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Application of biochar-coated urea controlled loss of fertilizer nitrogen and increased nitrogen use efficiency

Yiman Jia¹, Zhengyi Hu^{1,2,3*} , Yuxin Ba⁴ and Wenfang Qi⁵

Abstract

Background: The use of biochar-based N fertilizers have been considered among the most effective strategy for reducing nitrogen loss and improving nitrogen use efficiency (NUE). However, effect and mechanism of biochar-coated urea (BCU) controlling the loss of nitrogen from soil and NUE are rarely reported.

Methodology: In this study, a 65-d culture pot experiment of oilseed rape was used to investigate the impact of BCU on nitrogen leaching, ammonia volatilization, soil nitrogen concentrations, soil pH, nitrogen uptake, NUE and oilseed rape biomass as compared with urea and urea combined with biochar at same nitrogen level.

Results: Results showed that the application of BCU could minimize nitrogen loss mainly by reducing nitrate leaching loss; which could be attributed to the slow-release performance of BCU, followed by biochar induced adsorption/fixation of nitrogen due to the porous nature and surface functional groups of biochar. However, the application of BCU enhanced ammonia volatilization due to the increase of soil NH_4^+ -N concentration and pH value of microenvironment around urea by BCU. The application of BCU increased NUE by about 20% when compared with urea, since BCU reduced losses of nitrogen fertilizer and increased concentration of nitrogen in the soil as well as nitrogen uptake in oilseed rape. Furthermore, the reduction of nitrogen application by 20% when BCU served as a nitrogen source not only reduced nitrogen loss but significantly improved NUE, with no negative effect on the biomass of oilseed rape.

Conclusion: BCU can serve as a promising control release nitrogen fertilizer for reducing loss of nitrogen and increasing NUE. However further investigations are required to validate the dosage-effect relationship of BCU on crop yield at the field scale.

Keywords: Biochar, Biochar-based fertilizer, Slow-release coated urea, Ammonia volatilization, Nitrogen leaching, Nitrogen use efficiency

Background

The large amount application of nitrogen fertilizer has made great contribution to satisfy the continuously increasing food demand in China. However, loss of nitrogen fertilizer from soils of farmland via runoff, leaching, and ammonia volatilization, etc. [1, 2] not only results in the low nitrogen use efficiency (NUE) and high

production cost, but also increases environmental risk, since large amounts of nitrogen from agricultural fields may deposit in neighbouring ecosystems and lead to acidification and eutrophication of natural ecosystems [3–6]. Application of nitrogen in China averages 305 kg N per ha compared to 74 kg N per ha worldwide, but nitrogen use efficiency is only 25% compared to 42% worldwide [7, 8]. Therefore, how to control the loss of nitrogen nutrient and further improve the NUE have become a major concern in agricultural production in China.

Biochar, the product of thermal degradation of biomass resources in the absence of air (pyrolysis), has

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several properties that make it an efficient material to reduce nitrogen loss and improve NUE [9–11]. Beck et al. observed that the NO_3^- -N and total nitrogen loss from soil through runoff was reduced by 97% and 87%, respectively, when applying 7% mixed material biochar (walnut shell, rice shell, coconut shell, etc.) into ryegrass trays [12]. The reduction of nitrogen loss and improvement of NUE could be attributed to the porosity, large specific surface area, surface charges, variety of surface functional groups and a small amount of active carbon present in biochar [13–15]. These properties of biochar could increase soil water holding capacity, adsorb inorganic nitrogen, influence nitrification and denitrification of nitrogen in soil, increase microbial biomass, and change soil structure of bacterial community [16–19].

The application of biochar can be either direct into soil or in the form of biochar-based fertilizer. Direct application is the simplest and most convenient way [20, 21]. However, the storage, transportation and soil application of biochar are challenging because biochar is brittle, or has wide particle size distribution and low density [22]. Furthermore, a single amount of biochar for soil amendment at high rates of 20–50 t ha⁻¹, makes the economic feasibility for farmers questionable [23]. Biochar-based fertilizers are prepared by mixing biochar with inorganic fertilizer using physical or chemical methods (biochar-mixed fertilizer) [24–26] or coating biochar with binder outside inorganic fertilizer particles (biochar-coated fertilizer) [27–29]. Shi et al. prepared a granular biochar-mineral urea composite (Bio-MUC) by blending urea with green waste biochar supplemented with clay minerals of bentonite and sepiolite and observed that cumulative N release as NH_4^+ -N was significantly smaller by >70% from Bio-MUC than from urea in the leaching experiment over 30 days [25]. Wang et al. observed that nitrogen loss, ammonia volatilization and leaching nitrogen was 43.5%–45.5%, 3.7%–21.7% and 49.8%–52.1% lower respectively after application of BCU than urea at nitrogen application rates of 320 and 280 mg N/kg soil in pot experiment [29]. Our previous studies have successfully developed a series of BCU with satisfactory nitrogen slow release performance [15]. However, effects of biochar-coated urea on loss of nitrogen fertilizer and nitrogen use efficiency need to be validated.

The present objectives were to (1) investigate the characteristics of nitrogen fertilizer loss in soil applying BCU and NUE under vegetable-growing condition; (2) compare effects of nitrogen loss and NUE between BCU and urea; (3) compare effects of nitrogen loss and NUE between BCU and BCU combined with biochar. It is anticipated that the present work will provide a measure for controlling agricultural non-point source

pollution and introduce a new option for the high-value utilization of biochar prepared by pyrolysis of biomass resources.

Materials and methods

Materials

Biochar used for BCU was prepared based on pyrolysis of vinasse in a fixed-bed heating furnace. The pyrolysis temperature was 600 °C and the pyrolysis time was 90 min. The pH, specific surface area, ash content, C content, H content, N content, O content, O/C molar ratio, and H/C molar ratio of biochar were 8.88, 172.48 g/m², 29.89%, 61.32%, 1.62%, 2.79%, 1.66%, 0.02, 0.32, respectively. The microstructure, surface functional groups and carbon structures of biochar are presented in Additional file 1: Figs. S1–S3, respectively. BCU was manufactured by coating biochar outside urea with a coating machine [15, 30] (Fig. 1); First, urea was added to a coating machine which was already in operation at a speed of 80 rpm; Then, biochar and oxidized starch were sprayed into the machine in batches to coat biochar on the urea particles; Finally, resin and paraffin were coated outside the biochar layer by a spiral oscillator and a high-pressure spray gun, respectively. The percent of biochar in BCU was 22.56%. The nitrogen content of BCU was 33.67%. The carbon content of BCU was 31.53%. The nitrogen release properties of BCU were presented in our previous study [15].

