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HIGHLIGHTS

- N from the urea was bound strongly by the functionalised surfaces of the biochar.
- Biochar-mineral urea composite reduced the N leaching in soil.
- Biochar-mineral urea composite was more effective on the retention of NH_4^+-N.
- Biochar-mineral urea composite increased maize root growth and N use efficiency.

GRAPHICAL ABSTRACT
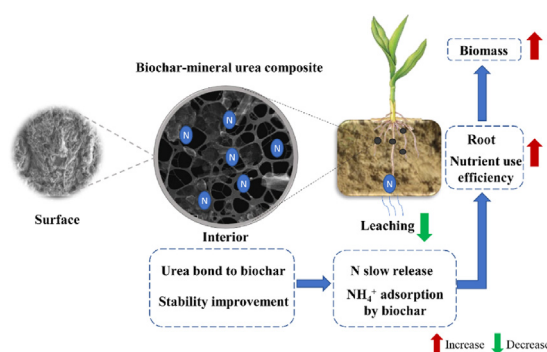
ARTICLE INFO

ABSTRACT

Over use of N fertilizers, most commonly as urea, had been seriously concerned as a major source of radiative N (Nr) for severe environment impacts through leaching, volatilization, and N_2O emission from fertilized croplands. It had been well known that biochar could enhance N retention and use efficiency by crops in amended croplands. In this study, a granular biochar-mineral urea composite (Bio-MUC) was obtained by blending urea with green waste biochar supplemented with clay minerals of bentonite and sepiolite. This Bio-MUC material was firstly characterized by microscopic analyses with FTIR, SEM-EDS and STEM, subsequently tested for N leaching in water in column experiment and for N supply for maize in pot culture, compared to conventional urea fertilizer (UF). Microscopic analyses indicated binding of urea N to particle surfaces of biochar and clay minerals in the Bio-MUC composite. In the leaching experiment over 30 days, cumulative N release as NH_4^+-N and of dissolved organic carbon (DOC) was significantly smaller by >70% and by 8% from the Bio-MUC than from UF. In pot culture with maize growing for 50 days, total fresh shoot was enhanced by 14% but fresh root by 25% under Bio-MUC compared to UF. This study suggested that N in the Bio-MUC was shown slow releasing in water but maize growth promoting in soil, relative to conventional urea. Such effect could be related mainly to N retention by binding to biochar/mineral surfaces and partly by carbon bonds of urea to biochar in the Bio-MUC. Therefore, biochar from agro-wastes could be used for blending urea as combined organo/mineral urea to replace

mineral urea so as to reduce N use and impacts on global Nr. Of course, how such biochar combined urea would impact N process in soil-plant systems deserve further field studies.

1. Introduction

Excessive N fertilization in agriculture had been seriously concerned as a major source of radiative N (Nr), causing severe environmental problems of water quality and of nitrous oxide (N_2O) emissions (Ju et al., 2006). Nitrogen fertilizer was consumed as much as 33 million tons per year in China's agriculture (Huang, 2014) but contributed by 72% to total nitrogen input in terrestrial ecosystems of China (Zhang et al., 2013). Particularly, annual N_2O emission from fertilized croplands of China contributed by 24% on average to the global total over 2007–2016 (Yue et al., 2019). The low N use efficiency (about 30–40%) but high risk due to N leaching, volatilization and N_2O emissions of N in fertilizers had been also heavily addressed as a global issue of Nr, challenging the global environmental sustainability (Gonzalez et al., 2015). Thus, to reduce N release but enhance plant utilization of N fertilizer had been a priority demand for sustainable agriculture globally.

Biochar had been known as a solid product of thermal decomposition of biomass in an oxygen-limited environment (Lehmann and Joseph, 2015). Under pyrolysis normally at temperature of 350–600 °C, biochar was produced as char material with organics from bio-wastes transformed mostly into recalcitrant carbon and surface area and porosity greatly enhanced, helping to retain nutrients, particularly N, in soil and solution and (Bian et al., 2016; Jaafar et al., 2015; Jindo et al., 2014; Joseph et al., 2010; Lehmann and Joseph, 2015, Li et al., 2018a). However, N retention capacity by biochar could vary with feedstocks and pyrolysis temperature used for biochar production (Li et al., 2018b). In China, agricultural bio-wastes had been increasingly recommended to produce, through engineered pyrolysis systems, biochars high in stable carbon and nano-sized porosity as well as in moisture and nutrient retention capacity (Pan et al., 2017). With improved availability of P and K as well as Si but reduced availability of potentially toxic metals and removed of medicine chemicals or antibiotics, these biochars had been widely applied as soil amendment, often at rates between 20 and 50 t ha^{-1}, to improve soil fertility and crop production and to immobilize heavy metals as well as to enhance soil carbon sequestration (Bian et al., 2014; Liu et al., 2019).

Application of large quantities of biochar in fields (especially cereal crops) by means of recycling biowastes could not provide a positive return on investment in agriculture (Clare et al., 2014, 2015). Instead, small quantity of functionally enhanced biochar products could be a low cost but high efficiency solution such as novel nano-biochar to tackle metal contamination in soils (Li et al., 2019). Likewise, small amount of biochar to blend chemical nutrients showed highly increased nutrient agronomic efficiency and plant growth promotion, potentially shifting paradigm of mineral fertilizers for green agriculture with an emerging technology of biochar-based compound fertilizer (BCF) (Joseph et al., 2013). Such BCF could provide net income through increased yield but reduced chemical fertilizer use and greenhouse gas emission (Qian et al., 2014; Zheng et al., 2017).

