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Hybrid brown coal-urea fertiliser reduces nitrogen loss compared to urea alone

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ABSTRACT

Synthetic nitrogen (N) fertilisers, such as urea, are susceptible to rapid dissipation from soil. More gradual release of mineral N from fertiliser may reduce the off-site movement of mineral N, thereby enhancing N supply to crops and minimising negative off-site impacts. We hypothesised that granulation of urea with humified brown coal (BC) delays mineral N release and maintains higher concentrations of N in soil than conventional urea granules. Four different brown coal-urea granules, with C:N ratios of 1-10, were prepared by pan granulation. Advanced spectroscopic and X-ray powder diffraction (XRD) techniques confirmed loading of urea-N into the BC structure. Nitrogen-release from BCU granules was slower than from urea, resulting in higher N retention over a longer period for increasing growth and N uptake by crop plants. This trend increased with higher loading of BC, emphasising the significant role of BC in N retention. These findings support the hypothesis that BC is suitable for developing slow release N fertilisers.

Keywords: Brown coal, urea, pan granulation, slow release fertiliser, fertiliser N use efficiency.

1. Introduction

Nitrogen is one of the most important, and limiting, nutrient elements for ecosystem provisioning services (Jackson et al., 2008). Urea is the dominant and main source of N input in many crop production systems world-wide because of its high N content. Unfortunately, the use-efficiency of urea fertiliser is very poor and recovery of N in soil-plant systems seldom exceeds 50% of applied N (Raun et al., 2002). The low N-use efficiency of urea is associated with N losses by leaching, denitrification and volatilisation (Fageria and Baligar, 2005). This is a major challenge for farmers worldwide, since the lost N represents both an economic cost and an environmental burden, as off-site N transport in water pollutes both surface and ground water, whilst nitrous oxide contributes to greenhouse gas accumulation in the atmosphere (Vitousek et al., 1997). The widespread loss of organic matter from arable soils has been implicated as one factor contributing to poor fertiliser N-use efficiency, because soils depleted in organic carbon are often impaired in their ability to retain N (Accoe et al., 2004). Furthermore, studies show that the carbon sequestration potential of soil is intricately linked with sequestration of other nutrients, especially N (Dong et al., 2009).

There is an increasing interest in the application of organic fertilisers (Das and Adhya, 2014; Hargreaves et al., 2008; Li et al., 2015), as they can contribute to climate change mitigation through C sequestration, and supply organic matter to soil at the same time (Diacono and Montemurro, 2011). Organic matter improves soil water holding capacity, soil buffering capacity, cation exchange capacity, soil structure, and increases the

availability of plant nutrients by increasing microbial biomass and their activities (Ge et al., 2009). Traditionally, organic fertilisers in the form of cow-dung, compost, farm yard manure, poultry litter, municipal wastes and humic substances were applied in various forms and in large amounts to improve crop productivity (Hargreaves et al., 2008; Imbufe et al., 2005; Loecke et al., 2004; Mondini et al., 2008). Efficient use of manure as a fertiliser is complicated by the imbalance of nutrients, variability in sources, difficulties in estimating nutrient availability, relatively low nutrient concentration and very large application rate limiting the distances manure can profitably be transported for use as a fertiliser (Albiach et al., 2001; Edmeades, 2002; Hargreaves et al., 2009; Quilty and Cattle, 2011). However, fortification of inorganic fertilisers with humified organic matter could enhance fertiliser use efficiency and return organic matter back into soil, restoring soil health and improving crop yield in a more sustainable manner (Ahmad et al., 2008).

Considerable scientific evidence indicates that combining natural organic materials high in humic substances with N fertiliser, leads to more efficient nutrient uptake by plants and decreased N losses in the environment from excess N fertiliser application (Debska et al., 2002; Kwiatkowska et al., 2008). In recent years, organic amendments other than traditional manures have been investigated for their potential to restore soil organic matter levels and provide associated benefits (Kim Thi Tran et al., 2015). Brown coal (BC), also known as lignite, is one such substrate, as it is high in humic acid content and contains ion exchange groups capable of complexing or adsorbing nutrients (Kwiatkowska et al., 2008). The high porosity of BC further enhances its capacity for adsorption and absorption of

nutrient ions on its porous surfaces (Karczewska et al., 1996). The chemical structure of BC include aromatic rings, bridges such as alkyl, ether or ester linkages and side chains such as alkyl, carboxyl and hydroxyl groups and exhibits properties similar to those of soil humic acids (Kwiatkowska et al., 2008). The porous structure and functional groups of BC are very important for better nutrient retention and microbial activity. For example, ammonia-N may be abiotically fixed to humic acid (Bosatta and Agren, 1995) when the C:N ratio is higher than 10 (Knicker et al., 1997).

Brown coal may reduce volatilisation loss of N from urea-fertilised soil by inhibiting urease enzyme activity, thus increasing urea-N availability for plants (Bollmann and Laanbroek, 2001; Sun et al., 2016). More recently, Rose et al. (2016) demonstrated that granulation of urea with BC alters the dynamics of fertiliser N in soil compared with unmodified urea, including reductions in mineral N leaching and nitrous oxide emissions. There is therefore, strong evidence to support ongoing research into optimisation of brown coal-urea fertilisers to provide a product with both slow release and immediate nutrient availability properties. Moreover, refinements in the preparation of such organo-mineral fertiliser granules are required to maintain granule integrity for soil application through currently used machinery. This study aimed to manufacture and characterise a number of different BC-urea fertiliser blends, and to quantify the subsequent N release patterns as a basis for the formulation of improved fertiliser granules that minimise N losses in agricultural use. Two field experiments were conducted to assess the performance of BCU granules for improving crop N acquisition.

2. Materials and methods

2.1. Preparation of brown coal-urea granules

Brown coal-urea (BCU) granules were prepared in Feeco International, Pakenham, Victoria using propriety granulation technology. Air-dried Loy Yang BC collected from the Latrobe Valley, Victoria, Australia, was used for the preparation of the fertiliser granules. The physical and chemical characteristics of the BC used in this study are given in Table 1.

