



## Research article

# Application of nano-urea in conventional flood-irrigated Boro rice in Bangladesh and nitrogen losses investigation

Md Abdullah Al Asif<sup>a,1,\*</sup>, Farah Mahjabin<sup>a,d,1</sup>, Sourav Kumar Singha<sup>b</sup>,  
 Mohammad Mofizur Rahman Jahangir<sup>a</sup>, Sheikh Manjura Hoque<sup>c,\*\*</sup>

<sup>a</sup> Department of Soil Science, Bangladesh Agricultural University, Mymensingh, 2202, Bangladesh

<sup>b</sup> Bangladesh Food Safety Authority, Dhaka, 1000, Bangladesh

<sup>c</sup> Materials Science Division, Atomic Energy Centre Dhaka, Dhaka, 1000, Bangladesh

<sup>d</sup> School of Science, Western Sydney University, Richmond, NSW, Australia

## ARTICLE INFO

## Keywords:

Nanourea

Scanning transmission electron microscopy (STEM)

EDS mapping

Hydroxyapatite (HAP)

N use efficiency (NUE)

## ABSTRACT

Bangladesh stands third in global rice production while complete modernization of rice production is not fully enforced. The boon of nano agriculture might circumvent the challenge of increasing the yield with minimal ecological damage. Nanofertilizer might be one of the solutions to address the problem of modern agriculture confronting environmental hazards owing to the excessive use of synthetic fertilizers by farmers in Bangladesh. We synthesized nanourea by chemical co-precipitation (CP) and hydrothermal (HT) methods in an attempt to develop environmentally friendly nanofertilizers. We characterized the nanourea and confirmed the functionalization of nanohydroxyapatite (nHAP) with urea by scanning transmission electron microscopy (STEM)/EDS mapping. The CP method produced particle dimensions of 45.62 nm for length and 14.16 nm for width. In comparison, the readings obtained through the HT method were around 74.69 nm and 20.44 nm for length and width, respectively. The field application of nanourea demonstrated impressive results, indicating a significant relationship between the particle size of nanourea and its impact on several agricultural factors. The grain yield using traditional synthetic fertilizer (urea) ranged from 6.47 to 6.52 t ha<sup>-1</sup> with a very low NUE of 35.8–36.34 %. Contrarily, the grain yield was found from 6.52 to 6.84 t ha<sup>-1</sup> and the obtained NUE ranged from 57.58 to 71.0 % using nanourea of the same concentration calibrated with traditional urea by two methods. Additionally, nanourea treatments having 25 % less nitrogen (N) provided higher total N (TN) in grain suggesting possible nutritional enrichment while checking the yield penalty and substantial increase in N use efficiency (NUE). However, further upscaling of this research on a field scale is necessary to confirm the findings.

## 1. Introduction

In the quest to solve the expanding global crisis of hunger, food insecurity, and malnutrition, new UN studies highlight a disturbing

\* Corresponding author. Bangladesh Agricultural University, Mymensingh – 2202, Atomic Energy Centre, Dhaka, 4 Kazi Nazrul Islam Avenue, Dhaka, 1000, Bangladesh.

\*\* Corresponding author. Bangladesh Agricultural University, Atomic Energy Centre, Mymensingh – 2202, Dhaka, Bangladesh.

E-mail addresses: [asif.1702062@bau.edu.bd](mailto:asif.1702062@bau.edu.bd) (M.A.A. Asif), [manjura\\_hoque@yahoo.com](mailto:manjura_hoque@yahoo.com) (S.M. Hoque).

<sup>1</sup> These authors contributed equally.

<https://doi.org/10.1016/j.heliyon.2024.e37150>

Received 9 May 2024; Received in revised form 1 August 2024; Accepted 28 August 2024

Available online 30 August 2024

2405-8440/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>).

trend: the world is becoming progressively away from its aim of eradicating these challenges by 2030. The number of people impacted by hunger increased to an estimated 828 million in 2021, up around 46 million from the previous year and 150 million since the commencement of the COVID-19 epidemic [1]. With rice providing a basic food for millions of people, the importance of rice growing in Bangladesh becomes evident against this backdrop. Winter rice, also known as boro rice, is a crucial component of Bangladesh's agricultural environment. Accounting for approximately 53.8 % of the nation's annual rice production [2], Boro rice stands as a cornerstone of the country's agricultural output and food security endeavors. However, against the backdrop of burgeoning global population projections—expected to exceed 9.7 billion by 2050—the imperative to enhance agricultural practices for sustainable rice productivity becomes increasingly urgent.

In order to fulfill rising food demands, the intensification of current agricultural methods has long relied upon the extensive use of chemical pesticides, fertilizers, and crop types that have undergone genetic modification [3]. The use of nitrogen (N) fertilizers to improve soil inadequacies and support crop development is central to this paradigm. Nevertheless, the careless use of traditional nitrogen fertilizers has led to a host of environmental issues, including reduced nitrogen use efficiency (NUE), acidification of the soil, emissions of nitrous oxide, and eutrophication of aquatic environments [4–6]. In the context of paddy fields, nitrogen retention within the soil fluctuates between 10 % and 35 %, with substantial nitrogen losses occurring via gas (ammonia volatilization and denitrification) and water (runoff, leaching, and lateral seepage) pathways [7–10]. Moreover, the proximity of urea application to seeds poses a risk of seedling damage due to ammonia release, further complicating nitrogen management practices [11]. The use of nitrogen (N) fertilizers to improve soil inadequacies and support crop development is central to this paradigm. Nevertheless, the careless use of traditional nitrogen fertilizers has led to a host of environmental issues, including reduced nitrogen use efficiency (NUE), acidification of the soil, emissions of nitrous oxide, and eutrophication of aquatic environments [12–14].

Because of their biocompatibility and biodegradability, hydroxyapatite (HAP) nanoparticles in particular have attracted interest as a promising option for sustainable nutrient delivery in agricultural contexts [15–17]. HAP nanoparticles have several uses, but one that deserves further investigation is as possible nitrogen transporters for plant nutrition Kottegoda et al., 2017. Additionally, it has also been found that nanourea synthesized using HAP and urea has a slower N release rate in the field condition than the conventional urea due to the presence of a moderately strong H-bond [18]. But even with the bright future of nano fertilizers, there is still little study being done in Bangladesh on the manufacture and use of nanourea.

In this vein, the current study endeavors to address this gap by developing two distinct types of nanourea—utilizing nano-hydroxyapatite (nHAP) and synthetic N fertilizer (urea)—via chemical co-precipitation (CP) and hydrothermal (HT) methods. Designated as  $S_W$  and  $S_H$ , respectively, these nanourea variants are anticipated to exhibit differential characteristics in particle size, shape, and crystallinity, thereby influencing crop yield and nitrogen release dynamics. Moreover, this study undertakes a comprehensive investigation into the interactions between these nanohybrids and the soil-plant environment within a rice field, encompassing diverse agronomic properties. It is hypothesized that the incorporation of urea into the matrix of nHAP will confer slow-release properties upon the resulting nanourea, thereby reducing solubility in field conditions and necessitating fewer application frequencies compared to the recommended rate of the conventional urea in Bangladesh—thus offering potential economic savings for farmers and the nation at large.

## 2. Materials and methods

### 2.1. Materials

Calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] (Merck, Germany), phosphoric acid [ $\text{H}_3\text{PO}_4$ ] (RCI Labscan, 85 %) and Ethanol [ $\text{C}_2\text{H}_5\text{OH}$ ] (RCI Labscan) were used during the synthesis of nanoparticles. Urea was purchased from the local market to ensure farmer's grade.

### 2.2. Preparation of nanourea

#### 2.2.1. Preparation of HAP by CP method

Two different precursor substances calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) were selected for the synthesis of HAP [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] nanoparticles. At first, 0.6M of  $\text{H}_3\text{PO}_4$  solution (1.73 ml, 43.82 ml deionized water) was added dropwise in the suspension of 1M  $\text{Ca}(\text{OH})_2$  under stirring. The magnetic stirring was carried out at 500 rpm at room temperature for 30 min. The reaction that was used to produce  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  nanoparticles. The precipitated sample was then washed three times by centrifugation at 13000 rpm for 20 min using deionized water and dried at 75–80 °C for approximately three days.

#### 2.2.2. Preparation of HAP by HT method

A pressure reactor vessel (Parr Instrument Model- 4576, 5000 psi and 500 °C) was used for the synthesis of HAP [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] by HT method. Initially, 180 ml of  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{PO}_4$  with the correct stoichiometric ratio was transferred into the reactor vessel. Then the reactor was assembled and placed into its position and the stirring shaft was put into its place. The water line related to the vessel was turned on. The gas pressure was controlled with the Ar gas followed by turning on the heater. The temperature was set at 300 °C, with the accompanying pressure of 1250–1300 psi inside the reactor. The pressure, temperature, and reaction time were monitored in the controller. The reaction was carried out for 4 h. When the reactor temperature came down to room temperature, the reactor vessel was ready to be dismantled. Before dismantling, it was ensured that the pressure inside the reactor chamber was released. The synthesized HAP was collected from the reactor, centrifuged at 12000 rpm for 20 min, and dried for three to 4 h in the hot plate at 75–80 °C.

### 2.2.3. Synthesis of nanourea

The synthesized HAP nanoparticles by CP and HT were then separately mixed with 30–40 ml of water (enough to wet the whole powder roughly) and sonicated for 45 min to disperse the aggregated and powdered HAP nanoparticles into individual nanoparticles. A saturated urea solution was prepared to mix with the sonicated HAP nanoparticles maintaining a ratio of urea: nHAP to 5:1. The nHAP and urea mixtures were stirred overnight to ensure thorough mixing. Then, the excess liquid was decanted followed by removing excess urea by centrifugation at 11000 rpm for 15 min using deionized water with subsequent drying.