Urea had been used as a conventional chemical N fertilizer, supplying 67% of total N in China's agriculture (Zhang et al., 2013). Reducing N release while sustain plant N nutrition would be a priority demand for biochar technology in China's green agriculture

(Pan et al., 2015). While biochar amendment helped to slow N release from soil fertilized with chemical NH_4Cl in an agricultural soil (Wen et al. 2017), wood biochar could react with urea N in solution urea with heat and slowed N releasing due to enhanced surface retention of ammonium on biochar (Manikandan and Subramanian, 2013). Chemical nutrients could be mechanically mixed with bentonite clay and biochar to produce biochar blended compound fertilizer at ambient condition (Joseph et al., 2013). With engineered biochar technology, biochar, clay and chemicals were mixed but reacted in a steam environment to produce a firm granular composite of biochar-mineral compound fertilizer (BCF) (Pan et al., 2017). Steam blending could lead to formation of organo-mineral aggregates, enabling N binding to biochar carbon matrix (Joseph et al., 2013). In other side, bentonite had been often applied as clay minerals for blending chemical N forms so as to protect the structure and thus mechanical strength of biochar blended granular fertilizer (Wei, 2017). Whereas, sepiolite had been extensively used as a mineral binder for chemicals, organic pollutants and heavy metal in soils (Mohammadi et al., 2019; Qin et al., 2019). With a structure of zeolite-like channels, sepiolite was recognized as a gel for suspension and also a binder in fertilizer manufacture, due to its strong adsorption of mineral and organic compounds onto their surfaces (Frost et al., 1998). Therefore, both of these two minerals could be considered as mineral agent promoting aggregation of biochar and urea when reacted, and providing extra adsorption for further enhancing N retention in the produced compound fertilizer.

In this study, with use of woody biochar as basal carrier and sepiolite and bentonite as mineral binder, is to test 2 hypothesis: (1) retention of N from urea could be enhanced through reaction and surface adsorption in the biochar-blended urea; and (2) N release could be reduced but supply for plant growth could be improved with application of the prepared compound urea. The study is aimed to provide insights if biochar blended urea could be used as an alternative for chemical urea to reduce N leaching loss but to enhance N nutrition to crops in agriculture.

2. Materials and methods

2.1. Materials

Biochar in this study was produced via pyrolysis of urban green waste collected from vegetation parks in Nanjing City. Being composed of dead branches, leaves, tree prunings and lawn cuttings, the collected green waste was crushed to chops in a diameter of <2 cm, air-dried and homogenized. Pyrolysis was performed in a rotary kiln under oxygen-limited environment under temperature in a range of 450–550 , with a residence time of 50 ± 10 min (Zhang, 2018). With such pyrolysis technology, each tonne of dry biomass yielded 246.3 kg of biochar on average. A portion of bulk biochar was ground to pass through a 20-mesh sieve and homogenized before use for blending fertilizer. The biochar was dark soft alkaline (pH in water of 10.1) solid material with a cation exchange capacity (CEC) of 7.4 cmol kg^{-1}. It contained organic carbon (OC) of 607.9 g kg^{-1}, total N of 12.2 g kg^{-1}, total P of 4.3 g kg^{-1} and total K of 15.6 g kg^{-1} with an ash content of 17.0%. The biochar particles had a filling density of 0.28 g cm^{-3}, a Brunauer-Emmet-Teller

(BET) surface area of 9.22 m^2 g^{-1} and micropore volume of 0.01 cm^3 g^{-1} (Fig. S1).

Clay minerals of bentonite and sepiolite were provided as commercial powder product (particle size <2 μm) by Shanghai Ryon Biological Technology CO., Ltd. Respectively of bentonite and sepiolite, the key properties were: pH (H$_2$O) of 10.1 and 9.3, CEC of 1.0 and 18.0 cmol kg^{-1}, bulk density of 2.65 and 1.75 g cm^{-3}. Purchased from Xilong Scientific CO., Ltd, the used chemical urea contained N of 46% and OC of 20%. All these materials were ground to pass through a 1.0 mm nylon sieve and homogenized before use.

Wood vinegar was provided by Nanjing Qinfeng Straw Biomass Technology Co Ltd. This material was a by-product of pyrolysis of maize residue in an oxygen-free rotatory kiln at temperature of 450 °C. Resulting from condensing the organic gas volatilized during pyrolysis, the solution was filtered to remove tar and particulate impurities and stored in sealed dark tank as the wood vinegar stock. The key properties of the wood vinegar used were: pH 4.1, electric conductivity of 8.7 ms cm^{-1}, and mineral nutrient of N, P and K respectively of 2.6 g L^{-1}, 36.8 mg L^{-1}, and 268 mg L^{-1}.

The soil used for experiment was collected from topsoil in a farm located in Xuji village (34°04′N, 116°93′E), Duji District, Huaibei Municipality, Anhui Province, China. The soil was air-dried, ground to pass through a 1 mm sieve and then homogenized. The soil had a pH (H$_2$O) of 8.0, an OC content of 11.35 g kg^{-1}, total N of 0.98 g kg^{-1}, and available P and K respectively of 14.6 and 120.3 mg kg^{-1}, as well as a bulk density of 1.37 g cm^{-3}.

2.2. Preparation of biochar-mineral urea composite

Preparation of biochar-mineral urea composite was basically following Liu (2016), using a mass ratio of mineral:biochar:urea being 9:5:10 but that of bentonite:biochar being 12:10. For this, portions of materials mentioned above, 10.0 g of urea, 5.0 g of biochar, 6.0 g of bentonite and 1.5 g of sepiolite were respectively weighed, mixed thoroughly and homogenized into a plastic dish. The mixture moisten with distilled water was agitated gently so as to form aggregate pellets. Add another 1.5 g of sepiolite to the dish and agitated again until all the added materials were completely mixed and stabilized as firm aggregated granules. A certain volume of wood vinegar diluted by 200 times (about a mass proportion of 10% to the formed granular material) was sprayed evenly onto the granules until they were moist. Subsequently, these resultant moist granules were dried in an oven at 60 °C for 3 h and stored as stock of biochar blended urea composite (Bio-MUC) for further test. As shown in Fig. S2, the obtained Bio-MUC material was black granules of 2–3 mm in diameter and of 14.06 N in hardness, containing OC of 20.0%, total N of 16.10%, total K of 0.36% and total P of 0.07% as well as Ca and Mg respectively of 1.5% and 2.8%.

