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Green synthesis and evaluation of calcium-based nanocomposites fertilizers: A way forward to sustainable agricultural

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ABSTRACT

Only 47% nitrogen of fertilizer is taken up by a plant whereas more than 40% nitrogen of total applied fertilizer is lost to environment that causes several environmental as well as economic consequences. Slow-release fertilizers are considered as a possible large-scale solution for nitrogen loss. The present study aims to stabilize urea by coating with four different materials including calcium phosphate (CP), gypsum powder (GP), calcium nitrate (CN), and gelatin (G) individually and in combination for slow release of nitrogen to sorghum crop. The physical and chemical characteristics of coated urea were examined by FT-IR, powder XRD, SEM, and crushing strength. Results showed that coating of CP, GP, and CN over urea was uneven and rough while G coating was smooth and admirable, and no pore was observed on the surface and indicated a weak water-urea interaction. Similarly, CPG coating over urea showed a maximum crushing strength of 2.38 N/m². Slow-release and soil leaching analysis revealed that G coated urea showed the maximum 39.12 and 779.36 ppm nutrient loss after 15- and 480-min treatment, respectively which is much better than uncoated urea (99.81 and 993.65 ppm). Results reported that the maximum plant height, diameter, and chlorophyll were observed as 132.91 ± 1.52 cm, 24.56 ± 1.00 mm, and 56.30 ± 1.03 mg/m² with CNG coated urea. Similarly, CNG also revealed the maximum dry matter yield (DMY) of 25226.15 kg/ha in shoots and 2633.50 kg/ha in roots, nitrogen uptake (NU) of 18153.75 kg/ha in shoots and 233.99 kg/ha in roots, and apparent nitrogen recovery (ANR) of 71.14% in shoots and 4.55% in roots. It is concluded that CNG coated urea showed better DMY, NU, ANR, and pot analysis, and it is recommended as a slow-release fertilizer for large scale application to minimize nutrient loss and maximize crop production.

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1. Introduction

Fertilizers are considered as one of the most influential input materials for better crop production and reduction of ammonia emissions. Fertilizers are usually applied to soil in liquid or prill

form to fulfil the nutrient deficiency necessary for crop growth. Nitrogen is an important nutrient for the plant's growth and development and is considered a vital macronutrient in soil (Trenkel, 2010). Healthy plants contain about 4% nitrogen in their above surface tissues, which makes nitrogen a much higher concentrated nutrient compared to other nutrients like carbon, oxygen, and hydrogen because these nutrients (carbon, oxygen, and hydrogen) did not impact soil fertility like nitrogen (Pan et al., 2016). Nitrogen is a major component for different plant operations including the function of chlorophyll, formations of a building block of protein (amino acids), and also acts as an energy transferable compound in different chemicals such as ATP (adenosine triphosphate) (Albornoz, 2016; Schulze et al., 2019).

If nitrogen content is low, the growth of plants will be affected, and plants will not be able to perform all necessary functions

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(Schulze et al., 2019). However, to fulfil the nitrogen requirement different nitrogen-containing fertilizers including ammonium sulphate, calcium ammonia nitrate, anhydrous ammonia, ammonium chloride, and urea applied to the soil for a better crop production. Among all nitrogenous fertilizers, urea is one of the most important and commonly used fast-released N-fertilizer because of its low cost, better productivity, and high nitrogen content (46%) availability. Besides, high integration and easy availability of production materials make urea as one of the most important factors in plant development (Garcia et al., 2018; Hussain et al., 2021).

According to emerging evidence, urea is a neutral organic compound that could not be directly absorbed by plants without hydrolyzed. However, insufficient and fast release of urea resulted in a loss of urea in the form of ammonia leading to low nitrogen use efficiency (Ni et al., 2011). The release rate of nitrogen is much higher than the uptake rate of plants. So, nutrients are lost due to leaching and run-off from the soil and cannot be properly utilized by plants and soil (Azeem et al., 2014). Accumulated data revealed that more than 40% of nitrogen is lost every year into the environment without being absorbed by plants and can cause severe environmental (ammonia emission) and economic consequences (Pereira et al., 2015). These situations urged scientists to find more alternative ways to reduce nitrogen loss as ammonia and increase crop production by delivering the urea in a slow and sustained manner (Elhassani et al., 2019).

Slow-release fertilizers (SRFs) are considered as one the most efficient and environmentally friendly alternative methods to manage nitrogen loss. SRF has superiority over other conventional alternative nutrient loss methods like urease inhibitors due to its low cost, less application frequency, better nutrient sustainability, and fewer growth-related negative effects associated with overdose (Naz and Sulaiman, 2016). SRF can be achieved in a variety of ways but the coating or encapsulation method is considered as one of the promising methods due to better holding ability of water-soluble, impermeable, or impervious materials over common soluble manure. Besides, the coating method controls the infiltration of water and melting point, and it is best to adapt the nutrients and needs of plant (Saha et al., 2018; Ye et al., 2020b).

Conventionally, different slow-release coating fertilizers such as polymer-coating fertilizers, woodchips-based fertilizers, petroleum-based coating fertilizers, and other layered base fertilizers (mesoporous hydroxyapatite, montmorillonite clays, and layered double hydroxide) have been applied into the soil to improve nitrogen use efficiency (NUE), but are limited to desired outcomes (Elhassani et al., 2019; Kottegoda et al., 2017; Naz and Sulaiman, 2016). Legras-Lecarpentier et al. (2019) reported that 100% lignosulfonate-bases granules significantly released all of the potassium phosphate and potassium nitrate over five days. They also revealed that incorporation of 1% alginate could effectively increase the release rate of fertilizer over 25 days. Chen and co-workers experimented on biomimetic hydrophobic water-based polymer coating urea (BCU) and demonstrated that modified urea showed remarkable releasing behaviours up to 87.52% on 56th day (Chen et al., 2020).

Riyajan et al. (2012) used $K_2S_2O_8$ as a binder along starch to prepare slow-release urea coatings at 60 °C. The results of this experiment were not satisfactory due to very shallow surface and easy penetrability of water in the coating. Similarly, Niu and Li (2012) experimented on starch-g-poly(vinyl acetate) (St-g-PVAc) as coating material over urea, and observed that hydrophobic PVAs significantly reduced the swellability of starch matrix that could be reached up to 48 h in water, which indicated as a long-time holding method (Naz and Sulaiman, 2016). However, the cost of this coating was also expensive and thus not suitable for industrial use. Ito et al. (2005) used a different approach for coating of urea. They coated two different mixtures such as wax and isobutyl-

dendiurea (IBDU) on urea making two different layers on urea for making a selective release. A double coating showed much better results than a single coating because moisture interacts with the outer layer and it is unable to fully penetrate.

However, these types of coatings required more energy and time to produce coated urea with a double layer. The coatings were effective at lower temperatures but once the temperature was elevated the coating start bursting due to thermal difference and making it useless to coat with these types of combinations. Although different SRF methods have shown somehow better results; however, these are not acceptable on a commercial level due to non-degradability, pH alternation, presence of microorganisms, and moisture content (Babadi, 2015; Naz and Sulaiman, 2017; Ruark, 2012). However, there is a need to develop a better coating method to overcome nitrogen loss and improve crop production without disturbing soil fertility. For the first time, calcium coating materials such as calcium phosphate, calcium nitrate, gypsum powder, and gelatin are used individually as well as in combination as slow-release fertilizers to slow down the hydrolysis of urea to improve the nitrogen use efficiency of crops.