Table 1

Physical and chemical properties of the Victorian brown coal used in this study

Property		Property	
Moisture (%)	62.2	Phosphorous (%)	0.01
pH (H ₂ O)	4.45	Potassium (%)	0.02
Ash (%)	1.46	Aluminium (%)	0.02
Volatile matter (%)	51.4	Manganese (mg kg ⁻¹)	53
Total carbon (%)	66.8	Copper (mg kg ⁻¹)	<1
Hydrogen (%)	4.93	Molybdenum (mg kg ⁻¹)	2.69
Nitrogen (%)	0.58	Cobalt (mg kg ⁻¹)	2.13
Sulphur (%)	0.42	Nickel (mg kg ⁻¹)	6.72
Oxygen (%)	24.3	Zinc (mg kg ⁻¹)	3.19
Silica (%)	0.34	Selenium (mg kg ⁻¹)	18.4
Iron (%)	0.13	Cadmium (mg kg ⁻¹)	0.82
Calcium (%)	0.04	Lead (mg kg ⁻¹)	7.23
Magnesium (%)	0.08	Chromium (mg kg ⁻¹)	<1
Sodium (%)	0.11	CEC (cmol _c kg ⁻¹)	76.3
Chlorine (%)	0.14		

Four different brown coal-urea (BCU) granules were prepared by mixing BC and urea on the basis of C:N ratios presented in Table 3. The urea blended in this study was supplied by Elders Agribusiness Company, Australia (elders.com.au). Various amount of urea and BC were blended to match with the theoretical C:N ratio based on the C and N content of BC and urea, respectively. The BC and urea were powdered prior to mixing in a pin mixer to form seed granules. Starch and molasses were used as binders to assist the granulation process and increase granule strength. Seed granules were subsequently developed in a pan granulator and dried in a rotary drum oven between 180 to 200 °C to reduce the moisture content to 4-5%. A schematic of the granulation process of BCU preparation is shown in Fig. 1.

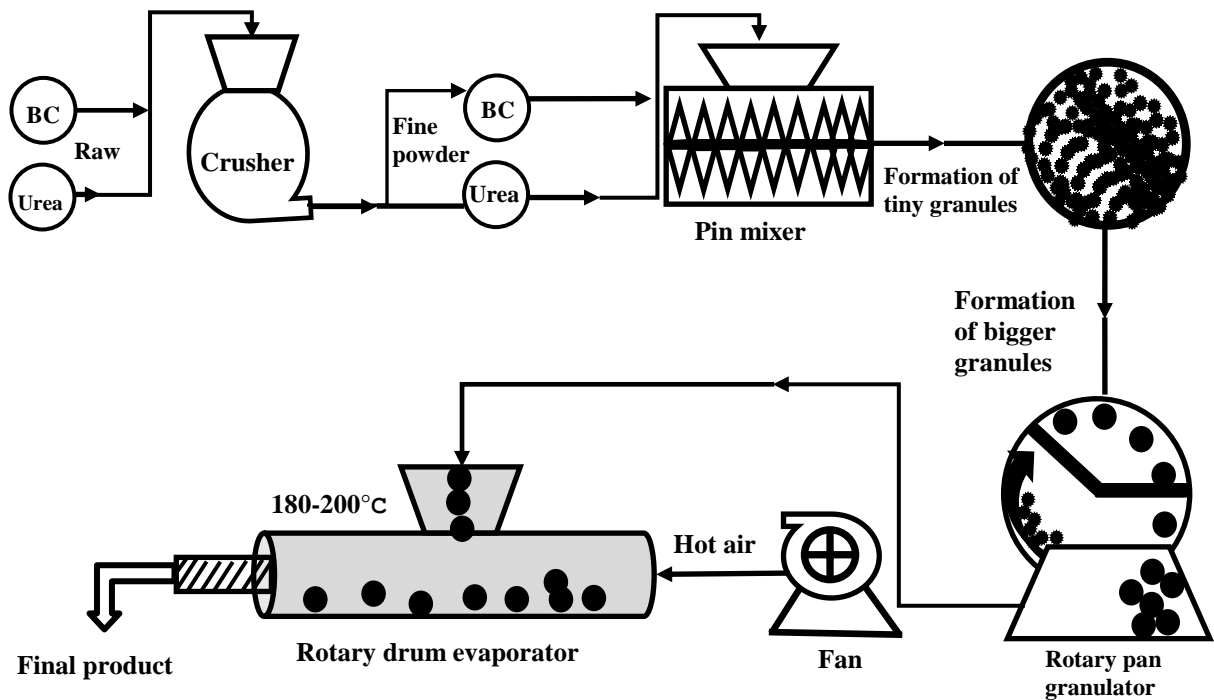


Fig. 1. Schematic of granulation process of BCU granules preparation

2.2. Characterisation of BCU granules

2.2.1. Physical and chemical properties of BCU granules

Granule particle size, moisture content, crush strength, and CHN composition were measured as follows. The size of fifty randomly selected granules from each blend was measured using slide calipers. The moisture content of the product was calculated based on the product mass before and after oven drying at 105 °C for 4 hours according to equation 1.

$$\text{Moisture content (\%)} = 100 \times \frac{\text{wet product mass} - \text{dry product mass}}{\text{wet product mass}} \quad (1)$$

Equation 1: Product moisture content

Single particle compressive crush strength tests were carried out on granules using a bench top scale Instron testing machine (Chattillon, 50LBF, AMETEK). The maximum force applied to break the granule was measured. A minimum of 20 granules from each of the BCU blends were tested and the mean and standard deviation of the crush strength were determined. The weight of 20 individual granules were measured and averaged. The C, H and N content of the samples were determined by combustion using a high-frequency induction furnace CHN analyser (Vario Micro Cube).

2.2.2. Structure analysis of BCU of the granules

The chemical structures of the BCU granule (C:N=1.5), unmodified urea and BC were characterised using Fourier Transform Infrared Spectroscopy (FTIR), ¹³C Solid State nuclear magnetic resonance (NMR) spectroscopy and powder X-ray diffraction (PXRD).

The FTIR spectra of very finely powdered samples were obtained in the wave length range of 400 to 4000 cm^{-1} with a FTIR spectrophotometer using the Attenuated Total Reflectance (ATR) technique. ATR spectra were acquired using a golden gate single bounce diamond ATR mounted in a nitrogen purged Bruker Equinox 55 FTIR spectrometer, equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The samples were kept in good optical contact on the diamond surface with a consistent application of low pressure. A background spectrum of a blank diamond was used to generate transmission spectra. Solid State ^{13}C NMR spectra were determined using a Bruker 100 (^{13}C) MHz spectrometer with cross polarisation-magic angle spinning (CP/MAS). Mineralogical and structural characteristics of urea, BC and BCU granules were determined by X-ray diffraction analysis of powdered samples using a Bruker D8 Advanced Powder X-ray Diffractometer at a scanning speed of $2^\circ\theta \text{ min}^{-1}$.

2.2.3. Water absorbency of BCU granules

Accurately weighed BCU granules ($5\pm 0.1 \text{ g}$) were immersed in 20 mL of deionised water and allowed to soak at room temperature for 10 min. The swollen granules were isolated from non-absorbed water and weighed (Wu et al., 2008). The water absorbency (WA) was calculated using the equation 2:

$$WA = \frac{M - M_0}{M_0} \quad (2)$$

Equation 2: Water absorbency measurement

Where, M and M_0 denote the weight of wet granules and dry granules, respectively.

