Front. Agr. Sci. Eng. 2024, 11(2): 326–343 https://doi.org/10.15302/J-FASE-2024571

RESEARCH ARTICLE

Biochar-compost-based controlled-release nitrogen fertilizer intended for an active microbial community

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KEYWORDS

Soil microbial community, biochar, compost, controlled-release nitrogen fertilizer, polylactic acid, spray coating.

HIGHLIGHTS

- Biochar-compost-based controlled-release urea fertilizer (BCRUF) pellets with an active microbial community were successfully synthesized.
- The releasing time of 80% N in BCRUF was 4–6 h in the water and 192 h (8 days) in soil.
- Processing parameters of BCRUF fabrication was influencing the microbe populations in the pellets.
- The BCRUF showed very promising characteristics to improve NUE and sustainability in agricultural production.

Received December 26, 2023;
Accepted April 25, 2024.

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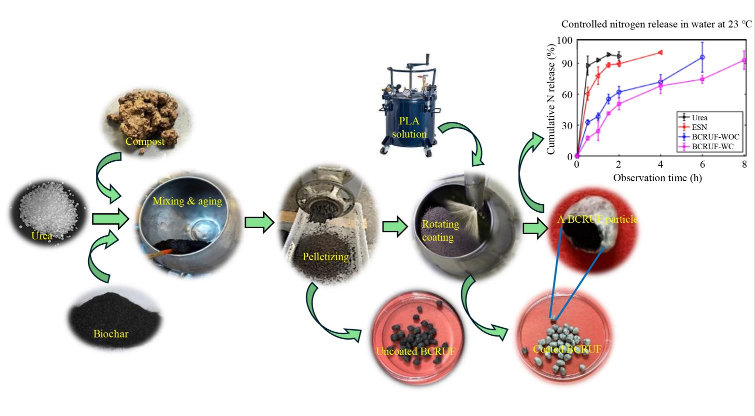
GRAPHICAL ABSTRACT



ABSTRACT

Nitrogen (N) fertilizers in agriculture suffer losses by volatilization of N to the air, surface runoff and leaching into the soil, resulting in low N use efficiency (NUE) (< 50%) and raising severe environmental pollutions. Controlled-release nitrogen fertilizers (CRNFs) can control the release of N nutrients to NUE in crop production. Different methods were used to develop new CRNFs. However, different CRNF technologies are still underdeveloped due to inadequate controlling on N releasing time and/or unsustainable diffusion. The study on the influences of CRNF processing parameters on microbial conditions are lacking when the CRNFs composed of various bio-ingredients such as biochar, composts, and biowaste. The complexity of processing methods, material biodegradability, and other physical properties make current CRNFs of questionable value in agricultural production. This research aims to develop a novel biochar-compost-based controlled-release urea fertilizer (BCRUF) to preserve microbial properties carried by the compost. The BCRUF was synthesized by pelletizing the 50:50 (dry, wt/wt) mixture of biochar and compost. BCRUF was loaded with urea and then spray-coated with polylactic acid (PLA). The releasing time of two types of BCRUFs, coated and uncoated with PLA, for 80% of N release in water was up to 6 h at three different temperatures (4, 23, and 40 °C), compared to conventional urea fertilizer and commercial environmentally smart N (ESN) fertilizer. The releasing time of coated BCRUF for 80% N release in soil was up to 192 h (8 days). Fourier-transform infrared spectroscopy (FTIR) analysis revealed that no new functional groups were found in the release solution, indicating no new chemical hazards generated. The differential scanning calorimetry (DSC) tests also verified that its thermal stability could be up to 160 °C. The microbe populations in the BCRUF pellets were reduced after the pelleting and drying processes in BCRUF fabrication, but a few bacteria can endure in the air-drying process. BCRUF pellets soaked in water for 4 days retained some bacteria. The BCRUF showed very promising characteristics to improve NUE and sustainability in agricultural production.

1 Introduction

Urea is applied in crop production to supplement nitrogen available to the crop from the soil. Standard prilled urea absorbs moisture quickly (generally in 24–48 h) and changes to ammonium bicarbonate[1]. In the field, the natural process resulting from the activity of the enzyme urease converts urea into ammonium bicarbonate. It is also vulnerable to losses like ammonia volatilization, leaching through soil particles, surface runoff and washing away of NO_3^- in water in different forms[2,3]. In water, ammonium cations tend to be converted to volatile ammonia[4]. Consequently, urea applied to the soil surface or plant foliage may lose over 50% N[4]. This incurs an economic loss for the growers and an adverse environmental impact on humankind in the atmospheric N cycle (climate change through N_2O emissions). Thus, the fertilizer industry is working on improving fertilizer N use efficiency (NUE)[5]. Modern fertilizer development attempts to invent ways to limit N losses to the environment, for example, through controlled-release N fertilizers (CRNFs). The fundamental principle behind CRNFs is to supply N nutrients to the crops to increase NUE and reduce N losses in the environment[6,7]. However, due to associated costs and lack of effective technologies, CRNFs represent < 1% of agricultural fertilizer applications[8].

CRNFs are a sustainable approach to nutrient management in agriculture. They are designed to release N nutrients gradually over an extended period using different methods. For example, polymer coated CRNFs consist of a polymer coating that controls the release of nutrients by regulating the diffusion rate of water into the granule, affecting nutrient diffusion from the granule[9]. Precise control is obtainable but comes at a higher cost, and the degradation of coating material is not sustainable. Sulfur-coated CRNFs provide nutrient control with environmental factors but are less accurate than polymer-coated CRNFs. Agricultural sustainability now demands new CRNFs that control N nutrient release with microbial and chemical activity[9,10]. Using biobased ingredients in fertilizer for chemical bonding to reduce N losses has attracted research attention. In recent years, biochar, a bio-ingredient derived from the pyrolysis of agricultural residues and/or wood wastes, has become a common ingredient for formulating new CRNFs[11]. Biochar is a carbon-rich product that is now commonly used for soil amendment and has some binding affinity that helps capture some ions in the soil[11,12]. Its surface functional groups (e.g., –OH and –COOH) trap the NH_4^+ ions from the fertilizers or soil and reduce the vaporization of the mineral fertilizer[10]. It also helps to neutralize soil pH and increases carbon sequestration. For this reason, it has recently been adopted as a bioeconomic fertilizer ingredient[12].

Applying biochar as a direct natural amendment is associated with reductions on spreading loss of 25% and a surface runoff loss of 20%–53%[13,14], but its powder may irritate human skin, eyes, and respiratory system[15]. Research found that using biochar as an additive to compound fertilizers creates a problem for granule preparation[8,16,17]. Adding secondary substances, such as starch[18], kaolin[15], and bentonite[16,19], can overcome this problem. However, adding starch can cause affinity for water molecules that will increase the N dissolve rate of the fertilizer. This ability comes from free –OH groups interacting with the glucose units and the water molecules. The –OH groups interact with water molecules by hydrogen bonding that may compromise the controlled-release characteristics[20]. Bentonite and kaolin, in contrast, enrich the soil with minerals that are not good for the long-term[6,10,13].

Thus, adding organic substances with biochar-based CRNF is now a focus of research as it has no negative impact on soil but is microbially beneficial, such as compost, manure, and biowaste[21,22]. These bio-substances are helpful for soil but do not replace mineral fertilizer use[23]. Also, using organic amendments can cause risks to human health if not appropriately managed[24]. Applying soil organic matter facilitates efficient biological nutrient cycling, which is crucial for successful soil management and agricultural productivity strategies for overcoming the negative effects of mineral fertilizer[25].

With the challenges that have arisen in combining mineral fertilizer and bio-substances, biochar and compost have been tried as a solution. The porous structure of biochar provides a large surface area for nutrient adsorption and is helpful for a stable microbial community. Being rich in carbon, biochar significantly contributes to soil carbon sequestration, which is important for the mitigation of climate change. Its neutral pH is useful in both acid and alkaline soils. Liu et al.[26] found that applying biochar reduces the use of organic and mineral fertilizers, improves agronomic traits and yield, and positively affects soil nutrients and microorganisms. Compost, in comparison, is rich in microbe, organic matter, and mixed nutrients. It can provide essential nutrients to improve soil structure. It contains a diverse range of microorganisms beneficial for soil and plant health. It can also buffer soil pH, making it conducive to plant growth in addition to its nutritional benefits[27]. Naeem et al.[28] studied its potential in a pot experiment, reporting a boost in maize yield with the combined application of biochar, compost, and fertilizer compared to these as individual treatments. Trupiano et al.[29] did a similar study on lettuce plants and reported that combining biochar and organic compost has a positive impact on soil biophysical and chemical characteristics that improved crop productivity over time. Liu et al.[30] and Agegnehu et al.[31] also reported the positive impact of combining compost with biochar for soil fertility improvement, with Agegnehu et al.[31] extending their research on maize yield response to greenhouse gas (GHG) emissions.

