among the three BNF treatments. The BNFs significantly increased the biomass of winter wheat in contrast to CK, BC, and AN, and there were no significant differences among the three BNF treatments. In comparison to the CK treatment, the other treatments increased the wheat biomass by 6.98–26.90%. Therefore, biochar and BNFs have the potential to increase the biomass and grain yield of winter wheat when used as a soil amendment.

Nitrogen Utilization Efficiency in Response to BNF Application

As shown in Fig. 4, the nitrogen apparent utilization efficiency (NAU) of BNFs was significantly higher than that of the AN treatment, where the highest NAU was observed for the RP-BNF treatment. The NAU observed with the RP-BNF treatment was 34.74% higher than that

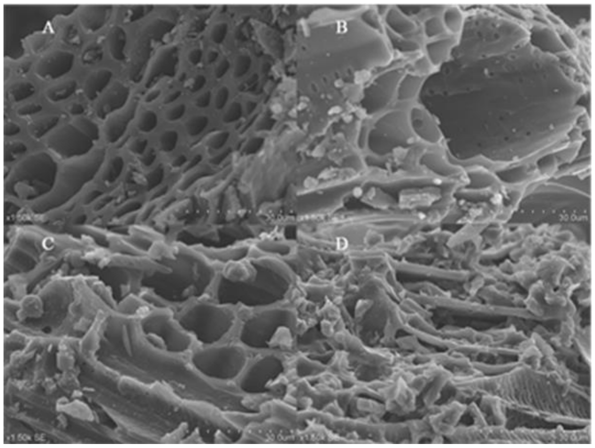

Fig. 1: Observations of the microstructure of biochar and BNFs. A) SEM micrograph of biochar, B) SEM micrograph of BP-BNF, C) SEM micrograph of AP-BNF, and D) SEM micrograph of RP-BNF. All micrographs were captured using the same magnification (1500 X)

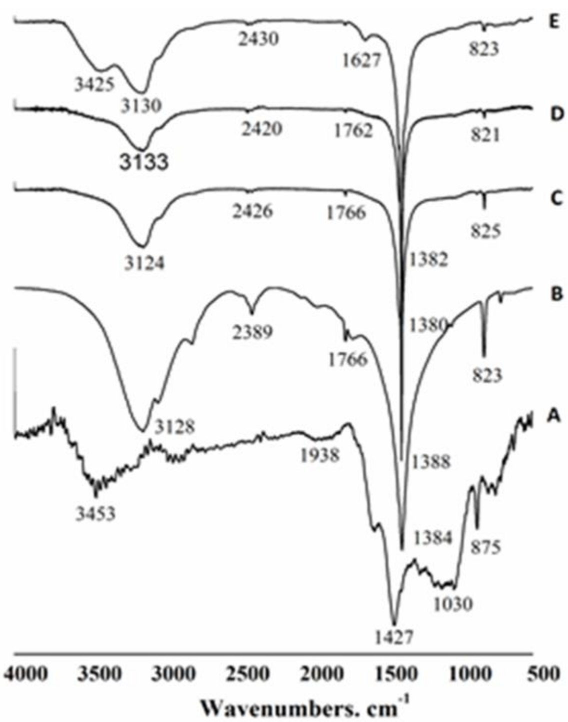

Fig. 2: Fourier transform infrared spectroscopy (FTIR) spectra of biochar, ammonium nitrate, and BNFs. A) Biochar, B) ammonium nitrate, C) BP-BNF, D) AP-BNF, and E) RP-BNF. Labels represent the peaks of the FTIR. 3450cm^{-1}: -OH; 3130 cm^{-1}: N-H; 3000 cm^{-1}: C=C; 1940 cm^{-1}: C=O; 1430 cm^{-1}: C-O; 1380 cm^{-1}: NO_3^-

with the CK treatment, and significantly higher than that with the AP-BNF treatment. However, the NAU was not significantly different between the BP- and RP-BNF treatments. The nitrogen harvest index (NHI) with the AP-