## 2.3. Characterization of structural properties of nanourea

### 2.3.1. X-ray diffraction

The XRD patterns of all synthesized samples were recorded using an X-ray diffractometer (XRD), Model: SmartLab SE, Rigaku, Japan. Thermofisher USA's Transmission Electron Microscopy (TEM), model TALOS 200X was used to examine the sample's size and morphology operated at 200 kV.

### 2.3.2. Fourier transform infrared spectroscopy (FTIR)

The Fourier Transform Infrared Spectroscopy analysis was made using the Jupiter, UK-based STA, 449 F3 FTIR spectroscopy, to determine the chemical structure and the bonding nature of the composites.

### 2.3.3. Evaluation of thermal properties (thermogravimetric analysis)

A thermogravimetric analyzer (model: TG/DTA6300, Seiko Instruments Inc. EXSTAR6000, Japan) was employed to conduct thermal analysis on various materials within a temperature span of 25–1000 °C under both air and nitrogen environments. This analysis encompassed thermogravimetric, differential thermogravimetric, and differential thermal measurements.

## 2.4. Field trial

### 2.4.1. Experimental site and soil description

A field trial of nanourea in Bangladesh was undertaken at the Soil Science field laboratory (Latitude: 24°43'04.8" N; Longitude: 90°25'32.7"), Bangladesh Agricultural University, Mymensingh. A pot experiment at the field site was carried out where all the biotic and abiotic environmental factors were alike in a real rice field. The soil was collected from a field where typically R-R-R (Boro rice- T. Aus rice- T. Aman rice) cropping pattern is followed and the soil is characterized as a Non-calcareous Dark Gray Floodplain soil (Aeric Haplaquept in US Soil Taxonomy) and belongs to agro-ecological zone-9, Old Brahmaputra floodplain soil [19]. The soil had a silt loam texture, an almost neutral pH (6.4), and a total nitrogen (TN) content was 0.126 %. The area experienced a sub-tropical monsoon climate with average annual temperatures of 26 °C, 1800 mm of rainfall, and 85 % relative humidity.

### 2.4.2. Experimental setup and cultural management

In a Completely Randomized Design (CRD), the nanourea  $S_W$ , received four (4) replications and five (5) treatments, whereas,  $S_H$  received four (4) replications and four (4) treatments. The following treatments were assigned in the pots for this study: T0: Control (no nutrient or fertilizer), T1: Urea (Conventional N fertilizer) at 100 % recommended dose (RD), T2: 100 %  $S_W$  and  $S_H$  at 100 % RD of urea, T3: 75 %  $S_W$  and  $S_H$  at 75 % RD of Urea, T4: 50 %  $S_W$  at 50 % RD of Urea. A field layout is provided for better understanding (Fig. 1). Around 600–700 kg of soil was collected from the field and hard clods were broken into numerous small fractions so that the seedlings would not have to face difficulties to be established. Unexpected plants, residues, weeds, and stubbles were removed from the soil

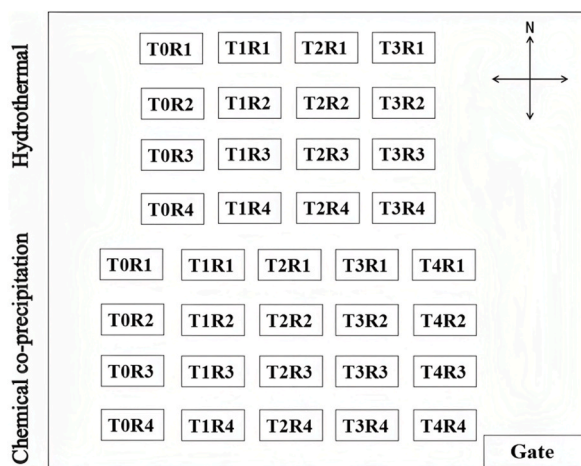


Fig. 1. Layout of the pots in the field.

before being placed in the pots. The number of pots was 36 of which 20 received  $S_W$  and 16 received  $S_H$  nanourea. Pots were filled with around 10 kg of soil, which were air and sun-dried. The area of the pot was  $0.064 \text{ m}^2$ . A composite sample of the dried soil was appropriated for chemical analysis, specifically for pH and TN. Rice was grown during the winter season, popularly known as the Boro season and the variety used was BRRI dhan28 as a trial crop. Seedlings were transplanted on 25 January 2023 in our experimental pots. From that day, seedlings were kept flooded with water for about 15 days for seedling establishment.

Urea  $144 \text{ kg N ha}^{-1}$ , TSP (Triple Superphosphate)  $21 \text{ kg P ha}^{-1}$ , MoP (Muriate of Potash)  $60 \text{ kg K ha}^{-1}$ , Gypsum  $8 \text{ kg S ha}^{-1}$  and Zinc sulphate ( $\text{ZnSO}_4$ )  $1.5 \text{ kg Zn ha}^{-1}$ . Fertilizers were applied based on the amount of soil in each pot (weight basis). Except for urea, all other chemical fertilizers were applied just before transplanting. Urea was applied in three splits (3) whereas nanourea was applied in two. For each pot, maintaining the BARC fertilizer recommendation,  $0.7 \text{ g TSP}$ ,  $0.8 \text{ g MP}$ ,  $0.3 \text{ g Gypsum}$ , and  $0.05 \text{ g ZnSO}_4$  were provided. For  $T_1$ , a total of  $2.09 \text{ g}$  of urea was provided maintaining  $0.7 \text{ g}$  for each of the three splits. Nanourea ( $S_W$  and  $S_H$ ) were applied in  $T_2$  in total amounts of  $3.03 \text{ g}$  and  $1.51 \text{ g}$  for each of the two splits due to the 45 % surface coating of urea. For  $T_3$  and  $T_4$ , a total of  $2.27 \text{ g}$  and  $1.51 \text{ g}$  of nanourea were supplied where  $1.13 \text{ g}$  and  $0.76 \text{ g}$  were used respectively for each of the two splits. Split application of urea was maintained conventionally, generally 15, 30, and 45 days after transplanting (DAT) whereas the first and the last split of nanourea were provided at 15 DAT and 40 DAT.

In nursery beds, boro rice seedlings were raised for 35–40 days before being carefully taken out and planted in pots. Each pot contained one seedling. Intercultural operations such as irrigation, weeding, and pest control were carried out as necessary to provide and maintain a conducive environment for regular agricultural growth and development. The crops were harvested when they had

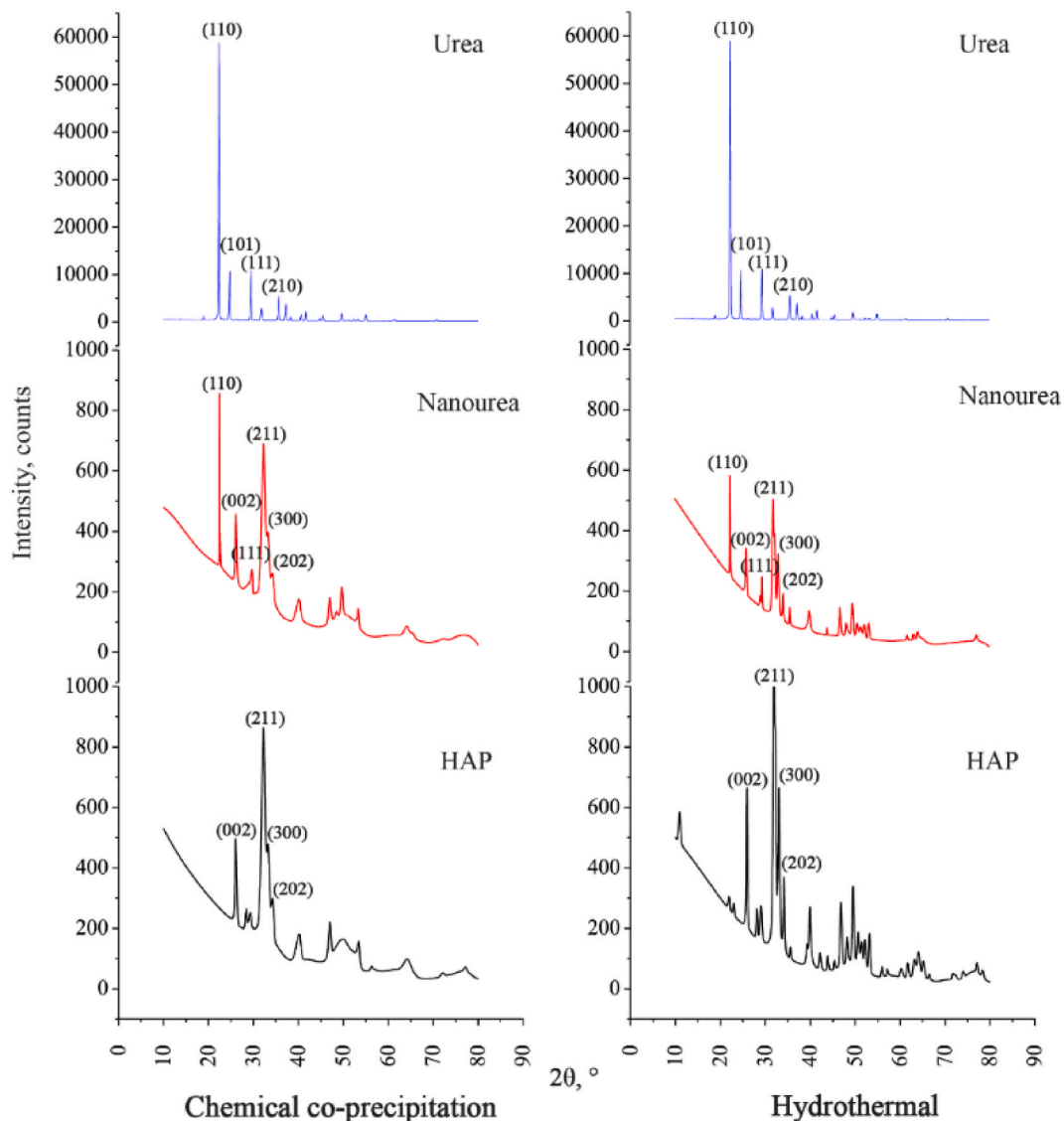


Fig. 2. XRD patterns show peak overlapping among urea, nanourea, and HAP.

reached physiological maturity. The whole seedling from each pot was collected and threshed on a threshing floor.