2. Materials and methods

2.1. Reagents

Calcium nitrate tetra hydrate ($CaH_8N_2O_{10}$; 98.50% pure), calcium phosphate ($Ca_3(PO_4)_2$; 96.00% pure), calcium sulfate ($CaSO_4$; 98.00% pure), potassium chloride (KCl; 99.30% pure), potassium dichromate (crystal) ($K_2Cr_2O_7$; 67.40% pure), sulfuric acid (H_2SO_4 ; 97.00% pure), ferrous ammonium sulfate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$; 99.00% pure), diphenylamine ($C_{12}H_{11}N$; 99.90% pure), potassium sulfate (K_2SO_4 ; 99.60% pure), copper sulfate ($CuSO_4$; 98.00% pure), sodium hydroxide (NaOH; 95.00% pure), phosphoric acid concentrated (H_3PO_4 ; 85.00% pure), Tris(hydroxymethyl)aminomethane ($C_4H_{11}NO_3$; 99.00% pure), ammonium sulfate ($(NH_4)_2SO_4$; 99.00% pure), ammonium chloride (NH_4Cl ; 95.00% pure), ammonium hydroxide (NH_4OH ; 30–32% pure), chloroform ($CHCl_3$), sodium bicarbonate ($NaHCO_3$; 99.50% pure), 4-Nitrophenol ($C_6H_5NO_3$; 99.00% pure), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$; 99.00% pure), potassium antimony(III) tartrate hydrate ($C_8H_{10}KO_{13}Sb$; 99.00% pure), L-ascorbic acid ($C_6H_8O_6$; 98.00% pure), potassium dihydrogen phosphate (KH_2PO_4 ; 99.50% pure), ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$; 99.00% pure), murexide ($C_8H_8N_6O_6$; 99.00% pure) and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$; 99.00% pure) were purchased from Sigma-Aldrich (USA). Gelatin ($C_{102}H_{151}O_{39}N_{31}$; 99.30% pure), boric acid (H_3BO_3 ; 99.95% pure), 1,10-Phenanthroline monohydrate ($C_{12}H_{10}N_2O$; 99.00% pure), acetic acid (glacial) (CH_3COOH ; 99.40% pure), eriochrome black T ($C_{20}H_{12}N_3O_7SNa$; 90.00% pure), 4-Dimethylaminobenzaldehyde ($C_9H_{11}NO$; 99.00% pure) were obtained from Daejung Chemicals, Sweden. Urea (46% N) was purchased from Fauji Fertilizer Company Limited, Pakistan.

2.2. Coating of materials

Four different calcium-containing materials such as calcium phosphate (CP), gypsum powder (GP), calcium nitrate (CN), and gelatin (G) were taken for urea coating. 5 g of each material was dissolved in 100 mL water (H_2O). Each sample was heated at 50 °C for 30 min and put on continuous stirring for 24 h. The sample mixtures were coated using Fluidized Bed Coater (YC-1000 Mini Spray Granulator, Shanghai, China). The coater was operated at standard coating conditions at 80 °C and 4 bar pressure. Similarly, different combinations of coating materials such as calcium

phosphate-gelatin (CPG), gypsum powder-gelatin (GPG), and calcium nitrate-gelatin (CNG) were also used as coating material over urea. 5 gm of calcium phosphate, gypsum powder, and calcium nitrate, and 3 gm of gelatin were dissolved in 100 mL water in a beaker and kept on a magnetic stirrer (MS-500, INTLLAB) for 24 h by following the same method of a coating as individual material. The samples were coated in the fluidized bed coater and dried under vacuum to a constant weight.

2.3. Characterization

Fourier Transform Infrared Spectroscopy (FT-IR) of uncoated and coated urea granules were carried out using PerkinElmer Spectrum 100 spectrometer in the wavenumber range of 500 to 4000 cm^{-1} . Urea granules were crushed into fine powder form, and 2 mg of powder was mixed with 200 mg potassium bromide (KBr) for FTIR analysis (Karimi et al., 2016). Powder X-ray Diffraction (XRD; STOE Germany) of uncoated and coated urea was carried out to check the crystallinity of polymeric and inorganic films. XRD analysis was performed over a scan angle of 2θ from 5 to 60° with a scan speed of 2 deg/min, step size of 0.4° , and step time of 1 sec. Scanning electron microscopy (SEM; S-4700 Hitachi, Japan) was used to study the surface morphology of coated and uncoated urea samples.

Prior to the examination, gold sputtering was done on urea granules by anion sputtering machine JFC-1500 of JEOL Ltd (Japan). The gold coating was done up to 250 Å on the granules. The surface morphology of granules sample was analyzed with a secondary electron detector using the accelerating voltage of 10 kV (Beig et al., 2020b). The crushing strength of granules was measured using Universal Tensile Machine (AGX Plus). Coated urea granules were randomly selected from the sample batch. During the test, urea granules were employed against a calculated amount of stress through a metal plunger. The force where urea granules were cracked was noted as a measure of its strength (Fertahi et al., 2019).

2.4. Slow-release analysis of coated urea

Slow-release analysis of coated urea was performed to check the efficiency of coated urea in water and soil in terms of nitrogen release. The release of urea and nutrients were studied using a UV-visible spectrophotometer (Thermo Scientific, GENESYS™ 20, USA). 2 gm of urea prill samples were taken in a 1 L glass beaker and filled with de-ionized water up to mark. 2 gm of sample aliquots was taken from the center of beaker at different time intervals of 3, 6, 9, 12, 15, 30, 60, and 120 min and dilution was done to 10 mL for absorbance measurement using a UV-visible Spectrophotometer. The beaker was put on magnetic stirring for 15 s before collection of samples. 10 mL sample was collected from 50 mL flask containing diluted sample into the 50 mL volumetric flask and then add 1 mL HCl (1:1) and 5 mL p-Dimethyl amino benzaldehyde solution in it along with de-ionized water to make it up. Finally, absorbance was noted using a wavelength of 418 nm to calculate the efficiency of unknown concentration coated urea using Eq. (1) (Phonchai et al., 2020). A total of six runs were carried out at different urea concentrations (0, 20, 40, 60, 80, 100 ppm).

$$\text{Efficiency}(\%) = \frac{C_u - C_{cu}}{C_u} \times 100$$

where, C_u and C_{cu} are the concentrations of urea (ppm) in the uncoated and coated samples at 15 min, respectively.

Similarly, soil leaching was studied by using a soil leaching column. A soil leaching column (height 150 mm and diameter 30 mm) was designed using poly tetra-fluoro ethylene (PTFE) for an examination of release rates in soil. The soil was heated at 80°C to

remove any moisture before an examination, and then meshed (greater than 2 mm) for a better result. 1 gm of coated urea was placed at the center of column for each run. 1 gm of copper sulphate was added into 1 L of deionized water to avoid any nitrification in the soil in the presence of urea. Each run was of 8 h and readings were taken after 30 min each. The readings were taken using a UV-visible spectrophotometer (Thermo Scientific, GENESYS™ 20, USA) at 430 nm and 25°C . Total 11 runs were carried out at different urea concentrations such as 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 ppm. Finally, absorbance was noted using a wavelength to calculate the release rate of unknown concentration of coated urea (see Eq. (2)) (Ye et al., 2020a).

$$\text{Urea}(\text{ppm}) = \frac{\text{Absorbance} - Y.\text{intercept}}{\text{Slope from calibration curve}} \quad (2)$$

2.5. Pot analysis of coated urea

Pot analysis of coated urea was performed at the National Agriculture Research Centre (NARC) Islamabad, Pakistan to evaluate the crop production and its nitrogen uptake after urea application by taking sorghum as a test crop. The samples were tested by following the complete random design (CRD) of Response Surface Methodology (RSM). The diameter of each plot was 4 m^2 with an 8 kg soil carrying capacity. The pot analysis of coated urea includes the analysis of plant roots and shoots to check the efficiency of coatings in real conditions. Before urea application into the pots, the soil analysis was performed to examine the pH, electric conductivity, total organic carbon (TOC), organic matter, microbial biomass carbon (MBC), microbial biomass nitrogen (MBN), microbial biomass potassium (MBK), microbial biomass phosphorous (MBP) and extractable calcium of soil.