The soil for the pot experiment was red soil containing 2.1% organic matter, 56.73 mg kg⁻¹ total nitrogen, 3.54 mg kg⁻¹ available phosphorous, 3.54 mg kg⁻¹ available potassium and a pH of 5.94. Calcium superphosphate ($\text{CaP}_2\text{H}_4\text{O}_8$) was used as phosphate fertilizer and potassium sulfate (K_2SO_4) as potash fertilizer.

Pot experiment design

In this study, a pot experiment was conducted with eight treatments composed of two sources of nitrogen fertilizer, two rates of nitrogen fertilization and biochar (Table 1). In detail, No fertilizer (CK), urea at 100% N rate (U1), urea at 80% N rate (U2), biochar combined with urea at 100% N rate (U1 + B), biochar combined with urea at 80% N rate (U2 + B), biochar-coated urea at 100% N rate (BCU1), biochar-coated urea at 80% N rate (BCU2), and biochar combined with biochar-coated urea at 100% N rate (BCU1 + B). Specifically, the amount of biochar added to the soil in the treatment of U1 + B and U2 + B was calculated according to the economic index cost of biochar and urea equivalent applied to the soil in the treatment of U1 + B and U2 + B were equivalent to that of BCU1 and BCU2 at the same N dose. The total amount of biochar added by BCU1 + B was the same as U1 + B. All these treatments were applied with 160 mg/kg P (366.4 mg/kg P_2O_5) and

62 mg/kg K (74.4 mg/kg K₂O). Each treatment was performed in triplicate.

The plastic pots were 20 cm in diameter and 14 cm in height, which were loaded from bottom to top with 100 mesh gauze, 1.5 cm of gravel (to cover the drain hole), 8.5 cm of soil (1500 g soil), and 3 cm of soil mixed with nitrogen, biochar, phosphate and potassium fertilizers (500 g soil), respectively. A plastic tray was placed at the bottom of each pot for collecting the leaching water. Ten four-day-old rapeseed seedlings (*B. campestris* L.) were transplanted to each plastic pot, and keeping five seedlings per pot on the 24th day of transplanting. Quantitative irrigation was carried out during the experiment using purified water for 500 ml each time. The positions of plastic pots were changed successively every day to reduce the error brought by position differences. The pot experiment lasted for 65 d.

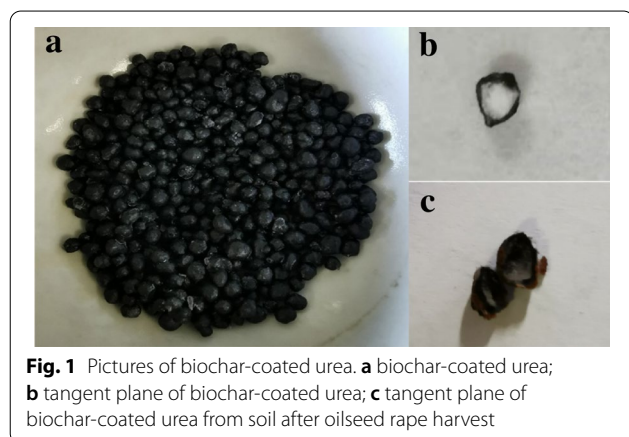


Fig. 1 Pictures of biochar-coated urea. **a** biochar-coated urea; **b** tangent plane of biochar-coated urea; **c** tangent plane of biochar-coated urea from soil after oilseed rape harvest

Sample collection and analysis

Volatilized ammonia was collected by closed chamber absorption method [29]. The schematic plot of ammonia volatilization collection was shown in Additional file 1: Fig. S4. Volatilized ammonia was absorbed by dilute sulfuric acid (0.01 mol/L) from the first day after fertilization and once a day for a total of 8 h each time. The ammonia volatilization every day was calculated by multiply the measured ammonia volatilization by three. The collection was stopped when the amount of ammonia volatilization under nitrogen fertilization treatments were similar to that under CK treatment for several consecutive days. The ammonium nitrogen of the absorption solutions was determined with the sodium salicylic hypochlorite spectrophotometry method (HJ 536-2009).

Watering for seven times was carried out during the whole pot experiment. The water flowing into the plastic tray was collected as leaching solution on the day of watering for analysis of TN, NH₄⁺-N and NO₃⁻-N. The volume of the leaching solutions was measured with a measuring cylinder.

At the end of the experiment, all the harvested oilseed rape plants were washed and dried in an oven at 105 °C for 30 min, and then dried at 80 °C to constant weight for estimation of the plant biomass. The dried plants were then ground for nitrogen analysis. The soil in each pot was thoroughly mixed, and part of the soil was taken for the determination of soil pH, TN, NH₄⁺-N and NO₃⁻-N.

The total nitrogen in solutions collected was determined with the alkaline potassium persulfate digestion-ultraviolet spectrophotometric method (HJ 636-2012); The total nitrogen in plant and soil was determined with 5E-CHN2000 elemental analyzer (Changsha kaiyuan

Table 1 Rates of applied nitrogen fertilizer as urea or biochar-coated urea and biochar or biochar in biochar-coated urea in soils

Treatment	Nitrogen application rate (mg/kg)	Equal amount of nitrogen used in field (kg/ha)	Percent of biochar applied in soil (%)	Amount of urea applied in soil (g/pot)	Amount of biochar applied in soil (g/pot)	Amount of BCU applied in soil (g/pot)
CK	–	–	–	–	–	–
U1	200	450	–	0.881	–	–
U2	160	360	–	0.705	–	–
U1 + B	200	450	0.5	0.881	10	–
U2 + B	160	360	0.5	0.705	10	–
BCU1	200	450	0.013	–	0.261	1.188
BCU2	160	360	0.010	–	0.209	0.950
BCU1 + B	200	450	0.5	–	10	1.188

CK, no fertilizer; U1, urea at 100% N rate; U2, urea at 80% N rate; U1 + B, biochar combined with urea at 100% N rate; U2 + B, biochar combined with urea at 80% N rate; BCU1, biochar-coated urea at 100% N rate; BCU2, biochar-coated urea at 80% N rate; BCU1 + B, biochar combined with biochar-coated urea at 100% N rate

Amount of biochar applied in soil for BCU1 + B treatment included 0.261 g/pot of biochar from coating material in biochar-coated urea and 9.739 g/pot of biochar powder

instruments Co., Ltd., China); NH_4^+-N in solutions was determined with the sodium salicylic hypochlorite spectrophotometry method (HJ 536-2009); and NO_3^--N in solutions was determined with the dual-wavelength ultraviolet spectrophotometric method (HJ/T 346-2007).