2.2.4. Water-holding capacity of soil amended with BCU granules

Loamy soil collected from Horsham, Victoria was used in this study. The physical and chemical properties of soil are presented in Table 2. Individual quantities (5 ± 0.1 g) of each different BCU granule were well-mixed with 60 g of dry soil and kept in individual poly vinyl chloride (PVC) tubes (1.8 cm diameter and 25 cm long); the bottom of the tube was sealed using a permeable nylon fabric and weighed (W_1). Deionised water was added to the soil columns until saturation and drainage occurred. The tube was weighed (W_2) again when free drainage has ceased. Two control treatments, viz., with no BCU granules and with straight BC granules were also included to compare the results with BCU granules. The experiment was laid out in a completely randomised design with five replicates. The water-holding capacity (WHC%) of the soil was calculated using the equation of Wu et al. (2008).

$$WHC (\%) = 100 \times \frac{W_2 - W_1}{(W_2 - W_1) + 65} \quad (3)$$

Equation 3: Water holding ratio measurement

Table 2

Physical and chemical properties of soil

Property		
Australian soil order	Vertosol	Sodosol
USDA soil order	Xerertic Vertisol	NA
Texture	Clay loam	Sandy loam
Bulk density (g cm ⁻³)	1.10	1.40
Moisture (%)	7.26	14.6
pH (H ₂ O)	8.32	6.27
Total carbon (%)	1.31	2.1
Nitrogen (%)	0.09	0.16
Ammonium nitrogen (mg kg ⁻¹)	20.6	7.1
Nitrate nitrogen (mg kg ⁻¹)	7.7	11.2
Phosphorus (Colwell) (mg kg ⁻¹)	39	9.3
Calcium (cmol _c kg ⁻¹)	30.8	1.3
Magnesium (cmol _c kg ⁻¹)	6.4	1.7
Potassium (cmol _c kg ⁻¹)	2.18	5.3
Sulfur (mg kg ⁻¹)	1.8	2.7
Iron (mg kg ⁻¹)	24	11

2.2.5. Urease activity and water retention capacity of soil amended with BCU granules

To 100 g of soil, 5±0.1 g of the different BCU granules were mixed in a 250 mL plastic container. The soil was then saturated by adding 70 mL of deionised water slowly and weighed (W1). Two control treatments, viz., with no BCU granules or with straight BC granules were also included to compare the results with BCU granules. The experiment was laid out in a completely randomised design with five

replicates. The containers were maintained at room temperature and weighed (W_i) at every 5 days interval over a period of 30 days. The water retention capacity (WRC%) of soil was calculated using the equation of Wu et al. (2008). The urease enzyme activity in soil was measured according to the method of Kandeler and Gerber (1988)

$$7 \text{ days after different N fertilisers addition. } WRC (\%) = 100 \times \frac{W_1 - W_i}{\text{Weight of soil (g)}}$$

Equation 4: Water retention capacity measurement

2.2.6. Dissolution of N from BCU granules in water

A N dissolution incubation experiment was undertaken following the method of Dai et al. (2008). One gram of equivalent-N from each fertiliser blend preparation was accurately weighed and transferred into nylon mesh bags. The bags were subsequently placed into 250 mL plastic containers containing 200 mL of deionised water. The containers were incubated at $25 \pm 1^\circ\text{C}$ for 14 days. The bags were taken out of the containers at days 1, 3, 5, 7 and 14 of the incubation, and transferred into 250-mL new plastic containers containing 200 mL of deionised water. The experiment was laid out in a completely randomised design with five replicates. The solutions were filtered through $0.45 \mu\text{m}$ membrane filter and collected for urea-N, ammonium-N and nitrate-N analyses. The solutions were analysed colorimetrically for urea-N using P-dimethylaminobenzaldehyde following the method of Singh and Saksena (1979). Ammonium-N was quantified by reacting with salicylate and hypochlorite in a buffered alkaline solution contain sodium nitroprusside as a reductant (Forster, 1995). Nitrate-N (Nitrite) was determined by reduction of nitrate using

vanadium (III) combined with colourimetric detection by acidic Griess reaction (Miranda et al., 2001).

2.2.7. Field experiments

Field experiments were conducted to determine the effect of BCU blends on the biomass yield and N uptake by canola and wheat compared to commercial urea fertiliser. The field trials were carried out in the experimental field of Southern Farming System (SFS), Inverleigh (38°10'29"S and 144°03'99"E), Victoria, Australia. A temperate monsoon climate prevailed in this area with mean annual temperature and precipitation of 18.5°C and 551 mm, respectively. The key physicochemical properties of this soil are presented in Table 2. The individual plot size was 15 m² (10 m×1.5 m). The field was divided into four blocks and each block was treated as a replicate. A 1 m buffer zone was maintained in between two blocks. Before seed sowing the soil was treated with Boxer Gold to minimise the weed growth and Lorsban to control pests. Seeds were uniformly sown with a seed driller, maintaining a uniform seed to seed and row to row distance. For the canola trial, N was added at the rate 70 kg ha⁻¹ from urea and BCU 2. For the wheat trial, the soil was treated with various amounts N to get a yield response. The soil was fertilised with urea-N at 100% of the recommended dose (75 kg N ha⁻¹) and 75, 50 and 25% of the recommended N dose. For BCU blends, the soil was treated with 75, 50 and 25% of the recommended N dose from BCU 1, BCU 2 and BCU 3, respectively. In both the canola and wheat trial a control treatment with no N was also included. In addition, monoammonium phosphate (MAP) was incorporated at a rate of 100 kg ha⁻¹ in all the plots except control plots. The experiments were laid out following a randomised complete block design. The canola

biomass was harvested at flowering stage. The biomass N content of canola was determined by combustion using a high-frequency induction furnace CHN analyser (Vario Micro Cube). The biomass N uptake by canola was calculated following the equation described by Finzi et al. (2007). Wheat was grown to maturity and grain yield was measured at harvest. The grain protein content of wheat was determined using Near Infrared Reflectance (NIR).

2.2.8. Statistical analysis

Statistical analyses were performed using the statistical software package IBM SPSS, version 20 (SPSS IBM, 2010). All tests of significance were carried out at $P < 0.05$. Normality testing of the data was conducted using the Kolmogorov-Smirnov goodness of fit test and equality of variances was tested using the modified Levene's test. One way analysis of variance (ANOVA) was performed and the multiple comparisons among the different treatments were done using a Scheffé test.

