Urea-Hydroxyapatite-Polymer Nanohybrids as Seed Coatings for Enhanced Germination

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Abstract

Modern agriculture practices play a vital role in fulfilling the doubling food demands of the increasing population. In particular, several attempts have been made to enhance the nutrient supply and plant uptake process in different growth stages of plants, but little effort has been made to enhance the nutrient status of the seeds at the seedling stage. At this stage of growth, phosphorus is the most essential nutrient, and the requirement is high, while nitrogen requirement is very low. This study focuses on developing a seed coating containing urea-modified hydroxyapatite nanocomposite to supply N and P to the seedlings in a controlled manner throughout the early growth stage. A nanohybrid based on urea-modified hydroxyapatite was synthesized using an in-situ sol-gel method and further combined with an alginate/cellulose polymer to develop the coating. Seed coating was realized using a dip coating method containing calcium chloride as the cross-linking agent. Seed germination experiments were conducted under laboratory conditions according to a randomized complete block design under constant light conditions, controlled humidity, and temperature. The structural features of the nanocomposite were studied using powder X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopic data was used to analyze the morphology. The formation of HA nanoparticles was confirmed by powder x-ray diffraction patterns that revealed the characteristic peaks for (002), (211), (300), and (202) planes of HA. Furthermore, the successful insertion of urea into the HA lattice was corroborated by both the powder X-ray diffraction and Fourier transform infrared spectroscopic techniques. Nanocomposite coatings of 50 -100 µm demonstrated excellent compatibility with the surfaces of the seeds. Seed coating composed of hydroxyapatite-urea (1:0.3) treatment revealed an increase of 124.6%, 147.6%, 100%, and 166.7% in average biomass, root length, number of roots, and maximum plant width, respectively, compared to the control, after 21 days of planting.

Keywords: Urea Modified Hydroxyapatite, Nanocomposite, Alginate, Carboxymethyl Cellulose, Seed Coating, Germination.

1. Introduction

With the increasing food demands of the global population, it is consequential to maintain the quality of the agricultural products using advanced technological applications (Ali et al., 2014, Prasad et al., 2014, Sharon et al., 2010, Xu et al., 2022). The emergence of a healthy plant depends on the seed's nutrient status. Among the many challenges of obtaining healthy seeds, attenuated nutrient capacity in seeds leads to seed deterioration, which is defined as deteriorative mutations occurring with the time that increase the seed's exposure to external conditions and decrease the viability and the survival of the seed, causing the loss of seed quality due to cytological, physiological and biochemical changes finally leading to seed death (Sarkar et al., 2012, Oni et al., 2022). Nitrogen, potassium, and phosphorous are the indispensable macronutrients in plants that are essential for germination, cell division, and root growth in the early stages of growth (Gunaratne et al., 2016, Silva and Uchida, 2000). The deficiency of these nutrients in plants shows chlorosis, early maturation in certain crops, lowering yield, and stunted growth due to poor cell division.

The recent efforts to infuse modern technology into the increase of food production have been particularly focused on the nanotechnology-based efficient and environmentally friendly agrochemicals (Kashyap et al., 2015, Kottegoda et al., 2014a, An et al., 2022, Rani et al., 2022).

In order to solve the problems associated with conventional fertilizers, such as premature loss, inefficient plant uptake, heavy metal contamination of living systems, and environmental pollution due to the increment of fertilizer consumption exponentially, scientists have put their fullest effort into increasing the use efficiency of fertilizers by incorporating plant nutrients into advanced delivery systems alias hybrid nanofertilizers (Ni et al., 2011, Savci, 2012b, Savci, 2012a, Azam et al., 2022). Since a biocompatible material hydroxyapatite (HA) and its derivatives showed promising results in such hybrid nanofertilizers systems (Abeywardana et al., 2021, Fernando et al., 2021, de Silva et al., 2022). HA has attracted substantial scientific interest due to its highly tailorable nature. HA [$Ca_{10}(PO_4)_6(OH)_2$] is a highly stable member of the apatite mineral family, and HA crystal is composed of closely packed Ca^{2+}, $PO4^{3-}$, and OH^- groups in hexagonal arrangement and space group of P63/m with lattice parameters a = b = 0.9423 nm and c = 0.6875 nm. The rich surface structure can be employed to fabricate nanohybrids possessing plant nutrients (Venkatasubbu et al., 2011).