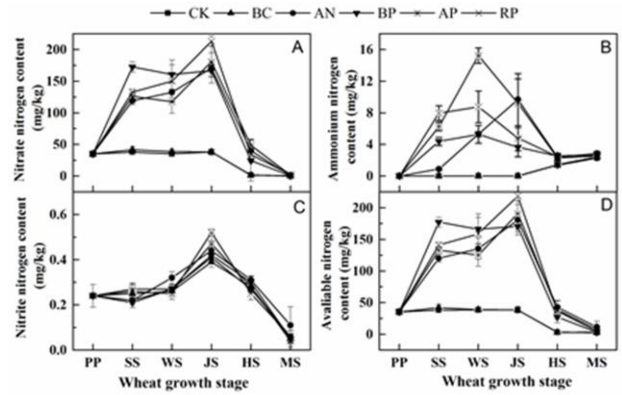

Fig. 3: Dynamic changes in soil available nitrogen during wheat growth. A) Nitrate nitrogen content, B) ammonium nitrogen content, C) nitrite nitrogen content, and D) available nitrogen content. PP: pre-planting, SS: seedling stage, WS: wintering stage, JS: jointing stage, HS: heading stage, and MS: maturation stage. All the values were based on four repetitions; the bars give SE values

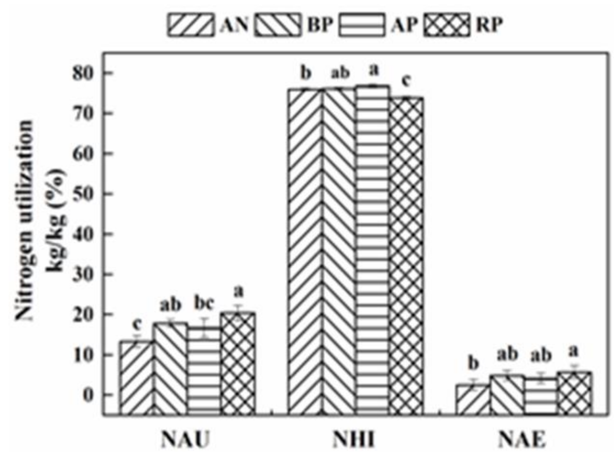

Fig. 4: Effects of different treatments on nitrogen utilization efficiency. Lowercase letters represent significant differences at $P<0.05$. All the values were based on three repetitions; the bars give SE values

BNF treatment was significantly higher than that with the RP-BNF and AN treatments. However, the difference was not significant in comparison to BP-BNF, indicating that the AP-BNF treatment effectively promoted the transformation of nitrogen into the wheat grain. The RP-BNF treatment resulted in the best performance for Nitrogen agronomic efficiency (NAE), with a significant increase of 56.72% relative to AN. In comparison to AN, the BP- and AP-BNF treatments did not exhibit significant differences. Thus, the analysis of NAU indicated that the RP-BNF treatment resulted in the best agronomic effects. In summary, in quantifying nitrogen utilization as a result of the various treatments, we conclude that the RP-BNF treatment was the most effective of the three BNFs.

Discussion

Research on biochar, inspired by investigations of *terra preta* (black soil) in Amazonia, has shown that biochar can improve soil properties and agronomic performance (Glaser and Birk, 2012). Several studies have also shown that the application of biochar to soil can influence soil properties, such as water holding capacity and microbial activity (Glaser *et al.*, 2002; Atkinson *et al.*, 2010). These results are in agreement with the observations of this study, where the well-developed pore structure and the high surface area of biochar particles endowed biochar with a high capacity for adsorption (Fig. 1 and 2). It has been several years since the idea that biochar can be used as fertilizer carrier was raised; however, very few studies have addressed this idea. Additionally, the research focus of the existing reports was biochar-compost (Agegnehu *et al.*, 2015), and they thus did not make full use of the strong adsorption characteristics. However, biochar-compost improves soil nutrient status and crop yield (Zhong *et al.*, 2006; Agegnehu *et al.*, 2015) and the BP-BNF in this study is a type of biochar-compost.

According to Fig. 1, we can know that a high quantity of internal pores and the large surface area of pore walls have the potential to serve as adsorption sites for nutrients. A small quantity of impurities was observed to adhere to the surface of biochar particles, which were likely ash salt crystals formed during pyrolysis. The highest incidence of crystals and flaky substances on the broken walls of biochar particles was observed in RP-BNF, and the surface microstructure even was blurred. The chemical reaction between ammonium hydroxide and nitric acid in the surface of biochar caused the most quantity ammonium nitrate adsorption, at the same time the maximum adsorption strength which can also be concluded in Fig. 2.