2.5.1. Soil analysis

The electrical conductivity of soil was found by a suspension of water to soil ratio of 2:1. The electrical conductivity was measured by EC meter (PAL-EC, China) after shaking the solution for 30 min at 25°C and standardizing the EC meter with 0.01 N KCl solution. The same solution was used for pH measurement using a pH meter (ResultsSevenExcellance™, Switzerland). Similarly, following Eqs. (3–4) were used to determine the total organic carbon (TOC) of soil (Mishra and Sarkar, 2020).

$$\text{Oxidizable organic carbon}(\%) = \frac{(V_{\text{blank}} - V_{\text{sample}}) \times 0.3 \times M}{\text{Weight of dry air} \times \text{soil}} \quad (3)$$

$$\text{TOC}(\%) = 1.334 \times \text{Oxidizable organic carbon}(\%) \quad (4)$$

where M is the molarity of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ solution, V_{blank} is a volume of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ solution is required to titrate the blank (mL), and V_{sample} is the volume of solution required to titrate the sample (mL).

A fumigation extraction strategy was utilized to measure microbial biomass carbon (MBC), microbial biomass nitrogen (MBN), microbial biomass phosphorus (MBP), and microbial biomass potassium (MBK) in the soil (Cheng et al., 2020; Estefan et al., 2013). 5 gm soil sample was taken in a test tube and put into a desiccator contain chloroform (ethanol-free) for 36 h. After 36 h, test tubes were removed from the desiccator and kept in a water bath for 120 min at 80°C . Fumigated and non-fumigated samples were extracted by adding 25 mL solution of 0.5 M K_2SO_4 , $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 0.5 M NaHCO_3 , 0.5 M $\text{C}_2\text{H}_7\text{NO}_2$ into a beaker for MBC, MBN, MBP, and MBK analysis respectively and shaken well at 500 rpm for 2 h using shaking orbital incubator (SHKA4000-1CE, Germany). Each solution was filtered off using Whatman no.

42 filter paper. Microbial biomass nitrogen (MBN) was determined by utilizing the Kjeldahl apparatus (Estefan et al., 2013). MBC was determined by multiplying the difference between organic content (OC) extracted by non-fumigated and fumigated residues with conversion coefficient K_c (0.45). Similarly, MBP and MBK were determined by the colorimetry method (Cheng et al., 2020).

2.5.2. Root and shoot analysis

Root and shoot analysis of sorghum crop was determined after the application of calcium coated urea. Root and shoot analysis include plants' dry matter yield (DMY), height and diameter, mineral nitrogen, ammonium nitrogen, and apparent nitrogen recovery (ANR). Plant height was determined by measuring the height of every plant in the plot and then the average was taken. Dry matter weight (DMW) was obtained by drying the shoot and root of plants for 24 h at 80 °C. The samples were dried in hot air and then placed in an oven for complete moisture removal. Leaf Area was calculated by measuring the average leaf length in a plot and multiplying it with a factor of 0.745. Kjeldahl digestion-automatic nitrogen analyzer was utilized to determine the nitrogen content in the plant. 5 gm of ground dry plant powder was added to the digestion tube. Then 3.5 g digestion catalyst mixture was added with 10 mL concentrated sulfuric acid (H_2SO_4) and swirl carefully. The mixture was heated for 3 h at 420 °C. After heating, the distillation process was performed to distill the ammonia with the help of 40% sodium hydroxide (NaOH) solution and boric acid (H_3BO_3) to capture and formed the solvated ammonium ions. Finally, titration was done with the help of 0.01 N H_2SO_4 . The following Eq. (5) was used to determine the ANR (%) of the plant (Estefan et al., 2013; Rashid et al., 2013).

$$\text{Nitrogen apparent recovery (\%)} = \frac{(N_s \text{ } DM_s) (N_0 \text{ } DM_0)}{TN_a} \quad (5)$$

where, N_s is N content in plant sample (kg N), DM_s is DM yield (kg/ha), N_0 is plant N content in the control treatment, and TN_a is the total amount of applied N (kg/ha) in the pots.

2.6. Statistical analysis

The statistical analysis was performed using IBM SPSS Statistics 26. The effects were analyzed by analysis of variance (ANOVA). The significance was tested at a 5% probability level. The least significant difference (LSD) tests were used for comparisons among different treatments (Beig et al., 2020b).

3. Results and discussions

3.1. Characterization of coated and uncoated urea

Fourier transformed infrared spectroscopy (FTIR) analysis of uncoated and coated urea was carried out to observe the presence of different functional groups within the wavenumber of 500–4000 cm^{-1} (see Fig. 1). The difference in peaks was used to observe the presence of various functional groups originated from different compounds by producing an infrared absorption spectrum. The prominent peak at 3439 cm^{-1} associated with uncoated as well as coated urea (coated with all materials like CP, GP, CN, and G) due to asymmetric and symmetric vibration of NH_2 . Results showed that a peak at 3256 cm^{-1} was attributed due to OH vibration, because of water absorption. Similarly, peaks at 2100, 2010, 1621, and 1465 cm^{-1} were associated with nitrile (C–N) stretching vibration, alkyne (C–C) stretching vibration, carbonyl (CO), and bending vibration of NH and CH stretching vibration of $O=C-NH_2$ respectively (Manivannan and Rajendran, 2011).

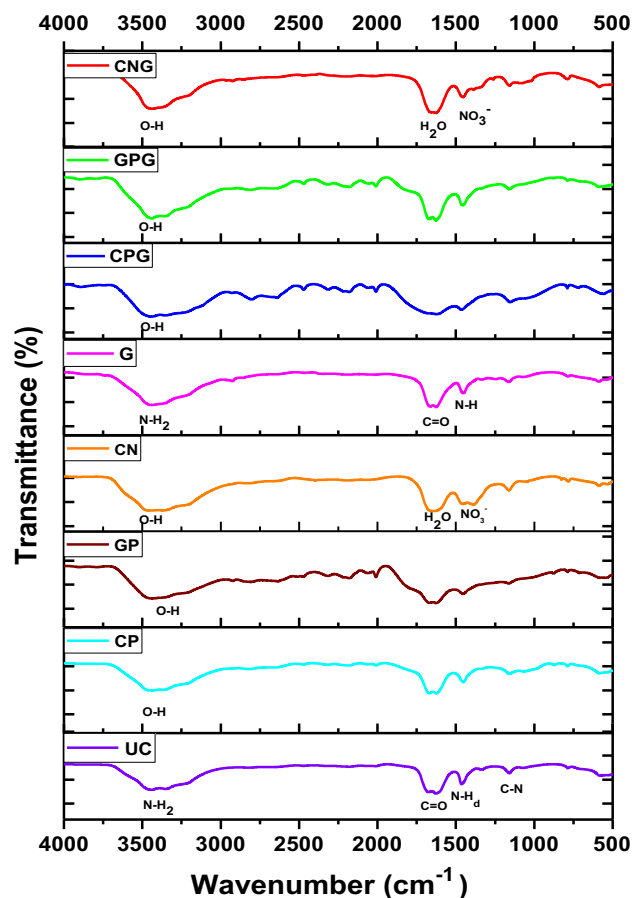


Fig. 1. FTIR spectra of uncoated and coated urea to check the presence of functional groups before and after coating.

In addition, the bands that appeared at 1465 and 1154 cm^{-1} of coated urea were attributed to $-CN$ stretching and $-C-O-C$ stretching vibration mode like in uncoated urea granule. C-H overtone stretching vibrations were also observed at 1154 cm^{-1} . Gelatin coated urea showed an N-H stretching peak at 3450 cm^{-1} . Similarly, 1640 and 1680 cm^{-1} peaks indicate the presence of $C=O$ in gelatin-coated urea. However, peaks of calcium phosphate and gypsum powder-coated urea were broad and fall in the range of 3500–3100 cm^{-1} and showed the presence of moisture with an O-H peak at 3300 cm^{-1} (Vollmer and Ayers, 2012; Wilson et al., 2010). The peaks of calcium nitrate coated urea were observed at 1600 and 1300 cm^{-1} due to N-O bond (Bhowmik et al., 2017; Shillito et al., 2009).