In previous research work done by our team, we have reported that hydroxyapatite-urea (HA-Urea) nanohybrid is capable of releasing nitrogen 12 times slower compared to pure urea confirming the applicability of HA-urea nanohybrids as a controlled release fertilizer (Kottegoda et al., 2013, Kottegoda et al., 2017, Gunaratne et al., 2016, Kottegoda et al., 2014b). Further, urea-HA nano-systems were developed, incorporated layered materials, and investigated the efficacy of these new formulations using rice and tea as model crops (Kottegoda et al., 2012, Kottegoda et al., 2017, Madusanka et al., 2017, Raguraj et al., 2020). Moreover, HA nanoparticles have been coated with citric acid and utilized as a slow-release P plant nutrient composition to improve the growth efficiency of corn (Samavini et al., 2018).

Only a few reports are available on the development of plant nutrient nano-systems to improve germination efficiency. Adhikari et al., 2016 have reported that Zn could be supplied to plants using microns scale (<3 µm) and nanoscale (<100 nm) ZnO powder at 25 mg Zn/g coated seeds and proven the efficacy using maize (Zea mays L.), soybean (Glycine max L.), pigeon pea (Cajanas cajan L.) and ladies finger (Abelmoschus esculentus L.) (Adhikari et al., 2016). Prasad and co-workers also have studied the

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effect of ZnO nanoparticles on the germination of peanut seeds (Prasad et al., 2012). 11Moreover, it has been reported that carbon nanotubes can penetrate seed coats and accelerate the germination efficiency (Khodakovskaya et al., 2009). Further, distinctive efforts have made to make protective, nutrient-incorporated, and insecticide-incorporated seed coatings as well (Xu et al., 2020, Paravar et al., 2022, Mohanraj et al., 2022).

In this study, the effect of a seed coating containing urea-modified hydroxyapatite nanoparticles on the germination efficiency of corn seeds is reported. Availability of both N (minor amount) and P nutrients enhanced the strength of the root system and the biomass of the early stages of the plant.

2. Materials and Methods

All chemicals and reagents used in this study were purchased from Sigma- Aldrich, USA, and were of analytical grade and used without further purification. Uncoated corn seeds were obtained from the Department of Agriculture, Gannoruwa, Sri Lanka.

2.1. Experimental Methods

2.1.1. Preparation of hydroxyapatite (HA) nanoparticles

HA nanoparticles were synthesized using the in-situ sol-gel method as explained by Kottegoda et al. A dispersion of calcium hydroxide (8.12 g) in distilled water (100 cm^3) was prepared. Orthophosphoric acid (0.6 mol dm^{-3}, 100.0 cm^3) was added dropwise under continuous agitation at 1000 rpm. The stoichiometry of the reaction was maintained such that Ca:P is 1.67, which is the stoichiometric amount in hydroxyapatite. The pH of the reaction mixture was maintained at 10 (Kottegoda et al., 2011, Kottegoda et al., 2017).

2.1.2. Preparation of hydroxyapatite-urea (HA-urea) nanohybrids

To prepare 1:1 HA-urea nanohybrid, urea (25.75 g) was added to prepared $Ca(OH)_2$ (1.0 mol dm^{-3}, 250 cm^3) dispersion and was stirred for one hour. Then, H_3PO_4 (0.6 mol dm^{-3}, 250 cm^3) in a separation funnel was added dropwise at a stirring speed of 1000 rpm. Similarly, HA-urea 1:0.3 and 1:0.6 ratios were prepared using the same method by adding 7.73 g and 15.45 g of urea, respectively.