However, very little work was reported on combining biochar and compost on CRNFs, even though the benefits are already established and well known for crop yield improvement. Based on the state of the arts using biochar and compost combined in CRNFs[28–31] in literature, this study was motivated by the emerging picture of biochar and compost mixes with mineral fertilizers (e.g., urea) to make new CRNFs. Mixed ingredients were pelletized as a novel fertilizer. The newly formulated biochar-compost-based controlled-release urea fertilizer (BCRUF) was coated with the biodegradable polylactic acid (PLA) solution to enhance its controlled-release characteristics.

This research compared the N nutrient release from coated and uncoated BCRUF (BCRUF-WC and BCRUF-WOC) at three different temperatures (4, 23, and 40 °C) and then compared the results with two commercial mineral fertilizers, urea and an environmentally smart N (ESN) fertilizer in water. The physical characteristics of the BCRUFs were also tested to explain their functions, such as water absorption and retention properties, biodegradability in soil burial and surface tests. The BCRUF microstructures and surface morphology were analyzed using scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), and other instruments. Microbial analysis was carried out to assess the microbial community that remained in the BCRUFs after pelletizing and drying at 23 ± 2 °C. The active microbial community in BCRUF fertilizer is an aspect of CRNF characteristics that have not previously been quantified. This research provide helpful information to improve NUE, reduce mineral fertilizer use, and sustainability in agricultural production.

2 Materials and methods

2.1 Materials

This research used the biochar derived from oat hull pyrolysis at 500 °C, which was purchased from Advanced Renewable Technology International, Inc., Des Moines, IA, USA (bulk density 178 $kg \cdot m^{-3}$). The particle size distribution was 0.5–2 mm for 90% biochar. This biochar was ground in a milling grinder and screened to a particle size of less than 0.45 mm. The organic carbon content, nitrogen content, ash content, and pH of the biochar were 78.7% (wt/wt), 0.71% (wt/wt), 4.38% (wt/wt), and 7.55, respectively. The compost was provided by a local farmer in South Dakota, USA. The main ingredients for the compost were woodchips, grass, and yard-plant stalks. The mixture of biochar-compost 1:1 (dry, wt%) was prepared using a rotary drum in the Biomaterials and Bioprocessing laboratory (BBL) at South Dakota State University (SDSU). This thoroughly mixed blend was kept in a plastic box covered with a black plastic bag for two weeks to allow microorganisms to uniformly colonize in the mixture. The commercial urea (46.7% N; 99% pure commercial grade) was purchased from Duda Energy LLC, Decatur, AL, USA for loading into the biochar-compost mixture. Granular PLA pellets were purchased from Solutions of Consequences LLC, Grand Rapids, MI, USA, and then dissolved in chloroform to prepare a 5 wt% of PLA solution as a coating material. The viscosity of the spray solution was 83 mPa·s, which was determined using a rotary viscometer (US Solid, Cleveland, OH, USA). The moisture contents of biochar, compost, and PLA pellets were found at 6.9%, 62.3%, and 0.3%, respectively, after analyzed using oven-dry methods. BCRUF pellet preparation and coating were done at room temperature (23 ± 2 °C) in the BBL. All chemical reagents under consideration were of analytical grade, and all measurements were repeated triplically.

2.2 BCRUF preparation

Figure 1 shows the flowchart of the new BCRUF preparation process. After receiving the compost, the debris and unwanted impurities that were not biodegradable, including any plastic or stone, were removed. Big soil molds were crushed into small particles. A ratio 1:1 (dry, wt%) of biochar to compost was mixed in a rotary pan for an hour. Afterward, the mixture was put in a plastic box for two weeks. After two weeks, 150 kg urea was mixed with 64.3 kg biochar compost in a rotary pan with water. Mixing continued for 1 h at 80 $\text{r}\cdot\text{min}^{-1}$ and then transferred to plastic containers. Plastic containers were kept uncovered in the laboratory. When the moisture of the mixture reached 20%, it was put again in the rotary pan for mixing as few crystals were produced during drying. Afterward, a commercial pelleting machine extrudes the mixture into pellets 2 mm round by 3–5 mm long. The process used standard industrial equipment to replicate industrial practices in fertilizer manufacturing. The undersized pellets were crushed and returned to the drum. The BCRUF pellets were dried at room temperature until the moisture level reached below 1%.

Only dry BCRUF pellets were coated. A customized spray coating setup was made for spraying 5% PLA solution (wt/wt) in the rotary drum. Initially, the rotary drum was loaded with 54 kg BCRUF pellets. A 20-L pressure tank (commercial spray paint pressure vessel with air powered mixing agitator, TCP Global, San Diego, CA, USA) full of PLA solution was connected to a spray gun (Syphon Spray Gun 79SG012, Guardair, Chicopee, MA, USA). The spray arrangement was adjusted to apply 9.1 $\text{kg}\cdot\text{h}^{-1}$ of 5% (wt/wt) PLA solution. During PLA spraying, the drum continuously rotated at a constant speed of 50 $\text{r}\cdot\text{min}^{-1}$. Occasionally, a hair dryer (1000 W) was used to heat the drum to hasten solvent evaporation. The spray lasted a few hours, then the pellets were removed from the drum and air-dried for a week to fully evaporate the solvent. Afterward, the pellets were reweighed to calculate the coating content (%).

2.3 Structural stability, buoyancy and strength of BCRUF pellets

Before other tests for the BCRUF pellets, coating content was determined for a BCRUF-WC sample. The coating content was measured on a weight percentage basis. Since the applied coating layer was too thin to separate it from the pellets the method of Rubel & Wei[17], Yu & Li[32] and others was used for determining coating content. Specially, 30 identical-sized pellets were carefully selected from BCRUF-WOC and BCRUF-WC batches and weighed separately to determine the weight difference after coating. The coating content (wt%) was calculated as:

$$\text{Coating content} = \frac{m_{\text{wc}} - m_{\text{woc}}}{m_{\text{woc}}} \times 100\% \qquad (1)$$

where, m_{wc} is the weight of 30 BCRUF-WC pellets and m_{woc} is the weight of 30 BCRUF-WOC pellets.

The protocol of Dubey & Mailapalli[33] was used to determine the structural stability of the BCRUF pellets in laboratory experiments. About 2 g BCRUFs were soaked in 100 mL deionized water for about 24 h, and the shape (deformation) of the pellets was observed. The start of distortion indicates the collapse of structural stability. Buoyancy was estimated using the techniques utilized in a patent CN111094215A[34]. About 300 BCRUF-WOC and BCRUF-WC pellets were scattered in an open bowl with 2 L of water, so the pellets had sufficient room and did not overlap on the water surface. Floating pellets were moved from the water surface after 1 min and counted.

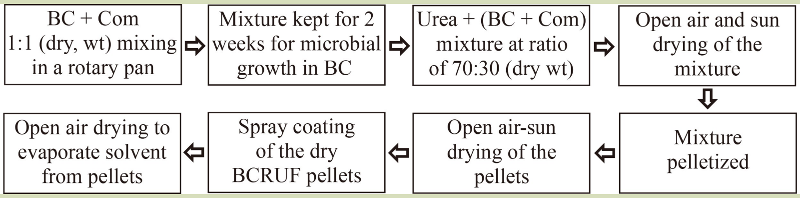


Fig. 1 Flow chart of the BCRUF-making process using urea, biochar (BC) and compost (Com). BC and Com were mixed initially and kept for microbial growth, and then urea was combined with the mixture. The air-dried mixture was pelletized to make BCRUF.

The flotation was calculated and expressed as floating pellets (%). A higher number of pellets floating indicates easy buoyancy and likely chances of being quickly washed away in surface runoff.