Powdered X-ray diffraction (XRD) was performed for crystalline characteristics of laboratory prepared slow-release urea fertilizer. Fig. 2 showed XRD spectrums of uncoated and coated urea. XRD results showed the dominant diffraction peaks at a 2θ value of 22°, 32°, 35°, and 40° for uncoated urea fertilizer. Beig et al. (Beig et al., 2020a) stated that the XRD spectrum of uncoated urea was observed at 2θ value of 22°, 24.5°, 29.5°, and 35°. Fig. 2 described that major XRD peaks for calcium nitrate (CN), calcium phosphate (CP), gypsum powder (GP), gelatin (G), calcium nitrate-gelatin (CNG), gypsum powder-gelatin (GPG), and gypsum powder-gelatin (GPG) coated urea were observed at 22°, but gelatin-coated urea also showed small peaks at 25°, 29°, 31.5°, and 40°. Honer et al. (2017) reported that calcium salt coating urea showed prominent XRD peaks at 22, 23.8, 31, and 46° (2θ degree). It was observed that there was no considerable difference between uncoated and coated urea granules which confirmed that no new

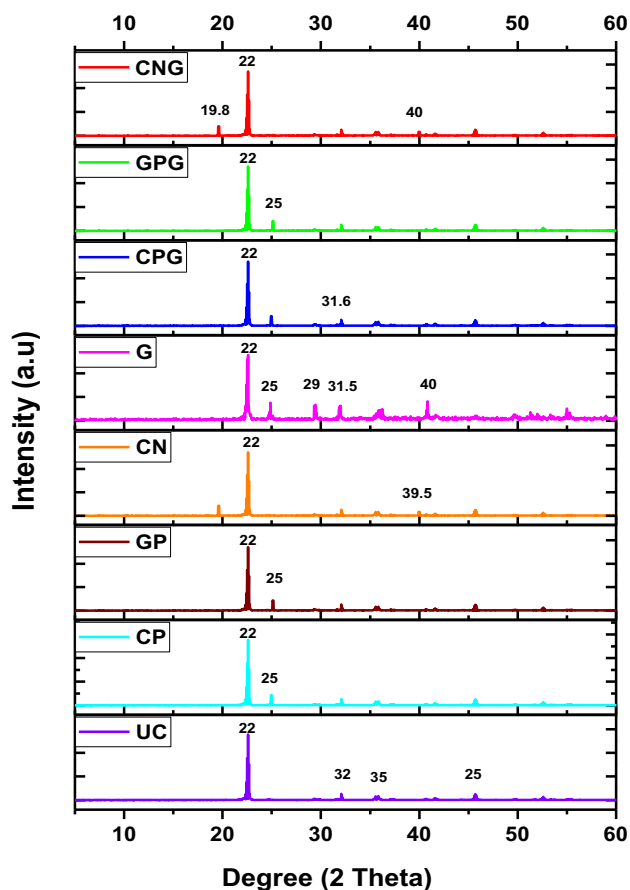


Fig. 2. X-ray diffraction analysis of coated and uncoated urea to confirm the crystalline characteristics of laboratory prepared slow-release urea fertilizer.

phase was formed or deformation in the structure of coated urea during coating process (Ayukawa et al., 2015).

The morphological structure of uncoated and coated urea was examined by scanning electron microscopy (SEM). The coating surfaces were examined for any pores and shape, and formulation of the outer structure of urea. Fig. 3 showed the SEM analysis of uncoated and coated urea at 2500 magnification. The magnification for uncoated urea revealed a rough and quite non-uniform surface with spots and edges that raised from few sides. Fig. 3 demonstrated that magnified SEM images confirmed the coating of calcium phosphate (CP) and gypsum powder (GP) on urea surface. The coating of both materials (CP and GP) was quite uneven and has small pores on the surface. The thickness of coating was enough to hinder the water interaction with urea surface. Pamungkas et al. (2020) demonstrated that an increase in granulation time could significantly improve the water absorption ability until 40 min. SEM results also showed that the coating of calcium nitrate (CN) on urea revealed a smooth and clean finish on the surface. Although CN coating was not perfectly spherical and have no big pores on the surface of urea making water-urea interaction difficult. It was observed that CN covers and bind on urea surface very well.

Fig. 3 indicated that gelatin (G) showed a smooth coverage on the surface of urea. No pore was observed on the surface which makes water-urea interaction difficult. Gelatin coating was well-shaped and almost spherical. Similarly, SEM results of calcium phosphate-gelatin (CPG) stated that the coating was rough and has very small pores on the surface. But the coating of gypsum powder-gelatin (GPG) and calcium nitrate-gelatin (CNG) showed a smooth coating. GPG and CNG coating has very small pores but an edgy structure makes water penetration difficult and proving

a holding structure for urea granules. Nevertheless, the presence of moisture on the surface of coated urea showed the capacity of the coating to hold water for a long term and provided a slow release of urea. However, the addition of gelatin could improve the compactness of materials and coating quality (Ramli, 2019).

To measure the resistance impact of uncoated and coated samples the crushing strength was analyzed, and results are presented in Fig. 4. Results showed that uncoated urea has 2.14 N/m² stress, while other coated urea by CP, GP, CN, G, CPG, GPG, and CNG reported 1.44, 2.10, 1.8, 2.18, 2.38, 2.27, 2.21 N/m² respectively. Results indicated that there was no significant difference in the crushing strength of uncoating and coating urea. However, all the coatings were well above the minimum standard of 1.5 N/m² (Qian, 2017). This indicated that no chemical reaction occurred, and the coatings were just on the surface of the urea that's why not increasing or decreasing strength of urea was observed. Beig et al. (2020a) reported that gelatin-coated urea showed a maximum 70 N crunching strength. Physical coatings do not increase the crushing strength in this small ratio.

3.2. Slow-release analysis and soil leaching of coated urea

Slow-release analysis of uncoated and coated urea for nutrients was performed in water and soil. UV-vis spectroscopy was used for the slow-release analysis of nutrients from uncoated and coated urea and results are presented in Fig. 5 (a). Results revealed that uncoated urea showed 21.25 and 99.81 ppm urea released after 3 and 15 min treatment respectively. Similarly, calcium phosphate (CP), gypsum phosphate (GP), calcium nitrate (CN), gelatin (G), calcium phosphate-gelatin (CPG), gypsum phosphate-gelatin (GPG), and calcium nitrate-gelatin (CNG) coated urea showed the minimum urea release of about 9.08, 8.16, 11.66, 6.33, 5.66, 0.92, and 2.41 ppm after 3 min treatment, while maximum urea release was observed as 49.91, 57.33, 44.25, 39.12, 47.91, 48.08, and 41.41 ppm after 15 min treatment.

Overall, a quick 15 min test concludes that the best coatings for slow release are in order of G, CNG, CN, CPG, GPG, CP, GP, and UC. Gelatin is a good binder for slow release coatings on the urea due to its property to hold cohesive agglomerates together and takes time to dissolve in water (Agubata et al., 2012). The other coatings also provide some resistance for water to reach the urea surface due to their physical interactions with the water and allowing time to delay the nitrogen release. The gelatin can decrease the nutrients release up to 3 times in water than that of uncoated urea. Shen et al. (2020) reported the slow release behaviour of urea for WSF with HNTs (halloysite nanotubes) and without HNTs in soil and distill water, and stated that WSF without HNTs showed the maximum release rate of urea of about 60.6 and 92.6% after 30 and 480 min. While WSF with HNTs showed the maximum release rate of urea of about 45.5 and 87.8% after 30 and 480 min, respectively.