2.3. Column experiment of N leaching

A column experiment (Fig. S3) was designed to test leaching of N from the Bio-MUC, using a plastic column of 5 cm in diameter and of 25 cm in height. The plastic column on the bottom was mounted with a 100-mesh nylon sheet, which had three small holes to allow drainage. In each column, 20 g acid washed quartz sand was spread evenly onto the bottom, onto which 150 g of test soil, described in Section 2.1, was packed to a height of about 10 cm in the column, prior to treatment.

Treatments for this test included soil without fertilizer as a control (CK), soil with urea fertilizer (UF) of 0.04 g per column and soil with Bio-MUC of 0.11 g per column (N rate same to UF). For treatment, the amount of test fertilizer was weighed and placed on the soil top in a column, to which another 100 g soil was evenly added and finally covered by another 20 g of the quartz sand. All the

treatments were performed in triplicates. Distilled water was added to the column to soil field capacity to allow soil stabilized for 1 day before leaching.

For leaching test, the column soil was irrigated with distilled water (100 ml each time) at a flow rate of 3.0 ml min^{-1} using a container controlled by a needle valve mounted on the column top (Fig.S3). A leaching was conducted on 1, 3, 5, 10, 15 and 30 days following fertilizer application and leachate was collected in a 250 ml glass bottle respectively following a leaching. All collected leachates were filtered through 0.45 um nylon filters and stored in an icebox in the dark at 4 °C prior to analysis. The leaching experiment was conducted at 25 ± 2 °C with a relative humidity of 65% in a greenhouse within the campus of the author's university.

2.4. Pot experiment for maize growth

For pot culture of maize, the test soil was sieved to pass a 20 mesh sieve and homogenized. The soil of 5.0 kg was weighed to a plastic pot of 28 cm in diameter and of 35 cm in height. Again, the treatment included a control (CK) soil without fertilizer application, soil with conventional urea (UF) at 1.00 g per pot and soil with biochar urea (Bio-MUC) at 2.85 g per pot. In all the fertilized pots, the amount of test fertilizers (0.46 g N each pot) was precisely weighed and thoroughly mixed with the soil before placing into the pot. In addition, 1.00 g of KH$_2$PO$_4$ was mixed to soil in each pot across treatments. Two seeds of maize cultivar Ludan 9088 were placed into 2 cm depth of soil in the pot. Seven days after germination, one plant remained in each pot and allow to grow for 50 days, from 2018-07-04 to 2018-08-024.

A treatment was performed in triplicates and all the pots were arranged in a randomized complete block design. During maize growth, all pots were moistened to field capacity (the maximum amount of water that the soil can hold), which was balanced with tap water, in 5 days interval over the 50 days growing course. Maize growing was maintained under 16 h of supplementary light per day but a daytime temperature in arrange of 20–30 °C during the whole growing period. The pot experiment was conducted also in a greenhouse within the university campus.

2.5. Material characterization

Characterization of biochar in terms of proximate analysis was done in accordance with the American Society for Testing and Materials (ASTM) D 1762–84 recommended for wood charcoal (Antal and Grønli, 2003). Biochar pH in water was measured following 1 h occasional stirring of biochar/water suspension (1:20, w/v). Biochar CEC of was measured with 1 M ammonium acetate

Table 1
X-ray photoelectron spectroscopy analysis of functional groups of Bio-MUC.

Peak name	Binding energy (eV)	Functional group	Relative proportion (at. %)
C1s A	284.75	C—C/C—H/C=C	19.7
C1s C	287.75	C=O	1.3
C1s D	286.52	C—O	6.0
C1s E	289.54	O=C—OH or O=C—N	4.8
N1s A	400.23	N—C=O	0.2
N1s B	398.37	NHC=O/NH$_2$—C	6.5
K2p3 A	293.79		0.3
Ca2s	439.37		1.1
Mg1s	1304.19		2.0
Na1s	1072.34		1.5
O1s	532.43		41.8
S2p	168.25		0.45
Si2p	103.14		10.9
Al2p	74.98		3.3

method (Sparks et al., 1996). Other rational chemical analysis were done following the procedure for soils.

The fourier transform infrared spectroscopy (FTIR) was employed to characterize the general organic composition both for biochar and the Bio-MUC. The materials were blended with KBr and pressed into a pellet. The absorbance spectra of these pellets were recorded between 4000 and 500 cm^{-1} using a Nicolet 6700 spectrophotometer (Thermo Scientific, USA) averaged of one hundred scans in a resolution of 4 cm^{-1}. In order to further distinguish the functional groups, a second derivative spectra analysis of the spectra was carried using the software of OMNIC (Rieppo et al., 2012).