### 2.5. Assessment of yield after harvesting

Initial weights of the rice grains and straw were recorded after harvesting. The final weights of the grain samples were appraised after oven drying (65 °C, 72 h) until a constant weight was found. Straw yields were calculated using a sun-dry basis.

### 2.6. Determination of total nitrogen, nitrogen uptake, and nitrogen use efficiency

A few days after harvesting, we collected soil samples from each pot to determine the final nitrogen concentration in the soil. TN concentration (%) was determined using the semi-micro Kjeldahl method [20].

Total N (TN), N uptake and N use efficiency (NUE) were calculated using the following formulae:

$$\text{Total N (\%)} = \frac{(\text{Sample} - \text{Blank}) \text{ ml} \times 0.01 \times 0.014 \times \text{Dilution factor} \times 100}{\text{Weight of Sample (g)}}$$

$$\text{Nutrient Uptake (kg / ha)} = \frac{\text{Nutrient Conc. (\%)} \times \text{Dry mass production (t ha}^{-1}\text{)}}{100}$$

$$\text{NUE (\%)} = \frac{\text{N uptake Fertilized plot (kg ha}^{-1}\text{)} - \text{N uptake Control plot (kg ha}^{-1}\text{)}}{\text{Total N input (kg ha}^{-1}\text{)}} \times 100$$

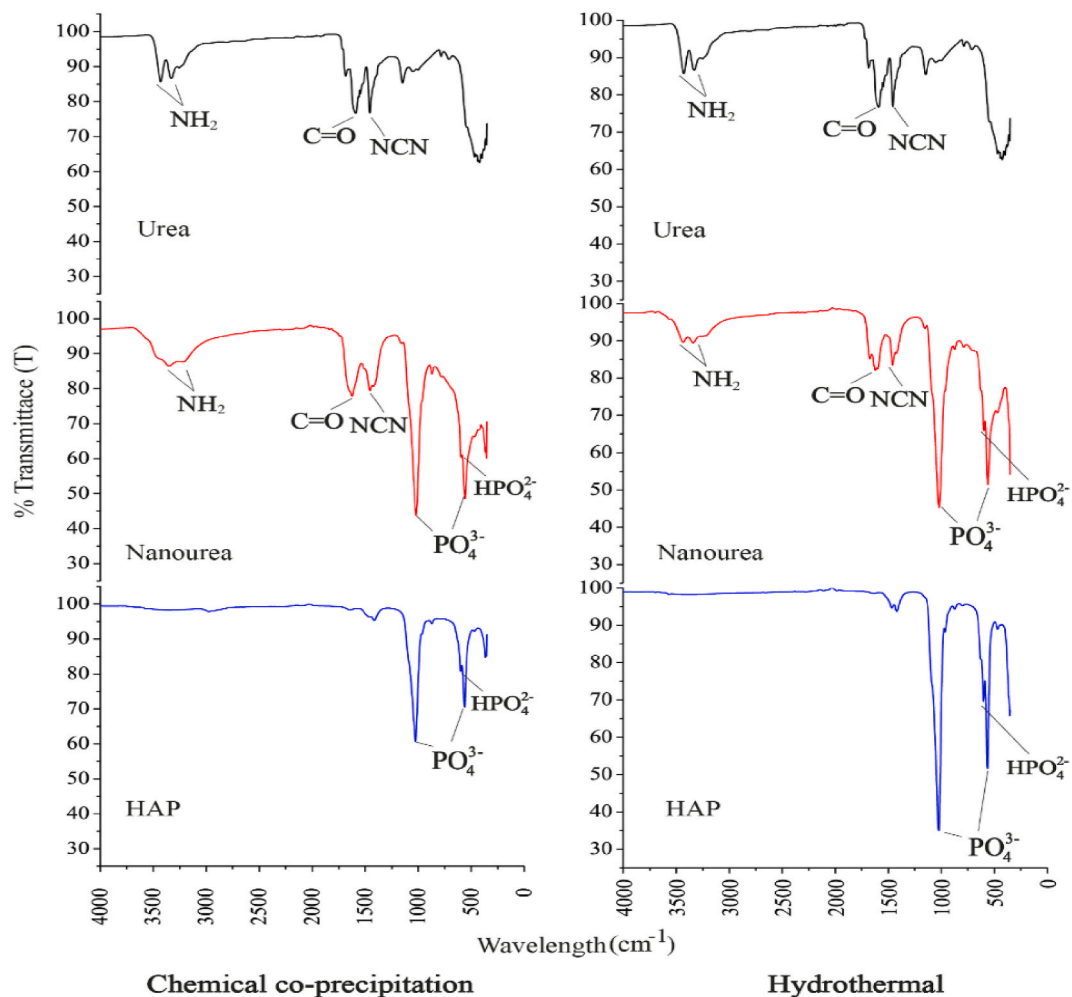


Fig. 3. FTIR spectra of  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{NH}_2$ , C=O, and N–C–N regions of urea, nanourea, and HAP.



## 2.7. Statistical analysis

Descriptive statistics such as mean, median, standard deviation, standard error, etc. were calculated to summarize the key features of the data set which provided a comprehensive knowledge about the data's central tendencies, dispersion, and distribution. Analysis of variance (ANOVA) and Tukey–Kramer multiple comparisons test were carried out using Statistix 10 and considered significant at  $p < 0.05$ .

## 3. Results and discussion

### 3.1. Structural properties of nanourea

#### 3.1.1. XRD

Fig. 2 shows X-ray diffraction patterns of urea,  $S_W$ ,  $S_H$ , and HAP in the bare state. The lattice parameters,  $a$  and  $c$  of  $S_W$  were 6.847 and 9.334 Å, and of  $S_H$  were 6.877 and 9.394 Å, respectively. The nanourea showed the lattice parameters for  $S_W$  as 6.831 and 9.329 Å and  $S_H$  as 6.887 and 9.386 Å, respectively. The grain size and lattice strain of  $S_W$  in the as-synthesized condition is 9 nm and 0.01349 and for  $S_H$  20 nm and 0.0065. The lattice parameters of  $S_H$  closely match with the bulk hydroxyapatite. The average grain size of  $S_W$  is much smaller than the  $S_H$ , while the lattice strain of  $S_W$  is higher than the  $S_H$ . The XRD patterns of both  $S_W$  and  $S_H$  bear the planes of urea and hydroxyapatite, for instance, 110 and 111 planes of urea and 002, 211, 300, and 202 planes of HAP. Peak shifts were prominent in the XRD patterns of HAP and nanourea revealing functionalization of HAP after the formation of nanourea. There is a large change in the lattice parameters between HAP and nanourea.

### 3.2. Fourier-transform infrared spectroscopy (FTIR)

Fig. 3 shows the FTIR spectrum of several characteristic bands of the HAP, urea, and nanourea synthesized by both chemical co-precipitation and hydrothermal methods. It revealed unique functional groups of urea molecules (N-C-N, H-N-H, and C=O) and HAP nanoparticles ( $PO_4^{3-}$ ,  $HPO_4^{2-}$ ) [21,22]. In the case of the chemical co-precipitation method, this is evident from the figure that the spectra of urea and nanourea coincided with each other from 1456  $cm^{-1}$  to 1458  $cm^{-1}$  for N-C-N bond, 1590  $cm^{-1}$  to 1622  $cm^{-1}$  for the functional group of C=O and 3218  $cm^{-1}$  to 3430  $cm^{-1}$  for N-H-N. In the case of HAP and nanourea, spectra coincided between 560  $cm^{-1}$  to 564  $cm^{-1}$  and 1024  $cm^{-1}$  to 1026  $cm^{-1}$  due to the presence of  $PO_4^{3-}$ . Additionally, peaks between 594  $cm^{-1}$  and 600  $cm^{-1}$  were aligned with  $HPO_4^{2-}$ . Contrarily for the hydrothermal method, the spectra of urea and nanourea coincided with each other between 1458  $cm^{-1}$  to 1460  $cm^{-1}$  due to the presence of N-C-N group, 1590  $cm^{-1}$  to 1624  $cm^{-1}$  for C=O bond and 3330  $cm^{-1}$  to 3430  $cm^{-1}$  for N-H-N. In the case of HAP and nanourea, spectra coincided between 560  $cm^{-1}$  to 564  $cm^{-1}$  and 1022  $cm^{-1}$  to 1024  $cm^{-1}$  for  $PO_4^{3-}$ . Additionally, peaks between 594  $cm^{-1}$  and 600  $cm^{-1}$  were aligned with  $HPO_4^{2-}$ . Therefore, it can be said that the peak positions of urea, nanourea, and HAP for both methods coincided nearly in a similar manner. However, the spectral shifts in both cases were visible. The nanourea showed spectrum shifts in the bands corresponding to C=O and C-N because of the weak chemical bonding