Similarly, Irfan et al. (2018) revealed that Zn-coated urea showed the minimum release rate of urea of about 4 ppm after 6 h that increase to 12 ppm after 26 h. Fig. 5 (b) presented the results of soil leaching for slow-release analysis of uncoated and coated urea. Results disclosed that uncoated urea showed a minimum 423.14 ppm urea loss after 30 min and a maximum of 993.65 ppm after 4 h treatment, respectively. Similarly, calcium phosphate (CP), gypsum phosphate (GP), calcium nitrate (CN), gelatin (G), calcium phosphate-gelatin (CPG), gypsum phosphate-gelatin (GPG), and calcium nitrate-gelatin (CNG) coated urea showed the minimum soil leaching of about 154.23, 168.15, 106.54, 32.15, 123.24, 151.24, and 95.52 ppm after 30 min treatment, while maximum soil leaching was observed as 906.34, 930.15, 882.53, 779.36, 868.25, 895.23, and 844.44 ppm after 4 h experiment.

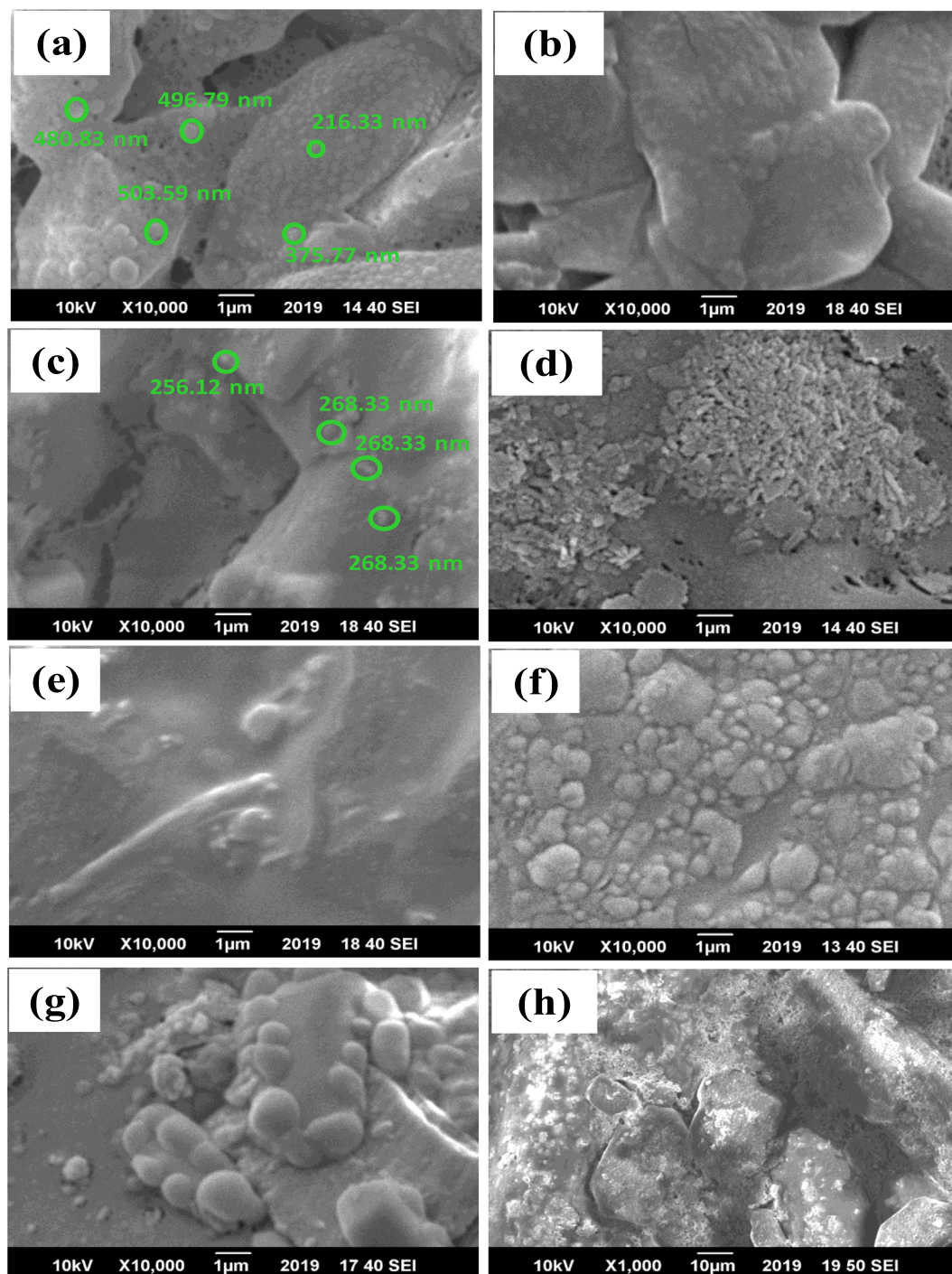


Fig. 3. Scanning electron microscopy (SEM) of calcium based coated urea; (a) CN, (b) CNG, (c) CP, (d) CPG, (e) G, (f) GPG, (g) GP, and (h) Uncoated urea.

Legras-Lecarpentier and co-workers revealed that lignin-based coated urea (lignosulfonates + 1% alginate) showed the maximum release rate of nutrients such as potassium nitrate and potassium phosphate of about 3.00 and 2.10 mg/mL respectively after the first day that decreases to about 1 mg/mL after 25 days (Legras-Lecarpentier et al., 2019). Wang et al. (2020) reported that SA8P10, SA8P15, SA6P15, SA8P25 coated urea showed the maximum FA leaching loss ratio of 56, 39.1, 48, and 34.2% respectively.

The gelatin showed the lowest release rate from all coatings. 8 h test for each sample results in the best coatings in order of G, CNG, CN, CPG, GPG, CP, GP, and UC. Gelatin plays a pivotal role in blocking the nutrients released in the soil also due to its long polymer

chain (Sathisaran and Balasubramanian, 2020). However, the usage of gelatin could decrease the nitrogen release up to over 2 times in the soil. Results showed that due to the good crystalline structure of all materials the coated urea gives a good resistive structure for the release of nutrients. Uncoated urea has no protection from water showed the quickest release rate of nutrients from all samples.

3.3. Pot analysis of coated urea

Pot analysis of coated and uncoated urea includes soil analysis before urea application, and root and shoot analysis after urea

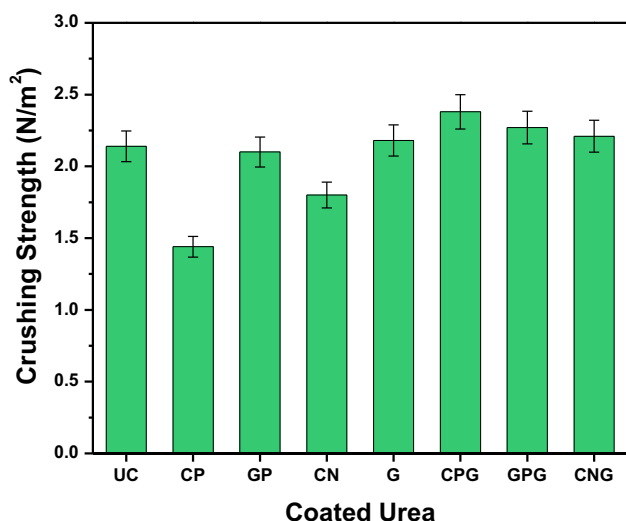


Fig. 4. Crushing strength of coated and uncoated urea to measure the resistance impact.