3. Results and discussion

3.1. Physical and chemical properties of BCU granules

The physical and chemical properties of the BCU granules and urea are presented in Tables 3-4. The moisture content of BCU granules varied from 2.9 to 3.6%. The moisture content of BCU granules were similar to that of urea (2.1%). The size of more than 90% of granules of different BCU blends fall in the range between 2-4 mm, with the average size of BCU granules equivalent to that of urea except for BCU 4 which was smaller and had the highest BC content. The individual granule weight of BCU 2 was significantly higher

compared to other granules including urea. As expected, all BCU granules contained a higher %C and lower %N compared to commercial urea. BCU 1 granule contained the highest %N (21.45%) and lowest %C (39.81%) and BCU 4 granule containing the lowest %N (5.74%) and highest %C (53.83%). A significantly ($P<0.05$) higher amount of C was measured in the individual granule of BCU 2 compared to other BCU granules and urea, while each urea granule contained significantly ($P<0.05$) higher and about double the amount N compared to BCU 1 granules. No significant ($P>0.05$) differences were observed in the N content of individual granules of BCU 1 and BCU 2 but the N content of these granules were about ten times higher than that of BCU 4.

Table 3

Physical properties and characterisation of BCU granules (values are mean \pm standard error, N = 5)

Granules	C:N ^T	C:N ^A	Moisture (%)	Size (mm)	Crush strength (kg)	Water absorbency (g g ⁻¹)	Weight granule ⁻¹ (mg)
BCU 1	1.0	1.8	2.89 \pm 0.11a	3.33 \pm 0.21a	4.75 \pm 0.37a	0.62 \pm 0.02b	49 \pm 1.2ab
BCU 2	1.5	2.7	3.56 \pm 0.09a	3.43 \pm 0.19a	6.69 \pm 0.44a	0.85 \pm 0.02b	58 \pm 1.3a
BCU 3	3.0	5.4	3.40 \pm 0.05a	3.19 \pm 0.14a	2.38 \pm 0.06b	1.03 \pm 0.06b	34 \pm 1.4c
BCU 4	10.0	10.8	3.21 \pm 0.13a	2.89 \pm 0.13c	0.42 \pm 0.03c	1.70 \pm 0.05a	18 \pm 1.1d
Urea	ND	ND	2.19 \pm 0.06a	3.36 \pm 0.23a	5.28 \pm 0.20a	ND	45 \pm 1.3b

ND: Not determined, T= Theoretical and A= Actual

The values with different letters differ significantly according to Scheffé-test at $P<0.05$.

Brown coal has previously been explored as a potential substrate for a slow release nitrogenous fertiliser by exploiting its extensive reactive surface area and humic acid content (Rose et al., 2016). Addition of humified BC to soil altered N cycling and dynamics in soil (Kim Thi Tran et al., 2015; Paramashivam et al., 2016; Rose et al., 2016; Sun et al., 2016). In this study, four formulations of urea-enriched BC granules were successfully made using the pan granulation technology (Fig. 1) to increase the understanding of mechanisms of N retention by BC. The N content of the dried products at all C:N ratios was close to the theoretical N content determined from the initial amount of urea addition to the wet coal (Table 3). The slightly lower N content in the BCU granules compared to the expected values may be due to the gaseous loss of N in drying process as has previously been observed for BCU granules produced using a simultaneous granulation and super-heated steam drying process (Rose et al., 2016). However, in contrast to Rose et al. (2016), no urea crystals were observed on the surface of BCU granules, indicating homogenous mixing of BC with the urea. This might be due to the effect of the pin mixing process of granulation, which improves agglomeration and densification to facilitate better N distribution and retention by BC after granulation. More than 90% of the BCU granules produced were of a suitable size for commercial use (2-4 mm), with low moisture content for practical long term storage and transport.

The mean crush strength of different BCU granules ranged from 0.42 to 6.69 kg. Most of the BCU granules maintained the standard fertiliser crush strength except BCU 4 which was lower. The crush strengths of BCU 1 and 2 were not significantly different ($P>0.05$)

from that of commercial urea. Formulation BCU 2 produced the hardest granules with a maximum crush strength and numerically higher than that of urea and the other BCU granules. The crush strength of fertiliser granules is another important characteristics determining its suitability for handling by farm machinery, and also its stability and degradation in the environment. The crush strengths of the dried BCU 1 and BCU 2 granules were statistically similar to commercial urea and other available fertilisers currently used in agriculture (Table 3). For handling purposes the granules crush strength should be at least 1.4 kg, and a crush strength ≥ 2.27 kg is highly desirable (Hignett, 1985).

Table 4

Chemical characterisation of BCU granules (values are mean \pm standard error, N = 5)

Granules	C (%)	H (%)	N (%)	C granule ⁻¹ (mg)	N granule ⁻¹ (mg)
BCU 1	39.81 \pm 0.05b	5.83 \pm 0.09a	21.45 \pm 0.08b	19.51 \pm 0.07b	10.54 \pm 0.02b
BCU 2	45.43 \pm 0.07b	5.82 \pm 0.2a	17.31 \pm 0.08b	26.24 \pm 0.05a	10.11 \pm 0.02b
BCU 3	48.40 \pm 0.16ab	4.81 \pm 0.08a	8.33 \pm 0.11c	16.22 \pm 0.04c	2.83 \pm 0.02c
BCU 4	53.83 \pm 0.09a	5.22 \pm 0.1a	5.74 \pm 0.11c	9.69 \pm 0.02d	1.12 \pm 0.01c
Urea	19.22 \pm 0.08c	6.41 \pm 0.04a	45.72 \pm 0.06a	8.61 \pm 0.02d	20.50 \pm 0.06a

The values with different letters differ significantly according to Scheffé-test at P<0.05.

3.2. Water absorbency, holding and retention capacity of BCU granules in soil

Blending of BC with urea increased the water absorbency, water holding capacity and retention of water in the soil used in this study (Table 3 and Fig. 2). The water absorbency increased gradually with an increase in BC content of the granules. The water absorbency

of urea and BC granules were not measured due to their instability in water. Among the granules, BCU 4 showed significantly higher water absorbency compared to other granules. Significantly higher water holding capacity was observed in soil amended with BC only and BCU granules compared to urea and control soil. Among the different granules, BCU 4 had the greatest increase in water holding capacity and cumulative water retention capacity of soil.