X-ray photoelectron spectroscopy (XPS) was also carried out on the Bio-MUC granules. One selected particle of the Bio-MUC respectively before and after leaching for 30 days in the column experiment was examined using a scanning electron microscope (SEM – Hitachi SU8010), fitted with a Bruker energy dispersive X-ray spectrometer (EDS). The particles were mounted on an Al stub and coated with Au. To provide detailed crystallographic and micro-chemical analysis, both transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) was undertaken using JEOL ARM200F. The near-surface regions of the granule were analysed by electron energy loss spectroscopy (EELS) and an EDS.
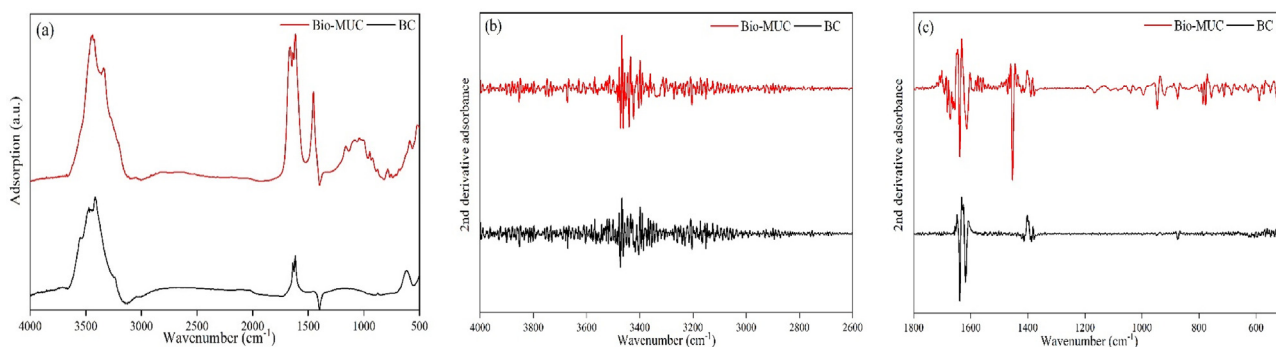

Fig. 1. FTIR spectra (a) and second derivative spectra (b, c) of the biochar and Bio-MUC.
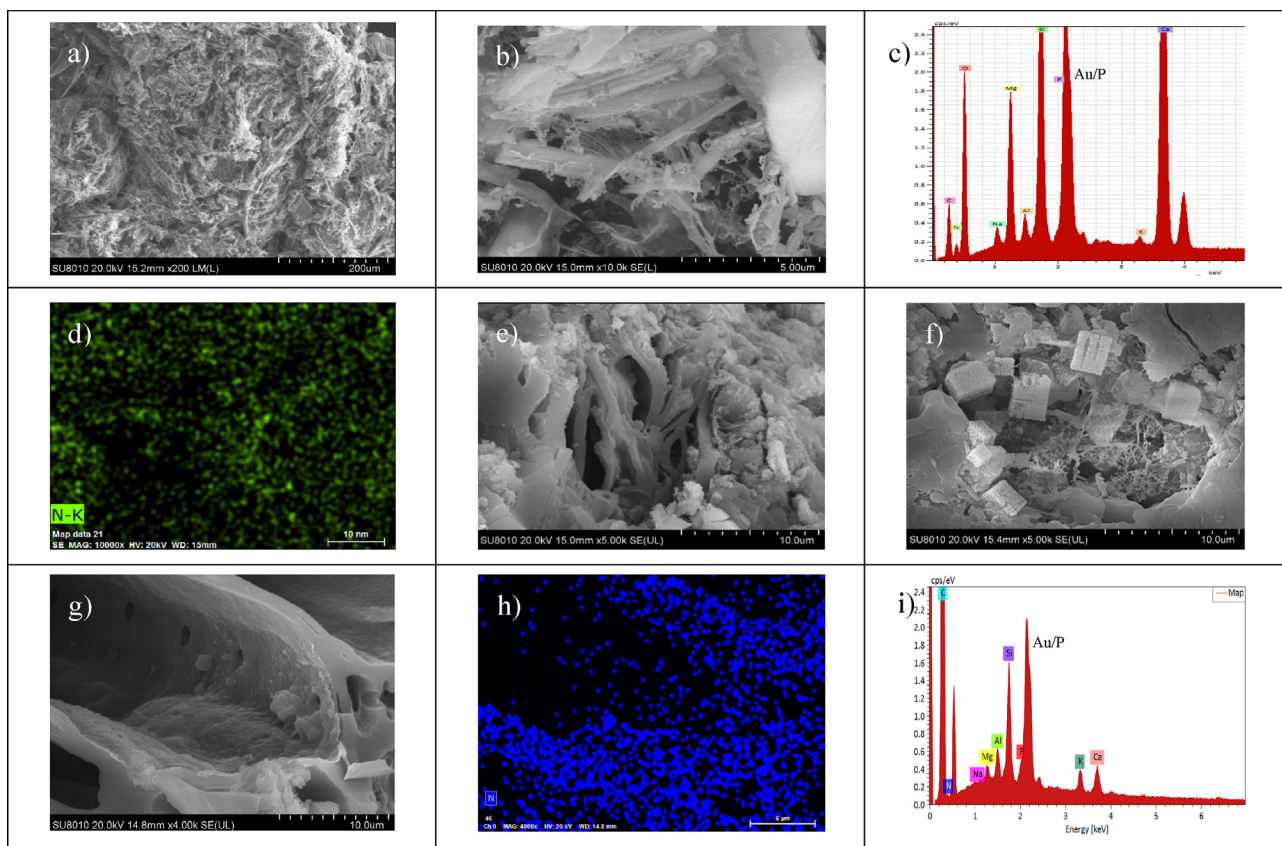

Fig. 2. SEM analysis of the Bio-MUC granule showing: a) secondary electron (SE) image of the surface of the granule. b) Detailed SE image showing sepiolite (thin crystallites) around a much coarser bentonite particle; c) EDS spectrum of a). The intense peak (Au/P) is predominantly due to the gold conductive coating; d) distribution of N throughout the mineral and the carbon phase. Internal structure of the Bio-MUC granule showing: e) secondary electron (SE) image of a fragment of biochar encased in minerals rich in N; f) SE image of cuboidal urea crystals surrounded by a range of minerals. Biochar fragments removed Bio-MUC following column leaching testing: g) Secondary electron (SE) image of a pore of biochar; h) N EDS map of g) and i) EDS spectrum of g).

2.6. Chemical analysis of minerals, soil, fertilizer and plant

Measurements of basic physico-chemical properties of clay minerals and soil, including pH, CEC and/or EC, and contents of OC, N, P, K and/or total ash, were all conducted following Lu (1999). For urea and Bio-MUC, however, contents of OC and total N were measured using methods recommended with Chinese fertilizer standard (GB/T 8572-2010) while those of P, K, Ca and Mg were measured using inductively coupled plasma mass spectrometry (ICP-MS). In addition, granule strength of Bio-MUC was measured using a granulometer (KQ-2, Particle strength tester, Nanjing Kehuan Analytical Instrument Co. Ltd, 2017).