The abundant hydroxyl, carboxyl, and carbonyl functional groups detected on the surface of biochar particles are thought to be involved in chemical adsorption and the reaction of biochar with ammonium nitrate and feed stocks of AN synthesis. The terminal –OH adsorption peak occurred in RP-BNF, whereas the N-H adsorption peak of NH_4^+ weakened and shifted to the long-wave period, confirming that a chemical reaction took place in the preparation of RP-BNF. The absorption wavelength observed in the range of 820–1300 cm^{-1} resulted from the interactive effect of NO_3^- and C-O in biochar, implying a strong chemical bond between these two groups. A similar phenomenon also occurred with respect to AP-BNF and BP-BNF, for which the only peak appeared at 3130 cm^{-1}, indicating that there was no distinct chemical reaction between ammonium nitrate and biochar. The absorption peak intensity of the high wave number and fingerprint region of AP-BNF was slightly higher in comparison to that of BP-BNF, as this is the region where the intermolecular hydrogen bonds between ammonium nitrate and biochar in AP-BNF are formed. These bonds weaken the intramolecular and intermolecular hydrogen bonds in ammonium nitrate, thereby enhancing the binding force of ammonium nitrate and biochar. As a result, ammonium ions are more readily adsorbed, thereby explaining why the sustained release effect of AP-BNF was greater than that of BP-BNF. In summary, the decreasing order of the nitrogenous nutrient adsorption of the three types of BNFs was RP-, AP-, and BP-BNF. At the same time, the denser peaks in the vicinity of 3000 cm^{-1} were attributed to the vibration of olefinic or aromatic ring stretching, which indicates that the carbon atoms in biochar existed in aromatic rings and carbon-carbon double bonds, and were thus structurally stable.

Therefore, we are absolutely sure biochar can be used as a fertilizer carrier to delay the release of nutrients into the soil, reduce fertilizer nutrient loss to leaching, and improve the utilization rate of fertilizer nutrients (Zhong *et al.*, 2006; Magrinibair *et al.*, 2009). In the present study, there were no significant differences among the three BNF treatments with respect to available nitrogen under the tested field conditions. This is likely a result of the various complex interactions among microbes, enzymes, and the root systems of crops, as the release of nitrogen from different BNFs has been shown to be affected by biochemical cycles in the soil (Wu *et al.*, 2014). According to a previous study (Kimetu *et al.*, 2010), application of biochar to soil has the ability to effectively improve the quantity of organic matter in soil, as biochar is rich in organic carbon. However, we observed no such effect in the present study, likely owing to the relatively small dosage of biochar, and thus organic matter was decomposed more than it was accumulated. Additionally, the C/N ratio of all treatments was less than 15, indicating that the decomposition of organic matter in the test soil was facilitated, and that nitrogen mineralization was significantly accelerated. Thus, this phenomenon is likely to cause a decrease in nitrogen content. The total phosphate and potassium contents of test soils displayed declining trends, likely because biochar and BNFs capture soil potassium and phosphorus that tend to be fixed by calcium, aluminum, and iron in soils.

In our preliminary study (Zhang *et al.*, 2014), experiments evaluating accumulated release of BNFs in water (Fig. 3) and cumulative nitrogen leaching from BNFs in a soil column (Fig. 4) showed that the best slow release of BNF occurred from RP-BNF, successively followed by AP- and BP-BNF, which concur with the results of Fig. 1 and 2 in this study. The effect of biochar on physical adsorption of ammonium nitrate in the processing of RP-BNF likely caused these results. However, there was no significant positive effect of BNF in the field of BNF in comparison to the other new synthetic fertilizers (i.e., polymer-coated fertilizers). This is because the development of new synthetic fertilizers prioritizes the controlled release of nutrients, achieving an ideal effect through coating to control the release of nutrients (Shaviv *et al.*, 2003), whereas the ammonium nitrate load effect of BNFs is strongly dependent on the electrostatic attraction or physical adsorption of chemical bonds, even in the case of fertilizer crystals attached to the surface of biochar, and thus the slow-release effect of carbon and nitrogen is limited. However, after nutrients are released, biochar can continue to improve the soil properties, in stark contrast to synthetic fertilizers. The short-term nature of the study likely also contributed to the indistinct effect of BNFs.

Conclusion

The BNF can improve the soil properties more than the synthetic fertilizer. Moreover, as revealed from quantifying nitrogen utilization, the RP-BNF treatment was the most effective of the three kinds of BNFs.

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