Data treatment and statistical analysis

The nitrogen absorption amount of oilseed rape was calculated with Eq. (1):

$$M_{NR} = C_{NR} \times M_R \tag{1}$$

where M_{NR} is the nitrogen absorption amounts (mg/pot) of oilseed rape; C_{NR} is nitrogen concentration of oilseed rape (%); M_R is the oilseed rape biomass (mg/pot).

The NUE was calculated with Eq. (2):

$$E_N = 100 \times (M_{NRF} - M_{NRC})/M_N \tag{2}$$

where E_N is the NUE (%); M_{NRF} is the nitrogen absorption amount (mg/pot) of oilseed rape with fertilized treatments (mg/pot); M_{NRC} is the nitrogen absorption amount (mg/pot) of oilseed rape with CK treatments (mg/pot); M_N is the amount of nitrogen application (mg/pot).

Graphical analysis was carried out using OriginPro 9.0 (OriginLab Corporation, Northampton, MA, USA). Statistical analyses (two-way ANOVA) were performed using SPSS Version 19.0 software (SPSS Inc., Chicago, USA). The least significant difference (LSD) was used to test for significance at $p < 0.05$ between the means.

Results

Effect of BCU application on ammonia volatilization

Ammonia volatilization was observed in all treated soils from the first day of the pot experiment (Fig. 2a).

Ammonia volatilization from CK continued until the 7th day of the experiment; from soils fed with urea until the 23th–25th day of the experiment (from U2 and U2 + B until the 25th day; from soils fed with U1 and U1 + B until the 23th day, and the 24th day, respectively); from soils fed with biochar-coated urea (BCU1,BCU2, BCU1 + B) until at least the 26th day of the experiment (Fig. 2a). The five obvious peaks of ammonia volatilization were observed from soils fed with biochar-coated urea (BCU1, BCU2, BCU1 + B) at the 5th day and 7th day, 9th day, 13th day, and 15th day of the experiment compared to only two peaks from soils fed with urea at the 5th day and 7th day of the experiment (U1, U2, U1 + B, U2 + B) (Fig. 1a). The highest peak of ammonia volatilization in U1 and U2 treatments appeared on the 5th day of experiment; in U1 + B and U2 + B treatments on the 5th day and the 7th day of experiment, respectively; in BCU1, BCU2, and BCU1 + B treatments on the 5th day, the 7th day and the 15th day of experiment, respectively (Fig. 1a). The highest peak values of ammonia volatilization followed the decreasing order as bellow: BCU1 > U1 > U1 + B; U2, BCU2 > U2 + B; BCU1 + B > U1 + B; U1 > U2 (Fig. 2a).

The cumulative ammonia volatilization followed the decreasing order as bellow: BCU2 > U2 > U2 + B; BCU1 > U1 > U1 + B; BCU1 + B > U1 + B. The highest cumulative ammonia volatilization (7.21–8.98 mg/kg) among treatments were observed from soils fed with biochar-coated urea, the lowest cumulative ammonia volatilization (3.39–3.91 mg/kg) among treatments were observed from soils fed with biochar combined with urea (Fig. 1b). Reduction rate of nitrogen fertilization as BCU by 20% (BCU2) was observed to reduce the cumulative ammonia volatilization by 24.42%.

Table 2 Cumulative leaching loss of NO_3^--N , NH_4^+-N and inorganic N in different fertilized soils during experiment for 65 days (mg/kg)

Treatments	NH_4^+-N	NO_3^--N	total nitrogen
CK	0.38 ± 0.04e	7.93 ± 0.98d	6.34 ± 2.19f
U1	4.47 ± 0.63a	60.62 ± 0.61a	78.03 ± 7.50a
U2	3.95 ± 0.55ab	55.31 ± 5.11ab	67.65 ± 1.23b
U1 + B	4.08 ± 0.21ab	57.11 ± 5.21a	74.95 ± 6.15ab
U2 + B	3.62 ± 0.03b	45.68 ± 7.28c	57.78 ± 6.10c
BCU1	2.74 ± 0.35c	48.61 ± 4.58bc	49.81 ± 2.33 cd
BCU2	2.10 ± 0.29d	41.67 ± 5.36c	42.94 ± 4.89de
BCU1 + B	1.68 ± 0.04d	40.44 ± 2.89c	41.35 ± 2.59e

CK, no fertilizer; U1, urea at 100% N rate; U2, urea at 80% N rate; U1 + B, biochar combined with urea at 100% N rate; U2 + B, biochar combined with urea at 80% N rate; BCU1, biochar-coated urea at 100% N rate; BCU2, biochar-coated urea at 80% N rate; BCU1 + B, biochar combined with biochar-coated urea at 100% N rate

Different letters in the same column indicate a significant difference at the 5% level according to the LSD test

Effect of BCU application on leaching loss of nitrogen in soil

Leaching loss of NH_4^+-N , NO_3^--N and total nitrogen were observed in all treatments during experiment, which gradually increased, and reached a maximum, and then gradually decreased (Fig. 2). The cumulative leaching loss of NH_4^+-N , NO_3^--N and total nitrogen in CK were significantly lower than other fertilization treatments during the whole pot experiment (Fig. 3, Table 2).

The greatest peak of leaching loss of NH_4^+-N from CK appeared on the 25th day of experiment (the third watering event), the greatest peak of leaching loss of NH_4^+-N from soil fed with urea (U1, U1 + B, U2 + B) on the 17th day of experiment (the 2nd watering event) excepting for U2, the greatest peak of leaching loss of NH_4^+-N from soil fed with biochar-coated urea (BCU1, BCU1 + B, BCU1 + B) on the 25th day of experiment (the third watering event) (Fig. 3a).