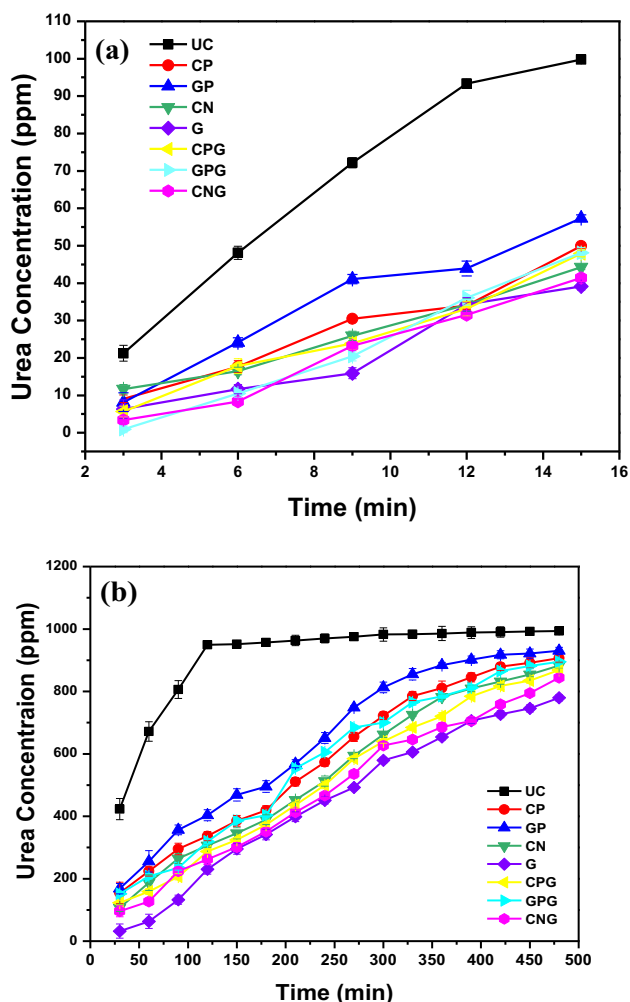


Fig. 5. UV-vis spectroscopy of uncoated and calcium-based coated urea; (a) Slow-release analysis and (b) Soil leaching.

application. Different parameters of soil were analyzed before urea application to sorghum crop.

3.3.1. Soil analysis

Soil analysis includes pH, electric conductivity (EC), total organic content (TOC) and organic matter, microbial biomass carbon (MBC), microbial biomass nitrogen (MBN), microbial biomass potassium (MBK), microbial biomass phosphorous (MBP), mineral nitrogen and extractive calcium.

3.3.1.1. pH, electric conductivity, total organic content. Fig. 6 (a) showed that pH of all samples was neutral and was in a range of 7–8. The uncoated urea or coatings does not change the pH of the soil. The pH of the soil was not disturbed much because all the coatings and binders are neutrals and do not affect the soil characteristics much. Fig. 6 (a) revealed the results of electric conductivity (EC) of inorganic salts content in the soil. Results reported that EC of all samples was below 200 $\mu\text{S/m}$. Results presented that coating of urea did not change the EC of the soil. The maximum EC of about 180 $\mu\text{S/m}$ was observed for gelatin-coated urea, while uncoated urea showed 125 $\mu\text{S/m}$ EC.

Total organic content (TOC) showed the presence of organics and microorganisms in the soil that convert the ammonia into nitrogen for plants and the results are presented in Fig. 6 (b). The present results disclosed that TOC and organic matter (OM) are affected by the application of coated urea. Calcium nitrate-gelatin (CNG) coated urea showed the maximum TOC and OM of about 8829.46 ± 82.89 kg/ha and 15350.92 ± 154.88 kg/ha followed by gypsum powder-gelatin (GPG) coated urea that displayed 7184.53 ± 19.30 kg/ha and 12402.02 ± 251.68 kg/ha respectively. The least TOC and OM of about 2410.73 ± 110.83 kg/ha and 4101.22 ± 60.07 kg/ha were noted for control in which no fertilizer was added.

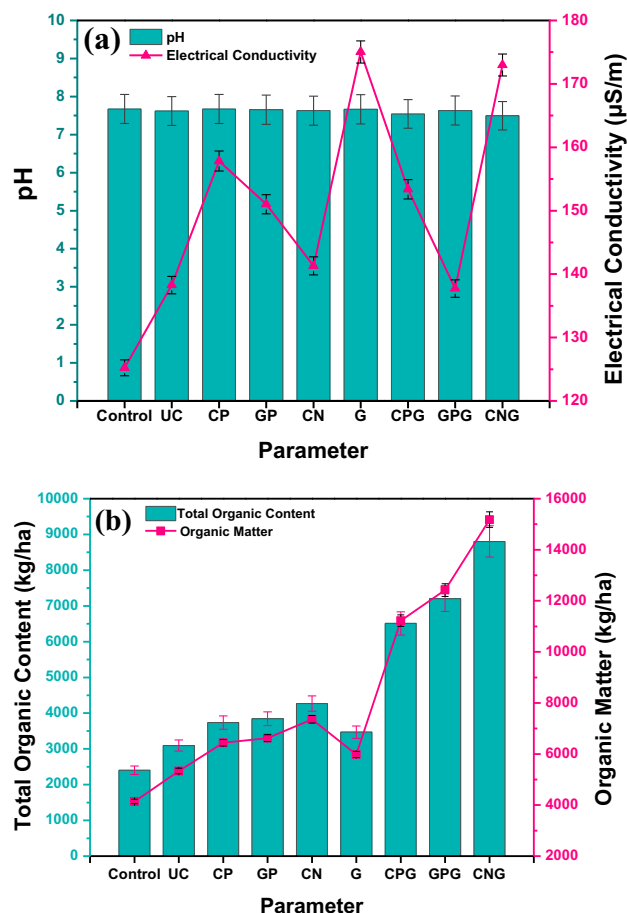


Fig. 6. (a) Electrical conductivity, pH, (b) Total organic content, and organic matter of uncoated and calcium-based coated urea.

3.3.1.2. Microbial biomass content. Fig. 7 (a,b) showed the results of different microbial biomass contents like carbon (MBC), nitrogen (MBN), potassium (MBP), and phosphorus (MBP). Fig. 7 (a) revealed that calcium nitrate-gelatin (CNG) showed the maximum MBC of 2.83 ± 0.024 kg/ha followed by gypsum powder-gelatin (GPG) of 2.47 ± 0.016 kg/ha, and calcium phosphate-gelatin (CPG) of 2.36 ± 0.03 kg/ha respectively. Fig. 7(a) also reported that CNG showed the maximum MBN of 1.45 ± 0.042 kg/ha followed by GPG with a value of 1.26 ± 0.012 kg/ha and CPG with a value of 0.94 ± 0.03 kg/ha. Similarly, Fig. 7(b) displayed the maximum MBP of about 0.12 ± 0.001 kg/ha for calcium phosphate-gelatin (CPG) coated urea followed by calcium phosphate (CP) coated urea 0.11 ± 0.001 kg/ha. While MBK does not change with the addition of uncoated as well as coated urea into the soil. The values were observed between 0.78 and 0.79 kg/ha for all samples. The results showed that the values of microbial biomass content changed with changes of coatings and displayed different results by using different coated fertilizers in the experiment. It is concluded that CNG coated urea showed better MBC and MBN, while CPG coated urea exhibited better MBP.