Concentrations of NH_4^+-N and NO_3^--N in the leachates were measured respectively with ultraviolet spectrophotometry and visible spectrophotometry (Lu, 1999). Total OC and N of leachates were measured with a C/N elemental analyzer (Jena multi N/C 3100, Germany, 2010).

Plant analysis was done only for maize samples collected at the end of the experiment (Growing for 50 days). Leaf chlorophyll content was determined using SPAD 502 m (Minolta Corporation, Japan). The height and stem diameter of maize plant were measured by a tape and a Vernier caliper respectively. Plant fresh biomass were measured by weight at harvest and dry biomass determined after oven drying at 105 °C for 3 h and subsequently at 80 °C for 6 h. Washed root samples were analysed for root char-

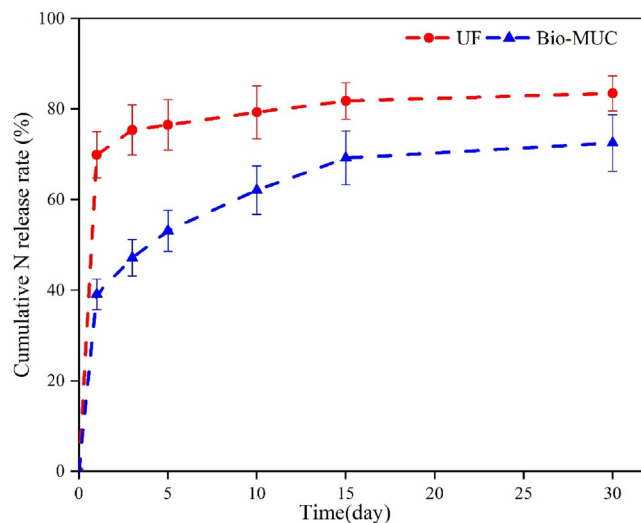**Fig. 4.** In-column leaching experimental data for cumulative N release rate of UF and Bio-MUC.