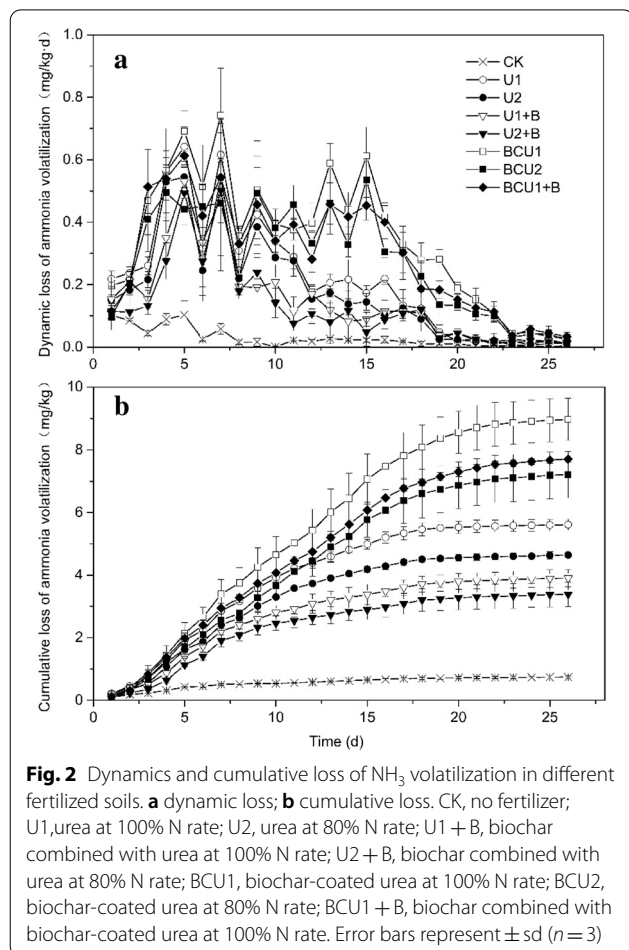
The cumulative loss of $\text{NH}_4^+\text{-N}$ was lower from soils fed with biochar-coated urea (BCU1, BCU1 + B, BCU1 + B) than from soils fed with urea (U1, U2, U1 + B, U2 + B) irrespective of N levels. Under the same level of nitrogen fertilization, the cumulative leaching loss of $\text{NH}_4^+\text{-N}$ in soils fed with BCU (BCU1, BCU2) were 38.67%–46.95% lower than that in soils fed with urea (U1, U2), which were 32.74%–42.22% lower than that in soils fed with urea mixed biochar (U1 + B, U2 + B). The cumulative loss of $\text{NH}_4^+\text{-N}$ was 11.17–23.68% lower from soils fed with low N level than from soils fed with high N level. The cumulative loss of $\text{NH}_4^+\text{-N}$ was 58.85% lower from soil fed with BCU1 + B than from soil fed with U1 + B (Fig. 3a, Table 2).

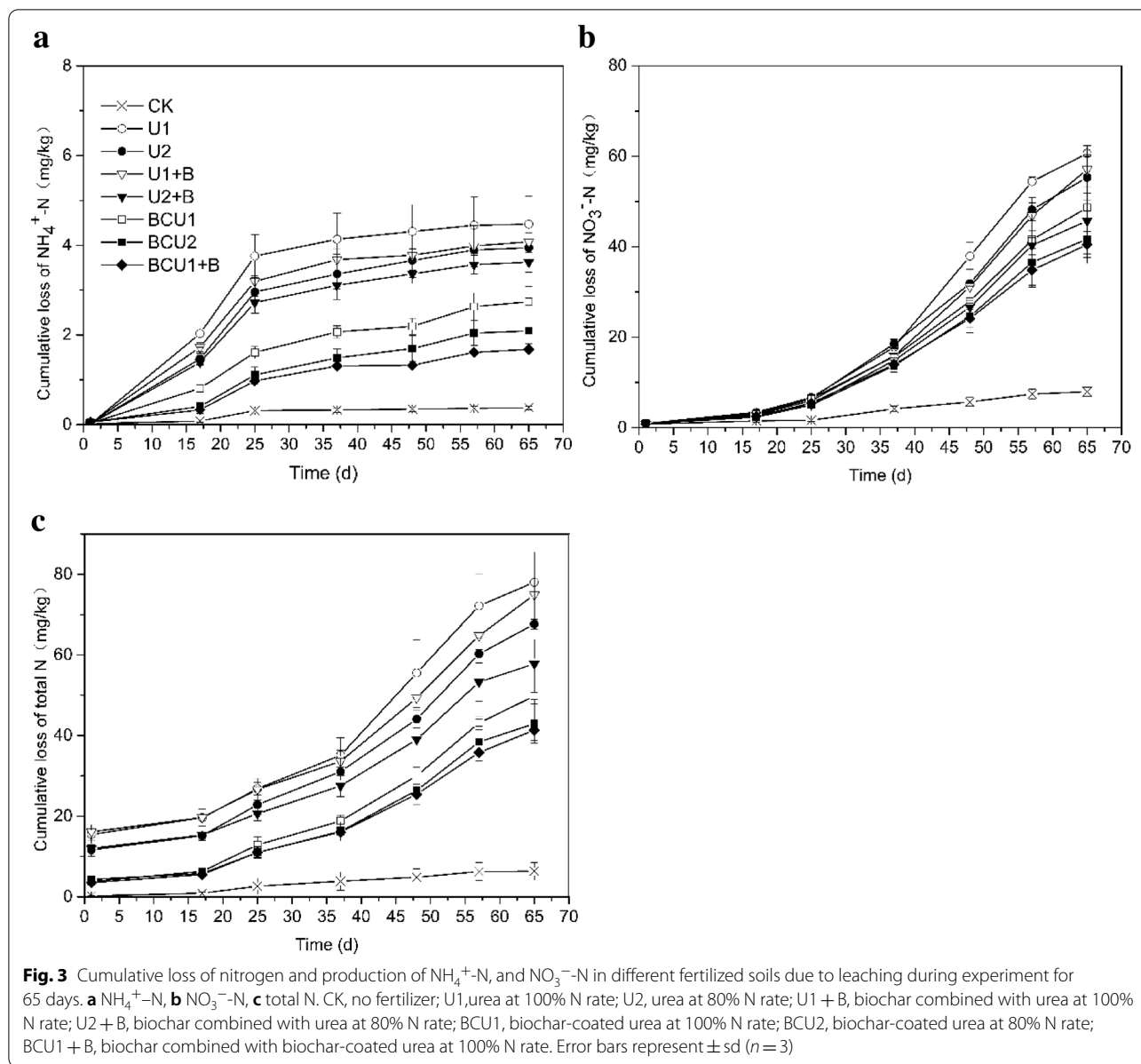
The greatest peak of leaching loss of $\text{NO}_3^-\text{-N}$ from all treatments appeared on the 57th day of experiment (the 6th watering event) except for U1 treatment (Fig. 3b). The leaching loss of $\text{NO}_3^-\text{-N}$ mainly occurred after 25 days of experiment (the third watering event), which accounted for more than 90% of the cumulative