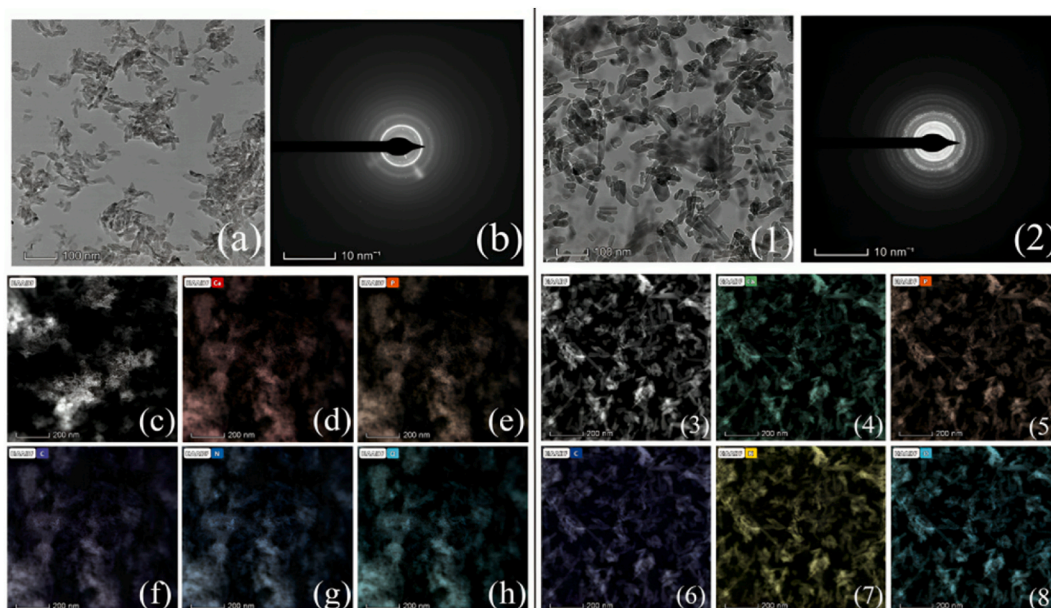


Fig. 4. TEM images of  $S_W$  (a–h) and  $S_H$  (1–8).

environment and variations in dipole motions. When nanourea was compared to urea, the spectral peak shift in H-N-H ( $3200\text{--}3430\text{ cm}^{-1}$ ) and peak widening were detected, indicating an induced change in the HAP nanostructures. When compared to bare HAP nanoparticles, the phosphate sites of the nanourea were found with lower intensities. Intramolecular interactions generated by urea doped on the surface of HAP nanoparticles changed the vibrational rhythm and caused spectrum shifts in the phosphate bands as reported by Sharma et al. [23]. The phosphate sites in the nanohybrids were occupied by the chemical reaction with urea. The data suggested that hydroxyapatite and urea interacted, presumably via hydrogen bonding. Kottegoda et al. [18] reported similar findings.

### 3.2.1. TEM

Fig. 4 shows the comparison of particle morphology of  $S_W$  and  $S_H$  in the TEM images. In both Fig. 4(a) and (1) represent the rod-shaped and clustered nanourea structures. Due to the hydrophilicity of HAP,  $S_W$  and  $S_H$  were in an elongated spindle-like cluster [23]. The average particle length and width of  $S_H$  were  $74.69 \pm 25\text{ nm}$  and  $20.44 \pm 6.17\text{ nm}$ , respectively which was 38.92 % and 30.88 % larger than  $S_W$  both in length and width. Figs. 4–1 shows the promoted growth of nanoparticles during hydrothermal synthesis because of high temperature and pressure Gyergyek et al., 2012 [24]. In addition, concentric diffraction rings in selected area (electron) diffraction (SAED) patterns of  $S_H$  showed the highest crystallinity than  $S_W$  (Fig. 4-b, 4-2). Synthesis of HAP in high temperature increased crystallinity which also supports our XRD results. A similar result was reported by Huang et al., 2019 [25].

Fig. 4 (c-h; 3–8) presents STEM-EDS elemental mapping of  $S_W$  and  $S_H$  where denotation of C, O, P, Ca, and N is blue, cyan, red, green, and yellow respectively. It can be concluded the presence of all molecules in the nanourea from the images. Images of a high-angle annular dark-field (HAADF) detector depict clear and wide edges of  $S_H$  due to its high crystallinity.

### 3.3. Thermal properties of nanourea

Fig. 5 shows the DTA/TGA traces of  $S_W$  and  $S_H$  samples in the bare state, urea, and  $S_W$  and  $S_H$ . Thermogravimetric traces for urea exhibited three stages: the first  $146.4\text{--}275.0\text{ }^\circ\text{C}$  with a 70.2 % weight loss corresponded to the formation of biuret, eqn (2), the second

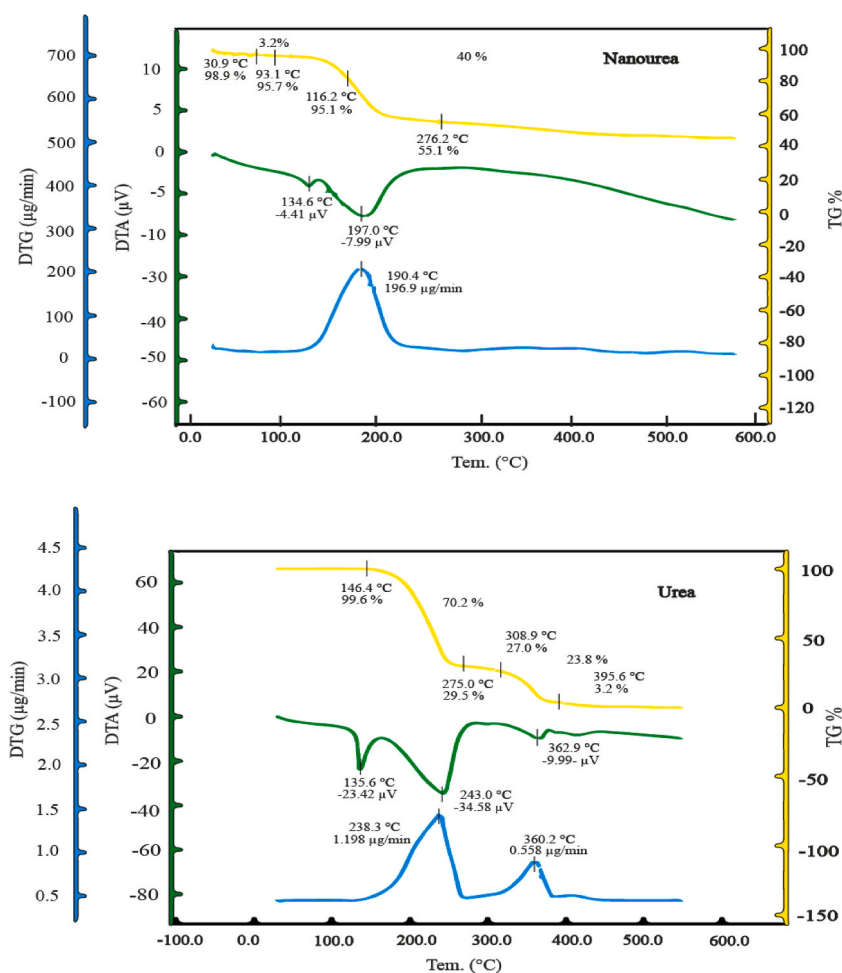
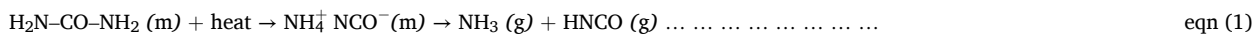


Fig. 5. TG/DTA result showing thermal property and weight loss of nanourea and urea.

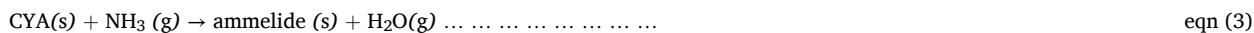
308.9–395.6 °C with a 13.3 % weight loss corresponded to the decomposition of urea to biuret and cyanic acid, and the production of a negligible amount of ammelide, eqn (4); and the third >395.6 °C with a 3.2 % weight loss represented the formation of cyanuric acid eqn (3). The reactions are given below:



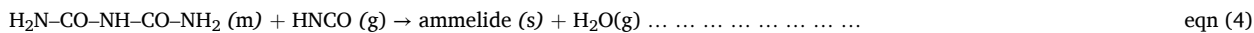
Urea ammonium cyanate ammonia cyanic acid



Urea cyanic acid biuret



Cyanuric acid ammonia



Biuret cyanic acid.

The decomposition began at the temperature of 146.4 °C, eqn (1) [26], and at about 160 °C, the reaction between intact urea and the urea decomposition product HNCO started to form biuret, eqn (2) [27]. The direct reaction of cyanuric acid that might produce cyanuric acid with accessible NH<sub>3</sub> (amination) was the conceptually simplest method of producing ammelide. This was a seemingly obvious method, but it could only happen in high pressure or at temperatures above 300 °C which existed during the decomposition process [28]. When NH<sub>3</sub> was taken out of the system during the commercial preparation of cyanuric acid in a kiln, less ammelide was typically produced. Although this would appear to be compatible with eqn (3), it is more likely that the scenario reflected how cyanuric acid is prepared in the laboratory as opposed to an industrial setting, where temperature gradients in the kiln may provide circumstances that are conducive to the creation of ammelide in this way. The direct reaction of biuret with HNCO, eqn. (4), which resulted in the synthesis of ammelide in our experiment, is a more likely parallel laboratory route that results in cyanuric acid [29,30]. There was an abrupt decrease in weight loss after 395.6 °C, which is the final decomposition temperature of urea [31]. For the nanourea, weight loss decreased gradually due to the loss of associated water and there was a sudden change at the temperature of 276.2 °C where most of the urea was decomposed. This result supports the finding of [32] revealing the attachment of urea nearly 45.9 %. The doses of nanourea were calibrated from this finding (referring to the section on materials and methods).