acteristics using WinRHIZO Pro. Roots were rinsed and scanned in a tray of distilled water using an Epson 1670 desktop scanner at 600 dpi. The WinRHIZO data were used to calculate root traits,
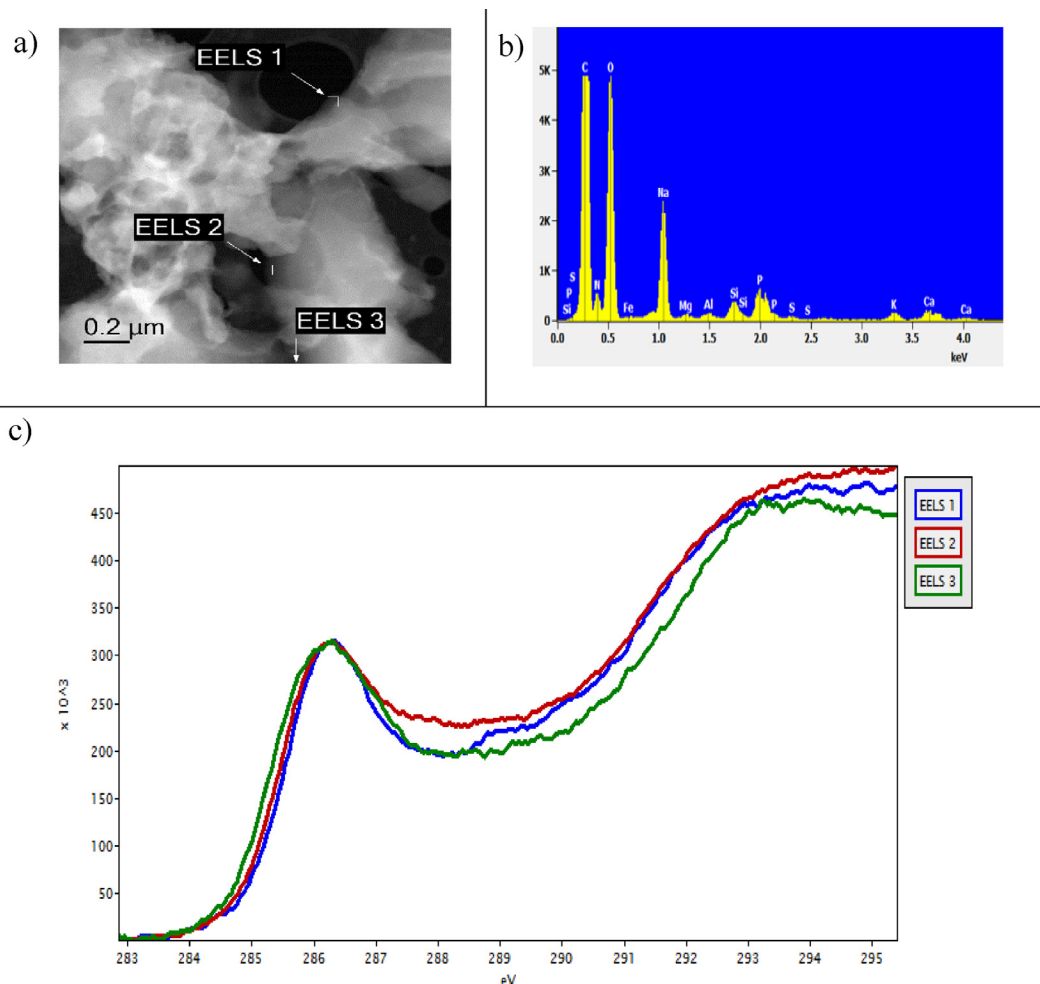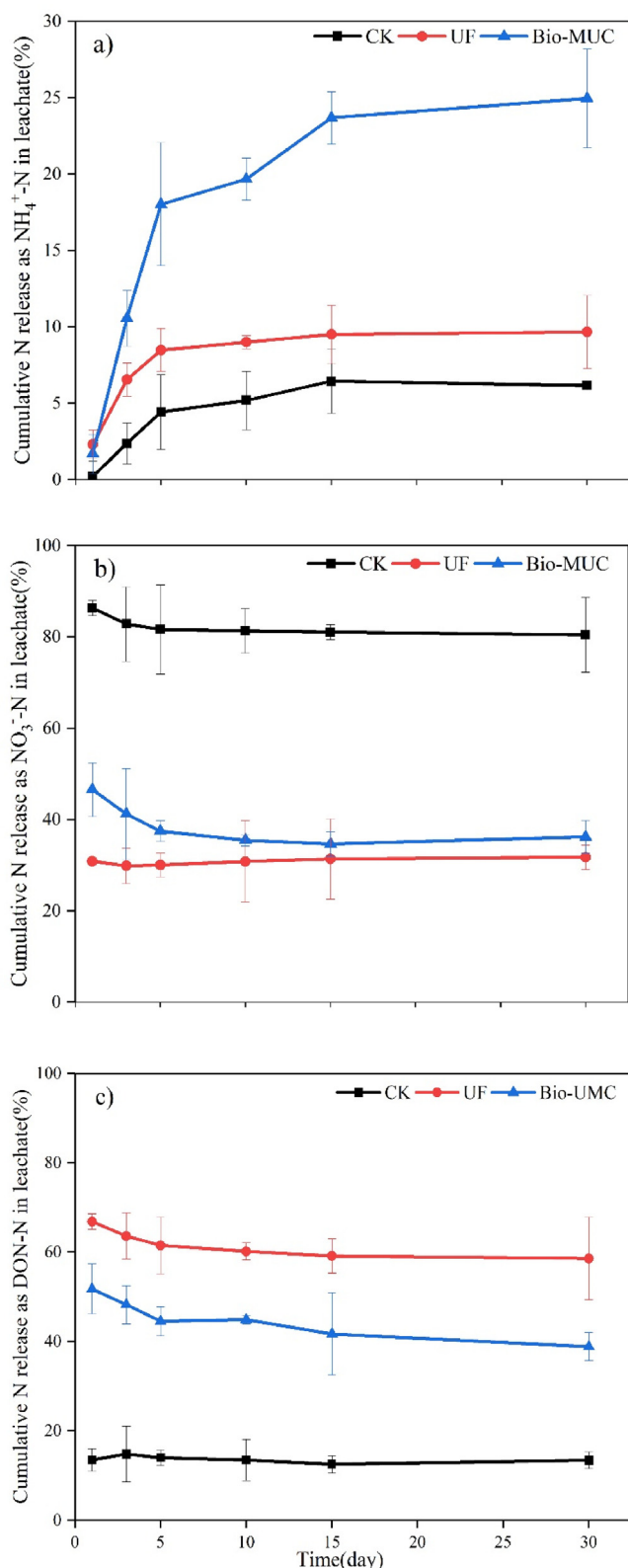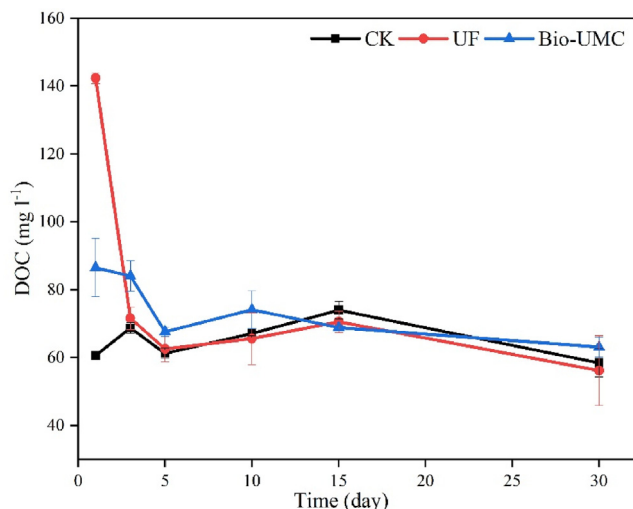

Fig. 3. a) A HAADF image; b) EDS spectrum of a); c) C K-edge EELS of the different areas of the biochar.

Fig. 6. Dissolved organic carbon (DOC) in leachates from leaching test of the control (CK), urea fertilizer (UF) and biochar-mineral urea composite (Bio-MUC) treated soils.

2.7. Data treatment and statistical analysis

Measurement data was expressed as mean and standard deviations of triplicated samples. All data was processed with Excel 2016 software. Statistical analysis was performed using the software SPSS 19.0 and Origin 9.0. The differences among the treatments were examined by one-way ANOVA, with a significance defined at $p < 0.05$.

3. Results and discussions

3.1. Structure of Bio-MUC

XPS results of the main functional groups and elements in the obtained Bio-MUC are given in Table 1. The main C functional groups in the Bio-MUC were aromatic and aliphatic (62%), followed by C—O bonds (19%, including phenolics, esters and alcohols) and carboxylic acids/ carboxamide (15%), but a much smaller proportion of ketones/ aldehydes (4%). The high peak of NHC=O/NH$_2$—C could indicate reaction of urea with some organic compounds in the biochar (Joseph et al., 2013). The high content of Si was from silicates in the clay minerals and, to minor extent, in the parent biochar (Liu et al., 2014).