For activities including material handling, storage, and spreading, fertilizer pellets must have sufficient strength[35]. In the storage, pellets are in contact with one another, so any crack in the pellets could result in caking. The strength of the pellets was estimated using the method described by Walker et al.[36]. The crushing force required for the pellets can accurately define the mechanical strength. The texture profile analyzer (Stable Micro Systems Ltd., Godalming, Surrey UK) was used to calculate the maximum crushing force needed to break the BCRUF pellets as their strength. Single pellets were placed under a 25-mm probe that moved with a speed of 10 mm·s^{-1}.

2.4 Nitrogen release patterns from BCRUF pellets

The N release patterns for the BCRUF pellets were determined by the protocol of Trinh et al.[7]. BCRUF-WOC, BCRUF-WC, urea, and ESN (Nutrient US LLC, Loveland, CO, USA) were added to the glass bottle containing 1.8 L deionized water. Placing the pellets in the water simulated the worst-case scenario for a fertilizer that may occur in the actual field, as previously described[8,37]. Ten mililiter water samples were collected from the glass bottle at set time intervals over 48 h. After sampling, each bottle was topped with the same amount of fresh distilled water. The N concentration in the water was determined by a simplified Kjeldahl method using a DR3900 spectrometer (320–1100 nm)[38]. Total N release (considering some vapor loss) curves were obtained as the cumulative release percentage versus time. Each test was repeated three times at three temperatures: low temperature (4 °C), room temperature (23 ± 2 °C), and elevated temperature (40 °C).

A soil column leaching test was performed to determine the N release profiles for BCRUF-WOC and BCRUF-WC compared to commercial urea and ESN described by Shi et al.[39]. Soil columns were arranged using nontransparent polyvinyl chloride pipes of 75 mm in diameter, with closing and opening options for leachate (Fig. 2). The bottom of the pipe was fitted with a hollow round cup that had a steel screen (i.e., a standard domestic sink stainer). The bottom of the tubes was filled with a 38-mm layer of quartz sand (> 1.2 mm) and rinsed with water to clean the inside of the pipe and the sand layer. Tubes were filled with around 6.8 kg of loosely packed loam (66.6% coarse sand and 4.5% clay) up to 380 mm. Fertilizer equivalent to 1.5 g N were placed in a 50-mm depth under the soil surface inside the columns. Treatments for this test included soil urea, ESN, BCRUF-WOC, and BCRUF-WC, and no fertilizer as a control. Each column was evenly filled with 100 g loam and 50 g sand (> 1.2 mm). On the first day, columns were wet to the predetermined water holding capacity of the soil (i.e., 550 mL).

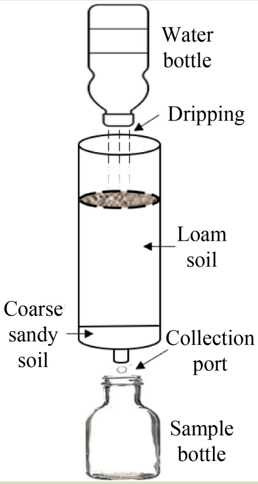


Fig. 2 Schematic of the leaching test column. The column had a coarse layer below 380 mm of test loam. A water bottle was inverted at the top of the column to apply 250 mm of precipitation by dripping.

During tests, the soil columns were rinsed with 250 mm·h^{-1} (~1 L water in 40 min) with a dripper attached to a plastic bottle and placed as shown in Fig. 2. The irrigation rate used was close to the summer precipitation in South Dakota, USA[40]. Every 4 days, leachate from each column was collected from the bottom of the column. The total leachate volume was recorded, and 10 mL samples were frozen with light in small plastic. All samples were centrifuged at 5000 r·min^{-1} for 10 min before being tested for N concentration by the photo spectrometer.

2.5 Water absorption and retention of BCRUF pellets

The rate of water absorption of BCRUF pellets was estimated using the method described by Cen et al.[8] using at 100% RH at room temperature. Oven-dried samples (2 g) of BCRUF-WOC, BCRUF-WC and ESN were placed inside a sealed bottle with water at the bottom. These sealed bottles had 100% RH at the water surface. A total of 36 bottles were prepared with samples for each type of fertilizer. Three bottles were opened at the particular observation time to weigh the pellets until the pellets became swollen. This is the maximum water absorption capacity under a fully saturated condition without any distortion of the pellet shape. The absorption (wt/wt) of each sample at different times was calculated using as:

$$\text{Water absorption} = \frac{m_w(t) - m_d}{m_d} \times 100\% \tag{2}$$

where, m_d and $m_w(t)$ represent the dry and partially water-saturated mass of the pellets at time $t = 0$ to $t = t$ equilibrium, respectively.

The water retention for BCRUF pellets was measured using the method described by Tarafder et al.[41]. A mixture of topsoil sieved to 0.7 mm mesh and oven-dried at 80 °C for 48 h was mixed with BCRUF-WOC and BCRUF-WC to determine water retention. 5 g of BCRUFs were mixed thoroughly with 100 g dried soil, then wet with 100 mL deionized water and mixed thoroughly by shaking. The bottles were weighed and kept at room temperature. As the water evaporated, the total weight of the bottle decreased. The bottles were reweighed every 3 days for a month. Each percentage water retention ratio was calculated as follows:

$$\text{Water retention} = \frac{m_t(t)}{m_i} \times 100\% \tag{3}$$

where, m_i and $m_t(t)$ are the weight of the bottle at time $t = 0$ and $t = t$, respectively.

2.6 Biodegradability of BCRUF pellets

The biodegradability of BCRUF pellets was tested by two different methods. The first was the surface pouch biodegradability test described by Carson & Ozores-Hampton[42] using nylon pouch bags 5 cm × 5 cm with a 50% opening. Ten gram of each BCRUF and ESN sample were placed in the bags and laid in the greenhouse soil bed at 6 cm spacing with sufficient bags for three replicates for each observation time. Water was applied by sprinkling every 3 days at a rate equivalent to 150 mm of precipitation. Observations were made weekly for 5 weeks. The greenhouse was maintained at 25 °C and ~65% RH. The second biodegradability test was a soil burial test in the field under natural conditions at South Dakota State University Research Farm in the Volga site from 12 June to 20 July, 2022. Pouch bags containing 5 g of each sample were buried under 4 cm of the soil and marked with flags. The bag weight was recorded weekly for 5 weeks after recovery from the soil. The weight loss between the initial (m_b) and final ($m_f(t)$) sampling times were used to calculate biodegradability as:

$$\text{Biodegradability} = \frac{m_b - m_f(t)}{m_b} \times 100\% \tag{4}$$

2.7 Caking and dustiness

Caking or fertilizer agglomeration is a problem for industrial fertilizer production and storage[36]. This occurs due to several internal mechanisms of fertilizer or environmental issues. BCRUF pellets capability to retain in the original state without caking was tested by taking BCRUF-WOC and BCRUF-WC for 9 months in a closely packed 1-L glass bottle. The status of the pellets was checked from the outside of the bottle. This was likewise done for boxes of pellets (~23 kg) in the laboratory. Dustiness of 6.8 kg of BCRUF-WOC and BCRUF-WC in separate experiments was assessed with a rotary drum pan rotated for 30 min as Suherman & Anggoro[43]. Any dust formed was screened using a vibratory seed cleaner (80W, 110V, 3 mm screener; Victor Farm Machinery, Henan, China).

2.8 SEM, differential scanning calorimetry, and FTIR analysis

The thickness of the coating layer controls the diffusion rate of the CRNFs. It is essential for determining the release rate in contact with soil. The surface morphology of the cross-sectional fertilizer pellets was studied using SEM (Hitachi S-4700, Tokyo, Japan). BCRUF pellets were cut in half with a sharp knife and coated with a thin layer of gold to prevent charging under the electron beam. A differential scanning calorimetry (DSC) analysis was carried out to analyzed thermal properties of the BCRUF using a PerkinElmer DSC 600 (Waltham, MA, USA) with a 20 $\text{mL}\cdot\text{min}^{-1}$ nitrogen. Ten milligram of the sample was weighed and sealed in an aluminum pan. The initial temperature was set to 20 °C, held for 1 min, and then heated to 425 °C with 10 $°\text{C}\cdot\text{min}^{-1}$ increments. FTIR was performed to observe the functional group in the raw material biochar, compost, and final fertilizer product. As powder, these were separately pelleted and pressed in the sample holder to measure the infrared spectra using Nicolet 6700 FTIR (Thermo Scientific, Waltham, MA, USA) to identify the contained compounds.