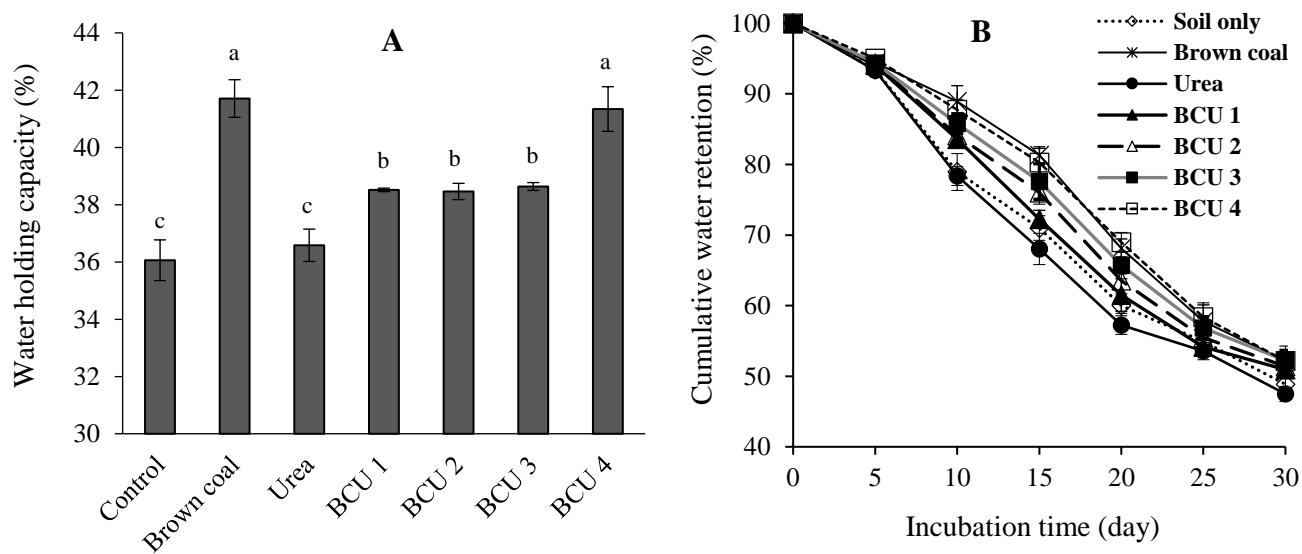


Fig. 2. Effect of BCU granules on the water holding capacity (A) and cumulative water retention capacity (B) of soil (values are mean \pm standard error, N = 5)

As such, three of the four BCU granules were found to be physically suitable as alternatives to currently available commercial N fertilisers. On average, the BCU granule can absorb 1 g of water by each g of granule. Thus, addition of BCU granules in soil could potentially increase the soil moisture content and water retention capacity of soil. This is supported by the water holding capacity and water retention capacity data in which BCU

granules amended soil showed significantly higher water retention in soil compared to urea and the control treated soil. This is similar to the findings of Xie et al. (2011), who reported that the addition of organo (wheat straw)-mineral fertiliser increased the water holding capacity of soil. Therefore, blending of BC with urea could be an option for increasing soil moisture and water retention for longer period of time in dry land and rain-fed agriculture, however the extent of the potential benefits at realistic application rates under field conditions requires further investigation.

3.3. Structural analysis of BCU granules

The FTIR spectra of BC, BCU (C:N=1.5) and urea are shown in Fig. 3. Blending of BC with urea decreased the peak intensity at 1250 and 1710 cm^{-1} which are assigned to carboxylic groups. Blending of BC with urea also decreased the phenolic group peak intensity at 3396 cm^{-1} . The increased peak intensities at 1053 and 3251 cm^{-1} indicate loading of urea-N into BC due to C-N and N-H stretching, respectively. The introduced urea mainly interacts with the carboxylic and phenolic groups of the BC.

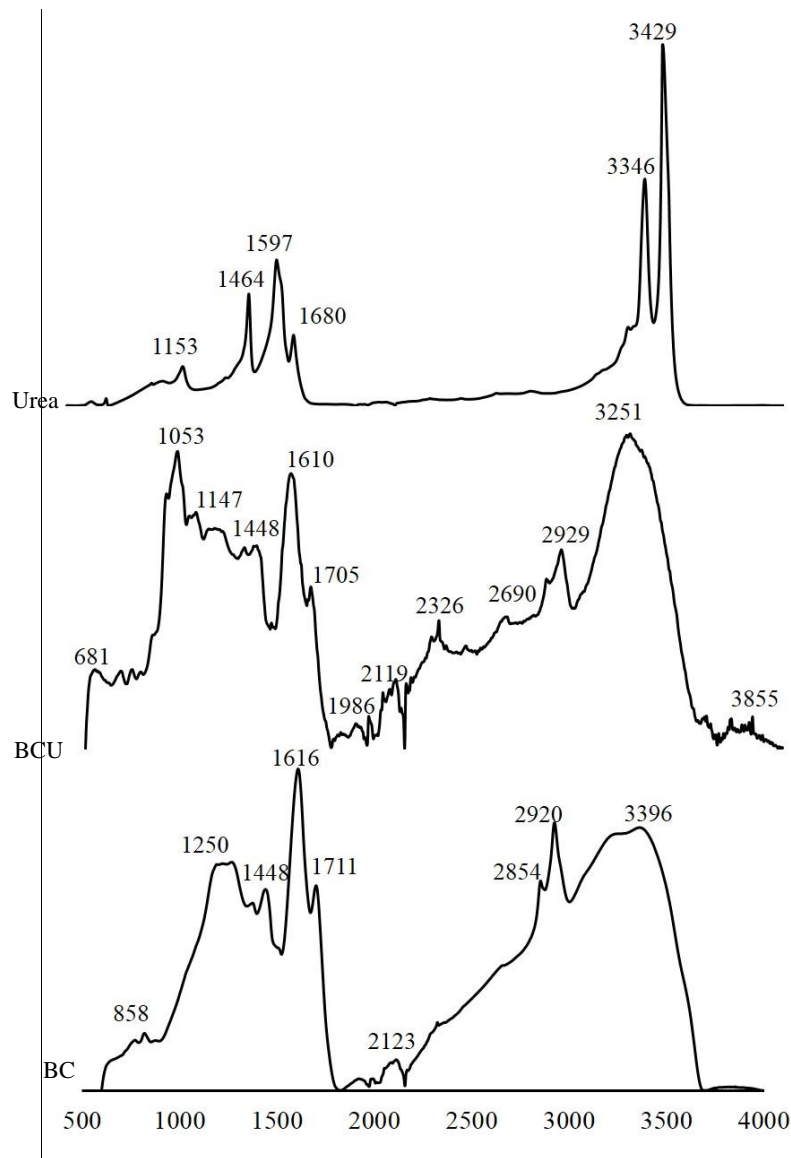


Fig. 3. FTIR spectra of urea (top), BCU granule (C:N=1.5, middle) and BC (bottom)

The NMR spectra of BC, BCU (C:N=1.5) and urea are shown in Fig. 4. Each NMR spectrum is grouped into three major regions for the integration purpose: 220 - 170, 170 - 77 and 77 - 0 ppm, corresponding to carboxyl/carbonyl, aromatic and aliphatic carbons respectively. Both the BC and BCU blend contain higher amount of carboxyl and aromatic C relative to their aliphatic C. No differences were observed in aliphatic carbon of BC and

BCU granules. Blending of BC with urea showed some interesting differences in the aromatic and carboxyl C compared to BC. The marked increase in the peak at position of 73 ppm clearly indicates the loading of N in BC by reacting with R-OH. Moreover, the decreased peak intensity at 125 ppm represents a decrease in carboxyl-C of BC. On the other hand, the increased peak intensity at 163 ppm could be the result of loading of the urea molecule in BC, based on a slight shift of the peak at 161 in the urea spectrum. The NMR spectra of BCU clearly indicates the loading of urea-N by chemical reaction with COOH or R-OH group of BC.