The FTIR spectra of the samples are presented in Fig. 1. As compared to the parent biochar, the Bio-MUC spectrum showed an increase in intensity at both the higher and lower wavenumbers. At high-wavenumber region 4000–1800 cm^{-1} (Fig. 1a), Bio-MUC had greater intensity of peaks associated N—H and/or O—H (~3500 cm^{-1}) especially those at 3620 cm^{-1} associated with the stretching vibration of Al—OH and Mg—OH of bentonite and sepiolite. The second derivative of the spectra (Fig. 1b) highlighted the higher concentrations of non-bonded N—H stretching peaks at 3467 cm^{-1}–3399 cm^{-1} in the Bio-MUC (Joseph et al., 2013). The second derivative spectra of the Bio-MUC (Fig. 1c), showed a high intensity of carbonyl stretching (C=O) in the range of 1642–1652 cm^{-1} attributed to amide groups, which was clear in the results of XPS (Table 1). This suggested reaction of C=O detected in the biochar with the N—H$_2$ from urea in the formed composite. There was a displacement of the N—H$_2$ deformation (at 1468 cm^{-1}, 1409 cm^{-1}) in the biochar to 1476 cm^{-1} in the Bio-MUC, again indicating reactions between the urea and the biochar. The FTIR of Bio-MUC at 1100–1000 cm^{-1} presented C—O stretching of car-

Fig. 5. The cumulative N release measured from column leaching experiments for control (CK), urea fertilizer (UF) and biochar-mineral urea composite (Bio-MUC) as a function of leaching time. Plots are shown for: a) NH$_4^+$; b) NO$_3^-$; c) dissolved organic nitrogen (DON).

morphology (root diameter classes) and topology (which quantifies root branching patterns). Analysis of plant N, P and K was performed following the procedure described by Lu (1999).

bohydrate/polysaccharide. The peaks at 1030, 930, 880, 780, 690, 560 and 463 cm^{-1} could be attributed to Si—O and/or Al—O, Al—O—Si, Fe—O contributed by the minerals in the Bio-MUC (Rafiq et al., 2017).

Fig. 2a and Fig. 2b illustrate the heterogeneity of the surface of the composite granule and Fig. 2c is a spectrum derived from a region containing minerals, biochar particles and urea. The biochar particle surfaces were seen covered by the mineral and urea. The sepiolite particles (Fig. 2b) were thin elongated crystals whereas the bentonite had a much coarser blocky shape. The N distribution (Fig. 2d) was quite uniform over the surface of the minerals. Fig. 2e and 2f illustrate the complex structure inside the granule. In some areas, small fragments of biochar had reacted with the N and in others while intact urea crystals remained largely surrounded by various minerals.

In the samples carefully collected following leaching, pores of the biochar in the leached Bio-MUC (Fig. 2g) were seen coated with an organo-mineral layer (Fig. 2i) that comprised both alumina-silicates and possibly compounds of K, Ca, Mg and Na. This suggested interaction of soil with biochar following the loss of urea in the composite as this organo-mineral layer was not detected in the fresh biochar. There was a small but detectable quantity of N both in the biochar and in this organo-mineral layer, suggesting a possible trap of N in the coated surface after leached out from the urea.

Fig. 3a illustrate binding of the clay minerals with the porous biochar. The EDS spectrum (Fig. 3b) of this area could point to a detectable concentration of nitrogen in the carbon matrix despite phase analysis of an EDS map indicated a detectable content of N in the mineral phases. C K-edge EELS-1 and EELS-2 in Fig. 3c indicated that the carbon had a high concentration of C/O functional groups near the mineral phases. EELS-3 indicated a much weaker occurrence of C/O functional groups apart from the minerals.

3.2. Dynamics of N and organic carbon release from Bio-MUC

There was a significant difference in the rate of N release between UF and Bio-MUC treatments (Fig. 4). Under UF treatments, 70% of urea N was leached out in first day following water treatment, compared to only 39% under Bio-MUC. Compared to UF, N was released from Bio-MUC at a significantly ($p < 0.05$) lower rate over the whole 30 days, being able to preserve more N in the fertilized soil to supply plant N utilization over a longer time (Kim et al., 2014). This could be supported by SEM examination, which indicated a proportion of N still present in the biochar left in the soil at the end of 30 days leaching. These were similar to findings obtained with more elaborate and costly produced organic N materials (Li et al., 2016; Wen et al., 2017; Yang et al., 2018b). In this study, preparation of the Bio-MUC was relatively much simple, being easily practiced with conventional manufacturing facilities.

There was no significant difference in soil pH after leaching (Table S1) between UF and Bio-MUC treatments. Accordingly, there was no difference in N loss via volatilization loss between the treatments (Fig. S4). As shown in Fig. 5, N release of organic N

Table 2
Maize plant traits over 50 days growing under different treatments.

Treatment	Fresh shoot (g pot^{-1})	Fresh root (g pot^{-1})	Plant height (cm)	Leaf SPAD
CK	98.36 ± 2.01b	21.70 ± 8.10b	136.50 ± 0.53a	19.40 ± 2.01b
UF	98.61 ± 3.72b	23.46 ± 5.02b	140.38 ± 0.21a	23.83 ± 1.99a
Bio-MUC	112.30 ± 10.5a	29.35 ± 2.75a	141.17 ± 0.76a	24.17 ± 1.27a

Values as mean ± standard error of triplicated samples. Different letters in a single column indicated a significant difference between treatments at $p < 0.05$.

Table 3
Maize root traits over 50 days growing under different treatments.