3 Results and discussion

3.1 Characteristics of the spray solution

The 5% (wt/wt) PLA solution was a semitransparent white liquid. The PLA takes 24–48 h to dilute in the solvent chloroform at room temperature. The solution was thick and sticky and quickly attached to the BCRUF surface. This coating material is reported[44] to be biodegradable and can create a suitable diffusion layer over the fertilizer pellets. The solidification of the made PLA solution depends on how fast the solvent evaporates, which can happen at room temperature and quicker at elevated temperatures. Figure 3 shows the DSC spectrum for the PLA. A specific change on the baseline at around 45 °C shows the transition glass temperature of PLA. The melting point of about 15 °C represents the fusion of the crystalline domains in the PLA chains. The thermal decomposition of PLA started at around 300 °C and ended at 370 °C. The FTIR spectrum in Fig. 4 shows characteristic absorption bands of PLA. For instance, the bands at 870 cm^{-1} attributed to the carbon-carbon bonds in the PLA backbone, methyl group vibration at 2944 cm^{-1} , and sharp peaks related to carboxyl group vibration in 1740, 1093, and 1182 cm^{-1}[35]. PLA coating exhibits less susceptibility to bursting effects than other inorganic-based coating materials derived from sulfur and minerals[43]. This attribute makes it more synchronous with the demands of plants.

3.2 Structural stability, strength, and buoyancy of BCRUFs

The structural stability and strength of BCRUFs confirm their capacity to sustain the manufacturing, application, and post-application processes. BCRUF pellets were coated and rotated continuously in a rotary pan for several hours. During coating, the pellets retained their original shape throughout the coating process. A negligible amount of dust was found as residue after the screening. This indicates dry structural stability for the pellets for both BCRUF-WOC and BCRUF-WC. BCRUF-WOC and BCRUF-WC pellets absorbed water quickly and were immersed in water at the bottom of the bottle. After 24 h, the pellets remained undistorted. The same process was repeated by placing the bottle in an incubator at room temperature but shaking it at 50 r·min^{-1}, which dispersed the BCRUF-WOC in 20 min and partially BCRUF-WC in 4 h. Complete dispersion of the coated fertilizer did not occur because of the network structure of the coating layer covering the fertilizer pellets.

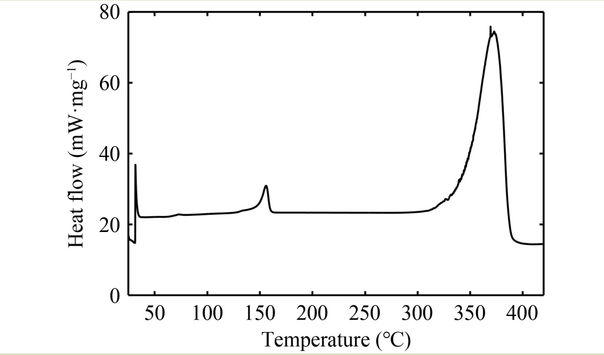


Fig. 3 Differential scanning calorimetry spectrum of polylactic acid solution showing the melting point above 150 °C and thermal decomposition initiated after 300 °C and ended at 370 °C.

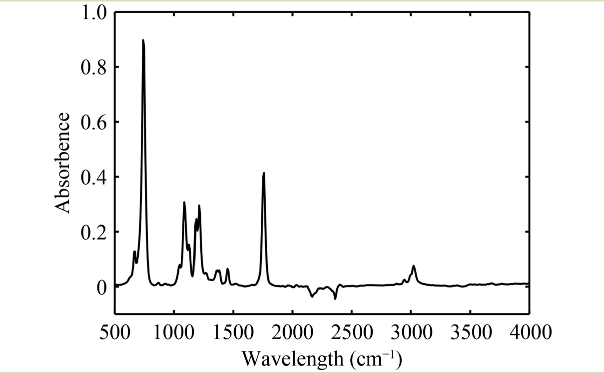


Fig. 4 Fourier-transform infrared spectroscopy spectrum for spray solution material spectra showing absorption bands of polylactic acid (PLA). The bands at 870 cm^{-1} attributed to the carbon-carbon bonds in the PLA backbone, methyl group vibration at 2944 cm^{-1}, and sharp peaks related to carboxyl group vibration in 1740, 1093, and 1182 cm^{-1}.

For BCRUF-WC, the coating content was 3.44% (wt/wt). Also, the compression test was performed to measure particle strength to understand the structural strength (Fig. 5). BCRUF-WOC and BCRUF-WC have strengths above 150 N with no significant difference. This is likely due to the amount of coating contents (3.44%, wt/wt) on BCRUF-WC pellets. Hofstee & Huisman[45] studied the fertilizer handling, transportation and spreading characteristics and stated that fertilizer pellets should have a compressive resistance of at least 15 N. However, BCRUF-WOC and BCRUF-WC have significantly different strengths than the commercially available ESN. Since the strength of BCRUF pellets was greater than the strength of ESN, BCRUFs should sustain mechanical handling as well as ESN. This strength is also higher than that of the strength found by Rubel & Wei.[16] and Walker et al.[36] for similar coating contents. Hofstee & Huisman[45] also discovered that the physical properties of fertilizer depend on the production process and additives such as conditioners. In this research, the pelletizing machine contributed to making such strong pellets.

The visual estimation of buoyancy showed that 100% of pellets for BCRUF-WOC remain floating in the water. In comparison, 95.3% of pellets from BCRUF-WC sank. BCRUF-WOC absorbs water more quickly than BCRUF-WC. Gaining weight helps pellets remain in position in the actual field, preventing

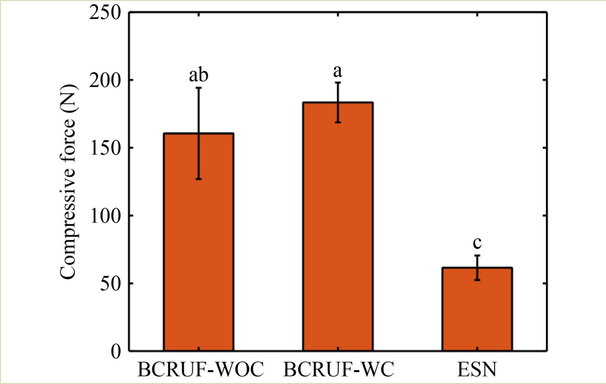


Fig. 5 Strength of the BCRUF-WOC and BCRUF-WC in comparison to ESN. The strengths of the BCRUF-WOC and BCRUF-WC are not significantly different, but they are significantly stronger from ESN.

wash away. BCRUF-WC was comparatively slower in absorbing water, and the PLA coating layer works as a foam layer to create some buoyancy that might cause a tendency to be washed away by the water. This phenomenon indicates the possibility of washing the coated pellets away with water. However, buoyancy would allow fertilizer to release gases directly into the air rather than entrapping them into water or soil. It is also helpful for controlling release, and the residue nutrient will remain inside pellets[46].

3.3 Nitrogen release patterns of BCRUF pellets

The N release study is related to analyzing nutrient release patterns of the synthesized BCRUF-WOC and BCRUF-WC. For PLA spray-coated BCRUFs, the number of cracks and pin holes is significant in controlling the rate of N release. The analyses were performed at three temperatures to see the effect of temperature on the release pattern by water immersion (Fig. 6) and soil column leachate test (Fig. 7) at room temperature. At room temperature (23 ± 2 °C), the N release in water from BCRUF pellets was slower than urea and ESN. More than 80% N diffused from urea and ESN in 0.5 h. Meanwhile, BCRUF-WOC and BCRUF-WC took 2 and 4 h to reach the 80% release. BCRUF-WC has the benefit of release control achieved by the coating layer in all three temperatures. Its release was always slower compared to other samples. Zhang et al.[47] reported that urea-loaded sawdust biochar with more than 80% urea release in 4 h. The release obtained by