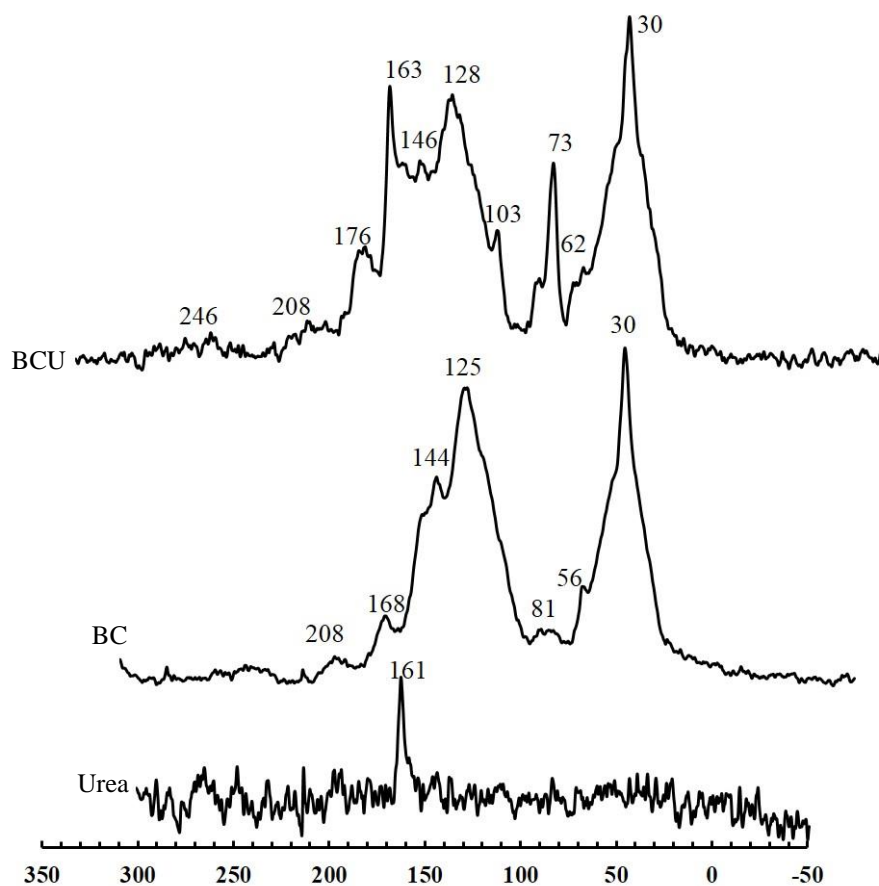


Fig. 4. ¹³C CP/MAS NMR spectra of urea (bottom), BC (middle) and BCU granule (C:N=1.5, top)

To monitor the structural changes and loading of urea into BC due to blending, the materials were analysed by XRD, as shown in Fig. 5. The BCU blend adopted a higher degree of crystalline order due to loading of urea or urea-N on to BC.

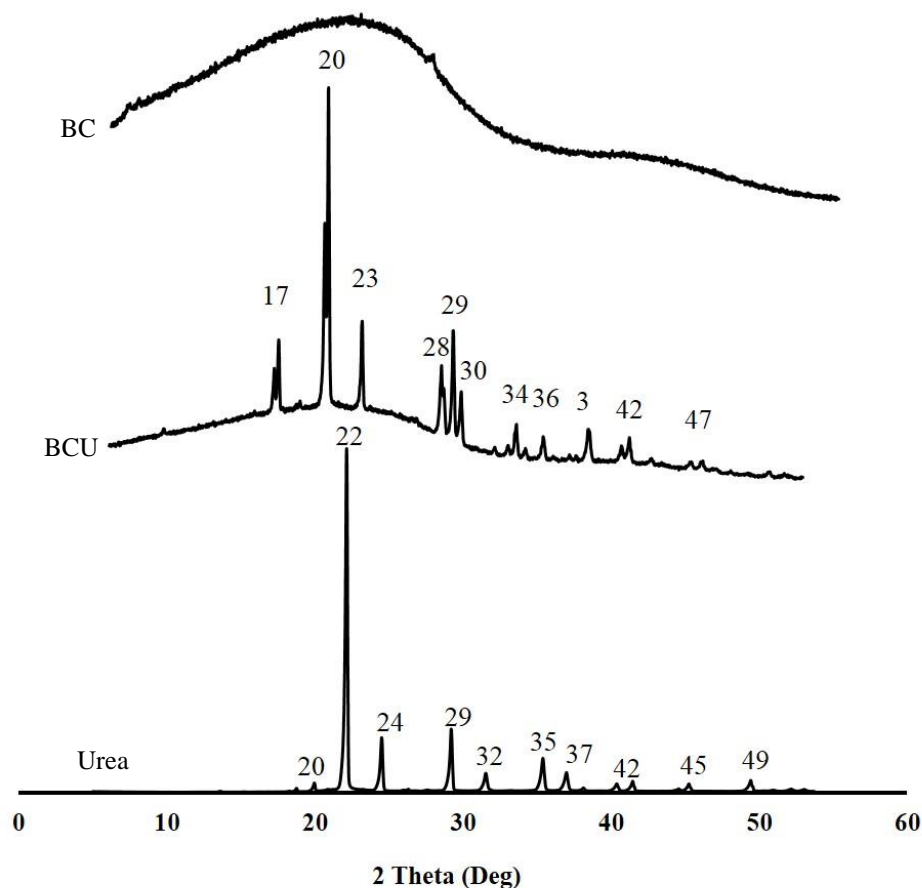


Fig. 5. Powder XRD patterns of urea (bottom), BCU granule (C:N=1.5, middle) and BC (top)

Results from FTIR and NMR of BC and the BCU blends support the hypothesis that the urea interacts with BC by chemical reaction with the carboxyl and phenolic groups of BC (Fig. 3-4). The decreased and shifted peak intensities in carboxyl and phenolic groups and appearance of new peaks in the BC clearly indicates the loading of urea-N or possibly other forms of N (e.g. $\text{NH}_4^+\text{-N}$ or $\text{NH}_3\text{-N}$) into the structure of BC. This is supported by XRD

analysis which showed an increased crystallinity in the structure of BCU granules compared with raw BC due to loading of urea-N into BC (Fig. 5). As previously highlighted, the enhanced agglomeration and densification of granules through pin mixing, may also have contributed to the altered crystalline structure of BCU formulations by loading of urea-N or NH_4^+ -N onto BC. These findings corroborate those of Kwiatkowska et al. (2008), who also identified similar chemical changes in mineral enriched BC using FTIR, and those of Manikandan and Subramanian (2013), who reported changes to FTIR and XRD spectra under loading of urea-N into biochar.