3.3.1.3. Mineral nitrogen and extractive calcium. Fig. 8 shows the results of mineral nitrogen (MN) and extractive calcium (ECa), which provide information about the presence of ammonium ions in the soil that was converted for plant utilization. CNG coated urea showed the maximum MN value with 37.96 ± 0.50 kg/ha followed by GPG (34.16 ± 1.62 kg/ha), and CPG coated urea (32.63 ± 1.35 kg/ha). The least value was noted for a control of about 4.23 ± 0.251

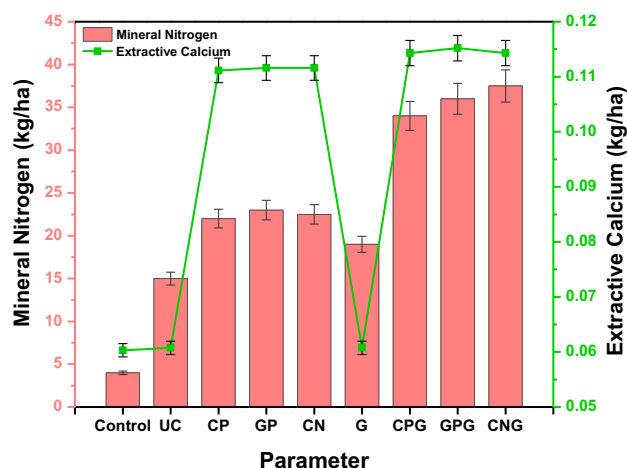


Fig. 8. Mineral nitrogen (MN) and extractive calcium (ECa) analysis of soil before and after urea coating.

kg/ha. Results also reported that GPG, CNG, CPG, CP, NP, and GP showed almost similar ECa (0.115 ± 0.001 kg/ha). While the control exhibited only 0.064 ± 0.0048 kg/ha ECa.

3.3.2. Root and shoot analysis of plant

Root and shoot analysis of plant after urea application consists of plant height and diameter, chlorophyll, dry matter yield (DMY), nitrogen uptake (NU), and apparent nitrogen recovery (ANR) analysis.

3.3.2.1. Plant height, diameter, and chlorophyll. Fig. 9(a) showed the results of plant height and diameter. CNG displayed the highest average plant height and diameter of 132.91 ± 1.52 cm and 24.56 ± 1.00 mm respectively because of the slow and gradual release of the urea. While control revealed the maximum plant height and diameter of about 75.23 ± 0.613 cm and 12.60 ± 0.40 mm. Wang et al. (2020) reported that SA8P10, SA8P15, SA6P10, SA8P25 coated urea showed the maximum plant (corn) height of 7.7, 7.1, 8.2, and 9.0 cm respectively after 13 days. Yang et al. (2017) reported that matrix-based urea showed the maximum plant height of 255.7 cm in the 2015 growing season (humid) and 226.9 in the 2016 growing season (dry) of the crop.

Fig. 9 (b) displayed that CNG coated urea showed the highest average plant chlorophyll of 56.30 ± 1.03 mg/m² followed by GPG coated urea which presented 51.5 ± 1.00 mg/m². While the minimum chlorophyll content was noted for gypsum coated urea which showed only 33.62 ± 0.83 mg/m². The control showed only 25.26 ± 0.76 mg/m² chlorophyll content that is minimum than all coated materials over urea. Outcomes of plant height and diameter changed with changes of coatings and showed different results by using different coated fertilizers. Yang et al. (2017) described that matrix-based urea indicated the highest chlorophyll α and chlorophyll β concentrations of about 38.7 and 79.9% in humid season and 19.8 and 158.2% in the dry season (dry).

3.3.2.2. Dry matter yield (DMY). Fig. 10 displayed the results of dry matter yield (DMY) of uncoated and coated urea in root and shoot of sorghum crop. Results stated that CNG coated urea showed the best DMY of 25226.15 kg/ha in shoots and 2633.50 kg/ha in roots followed by GPG and CPG coated urea which presented 22754.81 and 22729 kg/ha in shoot and 2633.5 and 2657.88 kg/ha in roots respectively. Similarly, gelatin (G) coated urea showed the maximum 16530.17 and 2421.51 kg/ha DMY in shoots and roots respectively. CP, GP, and NP showed almost the same DMY between

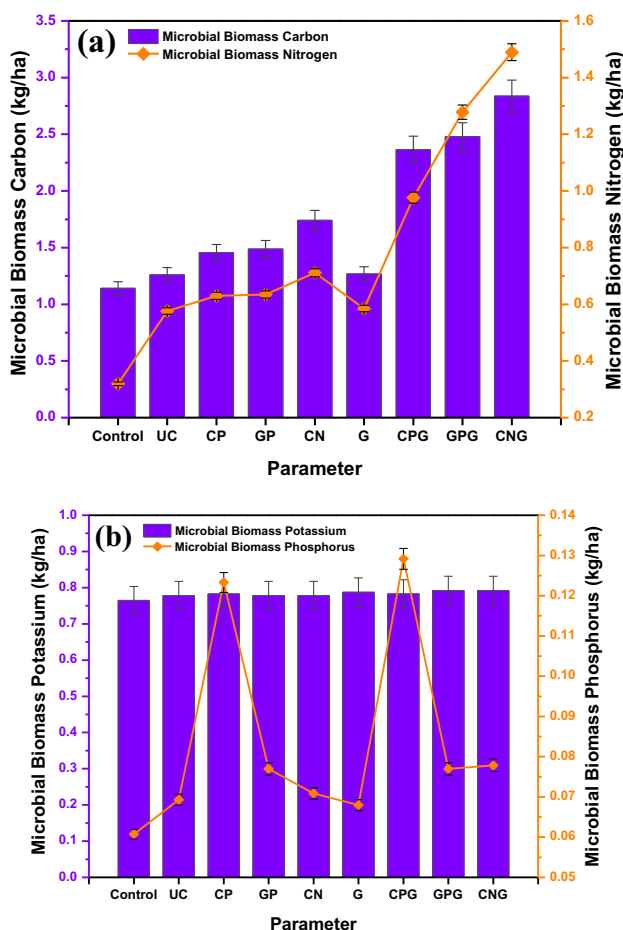


Fig. 7. Soil analysis ; (a) Microbial biomass carbon and nitrogen, (b) Microbial biomass potassium and phosphorus of coated and uncoated urea.

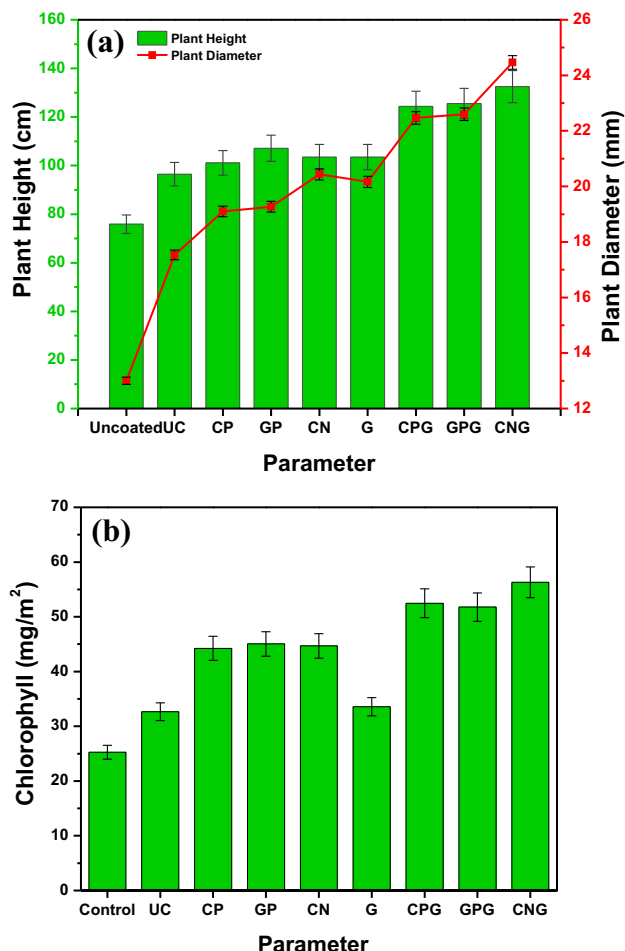


Fig. 9. Pot analysis; (a) Plant height, diameter and (b) chlorophyll of uncoated and calcium-based coated urea.