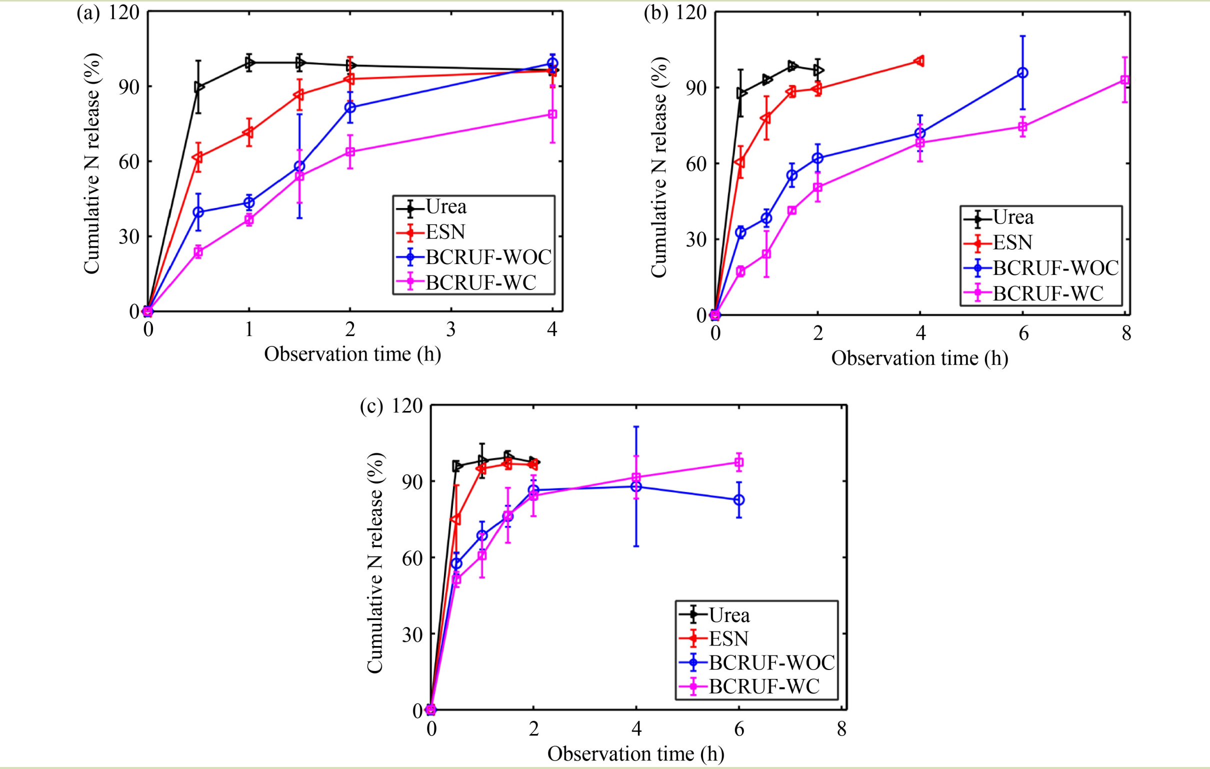


Fig. 6 Nitrogen release characteristics at three temperatures: (a) room temperature (23 ± 2 °C), (b) 4 °C, and (c) 40 °C. The release rate of BCRUF-WOC and BCRUF-WC at 4 °C was slower than at room temperature and 40 °C.

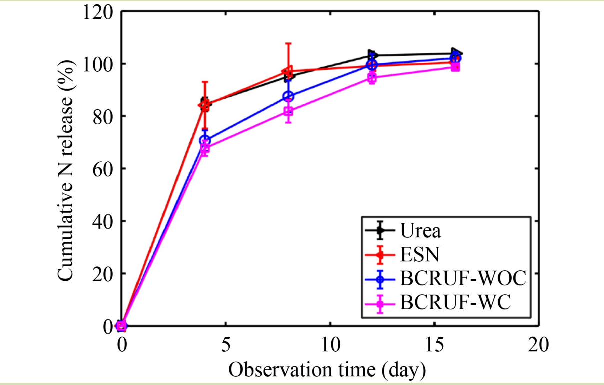


Fig. 7 Nitrogen release characteristics in the soil leaching test. The soil columns were rinsed every 4 days. BCRUF-WC controlled-release 8 days for 80% of the total N release.

Rubel & Wei[16] for biochar-based fertilizer was also quicker and faster than the BCRUF in this research.

In soil, the release of nutrients is much slower than in the water emersion test (Fig. 7). After saturating the columns with water, N release starts immediately N defused from the pellets into the soil. By day 4, urea and ESN had released about 84% of their N. By day 8, the remaining N had been released. No significant difference was observed between ESN and urea regarding release profile. The same phenomenon was observed for BCRUF-WOC and BCRUF-WC. By days 4 and 8, the N release for BCRUF-WOC was 70.6% and 87.5%, respectively. BCRUF-WC had released 67.7% and 81.8%, which is not significantly different from BCRUF-WOC. A soil column test by Shi et al.[39] showed that after 10 days, N release was less than 80%, but their rinsing rate was 3 mL·min^{-1}, which was considerably lower than the 25 mL·min^{-1} rinsing rate in the present study.

3.4 Effect of temperature on nitrogen release from BCRUF pellets

Urea is readily soluble in cold and hot water, so it tends to absorb moisture. At 40 °C, the N release for BCRUF-WOC was almost the same as at room temperature. After 2 h, it released around 90% N, indicating that the temperature did not impede N release from the uncoated pellets. For the coated BCRUF-WC pellets, the release at 40 °C was faster than at room temperature. Eighty percent of N was released after less than 2 h. The influence of the water convection might explain this variation in the N release profile relative to temperature. In general, elevated temperature accelerates the process of urea diffusion, and likewise for N release. Higher temperatures may enhance the breakdown of organic compounds like biochar and compost in the fertilizer, facilitating the release of nitrogen in forms more readily available for plant uptake[48]. Also, the glass transition temperature of PLA is around 45 °C, as shown by the DSC analysis. The polymeric chains are more flexible at this temperature and could have facilitated this diffusion.

Also, all samples under consideration had an accelerated release rate at 40 °C and a slower rate at 4 °C. For the low-temperature measurements (4 °C), the sample bottles were placed in the refrigerator, which reduced the convection of water and the diffusion rate of urea at the molecular level. The same experience is expected in the soil matrix. An elevated temperature also promotes N volatilization, leading to faster gaseous loss of N from BCRUF pellets. Urea and ESN release profiles did not demonstrate a significant difference from the release at 23 °C, as shown in Fig. 6(b). BCRUF-WOC and BCRUF-WC showed a slightly slower release at 4 °C, taking around 5 and 7 h to reach 80% N release, respectively. This can be attributed to the diminished tendency for chemical reactions, which subsequently slow the diffusion rate and the likelihood of gaseous volatilization. Since the BCRUFs are a mixture of biochar and compost and both ingredients are hydrophobic, low temperatures have reduced molecular interactions, resulting in the benefit of N control. The combined use of compost and biochar also produces synergisms that reduce N movement by capturing it inside pellets by organomineral stabilizing the fertilizer pellets. At low temperatures, molecular and rapid diffusion usually occurs[49]; the moisture absorption of the fertilizer pellets is influenced by the molecular processes occurring in front of the advancing liquid front. A temperature of 4 °C does not cause freezing of the water molecules, allowing easy transportation of the N from the fertilizer pellets.

In summary, the BCRUF samples demonstrated a significantly slower release in water compared to urea and ESN treatments in all three temperatures studied. The effect of the coating on the N release properties was more evident at lower temperatures (4 and 23 ± 2 °C). However, the difference in release times between coated and uncoated BCRUF was small at these temperatures. The non-uniformity of the coating layer can explain this. The holes in the coating layer (as evident in the SEM analysis) allow the water to penetrate quickly into the fertilizer core, facilitating the dissolution of urea. Thus, the coating process should be optimized to achieve better results.

3.5 Water absorption and retention of BCRUF pellets

Water absorption and retention of fertilizer can efficiently help manage soil moisture and reduce water consumption in the field. Under 100% RH, the BCRUF pellets were saturated with water after 18 h. BCRUF-WOC and BCRUF-WC did not differ in their water absorption (Fig. 8). Using PLA as a coating material results in a thin, flexible solid layer covering the pellets, which did not alter the water absorption or retention characteristics of the BCRUF pellets. For urea and ESN, this test was not possible as they absorbed water too quickly and liquified in relatively low humidity, which would result in the easy caking of uncovered urea and ESN and represent a problem for production and storage.