3.4. Urease activity in soil

The urease enzyme activity in soil was significantly influenced by the addition of N fertilisers (Fig. 6). Urease activity in the soil amended with BCU granules was substantially lower than in soil amended with commercial urea. Among the different BCU granules, the granules with a higher proportion BC generated a lower urease activity in soil with respect to the granules with a lower proportion of BC and higher N loading. A similar findings was reported by Bollmann and Laanbroek (2001) who found that incorporation of BC to soil inhibited the urease enzyme activity in soil.

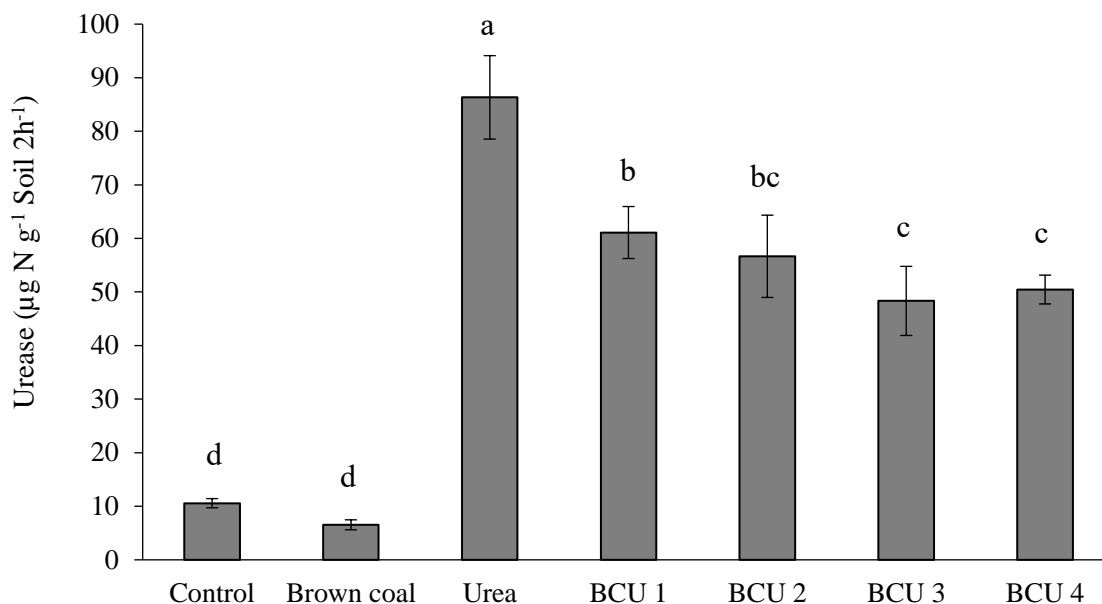


Fig. 6. Urease enzyme activity in soil 7 days after amendment with various N fertilisers (values are mean \pm standard error, N = 5)

3.5. Dissolution of N from BCU granules in water

Blending of BC with urea decreased the rate of N release into water compared to urea (Fig. 7A). In the case of urea, the release of N was very rapid and it reached almost 100% by day 3 of the incubation period. For the BCU granules, N release was delayed and after 14 days of incubation, only 73% of added N was released in water as urea-N. The BCU blends containing a higher proportion of BC content displayed lower and slower N release. A similar trend was also observed for the release of NH_4^+ -N from the granules. The release rate of NH_4^+ -N increased with increasing incubation time (Fig. 7B). No release of NH_4^+ -N was recorded for urea. The release of NH_4^+ -N for the granules indicates the partial hydrolysis of urea-N to NH_4^+ -N. No nitrate-N was released from either urea or from BCU granules during the incubation period.

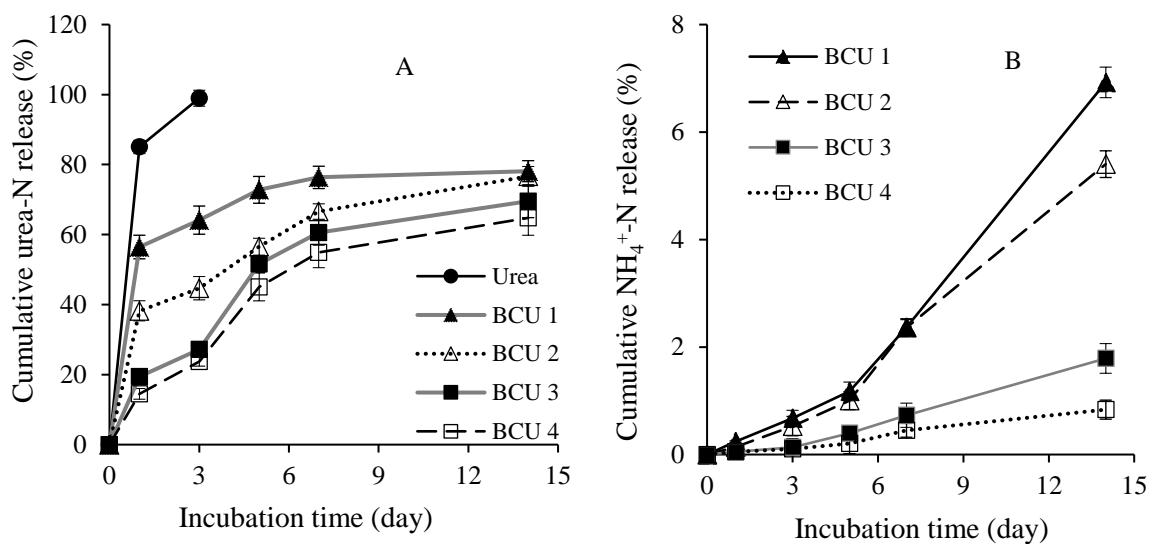


Fig. 7. Cumulative urea-N (A) and NH_4^+ -N (B) release in water from BCU granules and urea (values are mean \pm standard error, N = 5)

The delayed N release of N into water from the BCU granules supports the findings of Rose et al. (2016) who reported that granulation of BC with urea reduced the release rate of N in soil, resulting in N retention over a longer period of time. Importantly, our results show that after 14 days of incubation an average of only 73% of added N was released into water as urea-N from the BCU blends.