leaching loss of $\text{NO}_3^-\text{-N}$ during the whole experiment (Fig. 3b). Under the same level of nitrogen fertilizer, the cumulative leaching loss of $\text{NO}_3^-\text{-N}$ in soils fed with BCU (BCU1, BCU2) were significantly lower than that in soils fed with urea (U1, U2) (Table 2). Under the same level of nitrogen fertilizer, the cumulative leaching loss of $\text{NO}_3^-\text{-N}$ was 19.8% and 24.7% lower from soils fed with BCU1 and BCU2 than from soils fed with U1 and U2, respectively (Table 2); which was lower from soil fed with urea combined with biochar (U1 + B, U2 + B) than from soils fed with urea (U1, U2). The cumulative leaching loss of $\text{NO}_3^-\text{-N}$ from soils was lower with U1 + B treatment than with U1 treatment, but the difference was not significant ($p < 0.05$); which was lower with BCU1 + B treatment than with U1 + B treatment, with significant difference ($p < 0.05$) (Table 2).

The leaching trend of total nitrogen from soils was similar to $\text{NO}_3^-\text{-N}$, and $\text{NO}_3^-\text{-N}$ leaching loss was the main form of nitrogen leaching loss, accounting for 76–98% of total nitrogen leaching loss in fertilization treatments (Fig. 3, Table 2). However, the first leaching loss of total nitrogen from soils fed with urea (U1, U2, U1 + B, U2 + B) was much higher than that of $\text{NO}_3^-\text{-N}$ at the same level of nitrogen fertilization (Fig. 3c). The cumulative leaching loss of total nitrogen was 15.33% higher from soils fed with U1 than from soil fed with U2, which was 29.72% higher with U1 + B treatment than U2 + B treatment (Table 2). The cumulative leaching loss of total nitrogen followed the decrease order as below: U1 > U1 + B > BCU1, U2 > U2 + B > BCU2, and U1 + B > BCU1 + B (Table 2). In detail, the cumulative leaching loss of total nitrogen was 36.17% lower in BCU1 than in U1, and 33.55% lower in BCU1 than in U1 + B, it was also 36.5% lower in BCU2 than in U2; and 25.7% lower in BCU2 than in U2 + B (Table 2).

Obvious difference of cumulative loss of nitrogen fertilizer during experiment for 65 days was determined in dependence on the level of nitrogen fertilization, sources of nitrogen fertilizer, and application of biochar. Amount of cumulative nitrogen loss of nitrogen fertilizer followed the decreasing order as below: U1 > U1 + B > BCU1, U2 > U2 + B > BCU2; the percentage of cumulative loss of nitrogen fertilizer in nitrogen application followed the decreasing order as below irrespective of the level of nitrogen fertilization: urea (U1, U2) > biochar combined with urea (U1 + B, U2 + B) > biochar-coated urea (BCU1, BCU2); U1 + B > BCU1 + B (Table 3). Implying that both application of biochar-coated urea and biochar combined with urea could significantly reduce the loss of nitrogen fertilizer. However, the optimal measure of controlling nitrogen loss was biochar combined with biochar coated urea.





Effect of BCU application on soil pH and soil nitrogen concentrations

The pH of soils collected after harvesting oilseed rape ranged from 5.89 to 6.27, (Table 4). The greatest soil pH among treatments was observed in BCU1 + B treatment. The soil pH was greater in CK than in urea treatments (U1, U2) and in biochar-coated urea treatments (BCU1, BCU2). No obvious difference was found between CK and U1 + B or U2 + B soil pH. However, in BCU1 + B treatment pH was higher than CK (Table 4). Furthermore, the soil pH followed the decreasing order as below irrespective of nitrogen fertilization level: biochar combined with urea (U1 + B, U2 + B) > biochar-coated urea (BCU1, BCU2) > urea (U1, U2) (Table 4).

The concentrations of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and total nitrogen in soils fertilized with nitrogen were significantly higher than that in CK, which was higher in soil applied with high nitrogen levels than in soil applied with low nitrogen (Table 4). The greatest concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in soils among treatments was observed in BCU1 + B treatment; The greatest concentrations of total nitrogen in soils among treatments was observed in U1 + B treatment, followed by BCU1 + B treatment (Table 4). Furthermore, concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in soils followed the decreasing order: U1 + B, BCU1 > U1; U2 + B, BCU2 > U2. However, concentrations of total nitrogen in soils followed the decreasing

order as bellow: U1 + B > BCU1, U1; U2 + B > BCU2, U2 (Table 4).

Effect of BCU application on nitrogen uptake and nitrogen use efficiency

The nitrogen concentration and nitrogen uptake of oilseed rape in CK was lowest among all treatments (Table 5). The nitrogen concentration and nitrogen uptake of oilseed rape grown in soils fertilized with nitrogen were significantly higher than that in CK (Table 5). The concentration of nitrogen in oilseed rape followed the decreasing order as bellow: biochar-coated urea (BCU1, BCU2) > biochar combined with urea (U1 + B, U2 + B) > urea (U1, U2); no obvious difference between BCU1 + B and U1 + B. The uptake of nitrogen in oilseed rape under the same level of nitrogen fertilization followed the decreasing order as bellow: biochar-coated urea (BCU1, BCU2) > biochar combined with urea (U1 + B, U2 + B) > urea (U1, U2); BCU1 + B > U1 + B (Table 5).