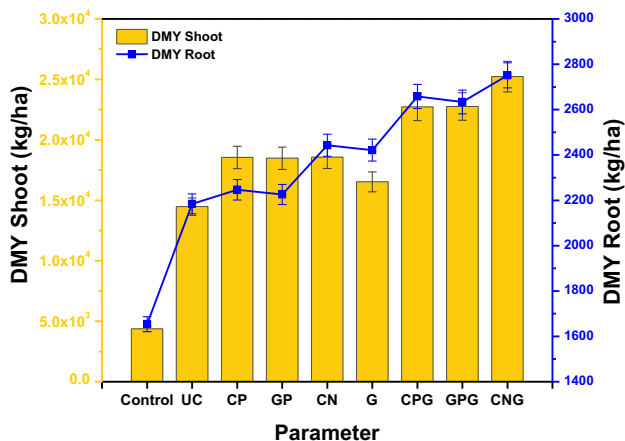


Fig. 10. Dry matter yield (DMY) of measurements of roots and shoots of uncoated and coated urea for pot crop analysis.

18449 and 18570 kg/ha for shoots and 2246.5–2372.5 kg/ha for roots. The least DMY value was noted for control with 4373.84 kg/ha in shoots and 1654 kg/ha in roots. It is concluded that coated urea indicated much better DMY than control and uncoated urea. Carvalho et al. (2016) demonstrated that urea coated with a polymer, NPBT, and CuB showed the maximum dry shoot biomass of 4858, 4750, and 4444 kg/ha with maximum grain

yield of 3629, 3687, and 3181 kg/ha respectively. Yang et al. (2017) reported that matrix-based urea showed the maximum grain yield of 8703 ± 221 kg/ha in 2015 growing season and 6892 ± 179 kg/ha in 2016 growing season of the crop.

3.3.2.3. Nitrogen uptake and apparent nitrogen recovery. Fig. 11 (a, b) presented the nitrogen uptake (NU) and apparent nitrogen recovery (ANR) results for roots and shoots of uncoated and coated urea. Results demonstrated that CNG coated urea displayed the best NU of 18153.75 kg/ha in shoots and 233.99 kg/ha in roots followed by GPG and CPG coated urea with 15445.98 kg/ha and 14721 kg/ha NU in shoots, and 15445.83 and 212.21 kg/ha in roots respectively. The least NU value was shown by control with 163.56 kg/ha in shoots and 11.50 kg/ha in roots. Fig. 11 (b) showed that CNG coated urea illustrated the maximum ANR value of 71.14% in shoots and 4.55% in roots. It is followed by GPG and CPG coated urea which presented 61.43 and 58.22% in shoots, and 3.67 and 3.64% in roots respectively. Similarly, gelatin (G), CP, GP, and NP coated urea showed the maximum 41.24, 29.55, 29.52, and 45.53% ANR in shoots, and 3.63, 2.16, 2.13, and 2.66% in roots respectively.

The uncoated urea showed a maximum ANR of 18.46% in shoots and 1.34% in roots of the sorghum plant. It is concluded that coated urea showed a much better ANR than uncoated urea in both roots and shoots. Li et al. (2017) reported that the maximum nitrogen uptake of about 138.2 and 42.4 kg/ha was observed for grain and straw of rice crop with polyurethane-coated urea. Similarly, degradable polymer-coated urea showed the maximum 132.6 and 39.8 kg/ha nitrogen uptake for grain and straw of rice crop respectively. They also stated that polyurethane-coated urea and degradable polymer-coated urea presented the maximum ANR of 40.8 and 37.5% for grain and 15.4 and 13.8% for the straw of rice

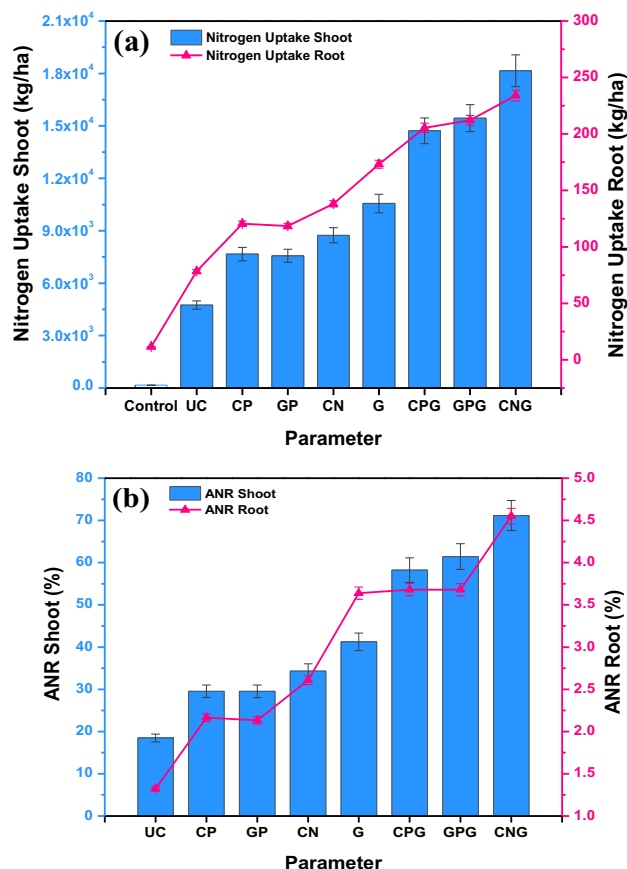


Fig. 11. Pot analysis; (a) Nitrogen uptake and (b) Apparent nitrogen recovery (ANR) for root and shoot of the plant after calcium-coated urea treatment.

crop during pot analysis. Carvalho et al. (2016) demonstrated that urea coated with a polymer, NPBT, and CuB showed the maximum apparent nitrogen recovery (ANR) of 68, 54, and 37% respectively for rice crop. Yang et al. (2017) reported that matrix-based urea showed the maximum ANR of 34% in 2015 growing season and 32.5% in 2016 growing season of the crop.

4. Conclusion

The main objective of the present study was to coat the urea with different coating materials individually and in combination to decrease the release rate of urea along with providing the necessary micronutrients to plants and soil. FTIR, XRD, SEM, and UTM were used to detect chemical changes, surface morphology, and crushing strength of the coated urea. Results revealed the confirmation of coating and described that gelatin-coated urea showed smooth and even coating over urea compared to other coated material and reported no specific pore for water-urea attraction. The field and slow-release analyses were performed on sorghum plants. The soil analysis revealed the maximum electric conductivity of 180 $\mu\text{S}/\text{m}$ for gelatin-coated urea, total organic content and organic matter of 8829.46 ± 82.89 kg/ha and 15350.92 ± 154.88 kg/ha for CNG coated urea, microbial biomass carbon of 2.83 ± 0.024 kg/ha, microbial biomass nitrogen of 1.45 ± 0.042 kg/ha, microbial biomass potassium of 0.79 kg/ha, microbial biomass phosphorous of 0.12 ± 0.001 kg/ha, mineral nitrogen of 37.96 ± 0.50 kg/ha and extractive calcium of 0.115 ± 0.001 kg/ha for CNG coated urea. Overall, it was concluded that calcium nitrate-gelatin (CNG) coated urea gave the best results of all samples. Together they both (calcium nitrate and gelatin) form a microporous structure from which the nutrients cannot cross and made a hindrance for water to enter the coating. Gelatin itself can also provide slow-release but it does not provide enough nutrients to the plants as they are provided when mixed with calcium compounds coatings. However, it is recommended as other binders such as carboxymethyl cellulose and starch should be tested in combination with gelatin to decrease the nutrient release rates. In addition, a nitrogen deficit fertilizer could be tested as a coating of urea for making a hindrance in nitrogen release.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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