Evidence from FTIR, NMR and XRD structural analysis suggests that the remainder of the N was retained by BC either by strong physical adsorption or by ion exchange with the acidic functional groups of BC. This could include (i) adsorption of urea-N or NH_4^+ -N on the reactive surface area and polar functional groups of BC by hydrogen bonding, decreasing the mobility of N (Sun et al., 2016), and/or (ii) partial hydrolysis of urea, releasing ammonia subsequently captured and measured as ammonium. The lower retention of N by the high N granules appears to be a consequence of oversaturation of sorption sites

within the BC matrix. This effectively increases the surface area of the crystalline urea and would promote faster dissolution and N release in water. The release of NH_4^+ -N from the granules indicates the partial hydrolysis of urea-N to NH_4^+ -N, likely to be caused by natural acidity of the BC and/or the presence of urease from microbial activity inherent in the BC (Kim Thi Tran et al., 2015). The NH_4^+ -N can exchange onto carboxyl site of the BC, assisting in its retention in the soil. Overall, these findings provide strong mechanistic support for the development of BCU blends as a slow release fertiliser for better N retention in the plant-soil system. Therefore, BCU blends can be used as a slow release N fertiliser for better N retention in soil-plant system for a longer period of time. As a results, it is anticipated that addition of BCU blends may also increase N availability and its use efficiency to crop plants by decreasing its losses in the environment.

3.6. *Field experiments*

Addition of BCU granule and urea to soil caused a significant increase in the dry matter yield of canola compared to control treatment which received no N fertiliser (Fig. 8. A). No significant difference in the dry matter yield of canola was observed between the plots treated with urea and BCU 2. Nevertheless, N uptake by canola was substantially higher in plots receiving N fertiliser as BCU compared to other treatments including those receiving an equivalent amount of fertiliser N as urea (Fig. 8. B). No significant differences in the grain yield of wheat were observed between any treatments, but slightly increased grain yield was noticed with the increase in N application rate (Table 5). In contrast, significant variation in grain protein content was determined among the various treatments (Table 5). The increased application of N fertiliser increased the grain protein content of wheat.

Although no significant difference in grain protein content was measured between urea and BCU treatments at N application rate higher than 55 kg N ha⁻¹, while grain protein was significantly higher from plots receiving BCU compared to commercial urea when the N was applied at the rate of 37.5 and 20 kg N ha⁻¹. The increased grain protein and N uptake by plants fertilised with BCU granules might be due to increased N availability in soil for longer period of time, as has been previously observed under glasshouse conditions in a sandy soil (Rose et al., 2016). The field results here demonstrate the potential agronomic value of BCU fertiliser and justify further research into the dynamics of N release, transport and plant availability from BCU fertiliser in different soils under various environmental conditions.

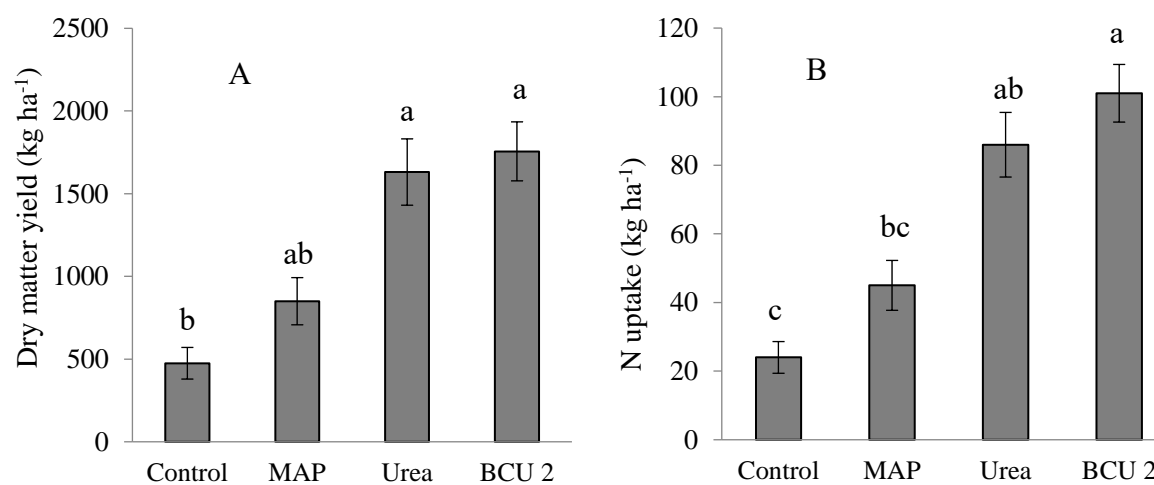


Fig. 8. Effect of BCU granules and urea on the dry matter yield (A) and N uptake (B) by canola (values are mean \pm standard error, N = 4)

Table 5

Effect of BCU granules and urea on the grain yield and protein content of wheat

Treatments	Yield (t ha ⁻¹)	Grain protein (%)
Control	5.43	9.4c
Urea (20 kg N ha ⁻¹)	5.53	9.4c
BCU 3 (20 kg N ha ⁻¹)	5.88	9.8b
Urea (37.5 kg N ha ⁻¹)	5.90	10.0b
BCU 2 (37.5 kg N ha ⁻¹)	6.03	10.5a
Urea (55 kg N ha ⁻¹)	6.08	10.5a
BCU 1 (55 kg N ha ⁻¹)	6.10	10.5a
Urea (75 kg N ha ⁻¹)	6.30	10.6a

4. Conclusions

Urea and BC were successfully blended and granulated using pan granulation technology. The granules formed were of an appropriate size and sufficiently strong for agricultural use. The loading of urea-N into BC was confirmed by FTIR, NMR and XRD characterisation. Granulation of urea with BC delayed the fertiliser N release, enhanced N retention in the granule and increased the moisture holding and retention capacity of soil compared to urea. Nitrogen retention increased concurrently with BC loading, emphasising the significant role of BC in N retention. Field experiments demonstrated increased N uptake by canola and grain protein content of wheat in BCU amended soil compared with the equivalent amount of N supplied in the form of urea. Based on the overall results and international fertiliser standards, BCU granules containing 8-17% N with a C:N ratio of 5.4

to 2.7 (i.e. BCU 3 and BCU 2 in this study) were shown to be the most suitable slow-release, enhanced efficiency N fertiliser for future research and application. This research has increased our understanding of how BC can be used as a substrate to develop improved slow release N fertilisers with a lower environmental hazard. Additional work is now necessary to study the effect of BCU granules on plant growth and N uptake in various soil types and under field conditions.

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