The water holding capacity of BCRUF-WOC and BCRUF-WC pellets was 27.0% and 24.5%, which was more than ESN. Therefore, BCRUF pellets can potentially improve the soil moisture holding capacity and reduce moisture loss from soil. In the water retention test, control soils that were not mixed with BCRUF pellets reached 44.6% moisture after 28 days (Fig. 9), whereas the moisture of soils with BCRUF-WOC and BCRUF-WC mixture were 47.3% and 48.2%, respectively, after 28 days. This is likely due to the porous structure of biochar that traps water molecules. Though not significant in the present study, the coating of fertilizers might help retain more moisture in the soil, as reported by Rubel & Wei[17] and Liu et al.[50]. A more pronounced effect on water absorption and retention was also found in the present study compared to previous research[8,17,50,51].

Among the ingredients used for making BCRUF-WOC and BCRUF-WC, biochar has a high surface area ($273\ g\cdot m^{-2}$) and porous structure that enables it to absorb and retain water within the soil. Mao et al.[52] report this for a biochar-based fertilizer, similar to the BCRUF pellets assessed in the present study. They found that when exposed to moisture, water molecules adhere to the surface of biochar pellets. Infiltration through the porous network through capillary action also extends water holding capacity. Compost reduces soil crusting, which helps with water absorption and penetration into the soil. Also, the polymer network of PLA did not significantly affect water absorption or retention despite the PLA itself being hydrophobic. The discontinuous nature of the coating, as shown in the SEM analysis, might be the reason for this effect.

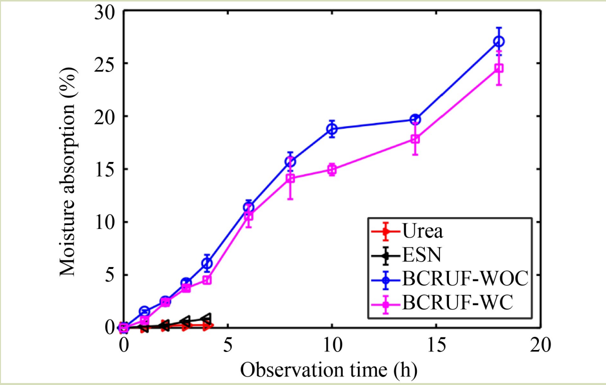


Fig. 8 Water absorption of test fertilizers at room temperature. Urea and ESN (environmentally smart nitrogen) absorbed moisture quickly compared to the WCRUF-WOC and BCRUF-WC.

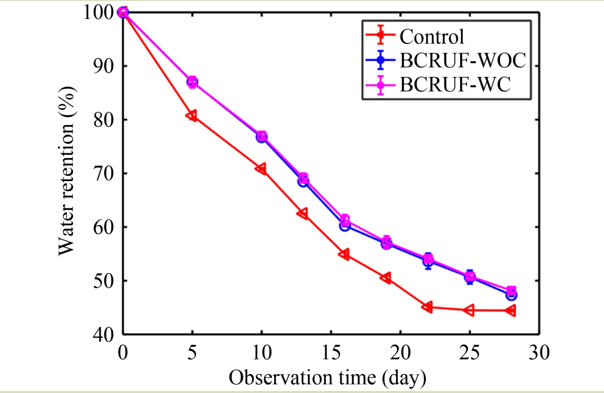


Fig. 9 Water retention of soil with and without BCRUF pellets at room temperature.

3.6 Biodegradability, caking, and dustiness of BCRUF pellets

Biodegradability assessment is essential for polymer-coated fertilizer (PLA in this case) to validate agricultural sustainability. The polymer shell that remains after a specified period is deemed toxic to the soil. On the surface, ESN was found to vanish after one week. In contrast, BCRUF-WOC and BCRUF-WC lost about 38% of their mass (by biodegradation) after 2 weeks, as shown in Fig. 10, but after 4 weeks, it was 78% and 67%, respectively.

Ketabchi et al.[53] observed 0.6%–3.7% decomposition in the first 30 days for a similar type of PLA-coated fertilizer. This indicates that the decomposition in the present study was faster and may have been enhanced by the core ingredients (e.g., biochar and compost) of BCRUF. In the soil burial test, BCRUF-WC lost 64% of its weight in 2 weeks and 72% by 4 weeks. The initial weight loss was quicker and became slower. The rapid mass loss occurred in the first 3 weeks as a significant portion of the urea diffused. The tests were terminated after 4 weeks as pellets became difficult to identify.

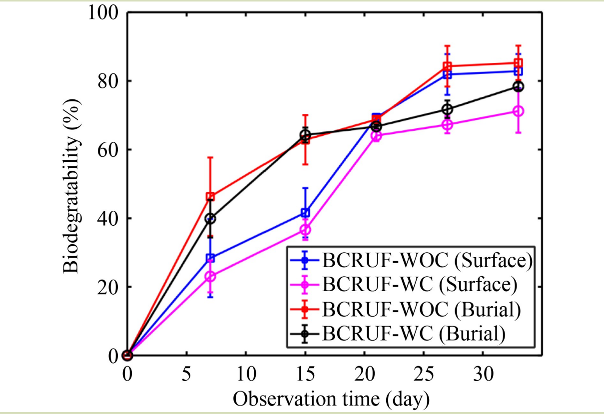


Fig. 10 Soil surface and subsurface biodegradability for the BCRUF-WOC and BCRUF-WC pellets. The weight-based biodegradability in the case of soil burial was faster than in the surface test.

In the burial tests, moisture comes into contact with pellets sooner. Thus, N leached from the pouch bags, but the pellets retained their shape. With time, microbial action, and moisture degraded the pellets. Therefore, the BCRUF-WC will completely degrade into micro components within 5–6 weeks after application.

During the observation of the pellets in glass bottles and storage boxes for 9 months, no caking or the tendency of caking was seen. This indicates the suitability of BCRUF-WOC and BCRUF-WC for storage and transport, and no further treatment is needed for caking prevention. BCRUF-WOC produced 27 g·kg^{-1} dust, and BCRUF-WC produced 7 g·kg^{-1} dust, which is negligible. Low dustiness is also favorable for preventing the caking of fertilizers.

3.7 SEM, FTIR, DSC analysis of BCRUFs

The SEM images of the cross-section of the BCRUF-WC pellets are given in Fig. 11. The microstructure of the standard biochar appeared in Fig. 11 with some clusters of urea molecules (highlighted in the figure). Biochar structure can vary depending on the feedstock used in the pyrolysis process. The biochar used in the present study had a porous structure with macropores and micropores (Fig. 11). Figure 11 indicates macropores about hundreds of micrometers in diameter that are believed to positively affect N release control and retention of water by holding these in the voids of the structure. The biochar used appeared to have no large clusters of micropores.

The outer solid layer of the coating created a smooth layer over the fertilizer core. The shallow spaces in the cross-sectional view also might be from the compost as it was not finely powdered and contained many small wood chips, broken nuts and nutshells, as evident in Fig. 11(b), a photo of the surface of a fertilizer pellet. The black spots are non-covered areas. The PLA coating had some holes and aggregates, which would have resulted from the coating process and solvent evaporation. Since compost and biochar ingredients at the microscopic level are similar, they are not distinguishable in the cross-sectional view.

Figure 12 shows the FTIR spectra for urea, compost, biochar, and BCRUF. The urea and BCRUF spectra have similar absorbance bands, indicating that no new functional groups were incorporated into the BCRUF. The characteristic NH_2 stretching vibrations of urea at bands around 3433, 3325, and 3255 cm^{-1} were evident in BCRUF spectra, meaning that urea features dominant over biochar[54]. The broad band between 3400 and 3500 cm^{-1} in the compost spectrum indicates the presence of –OH groups, but in the BCRUF sample, it seems to overlap with the NH_2 vibrations[42]. The peak at 2360 cm^{-1} in the biochar, compost, and BCRUF samples corresponds to the stretching vibration of aromatic C=C[49]. The 1481 and 1172 cm^{-1} peaks can be related to C–N axial deformation[55]. The biochar spectrum showed no characteristic absorption bands of functional groups such as acyl, carboxyl, or hydroxyl. It is evident that in this research, no modifications were made to the biochar that would reduce its capacity to absorb ions and protect the microorganisms.

Figure 13 shows the DSC curves for pure urea, ESN, BCRUF-WOC, and BCRUF-WC. For pure urea, the melting point started at 145 °C and ended at 180 °C, with the peak at 166 °C. For ESN, BCRUF-WOC, and BCRUF-WC, the melting point shifted to about 119 °C, ending at 149 °C, and peaking at 141 °C. Pure urea started to degrade at 200 °C, ESN at 171 °C, and the BCRUFs at 160 °C. This behavior shows that the coated samples were less thermally stable than pure urea. However, the BCRUFs had thermal properties similar to ESN.