### 3.4. Yields of rice grain and straw

All the treatments showed significant effects on rice yields for S<sub>w</sub> (both grain and straw) ( $p < 0.001$ ). Grain yields ranged from 4.56 t ha<sup>-1</sup> to 6.52 t ha<sup>-1</sup> for different treatments (Table 1). Treatment T<sub>3</sub> had a significantly higher yield (6.52 t ha<sup>-1</sup>) than the treatments T<sub>1</sub> (6.51 t ha<sup>-1</sup>) and T<sub>2</sub> (6.47 t ha<sup>-1</sup>) which were statistically alike. In addition, among the nanourea treatments, the highest (6.52 t ha<sup>-1</sup>) and the lowest (6.20 t ha<sup>-1</sup>) yields were generated by T<sub>3</sub> and T<sub>4</sub>, respectively, which were statistically different. Considering all the treatments, the lowest yield was found in T<sub>0</sub> (4.56 t ha<sup>-1</sup>). Overall, the grain yields in T<sub>3</sub>, T<sub>2</sub>, and T<sub>4</sub> were 42.99 %, 42.06 %, and 36.01 % higher than in T<sub>0</sub>. In the case of straw, treatments also showed significant effects ( $p < 0.001$ ). Straw yield varied from 5.41 t ha<sup>-1</sup> to 7.93 t ha<sup>-1</sup> for different treatments. The treatment T<sub>1</sub> produced the highest yield (7.93 t ha<sup>-1</sup>) followed by the second highest T<sub>2</sub> (7.21 t ha<sup>-1</sup>) which were statistically comparable. However, T<sub>3</sub> (6.85 t ha<sup>-1</sup>) and T<sub>4</sub> (6.83 t ha<sup>-1</sup>) were statistically different from T<sub>1</sub>. Among the urea-HAP treatments, the highest and the lowest straw yields were found in T<sub>2</sub> (7.21 t ha<sup>-1</sup>) and T<sub>4</sub> (6.83 t ha<sup>-1</sup>) which were statistically analogous. Straw yields in T<sub>2</sub>, T<sub>3</sub>, and T<sub>4</sub> were 33.29 %, 26.73 % and 26.23 % higher than T<sub>0</sub>.

Different results were obtained from S<sub>H</sub>. Grain yield responded positively to the treatments ranging from 4.61 t ha<sup>-1</sup> to 6.84 t ha<sup>-1</sup> and the effects were significant ( $p < 0.001$ ). From Fig. 5, it is evident that T<sub>2</sub> showed the highest grain yield (6.84 t ha<sup>-1</sup>) while T<sub>0</sub> supplied the lowest (4.61 t ha<sup>-1</sup>). The treatments T<sub>1</sub> and T<sub>3</sub> provided a yield of 6.47 t ha<sup>-1</sup> and 6.43 t ha<sup>-1</sup> which were statistically similar but differed from T<sub>2</sub>. Nanourea-treated pots (T<sub>2</sub> and T<sub>3</sub>) showed 48.4 % and 39.5 % higher yields than T<sub>0</sub>. In the case of straw yield, treatment effects were significant ( $p < 0.001$ ) and the yield ranged from 5.47 t ha<sup>-1</sup> to 8.44 t ha<sup>-1</sup>. The highest yield was

**Table 1**

Effect of different nanourea treatments on grain and straw yield of Boro rice (Here, T<sub>0</sub> = Control, T<sub>1</sub> = 100 % Urea, T<sub>2</sub> = 100 % urea-HAP, T<sub>3</sub> = 75 % urea-HAP, and T<sub>4</sub> = 50 % urea-HAP.).

Treatments	Chemical Co-Precipitation		Hydrothermal	
	Grain yield (t ha <sup>-1</sup> )	Straw yield (t ha <sup>-1</sup> )	Grain yield (t ha <sup>-1</sup> )	Straw yield (t ha <sup>-1</sup> )
T <sub>0</sub>	4.56 ± 0.1 c	5.41 ± 0.20 c	4.61 ± 0.14 c	5.47 ± 0.11 d
T <sub>1</sub>	6.51 ± 0.09 a	7.93 ± 0.36 a	6.47 ± 0.04 b	8.44 ± 0.07 a
T <sub>2</sub>	6.47 ± 0.1 a	7.21 ± 0.02 ab	6.84 ± 0.08 a	7.73 ± 0.11 b
T <sub>3</sub>	6.52 ± 0.07 a	6.85 ± 0.18 b	6.43 ± 0.1b	6.97 ± 0.07 c
T <sub>4</sub>	6.20 ± 0.12 b	6.83 ± 0.34 b		
Statistics (P < 0.05)				
Treatments	***	***	***	***



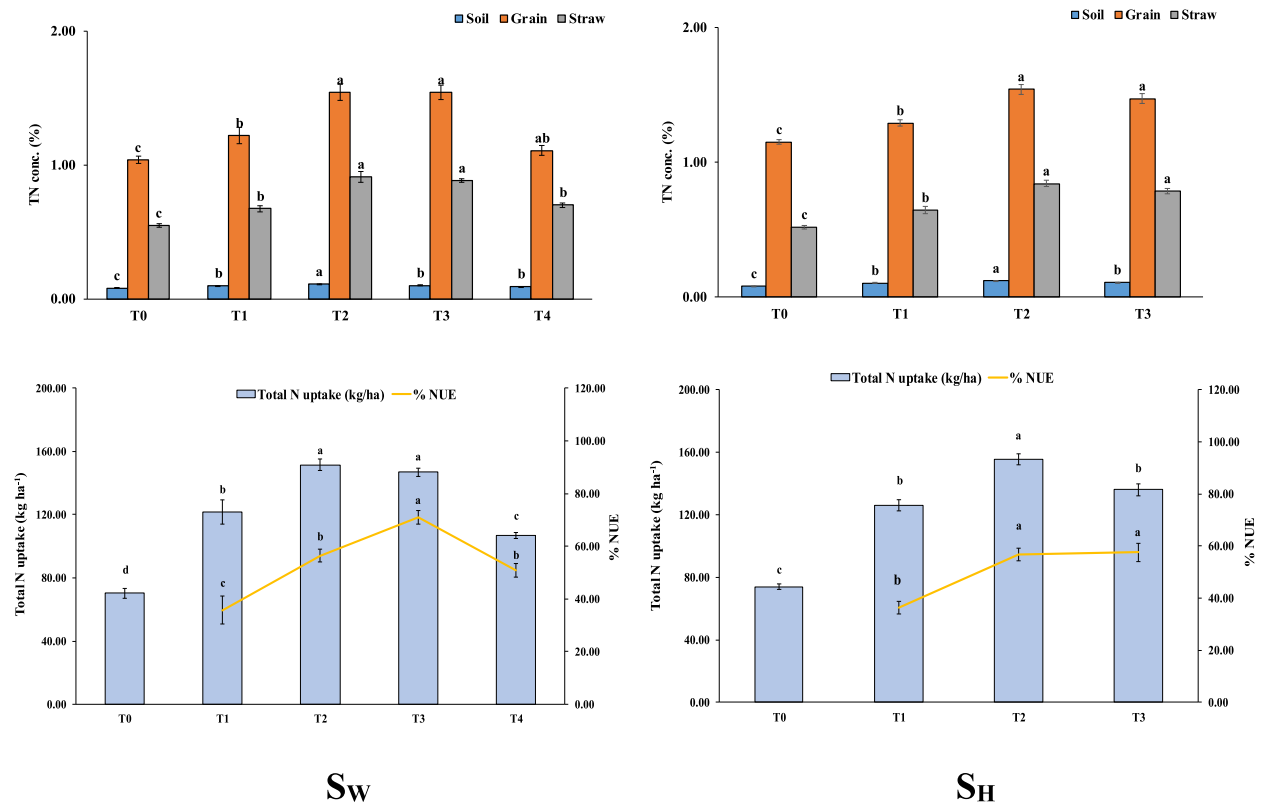
generated by T<sub>1</sub> followed by T<sub>2</sub>, T<sub>3</sub>, and T<sub>0</sub> (7.73 t ha<sup>-1</sup>, 6.97 t ha<sup>-1</sup>, and 5.37 t ha<sup>-1</sup>), respectively, where the latter three were statistically different from T<sub>1</sub>. Nanourea-treated pots (T<sub>2</sub> and T<sub>3</sub>) provided 41.3 % and 35.6 % higher yields than T<sub>0</sub>.

In this experiment, the conventional urea fertilizer was provided following the recommended dose in three splits [33] whereas the nanourea was applied in different doses in two splits. There was a large gap of 26 days between the first and the last split of the nanourea application whereas the urea was applied at a 14-day interval. The experiment revealed that a 75 % supply of S<sub>W</sub> produced a significantly higher yield where 100 % S<sub>W</sub> and 100 % synthetic urea shared similar kinds of data statistically. For S<sub>H</sub>, a 100 % supply of nanourea statistically outperforms the grain yield by 100 % synthetic urea. Therefore, the yield penalty was checked by nanourea in both cases. It happened because of the synchronization of the physiological N demand of the rice plants and N supply by the nanourea. Rice plant needs a relatively continuous N supply during their whole life cycle to sustain vegetative and reproductive growth. Only a fertilizer that has the property of a slow-release nutrient supplier can fit this criterion. Higher yield from nano fertilizer was reported by Al-Khuzai & Al-Juthery., 2020 [34] which aligns with the findings of this experiment. Yields can be variable as they depend on several factors, for instance, terrain, soil properties, variety, and climate [35,36]. In terms of straw and grain yield, the synthetic urea showed higher straw yield with lower grain yield compared to the nanourea produced in both methods. More vegetative growth is induced as synthetic urea was applied in three splits up to the 50 days of transplanting, whereas the application of nanourea in two splits created a stressed condition for rice plants to shift their growth from vegetative to reproductive. It was evident that flowering first occurred in nanourea-treated pots. The flowering of rice is delayed by one to four days due to N application and further application of increased amount of N fertilizer led to more late flowering [37]. Therefore, it is better to assess the potentiality of the nanourea from the following perspectives discussed below.