Treatment	Length (cm)	Surface area (cm^2)	Average diameter (mm)	Total volume (cm^3)
CK	3618.25 ± 509.32b	163.44 ± 23.32b	2.05 ± 0.39 a	7.14 ± 0.93b
UF	3976.03 ± 365.18 ab	179.88 ± 15.70 ab	2.19 ± 0.20 a	7.23 ± 0.68b
Bio-MUC	4716.01 ± 409.12 a	212.94 ± 19.04 a	2.58 ± 0.35 a	9.96 ± 0.81 a

Values as mean ± standard error of triplicated samples. Different letters in a single column indicated a significant difference between treatments at $p < 0.05$.
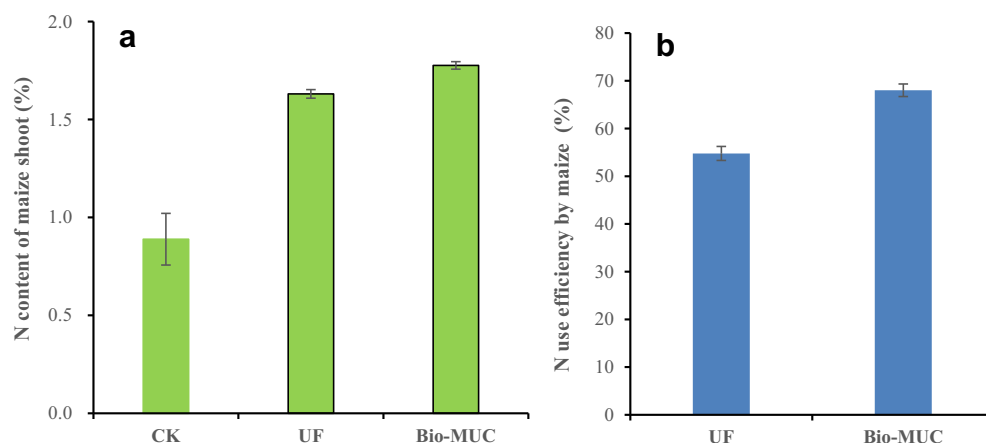
Fig. 7. Nitrogen content (a) and nitrogen use efficiency of (NUE) (b) by maize plants grown in control (CK), urea fertilizer (UF) and biochar-mineral urea composite (Bio-MUC) treated soils.

(DON) was 39–56% higher under UF than under Bio-MUC over the whole leaching course. This could suggest higher NH_4^+-N/NO_3^--N ratio and inorganic N/organic N ratio under Bio-MUC, being potentially more beneficial for plant N uptake and metabolism (Xu et al., 2012). Moreover, the proportion of NH_4^+-N to total dissolved N in the leachate varied across the leaching times (Fig. 5a). Under UF, this proportion was shortly increased over the first 5 days of leaching indicating a fast destruction of organic N bounds while this portion was kept increasing till 24% by 15 days following leaching experiment. This could be due to NH_4^+ adsorption onto or by functional groups such as —COO^- (—COOH), amino and —O^- (—OH) on the biochar surfaces (Yuan et al., 2011), compared to NH_4^+-N retention mainly due to hydrogen bonding and electrostatic interaction in soils (Cai et al., 2016).

The dynamics of DOC concentration in the leachate generally followed a negative exponential function with time (Fig. 6). DOC concentration peaked on day 1, being much higher under UF (142.34 mg L^{-1}) than under Bio-MUC (86.48 mg L^{-1}). Under UF treatment, DOC concentration sharply decreased to a stable level on day 3 following leaching. In contrast, DOC dynamics under Bio-MUC was more gently keeping a higher concentration until day 10 than under UF. This dynamic was more or less coincident with the total N release (Fig. 4), indicating a quick destruction of urea molecule to release both carbon and N shortly. However, the high content of organic carbon was mostly stable or recalcitrant (Lehmann and Joseph, 2015), microbial decomposition was weak and slow for biochar (Liu et al., 2016; Zhou et al., 2018). Again, some of labile organic carbon from both the biochar and urea could be bonded to the clay minerals (Yang et al. 2018a). Organic matter and mineral interaction revealed by SEM and STEM analysis could be significant in organo-mineral micro-aggregates in the Bio-MUC to protect OC from microbial attack (Pan et al., 2017) which was already recognized as a carbon stability (Yang et al., 2016) over the long run. However, there was no significant difference in soil organic carbon (SOC) content among the treatments though the addition of the fertilizers were so small.

3.3. Effect of Bio-MUC on maize growth

Compared to UF, Bio-MUC significantly ($p < 0.05$) improved maize growth (Tables 2 and 3) and increased N in the maize plant (Fig. 7). Fresh biomass of shoot and root was increased respectively by 13.8% and 25.1% under Bio-MUC than under UF though leaf activity and plant height unchanged. Meanwhile root volume was increased by 37.7% under Bio-MUC than under UF though other root traits not significantly affected (Table 3). Hereby N use efficiency was regarded as biomass production per unit of N fertilized and calculation using data from Fig. 7 suggested an increase in N use efficiency for biomass production was 24% higher under Bio-MUC than under UF. This could demonstrate a potential to improve N use efficiency with the biochar-mineral urea composite in dry croplands. This was addressed in a pot study by El Sharkawi et al. (2018) who reported a significant increase in N use efficiency by mustard spinach in sandy soil fertilized with a granular biochar-based fertilizer, compared to application of mineral fertilizer. This was possibly due to much enhanced root biomass and root volume to help plant uptake and translocate N to shoots. Biochar's role in improving root development had been recognized. And improved root growth could be a strategy to enhance resistance to environmental stress such as drought (Bruun et al., 2014).

4. Conclusion

This study demonstrated that biochar could be used to blend urea with proper mineral binder, which could enhance N retention through surface adsorption and organo/mineral interaction in the formed biochar-mineral-urea aggregated granules. Microscopic and spectroscopic analysis of the fresh and leached Bio-MUC showed that N from the urea could be bound strongly to the functionalized surfaces of the biochar carbon matrix. The biochar-mineral urea composite was shown capable of slow releasing and of preserving high ratio of ammonium to nitrate over a longer period, compared to chemical urea. Use of such Bio-MUC improved maize growth and nitrogen use efficiency for biomass production through increased N uptake and root development. Therefore, the biochar-mineral urea composite could be a solution to replace chemical urea so as to reduce chemical N loss in fertilized dry croplands. Of course, more field works deserve to elucidate how such fertilizer affect soil–plant and microbial interaction and therefore, modify soil and plant health in field conditions.

Declaration of competing interest

The authors declare no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.134424.

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