3.8 Effect of biochar and compost in nitrogen release

Biochar and compost, the main two ingredients of the BCRUF, can impact the N release dynamics of the fertilizer pellets. The functional groups in biochar are aromatic and heterocyclic carbons. These groups are stable due to their stable chemical structure[56]. Production of BCRUF-WOC did not introduce any new form of bonding or functional group that affects the

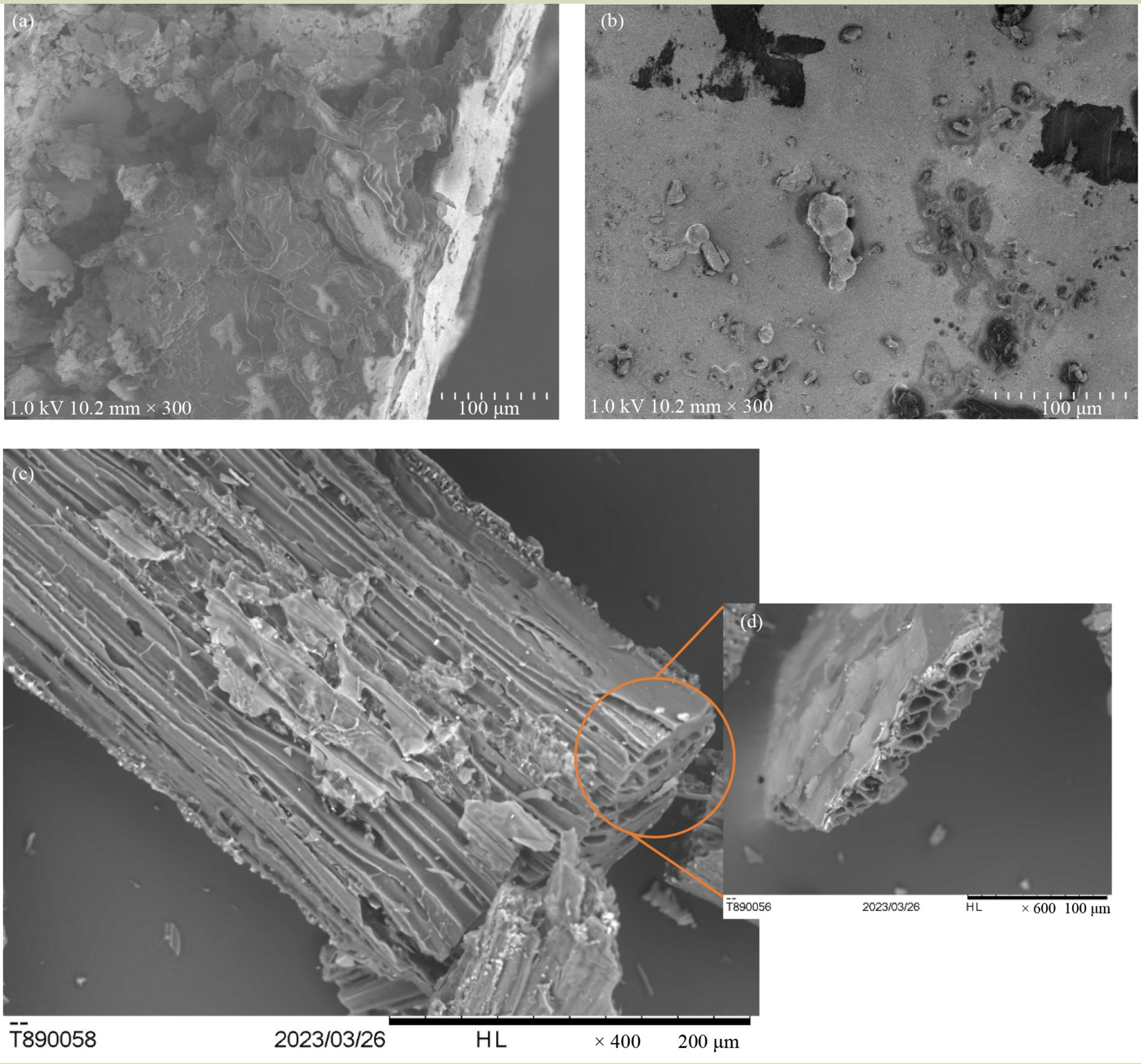


Fig. 11 SEM images of the BCRUF-WC at (a, b) × 300, (c) × 400 magnification, and (d) × 600 magnification

environment and the release. Thus, it can be assumed that the cation exchange capacity of biochar enables biochar to absorb and retain nutrients N in fertilizer. The release control contributed by biochar in BCRNF-WOC is thus provided by the porous structure and high surface area of biochar. In the field application of the biochar, it will slow the decomposition of organic matter, improving the release properties. The FTIR analysis evidenced no formation of new chemical bonds that might hold the nitrogen.

3.9 Microbial community in the BCRUF

The positive impacts of the BCRUF on growth and crop yield are limited to nutrient control and management. CRNFs developed so far can contribute to the slow or controlled-release of nutrients and soil amendment[57]. The concept herein includes retaining the microorganisms of bio-ingredients used for BCRUF making. Fertilizers carrying a microbial strain with controlled-release of nutrients with different functional groups can strongly promote plant growth, crop yields, and healthy agroecosystems. The BCRUF contains microorganisms after pelletizing and drying (done by Sprouting Soil, Newport, OR, USA). Incorporating bio-ingredients like compost is important for making new BCRUF as it is an effective, innovative way to process and pelletize BCRUF, keeping microorganisms inside the pellets. The future application of BCRUF in the soil will improve soil biology and

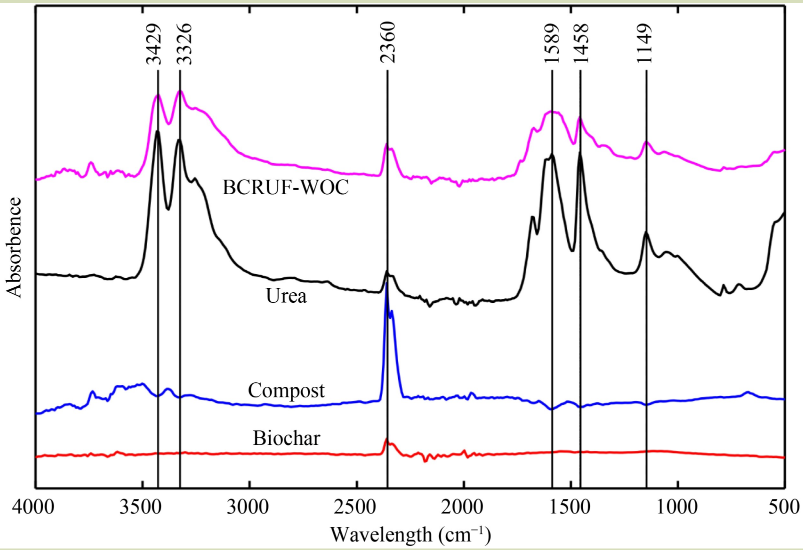


Fig. 12 Spectrum obtained by FTIR for biochar, compost, and urea used for making BCRUF. No new chemical compound formed through the preparation process indicates a safer use of BCRUFs in agriculture.