### 3.5. Nitrogen loss investigations

#### 3.5.1. Total nitrogen concentration

The effects were significant ( $p < 0.001$ ) for all the treatments on total N in soil (%), total N in grain (%), and total N in straw (%) (Fig. 6). For S<sub>W</sub>, TN% in soil ranged from 0.09 % to 0.11 % for different treatments. T<sub>2</sub> generated significant TN% in soil (0.11 %) followed by T<sub>3</sub> (0.10 %), T<sub>1</sub> (0.10 %), and T<sub>4</sub> (0.09 %) where the latter three were statistically analogous. TN% in soil for the nanohybrid treatments (T<sub>2</sub>, T<sub>3</sub>, and T<sub>4</sub>) were approximately 37.5 %, 25 %, and 12.5 % higher compared to T<sub>0</sub>, respectively. The residual N was 1 g per pot higher in T<sub>2</sub> treatments, estimated to be 200 kg ha<sup>-1</sup>, than the sole application of urea. TN% in grain ranged



**Fig. 6.** Total Nitrogen, Total N uptake, and % NUE obtained from S<sub>W</sub> and S<sub>H</sub> treatments (S<sub>W</sub> = nanourea synthesized by chemical co-precipitation method; S<sub>H</sub> = nanourea synthesized by hydrothermal method; T<sub>0</sub> = Control; T<sub>1</sub> = 100 % urea; T<sub>2</sub> = 100 % urea-HAP; T<sub>3</sub> = 75 % urea-HAP; T<sub>4</sub> = 50 % urea-HAP).

from 1.04 % to 1.54 % for different treatments. The highest value of TN% in grain (1.54 %) was found in both T<sub>2</sub> and T<sub>3</sub> followed by T<sub>1</sub> (1.22 %) and T<sub>4</sub> (1.11 %) where the latter two were significantly different ( $p < 0.001$ ). The lowest value was found in T<sub>0</sub> (1.04 %) which was different from all other treatments statistically. T<sub>2</sub> and T<sub>3</sub> showed nearly one and a half times higher TN% in grain compared to T<sub>0</sub>. Turning to the TN% in straw, the treatments showed significant effects ( $p < 0.001$ ). TN% in straw ranged from 0.55 % to 0.91 % for different treatments. T<sub>2</sub> rendered significant TN% in straw (0.91 %) followed by T<sub>3</sub> (0.88 %) and they were statistically comparable. The effect of T<sub>4</sub> (0.70 %) was statistically analogous to T<sub>1</sub> (0.67 %). The lowest value was found in T<sub>0</sub> (0.55 %). TN% in straw for T<sub>2</sub>, T<sub>3</sub>, and T<sub>4</sub> were around 1.67, 1.62, and 1.28 times higher compared to T<sub>0</sub>.

For S<sub>H</sub>, the effects were also significant ( $p < 0.001$ ) for all the treatments on total N in soil (%), total N in grain (%), and total N in straw (%). Surprisingly, the treatment T<sub>2</sub> had significantly higher N content in soil (0.12 %) compared to T<sub>1</sub> (0.10 %) and T<sub>3</sub> (0.11 %) where the latter two were statistically comparable. The treatment T<sub>0</sub> has a lower amount of soil TN (0.08 %). Therefore, T<sub>2</sub> and T<sub>3</sub> increased total soil N by 400 and 200 kg ha<sup>-1</sup>. For grain TN%, the treatment effects were also significant ( $p < 0.001$ ). The treatment T<sub>2</sub> generated the highest TN (1.54 %) followed by T<sub>3</sub> (1.47 %) which was statistically analogous. T<sub>1</sub> produced 1.29 % TN in grain which was statistically different. T<sub>0</sub> showed the lowest TN. In the case of straw, the trend was similar to grain for TN%. The treatment effects were significant ( $p < 0.001$ ). The highest TN (0.84 %) was generated by T<sub>2</sub> followed by T<sub>3</sub> (0.78 %) which was statistically analogous. T<sub>1</sub> produced 0.64 % TN in grain which was statistically different from T<sub>2</sub> and T<sub>3</sub>. T<sub>0</sub> showed the lowest TN in straw. As a slow-release fertilizer, S<sub>W</sub> & S<sub>H</sub> perfectly supplied the nutrients according to the plant's necessity and rendered a considerable amount of N in the soil. The treatment T<sub>2</sub> of S<sub>W</sub> and T<sub>2</sub> and T<sub>3</sub> of S<sub>H</sub> provided the soil with 200, 400 kg, and 200 kg N ha<sup>-1</sup>, respectively, which is enough to sustain the next season's rice production.

### 3.5.2. Total N uptake

The overall uptake of N was significantly influenced by the application of urea and different rates of nanourea ( $p < 0.001$ ) (Fig. 6). For S<sub>W</sub>, the uptake of N ranged from 70.26 to 151.44 kg ha<sup>-1</sup> for different treatments. The T<sub>2</sub> treatment (151.44 kg ha<sup>-1</sup>) generated the maximum N uptake, which was statistically analogous to the T<sub>3</sub> treatment (146.91 kg ha<sup>-1</sup>), followed by T<sub>1</sub> (121.75 kg ha<sup>-1</sup>), T<sub>4</sub> (107.00 kg ha<sup>-1</sup>), and T<sub>0</sub> (70.26 kg ha<sup>-1</sup>) where the rest three were statistically different. The T<sub>2</sub>, T<sub>3</sub>, and T<sub>4</sub> treatments had approximately two and one and a half times higher uptake in contrast to T<sub>0</sub>, respectively. Turning to S<sub>H</sub>, the N uptake ranged from 73.85 to 155.61 kg ha<sup>-1</sup>. Here, The T<sub>2</sub> treatment (155.61 kg ha<sup>-1</sup>) also generated the maximum N uptake, followed by T<sub>3</sub> (136.04 kg ha<sup>-1</sup>) and T<sub>1</sub> (126.18 kg ha<sup>-1</sup>) where the rest two were statistically analogous. The treatment T<sub>0</sub> showed the minimum uptake (73.85 kg ha<sup>-1</sup>). The T<sub>2</sub> and T<sub>3</sub> treatments had approximately two times higher uptake compared to T<sub>0</sub>.

### 3.5.3. N use efficiency (NUE)

N use efficiency (NUE) was significantly altered by the treatment effect ( $p < 0.001$ ) (Fig. 6). The S<sub>W</sub> treatments generated the maximum NUE compared to S<sub>H</sub> where T<sub>3</sub> of S<sub>W</sub> achieved maximum use efficiency (71.0 %), which was statistically different from T<sub>2</sub> (56.4 %) and T<sub>4</sub> (51.1 %) treatment. Besides that, T<sub>1</sub> treatment provided the minimum NUE (35.8 %). All the nanourea treatments of S<sub>W</sub> (T<sub>2</sub>, T<sub>3</sub>, T<sub>4</sub>) showed around 1.5 to 2 times greater NUE compared to urea (T<sub>1</sub>). In the case of S<sub>H</sub>, T<sub>3</sub> achieved maximum use efficiency (57.6 %), which was statistically equivalent to T<sub>2</sub> (56.8 %). However, T<sub>1</sub> provided the minimum NUE (36.3 %). All the nanourea treatments of S<sub>H</sub> (T<sub>2</sub> and T<sub>3</sub>) had shown around 1.5 times greater NUE compared to urea (T<sub>1</sub>).

Qureshi et al., 2018 [38] reported nanofertilizers as a controlled nutrient supplier that supports the properties of S<sub>W</sub> and S<sub>H</sub>. Nano fertilizers are highly reactive due to their large surface area [39,40], helping nutrients spread out in the soil and become more available to plants. This might be the possible rationale for enhanced N uptake in T<sub>2</sub> suggesting the treatment provided the rice plants with the necessary N, thus nutrient mining did not take place. The T<sub>3</sub> of S<sub>W</sub> can also be taken under consideration as it showed lower TN in soil but similar TN in grain and straw suggesting possible nutrient mining. In contrast, T<sub>3</sub> of S<sub>H</sub> showed higher TN in soil with nearly similar TN in grain and straw suggesting more consistency in sustaining soil fertility and nutritional enrichment. Amanullah et al., 2020. [41] found that nanofertilizers are available in soil for a longer period often covering the entire growing season. That is why nanourea was able to compensate for the soil TN while boosting the N content in grain and straw. Thus, it can be a sustainable option.

The TN in grain was notably higher in nanourea treatments compared to sole application of urea which certainly enhanced the nutritional quality of the grains. Increased N content in grains will ensure quality food for an increased population by enhancing gene expression and protein synthesis. Deo et al., 2022 [42] observed enhanced N content in grain for nano-DAP and Behboudi et al., 2018 [43] and Cakmak, 2000 [44] recorded similar findings for nano-zinc which may also fit for the nanourea. Additionally, the straw showed higher TN for nanourea treatments than sole urea. Therefore, the harvested straw can be incorporated into the soil as a way of conservation agriculture which may supply N to the next crop readily [45].

Rice plants in the T<sub>3</sub> of S<sub>W</sub> and S<sub>H</sub> showed the highest NUE (71.0 % and 57.6 %, respectively). Kottegoda et al., 2017 [18] reported 48 %, Sharmila, 2010 [46] reported 58 % and Gupta & Prakash, 2020 [47] reported a three-fold increase in NUE which is aligned with our findings. Since the TN in grain and straw was higher in nanourea treatments while the yield was quite similar to sole urea, N uptake was higher for those treatments generating higher NUE. However, T<sub>3</sub> of S<sub>H</sub> cannot meet the demand for other parameters, for instance, yield, TN in grain and straw, and N uptake compared to T<sub>3</sub> of S<sub>W</sub>. The T<sub>3</sub> of S<sub>W</sub> generated the highest efficiency when 25 % less N was supplied to the rice plants than the conventional practice. However, T<sub>3</sub> of S<sub>H</sub> showed higher N in soil compared to T<sub>3</sub> of S<sub>W</sub>. Higher N content in the soil means lower uptake and lower NUE. It can be due to the much slower N release and dissolution of the N in soil which becomes available to plants, lack of harmonization with the growth stages of rice plants, and way of reaction in the field temperature as they were also synthesized in high temperature.