The NUE followed the decreasing order as bellow irrespective of nitrogen fertilization level: biochar-coated urea (BCU1, BCU2) > biochar combined with urea (U1 + B, U2 + B) > urea (U1, U2); BCU1 + B > U1 + B (Table 5). Thus, it could be seen that application of biochar-coated urea could significantly increase NUE compared to urea application.

Effect of BCU application on oilseed rape growth

Biomass of oilseed rape was higher with high nitrogen fertilization level than low nitrogen level (Table 5). Furthermore, biomass of oilseed rape tended to follow the decreasing order as bellow: biochar-coated

urea (BCU1, BCU2) > biochar combined with urea (U1 + B, U2 + B) > urea (U1, U2), under high nitrogen fertilization level; biochar-coated urea (BCU1, BCU2) > biochar combined with urea (U1 + B, U2 + B), urea (U1, U2), under low nitrogen fertilization level; BCU1 + B > U1 + B (Table 5); but these differences were not significant ($p < 0.05$). Moreover, biomass of oilseed rape was higher in BCU1 treatment than U1 treatment (Table 5), implying that a 20% reduction in nitrogen application would not reduce biomass if urea was replaced with biochar-coated urea. Biomass of oilseed rape was significantly lower in U2 + B treatment than in U1 treatment (Table 5). It could be seen that a 20% reduction in nitrogen application would reduce biomass even if urea was combined with biochar.

Discussion

Effects and mechanisms of BCU application on controlling loss of nitrogen

The leaching, volatilization as NH₃-N and nitrous oxide, and runoff are main pathways of nitrogen loss in soil fertilized with nitrogen [31]. The leaching loss of total nitrogen, NH₄⁺-N and NO₃⁻-N, and volatilization loss as NH₃-N were considered in the present culture experiment, because nitrous oxide produced by denitrification was reported to account for only a small proportion of nitrogen fertilization (about 1%) [32], and no runoff during the present culture experiment. The results of the present experiment demonstrated that total loss of nitrogen via leaching, and NH₃-N volatilization accounted for 20.99–40.76% of nitrogen fertilization (Table 3). The total loss of nitrogen via leaching accounted for 72.42–83.07%, 3.42–5.92%, and 4.95–15.71% distributed in NO₃⁻-N,

Table 3 Cumulative loss of fertilizer nitrogen in soil and percentage of cumulative loss of fertilizer nitrogen in nitrogen application after the 65 d experiment

Fertilization treatments	Amount of N fertilization (mg/kg)	Leaching loss of fertilizer-N (mg/kg)			NH ₃ volatilization of fertilizer-N (mg/kg)	Total loss of fertilizer-N (mg/kg)	Percentage (%)
		Total N	NH ₄ ⁺ -N	NO ₃ ⁻ -N			
U1	200	71.69	4.10	52.69	4.87	76.56	38.28
U2	160	61.31	3.57	47.39	3.91	65.22	40.76
U1 + B	200	68.61	3.70	49.18	3.17	71.78	35.89
U2 + B	160	51.44	3.25	37.76	2.65	54.08	33.80
BCU1	200	43.47	2.37	40.68	8.24	51.70	25.85
BCU2	160	36.60	1.7	33.74	6.47	43.08	26.92
BCU1 + B	200	35.01	1.30	32.52	6.97	41.98	20.99

Amount of N fertilization: only nitrogen as application of urea or biochar-coated urea is considered due to very little nitrogen in biochar

Loss of N fertilizer = Fertilization treatment - CK

Total loss of fertilizer-N = Leaching loss of total N + NH₃ volatilization loss

% - Percentage of loss of fertilizer nitrogen in nitrogen application

U1, urea at 100% N rate; U2, urea at 80% N rate; U1 + B, biochar combined with urea at 100% N rate; U2 + B, biochar combined with urea at 80% N rate; BCU1, biochar-coated urea at 100% N rate; BCU2, biochar-coated urea at 80% N rate; BCU1 + B, biochar combined with biochar-coated urea at 100% N rate

Table 4 Concentration of nitrogen (mg/kg) and pH in different fertilized soils collected after harvesting oil rapeseed

Treatments	pH	NH ₄ ⁺ -N (mg/kg)	NO ₃ ⁻ -N (mg/kg)	Total nitrogen (mg/kg)
CK	6.17 ± 0.20ab	7.34 ± 1.07e	22.09 ± 0.848c	254.06 ± 9.38d
U1	5.95 ± 0.10bc	14.42 ± 1.75bcd	58.99 ± 3.22a	294.42 ± 16.81d
U2	5.89 ± 0.04c	11.72 ± 1.57d	40.46 ± 4.15b	277.01 ± 26.99d
U1 + B	6.19 ± 0.13ab	17.45 ± 3.47ab	62.29 ± 4.13a	485.61 ± 72.93a
U2 + B	6.18 ± 0.15ab	12.48 ± 2.11 cd	44.12 ± 7.11b	384.18 ± 77.35bc
BCU1	6.10 ± 0.10abc	15.68 ± 2.41abc	63.41 ± 3.44a	321.87 ± 16.76c
BCU2	6.03 ± 0.15abc	12.59 ± 1.61 cd	45.19 ± 2.37b	280.20 ± 25.85d
BCU1 + B	6.27 ± 0.02a	18.99 ± 1.03a	64.79 ± 8.11a	441.68 ± 26.83ab

CK, no fertilizer; U1, urea at 100% N rate; U2, urea at 80% N rate; U1 + B, biochar combined with urea at 100% N rate; U2 + B, biochar combined with urea at 80% N rate; BCU1, biochar-coated urea at 100% N rate; BCU2, biochar-coated urea at 80% N rate; BCU1 + B, biochar combined with biochar-coated urea at 100% N rate
 Different letters in the same column indicate a significant difference at the 5% level according to the LSD test

NH₄⁺-N, and NH₃-N respectively (Figs. 2, 3, Table 2). It followed that leaching loss of NO₃⁻-N was predominantly pathway of nitrogen loss in the present culture experiment.