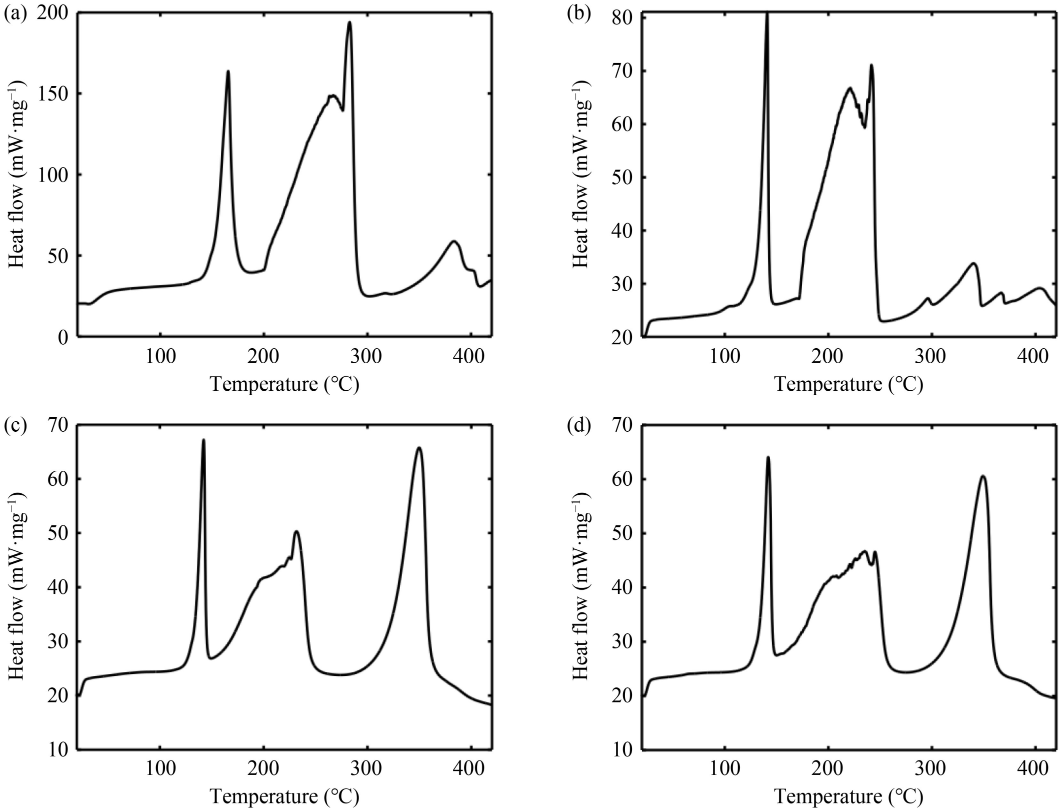


Fig. 13 Differential scanning calorimetry analysis for the (a) urea, (b) ESN, (c) BCRUF-WOC, and (d) BCRUF-WC.

minimize the sole use of chemical fertilizers. After pelletizing, BCRUF-WOC contained a reduced amount of microorganisms. The reason may be the reduction of moisture content from 15% to less than 1% inside the fertilizer pellets.

Ronga et al.[58] studied the effects of dewatering, composting and pelleting livestock manure to make biofertilizer, finding that composting and pelleting biowaste is a feasible and sustainable valorization method for biofertilizer. Sarlaki et al.[59] experimented on agro-biowaste to create a new biofertilizer by pelletizing, regarding the pelleted biofertilizer as a promising strategy to improve biowaste environmental and agronomic performance. However, pelleting is a mechanical process where biowaste undergoes moisture change, mixing, temperature change, pelleting under pressure, and chemical treatment[60]. In contrast, composting keeps the microbe populations high during the processing, maximizing the biofertilizer benefit[61]. It is suggested that the moisture level be kept at 40%–60%, pressure or mixing should be as low as possible, and chemicals should not be added to protect the microbes in compost.

However, the challenge for the biowaste processing industry lies in sustaining efficiency and retaining microbial population in the final biofertilizer product[62]. Reducing microbe populations and inconsistent microbial content may discourage farmers from using biofertilizers. Although making BCRUF did not involve any direct method to kill the microorganisms, the heat produced during pelleting might kill some microorganisms. Most available compost fungi and bacteria can take the heat stress above 100–140 °C for a few minutes (5–10 min). Exposure above this temperature can radically reduce the population in 20–30 s[63]. The raw mixture in the pellet machine was exposed at high temperatures as water vapor was released from the contact parts of the pellet machine, affecting the population of microorganisms. The ratio of fungi to bacteria dropped to 0.05 and fell outside the recommended range of 0.6–0.9 (Table 1). Another reason for the drop in microbial population is the transformation from anaerobic to aerobic fertilizer during air drying. Microorganisms that grow in anaerobic conditions usually cannot survive as well in an aerobic environment[64].

After air drying (< 1% moisture) and coating with PLA solution, the microorganism assessment was done again to determine the population of microorganisms. The BCRUF-WOC and BCRUF-WC dry samples were ground in a mortar and pestle to a semi-powdery consistency for analysis. The same samples were soaked to dissolve in water for four days and tested for microorganisms. This helps understand the microbial reactivity with the presence of water. A vast population drop has been found for BCRUF-WOC and BCRUF-WC (Table 2). The Fungi community turns to zero and has a low population of bacteria. The other essential microorganisms, protozoans, flagellates and amoebae also did not withstand the drying and coating processes. Soaking the pellets up to the complete diffusion of the pellets reactivates a few numbers of bacteria irrespective of any change in other microbial populations. This was also observed by Keena et al.[65] when they applied manure-based fertilizers in surface water. The nutrients released from fertilizer stimulate microbial growth, a process that reduces the dissolved oxygen content of the water.

4 Conclusions

This research successfully synthesized BCRUF that carries an active microbial community. Microorganisms can allow more nutrition control and management in future agriculture for plant growth and yield. However, pelleting and drying affected the microorganism population. Synthesized fertilizer pellets were strong and stable with negligible buoyancy. The pellet strength was above 150 N, comparable to a commercially available smart fertilizer. The N release characteristics were extended up to 4–6 h for 80% of the release in the water emersion test. BCRUF-WC controlled 80% N release to the soil for up to 192 h (8 days). Although PLA is not sensitive between 4 and 40 °C, release profiles were responsive to temperature change due to molecular action and diffusion rate of N in water

Table 1 Status of the microorganism after the fertilizer making processes

Microorganisms	Compost	BCRUF-WOC
Fungi ($\mu g \cdot g^{-1}$)	317 ± 253	11 ± 24
Bacteria ($\mu g \cdot g^{-1}$)	880 ± 147	211 ± 11
Actinobacteria ($\mu g \cdot g^{-1}$)	2.38 ± 1.73	1.46 ± 1.36
Fungi:Bacteria	0.36	0.05
Protozoa (total, × 10^3)	603 ± 177	16 ± 36
Flagellates ($\mu g \cdot g^{-1}$)	16304 ± 36457	0
Amoebae ($mg \cdot g^{-1}$)	587 ± 167	16 ± 36

Table 2 Status of the microorganism after air drying (< 1% moisture) and coating

Microorganisms	Without soaking		With four days of soaking	
	BCRUF-WOC	BCRUF-WC	BCRUF-WOC	BCRUF-WC
Fungi ($\mu g \cdot g^{-1}$)	0	0	0	0
Bacteria ($\mu g \cdot g^{-1}$)	73.3 ± 51.7	176 ± 84	337 ± 87	337 ± 66
Actinobacteria ($\mu g \cdot g^{-1}$)	0	0	3.05	2.78
Fungi:Bacteria	0	0	0	0
Protozoa (Total)	0	0	0	0
Flagellates ($\mu g \cdot g^{-1}$)	0	0	0	0
Amoebae ($\mu g \cdot g^{-1}$)	0	0	0	0

with temperature. The reduced tendency of moisture absorption, no dustiness, and cake-forming tendency gave this fertilizer highly suitable properties for attaining agriculture sustainability. The FTIR analysis indicated that no new chemical bonds had been created that could cause any harm to the crops and environment. The presence of moisture in BCRUF promotes the reestablishment of microbial communities. This provides a new option for a compost-biochar combined fertilizer to reduce the use of mineral fertilizers, help provide active microbes, and control N release.

Acknowledgements

This research received funding supports from the South Dakota Governor’s Office of Economic Development (POC2020-04), the USDA NIFA through the North Central Regional Sun Grant Center, and Hatch Projects (3AR652, 3AR689, and 3AH658) of the South Dakota Agricultural Experiment Station. UT-Battelle LLC partly authored this manuscript under contract DE-AC05-00OR22725 with DOE. The US Government retains, and the publisher acknowledges that the US Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript or allow others to do so for US Government purposes. DOE will provide public access to these federally sponsored research results per the DOE Public Access Plan.

Compliance with ethics guidelines

Robiul Islam Rubel, Lin Wei, Salman Alanazi, Abdulkarim Aldekhail, Anne C. M. Cidreira, Xufei Yang, Sanjita Wasti, Samarthya Bhagia, and Xianhui Zhao declare that they have no conflicts of interest or financial conflicts to disclose. This article does not contain any studies with human or animal subjects performed by any of the authors.

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