For controlled-release prilled fertilizer, there are two different ways of N release, (1) fertilizer dissolution within the prilled form, and (2) N diffusion from the prilled form into the soil solution. This process is predominantly mediated by soil temperature, soil

moisture, and time, with soil temperature identified as the primary factor determining the controlled release of N from fertilizers [48, 49]. Additionally,  $T_4$  of  $S_W$  also generated considerable NUE due to increased uptake by the plants while having 50 % less N rate, indicating maximum N mining from the soil comparing the TN with initial soil N. That means, though the uptake and NUE were higher in terms of dose in  $T_4$ , N mining in soil occurred simultaneously which is not a sustainable practice.

Overall, the NUE was high for the nanourea treatments ( $T_2$ ,  $T_3$ ,  $T_4$ ) both in  $S_W$  and  $S_H$ . Higher NUE means lower doses, supporting the hypothesis of reducing the number of split applications of urea ( $n = 2$ ) and decreasing the rapid solubility of conventional urea for checking N loss. Thus,  $T_3$  of  $S_W$  will be environmentally feasible as it has higher NUE which prevents N loss through different pathways, for instance, volatilization, leaching, and denitrification which is in agreement with Solanki et al., 2015 [50] and Chhipa & Joshi, 2016 [51]. Also,  $T_3$  can be a sustainable solution where lower N input (25 %) will be possible with a similar output of conventional fertilizer. The total soil N content (%) in  $T_3$  is similar to  $T_1$ , however, accounts for nearly similar uptake as  $T_2$ . The yield of  $T_3$  was also higher among the nano urea-treated pots. The NUE of  $T_3$  was higher than any other treatment. It is evident, that plants that received  $T_3$  treatment had a positive response to the nanourea along with a necessity of N which was supplied by the soil. Therefore,  $T_3$  of  $S_W$  is a sustainable option. For  $S_H$ , the treatment  $T_2$  had higher yield, TN in soil, grain, and straw, uptake, and nearly similar NUE to  $T_3$ . Therefore,  $T_2$  performed the best among different  $S_H$  treatments. Considering both types of nanourea,  $T_3$  of  $S_W$  with 25 % less N content and two split applications outperforms all other treatments suggesting environmental sustainability.

### 3.6. Economic feasibility of nanourea

Bangladesh is one of the largest importers of Urea in the world. The annual demand for urea is 2.9 million tons on average where 70 % of the demand is met with import. The average import cost of urea is \$645 per ton in Bangladesh which is definitely mining our foreign reserve every year. Additionally, the government of Bangladesh has to subsidize \$128 per ton of urea so that farmers can buy them at a lower cost to sustain crop production Uzzaman, 2023 [52]. However, it can be easily comprehended that any disruption in the supply chain of urea will negatively impact the country's overall production system. Therefore, it is necessary to seek alternatives to resolve the issue of sustainable rice production as the security of food for our country. Nanourea can take a leading role here. As nanourea can be synthesized in Bangladesh with the help of local experts and our recommendation is to use 25 % less than the amount farmers are currently using, our foreign reserve can be saved since less amount of urea has to be bought and transported. Farmers also have to buy less amount of fertilizer and transport less of the usual amount. Thus, it can save money for the farmers and reduce the overall cost of production. Moreover, nanourea can be produced in the country so the fertilizer cost would be lower. Therefore, the government doesn't have to subsidize more money here. All we need is to commercialize the production of nanourea. The country has several state-run urea production factories that can take the role of establishing and supplying overall infrastructure for the local experts. Last but not least, the indirect economic saving would be the lower environmental hazards due to the excessive use of urea. The indiscriminate use of urea could lead to different natural hazards that might cost a huge amount of public funds. This can be checked by this nanourea. Further investigation is necessary in this regard.

## 4. Conclusions

Our research on nanourea has revealed positive implications for sustainable rice production. The study has clarified the structure and properties of nanourea using a thorough set of investigations, including X-ray Diffraction, Fourier Transform Infrared Spectroscopy, and Thermogravimetric/Differential Thermal Analysis. The results have shown that nanourea has a slow-release tendency because of the urea molecules coated on nHAP. This slow-release property is crucial because it tackles the common problem of N loss in conventional urea fertilization methods. The field trial has provided more evidence of the usefulness of nanourea in rice farming. In comparison to standard urea applications, rice plants treated with nanourea have shown improved yields, greater N content in the grains and straw, and much higher NUE. The most effective treatment group,  $T_3$  of  $S_W$ , has suggested that nanourea can provide a sustainable nitrogen supply with a 25 % reduced N input, opening up a promising new path for agricultural methods that are both economically and environmentally sound. Given the growing global need for N fertilizers and the resulting difficulties in preserving soil fertility, minimizing nutrient losses, and assuring sustainable food production, this research is extremely pertinent. A potential answer to these problems can be found in the creative use of nanotechnology, as shown by the effective production and use of nanourea. However, as the very first field trial of nanourea that has been synthesized and trialed in Bangladesh, we acknowledge our limitations. A larger sample size would have given us more data and a robust statistical analysis. That is why we believe that further research is necessary to fully confirm its long-term effects, scalability, and economic sustainability within the diversified ecosystem.

### Data availability statement

Data will be made available on request.

### CRediT authorship contribution statement

**Md Abdullah Al Asif:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Farah Mahjabin:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sourav Kumar Singha:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Mohammad Mofizur Rahman Jahangir:** Validation, Supervision, Funding acquisition. **Sheikh Manjura Hoque:** Writing – review & editing, Visualization, Validation,

Supervision, Resources, Funding acquisition, Conceptualization.

### 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.

### Acknowledgments

The authors acknowledge Bangladesh Atomic Energy Commission, Dhaka, greatly.