The results of the present experiment also demonstrated that total loss of nitrogen via leaching, and NH₃-N volatilization accounted for 25.85–26.92% of applied nitrogen as biochar-coated urea (BCU1, BCU2) (Table 3). When biochar-coated urea was used as nitrogen fertilizer, the total loss of nitrogen accounted for 82.69–83.07%, 4.17–4.67%, and 14.38–15.27% distributed in NO₃⁻-N, NH₄⁺-N, and NH₃-N respectively (Figs. 2, 3, Table 2). It can be seen that leaching loss of NO₃⁻-N was the predominant pathway of nitrogen loss when biochar-coated urea was used as nitrogen fertilizer. Similar results were also obtained from the investigation of Wang et al., who observed that the nitrogen loss via leaching was higher than that via NH₃-N volatilization, and leaching loss of NO₃⁻-N was accounted for 51.6–95.7% of total nitrogen leached when biochar-coated urea was used as nitrogen fertilizer [29].

The results of the present culture experiment showed that application of coated urea could significantly reduce nitrogen fertilizer loss compared with application of urea alone, because the loss of nitrogen in soil fed with BCU was about 30% lower than that in soil fed with urea (Figs. 2, 3, Table 2); the loss of nitrogen fertilizer as biochar-coated urea (BCU1, BCU2) was 32.48–33.95% lower than that as urea (U1, U2). The main pathway of reducing loss of nitrogen fertilizer as BCU could contribute to reduce nitrogen leaching loss rather than loss of volatilization via NH₃-N, because volatilization loss via NH₃-N was greater in soils fed with biochar-coated urea (BCU1, BCU2) than in soils fed with urea (U1, U2) (Fig. 2). The NH₃-N volatilization loss of nitrogen fertilizer as biochar-coated urea was greater than that as urea under the same nitrogen fertilization level (Table 3). The mechanism of BCU application for reducing the leaching loss of nitrogen mainly included the following two aspects. Firstly, BCU used in this present experiment had good slow-release properties [15]. Slow-release fertilizer

Table 5 Concentration of nitrogen in oilseed rape, amount of oilseed rape nitrogen uptake, nitrogen utilization efficiency of fertilized nitrogen, and biomass of oilseed rape under different fertilized treatments

Treatment	Nitrogen in oilseed rape concentration (mg/kg)	Amount of oilseed rape nitrogen uptake (mg/pot)	Biomass of oilseed rape (g/pot)	Nitrogen utilization efficiency of fertilized nitrogen (%)
CK	58.77 ± 2.44c	78.54 ± 23.79c	1.33 ± 0.36c	–
U1	65.03 ± 0.86bc	200.65 ± 36.91b	3.09 ± 0.57ab	30.64
U2	64.40 ± 1.54bc	176.42 ± 46.77b	2.73 ± 0.66b	30.52
U1 + B	72.07 ± 5.06a	244.33 ± 47.79ab	3.41 ± 0.80ab	41.96
U2 + B	70.97 ± 5.82ab	188.83 ± 36.19b	2.65 ± 0.34b	34.27
BCU1	72.77 ± 3.54a	283.57 ± 48.10a	3.89 ± 0.58a	51.29
BCU2	70.63 ± 1.01ab	238.56 ± 57.87ab	3.38 ± 0.86ab	50.26
BCU1 + B	71.77 ± 4.39a	280.98 ± 24.45a	3.93 ± 0.48a	50.97

CK, no fertilizer; U1, urea at 100% N rate; U2, urea at 80% N rate; U1 + B, biochar combined with urea at 100% N rate; U2 + B, biochar combined with urea at 80% N rate; BCU1, biochar-coated urea at 100% N rate; BCU2, biochar-coated urea at 80% N rate; BCU1 + B, biochar combined with biochar-coated urea at 100% N rate
 Different letters in the same column indicate a significant difference at the 5% level according to the LSD test

was reported to delay the release of nitrogen fertilizer, and to extend the time for crops to absorb and use fertilizer nitrogen, ultimately to decrease leaching loss of nitrogen [33]. The present experiment observed that the cumulative leaching amount of total nitrogen, NH_4^+-N and NO_3^--N was lower in soils fed with BCU than in soils fed with urea, especially at the first leaching event (Fig. 3). This was because urea inside BCU was partially dissolved due to the barrier effect of the coated materials (biochar). Secondly, biochar with large specific surface area, and negative surface functional groups could increase soil water holding capacity and soil microorganism, nitrification and nitrogen adsorption (such as NH_4^+-N and NO_3^--N), ultimately to reduce nitrogen losses [18, 32, 34].

The present results demonstrated that the cumulative leaching loss of total nitrogen, NH_4^+-N and NO_3^--N were lower in soils fed with biochar combined with urea (U1 + B, U2 + B) than in soils fed with urea (U1, U2) at the same nitrogen fertilization level (Table 2). However, the dynamics of leaching of total nitrogen, NH_4^+-N and NO_3^--N in soils fed with urea combined with biochar were similar to those in soils fed urea (Fig. 3). Direct biochar application was found to reduce nitrogen loss from leaching, due to its adsorption ability to achieve nitrogen retention. However, the direct application of biochar did not achieve slow release of nitrogen fertilizer.

In the present study, compared with individual application of urea, urea combined with biochar significantly reduced loss of NH_3 volatilization, but biochar-coated urea significantly increased loss of NH_3 volatilization (Fig. 2). The ammonia volatilization loss of nitrogen fertilizer was reported to mainly relate to nitrogen release of fertilizer, residue of nitrogen in soil, ammonia adsorption/fixation, nitrification, and soil pH [29, 34, 35]. Zheng et al. observed that the ammonia volatilization was more likely to occur when soil pH was above 8 [11]. The pH values were slightly greater in soils fed with biochar-coated urea (BCU1, BCU2) than in soils fed with urea (U1, U2), which was within the range of acidity (Table 4). Therefore, the increase of bulk soil pH due to BCU application could not be the main factor for the increase of ammonia volatilization observed. High ammonia volatilization in soils fed with BCU compared to urea could be contributed to high soil NH_4^+-N concentration, because concentrations of NH_4^+-N were greater in soils fed with BCU than in soils fed with urea under the same nitrogen fertilization (Table 4); application of BCU prolonged the time of ammonia volatilization (Fig. 2). Moreover, coated biochar induced alkaline microenvironment outside urea could also contribute to ammonia volatilization. Puga et al. have observed that biochar as coating material increased ammonia volatilization of nitrogen

fertilizer, while application of biochar combined urea reduced ammonia volatilization [28]. However, reduction rate of nitrogen fertilization as BCU by 20% (BCU2) was observed to reduce ammonia volatilization loss. In conclusion, although the application of BCU increased ammonia volatilization, it significantly reduced nitrogen leaching, and ultimately reduced total nitrogen loss of nitrogen fertilizer.