### References

- [1] FAO UN Report, Global Hunger Numbers Rose to as Many as 828 Million in 2021, Newsroom (2022) (who.int).
- [2] A. Ahmed, M.M. Bakhtiar, Boro rice procurement in Bangladesh: Implications for policy, International Food Policy Research Institute (IFPRI, Washington, DC, 2020. <https://doi.org/10.2499/p15738coll2.133724>.
- [3] H. Chhipa, Nanofertilizers and nanopesticides for agriculture, *Environ. Chem. Lett.* 15 (2017) 15–22.
- [4] J.H. Guo, X.J. Liu, Y. Zhang, J.L. Shen, W.X. Han, W.F. Zhang, P. Christie, K.W.T. Goulding, P.M. Vitousek, F.S. Zhang, Significant acidification in major Chinese croplands, *Science* 327 (5968) (2010) 1008–1010.
- [5] D. Tilman, K.G. Cassman, P.A. Matson, R. Naylor, S. Polasky, Agricultural sustainability and intensive production practices, *Nature* 418 (6898) (2002) 671–677.
- [6] W. Zhang, Z. Dou, P. He, X.-T. Ju, D. Powlson, D. Chadwick, D. Norse, Y.-L. Lu, Y. Zhang, L. Wu, New technologies reduce greenhouse gas emissions from nitrogenous fertilizer in China, *Proc. Natl. Acad. Sci. USA* 110 (21) (2013) 8375–8380.
- [7] G.X. Cai, D.L. Chen, H. Ding, A. Pacholski, X.H. Fan, Z.L. Zhu, Nitrogen losses from fertilizers applied to maize, wheat and rice in the North China Plain, *Nutrient Cycl. Agroecosyst.* 63 (2002) 187–195.
- [8] X. Chen, C. Ma, H. Zhou, Y. Liu, X. Huang, M. Wang, Y. Cai, D. Su, M.A. Muneer, M. Guo, Identifying the main crops and key factors determining the carbon footprint of crop production in China, 2001–2018, *Resour. Conserv. Recycl.* 172 (2021) 105661.
- [9] P. Li, J. Lu, W. Hou, Y. Pan, Y. Wang, M.R. Khan, T. Ren, R. Cong, X. Li, Reducing nitrogen losses through ammonia volatilization and surface runoff to improve apparent nitrogen recovery of double cropping of late rice using controlled release urea, *Environ. Sci. Pollut. Control Ser.* 24 (2017) 11722–11733.
- [10] X.Q. Liang, Y.X. Chen, H. Li, G.M. Tian, W.Z. Ni, M.M. He, Z.J. Zhang, Modeling transport and fate of nitrogen from urea applied to a near-trench paddy field, *Environ. Pollut.* 150 (3) (2007) 313–320.
- [11] K. Lakshman, M. Chandrakala, P.S. Prasad, G.P. Babu, T. Srinivas, N.R. Naik, A. Korah, Liquid nano-urea: an emerging nano fertilizer substitute for conventional urea, *Chronicle of Bioresource Management* 6 (Jun, 2) (2022) 54–59.
- [12] M.C. DeRosa, C. Monreal, M. Schnitzer, R. Walsh, Y. Sultan, Nanotechnology in fertilizers, *Nat. Nanotechnol.* 5 (2) (2010), 91–91.
- [13] V. Karunaratne, N. Kottegoda, A. De Alwis, Nanotechnology in a world out of balance, *J. Natl. Sci. Found. Sri Lanka* 40 (1) (2012) 3–8.
- [14] N. Kottegoda, I. Munaweera, N. Madusanka, V. Karunaratne, A green slow-release fertilizer composition based on urea-modified hydroxyapatite nanoparticles encapsulated wood, *Curr. Sci.* (2011) 73–78.
- [15] J. Gómez-Morales, M. Iafisco, J.M. Delgado-López, S. Sarda, C. Drouet, Progress on the preparation of nanocrystalline apatites and surface characterization: overview of fundamental and applied aspects, *Prog. Cryst. Growth Char. Mater.* 59 (1) (2013) 1–46.
- [16] S. Sprio, M. Sandri, A. Ruffini, A. Adamiano, M. Iafisco, M. Dapporto, S. Panseri, M. Montesi, A. Tampieri, Tissue engineering and biomimetics with bioceramics, in: *Advances in Ceramic Biomaterials*, Elsevier, 2017, pp. 407–432.
- [17] A. Tampieri, M. Iafisco, S. Sprio, A. Ruffini, S. Panseri, M. Montesi, A. Adamiano, M. Sandri, Hydroxyapatite: from nanocrystals to hybrid nanocomposites for regenerative medicine, *Handbook of Bioceramics and Biocomposites* (2016) 119–144.
- [18] N. Kottegoda, C. Sandaruwan, G. Priyadarshana, A. Siriwardhana, U.A. Rathnayake, D.M. Berugoda Arachchige, A.R. Kumarasinghe, D. Dahanayake, V. Karunaratne, G.A. Amaratunga, Urea-hydroxyapatite nanohybrids for slow release of nitrogen, *ACS Nano* 11 (2) (2017) 1214–1221.
- [19] Brammer H., Antoine J., Kassam A.H., van Velthuisen H.T., Land resources appraisal of Bangladesh for agricultural development, *Agroecological regions of Bangladesh* (1988). Report 5: Land resources, v. 2-5: Land resources map and legend, Sherour - Jamalpur - Tangail (fao.org).
- [20] D.R. Keeney, D.W. Nelson, Nitrogen-inorganic forms, in: A.L. Page (Ed.), *Agronomy Monographs*, American Society of Agronomy, Soil Science Society of America, 2015, pp. 643–698, <https://doi.org/10.2134/agronmonogr9.2.2ed.c33>.
- [21] G.J.E. Poinern, R. Brundavanam, X.T. Le, S. Djordjevic, M. Prokic, D. Fawcett, Thermal and ultrasonic influence in the formation of nanometer scale hydroxyapatite bio-ceramic, *Int. J. Nanomed.* (2011) 2083–2095.
- [22] L.B. Sagle, Y. Zhang, V.A. Litosh, X. Chen, Y. Cho, P.S. Cremer, Investigating the hydrogen-bonding model of urea denaturation, *J. Am. Chem. Soc.* 131 (26) (2009) 9304–9310.
- [23] B. Sharma, L.O. Afonso, M.P. Singh, U. Soni, D.M. Cahill, Zinc-and magnesium-doped hydroxyapatite-urea nanohybrids enhance wheat growth and nitrogen uptake, *Sci. Rep.* 12 (1) (2022) 19506.
- [24] S. Gyergyek, M. Drogenik, D. Makovec, Oleic-acid-coated CoFe<sub>2</sub>O<sub>4</sub> nanoparticles synthesized by co-precipitation and hydrothermal synthesis, *Mater. Chem. Phys.* 133 (1) (2012) 515–522.
- [25] G. Huang, C.-H. Lu, H.-H. Yang, Magnetic nanomaterials for magnetic bioanalysis, in: *Novel Nanomaterials for Biomedical, Environmental and Energy Applications*, 2019, pp. 89–109.
- [26] A. Zabardasti, Theoretical calculation of equilibrium constant for keto-enol tautomerism in cyanuric acid, *Chem. Heterocycl. Compd.* 43 (2007) 1344–1346.
- [27] E. Kinne-Saffran, R.K.H. Kinne, Vitalism and synthesis of urea: from friedrich wöhler to hans A. Krebs, *Am. J. Nephrol.* 19 (2) (1999) 290–294.
- [28] P. Kumar, R.K. Gupta, D.S. Pandey, Half-sandwich arene ruthenium complexes: synthetic strategies and relevance in catalysis, *Chem. Soc. Rev.* 43 (2) (2014) 707–733.
- [29] K. Jug, On the development of semiempirical methods in the MO formalism, *Theor. Chim. Acta* 14 (2) (1969) 91–135.
- [30] X. Zhu, X. Zhou, Y. Jing, Y. Li, Electrochemical synthesis of urea on MBenes, *Nat. Commun.* 12 (1) (2021) 4080.
- [31] L. Stradella, M. Argentero, A study of the thermal decomposition of urea, of related compounds and thiourea using DSC and TG-EGA, *Thermochim. Acta* 219 (1993) 315–323.
- [32] P.M. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach, J. Brauer, Thermal decomposition (pyrolysis) of urea in an open reaction vessel, *Thermochim. Acta* 424 (1–2) (2004) 131–142.
- [33] FRG, Fertilizer Recommendation Guide-2018, vol. 1215, Bangladesh Agricultural Research Council (BARC), Farmgate, Dhaka, 2018.
- [34] A.H.G. Al-Khuzai, H.W.A. Al-Juthery, Effect of DAP fertilizer source and nano fertilizers (silicon and complete) spray on some growth and yield indicators of rice (*Oryza sativa* L. cv. Anber 33), *IOP Conf. Ser. Earth Environ. Sci.* 553 (1) (2020) 012008.
- [35] S.-L. Liu, C. Pu, Y.-X. Ren, X.-L. Zhao, X. Zhao, F. Chen, X.-P. Xiao, H.-L. Zhang, Yield variation of double-rice in response to climate change in Southern China, *Eur. J. Agron.* 81 (2016) 161–168.
- [36] Y. Xiong, Y. Xie, Q. Song, W. Zeng, The relationship between meteorological factors and rice yield in Liuzhi special zone, *Guizhou Agricultural Sciences* 10 (2009) 79–81.

- [37] T. Ye, Y. Li, J. Zhang, W. Hou, W. Zhou, J. Lu, Y. Xing, X. Li, Nitrogen, phosphorus, and potassium fertilization affects the flowering time of rice (*Oryza sativa* L.), *Global Ecology and Conservation* 20 (2019) e00753.
- [38] A. Qureshi, D.K. Singh, S. Dwivedi, Nano-fertilizers: a novel way for enhancing nutrient use efficiency and crop productivity, *Int. J. Curr. Microbiol. App. Sci* 7 (2) (2018) 3325–3335.
- [39] J.F. Liscano, C.E. Wilson, R.J. Norman-Jr, N.A. Slaton, Zinc Availability to Rice from Seven Granular Fertilizers, Arkansas Agricultural Experiment Station, Fayetteville, CA, USA, 2000 vol. 963.
- [40] K.S. Siddiqi, A. Husen, Plant response to engineered metal oxide nanoparticles, *Nanoscale Res. Lett.* 12 (1) (2017) 1–18.
- [41] Amanullah, H. Ullah, M. Soliman Elshikh, M.S. Alwahibi, J. Alkahtani, A. Muhammad, S. Khalid, Imran, Nitrogen contents in soil, grains, and straw of hybrid rice differ when applied with different organic nitrogen sources, *Agriculture* 10 (9) (2020) 386.
- [42] H.R. Deo, T. Chandrakar, L.K. Srivastava, N.K. Nag, D.P. Singh, A. Thakur, Effect of Nano-DAP on Yield, Nutrient Uptake and Nutrient Use Efficiency by Rice under Bastar Plateau, 2022.
- [43] F. Behboudi, Z. Tahmasebi Sarvestani, M.Z. Kassae, S.A.M. Modares Sanavi, A. Sorooshzadeh, Improving growth and yield of wheat under drought stress via application of SiO<sub>2</sub> nanoparticles, *J. Agric. Sci. Technol.* 20 (7) (2018) 1479–1492.
- [44] I. Cakmak, Tansley Review No. 111 Possible roles of zinc in protecting plant cells from damage by reactive oxygen species, *New Phytol.* 146 (2) (2000) 185–205.
- [45] A. Dobermann, T.H. Fairhurst, Rice straw management, *Better Crops International* 16 (1) (2002) 7–11.
- [46] R.C. Sharmila, Nutrient Release Pattern of Nano-Fertilizer Formulations, Tamil Nadu Agricultural University, Coimbatore, 2010.
- [47] C. Gupta, D. Prakash, Effect of nano-fertilizers on soil microflora, *Ann. Plant Sci.* 9 (2020) 3846–3859.
- [48] T. Fujita, C. Takahashi, S. Yoshida, H. Shimizu, Coated granular fertilizer capable of controlling the effect of temperature upon dissolution-out rate, Google Patents (1983). <https://patents.google.com/patent/US4369055A/en>.
- [49] O.R. Lunt, J.J. Oertli, Controlled release of fertilizer minerals by encapsulating membranes: II. Efficiency of recovery, influence of soil moisture, mode of application, and other considerations related to use, *Soil Sci. Soc. Am. J.* 26 (6) (1962) 584–587, <https://doi.org/10.2136/sssaj1962.03615995002600060020x>.
- [50] P. Solanki, A. Bhargava, H. Chhipa, N. Jain, J. Panwar, Nano-fertilizers and their smart delivery system, *Nanotechnologies in Food and Agriculture* (2015) 81–101.
- [51] H. Chhipa, P. Joshi, Nanofertilisers, nanopesticides and nanosensors in agriculture, *Nanoscience in Food and Agriculture* 1 (2016) 247–282.
- [52] S.A. Uzzaman, Bangladesh opens southeast asia's largest fertilizer factory, *Confluence* (2023, November 12). <https://theconfluence.blog/bangladesh-opens-southeast-asias-largest-fertilizer-factory/>.