Total loss of nitrogen fertilizer followed the decreasing order as below: $\text{BCU1} + \text{B} > \text{BCU1} > \text{U1} + \text{B}$ (Table 3). Implying that application of biochar combined with BCU was more conducive to reduce nitrogen fertilizer loss. However, additional biochar application will have to add additional cost. Therefore, application of biochar-coated urea could be a promising alternative measure for reducing loss of nitrogen. However, further investigations were required to validate dosage-effect relationship of BCU on the loss of nitrogen at the field scale.

Effects and mechanisms of BCU application on NUE

Coated fertilizer has incomparable virtues than other chemical fertilizers in improving NUE, reducing environmental pollution, and saving labour, because it could most likely match the nutrient release rate to crop's demand by coating materials design among controlled slow release fertilizers [36, 37]. The present results showed that the BCU used in the present study could effectively improve the NUE of fertilized nitrogen, because the NUE of biochar coated urea was significantly greater than that of urea irrespective of nitrogen fertilization level (Table 5). The mechanisms for BCU to improve the NUE of fertilized nitrogen mainly included the following aspects. Firstly, application of BCU reduced nitrogen loss due to its good slow-release and adsorption/retention properties of biochar as coating material. Puga et al. observed that the improvement of NUE for biochar-based fertilizers was related to the gradual release of nitrogen and the reduction of nitrogen leaching loss [38]. The BCU used in the present experiment had good slow release properties [15], and the total nitrogen loss in soil fed with BCU was about 30% lower compared with urea (Fig. 2, Table 2). Secondly, the application of BCU increased soil nitrogen residue, crop nitrogen uptake. The present results indicated that the concentrations of total nitrogen, NH_4^+-N and NO_3^--N of soils fed with BCU were greater than that of soils fed with urea under the same level of nitrogen fertilization (Table 4). Zheng et al. also observed that application of biochar enhanced fixation of nitrogen in soils [11]. Thirdly, the application of BCU increased crop nitrogen uptake. The present results showed that the nitrogen concentration and nitrogen uptake of oilseed rape was greater in BCU treatments than in urea treatments (Table 5). Liu et al. observed that

application of maize stover biochar improved NUE of urea and enhanced soil N availability to Ryegrass (*Lolium perenne* L.) [35].

The present results showed that the NUE for BCU1 + B and BCU1 was greater than that for U1 + B, but no difference of NUE between BCU1 + B and BCU1 was observed (Table 5). Implying that both application of biochar combined with urea, and biochar coated urea can improve NUE, but application of biochar combined with BCU could not result in further improvement of NUE compared with application of BCU. It could be seen that biochar combined with BCU can control loss of nitrogen, but can't improve NUE compared to the application of BCU. Additional biochar applications require additional costs. Therefore, application of BCU could be a promising alternative measure for improving NUE of nitrogen fertilizer. However further investigations are required to validate optimization of BCU fertilization levels at the field scale.

Moreover, reduction rate of nitrogen fertilization as BCU (BCU2) by 20% was not observed to decrease the biomass of oilseed rape. The biomass of oilseed rape was 10% higher with BCU2 treatments than U1 treatment, which was equivalent to U1 + B (Table 5). Therefore, application of BCU could be a promising controlled release nitrogen fertilizer for reducing loss of nitrogen and improving NUE without negative impact on plant yield.

Conclusions

The present study demonstrated that nitrogen fertilization as BCU could not only significantly reduce nitrogen loss but effectively improve NUE compared to urea. However, results showed that although volatilization loss of BCU was higher due to BCU-induced residue of $\text{NH}_4^+ - \text{N}$ nitrogen in soils, the total nitrogen reduction of BCU was lower. This was mainly because the application of BCU largely reduced the nitrogen leaching loss. The application of BCU significantly increased NUE of BCU compared with urea, which could contribute to the application of BCU-induced reduction of nitrogen fertilizer loss, increasing uptake of nitrogen in plant, and residue of nitrogen in soils. The reduction rate of nitrogen fertilization as BCU (BCU2) by 20% was not observed to decrease the biomass of oilseed rape. BCU combined with biochar was observed to further reduce the loss of nitrogen compared with BCU, but NUE was a little lower. Also, the additional biochar application inevitably increased the cost of fertilization. The application of BCU was more convenient to operate and could avoid the problems of biochar powder dispersion, compared with directly applying biochar into the soil. Therefore, the application of BCU could be a promising

control release nitrogen fertilizer for reducing nitrogen loss and improving NUE without any negative impact on plant yield. However, further investigations are required to validate the dosage-effect relationship of BCU on the loss of nitrogen, NUE, and crop yield at the field scale.

Supplementary information

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Additional file 1: Fig. S1. SEM images of biochar used for biochar-coated urea. **Fig. S2.** FTIR spectra of biochar used for biochar-coated urea. The band at 1570 cm^{-1} correspond to keto C=O stretching vibrations in esters or C=C stretching vibrations in alkene and aromatic compounds; The band at 1030 cm^{-1} correspond to C-O stretching vibrations in lignin derivatives or alcohols and phenols. **Fig. S3.** ^{13}C NMR spectra of biochar used for biochar-coated urea. Resonance region at 110–150 ppm indicated aromatic carbon. **Fig. S4.** Schematic plot of ammonia volatilization collection.

Abbreviations

NUE: Nitrogen use efficiency; BCU: Biochar-coated urea; Bio-MUC: Biochar-mineral urea composite.

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Authors' contributions

YJ and ZH designed the experiments and wrote the paper. YJ performed the experiments. YJ and WQ analyzed the data. YB provided guidance during experimental work. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analysed during this study are included in this published article (and its Additional file 1).

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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