2.1.3. Synthesis of Urea-HA-polymer nanocomposite seed coating

Urea-HA nanohybrid dispersion was made compatible with the seed prior to the application. Bio-compatible polymer materials have been used while preparing the coating (Ghanbarzadeh et al., 2010, Kenawy and Sakran, 1996, Lee and Mooney, 2012, Tønnesen and Karlsen, 2002, Benchabane and Bekkour, 2008). HA dispersion (10.00 cm^3) was added to a solution containing 10% (w/v) sodium alginate and stirred for 1 h. Then, carboxymethyl cellulose (CMC) sodium salt solution was prepared by dissolving 1.20 g of carboxymethyl cellulose sodium salt in 75.00 cm^3 of hot water (60 °C.) and allowed the solution to cool to room temperature. Sodium alginate and HA mixture was added to the carboxymethyl cellulose solution and stirred for a further 2 h.

2.1.4. Preparation of coated seeds

Seeds were dipped in the urea-HA polymeric dispersion and then dipped in calcium chloride solution (1.0 mol dm^{-3}) to facilitate the cross-linking process. The same procedure was repeated for other the three HA-urea ratios, 1:0.3, 1:0.6, and 1:1, to obtain coated seeds, as depicted in Figure 1. The seeds were dried in air for 48 hours at 50 °C.

Figure 1. Urea-HA-CMC/Alginate coated corn seeds.

2.2. Characterization techniques

2.2.1. Scanning electron microscopic (SEM) analysis

The formation of HA and HA-urea nanohybrids was confirmed using HITACHI SU6600 Scanning Electron Microscope. Samples were gold-sputtered using HITACHI, E-1020 ion sputter to overcome the charging effect. Imaging was carried out using secondary electron mode. Morphology of the coating compared to non-coated seeds, coating thickness and the compatibility of the coating with the seed surface were also analyzed using SEM imaging (Figure 2).

2.2.2. Fourier transform infrared spectroscopic (FTIR) analysis

Interactions in HA and HA-urea nanohybrids were analyzed in diffuse reflectance mode in a range of 400 cm^{-1} to 4000 cm^{-1} wavelengths using Bruker Vertex 80 coupled with Ram-FT module Fourier Transform Infrared spectrometer. The samples were 200 times diluted with spectroscopic grade KBr and analyzed using KBr as blank.

2.2.3. Powder X-Ray diffraction (PXRD)

The crystalline structures of HA and HA-urea were analyzed using PXRD patterns. Powdered samples were loaded onto a stub and were analyzed under Cu Kα radiation (0.1414 nm) over the 2θ range (5 - 80°) with a step size of 0.02 and scan speed of 2.0 degrees/min, using D8 Focus X-Ray diffractometer.

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2.2.4. Kjeldahl analysis

The total nitrogen content of coated and uncoated seeds was analyzed by the Kjeldahl analysis technique (Table 1). Approximately 1.0 g of the seed, 8.0 cm^3 conc. Sulphuric and one Kjeldahl selenium tablet were added into the Kjeldahl digestion tube. The sample was digested for 2 h at 400 °C in the digestion unit. Then, the sample was distilled in the distillation unit, and trapped ammonia in 4% (w/v) boric acid was titrated against 0.5 mol dm^{-3} HCl acid using screened methyl orange as the indicator. Each treatment was done in triplicates. The total nitrogen content was calculated.

2.2.5. Germination studies

Germination studies were carried out using the following treatments,

1. HA-coated seeds
2. Urea-HA-CMC/alginate (0.3:1 urea:HA ratio) coated seeds
3. Urea-HA-CMC/alginate (0.6:1 urea:HA ratio) coated seeds
4. Urea-HA-CMC/alginate (1:1 urea:HA ratio) coated seeds
5. Uncoated seeds

Germination trials were conducted according to Randomized Complete Block Design (RCBD). The experimental setup is illustrated in Figure 2. 16 replicates of each treatment were subjected to germinate under constant environmental conditions such as light (60 lux), humidity (60%), and temperature (26 °C). Plastic pots (80 nos.) of the same size and shape were taken, and an equal amount of cotton wool was added to each. Seeds were kept in between two folds of tissue paper in each pot. Water (50 mL) was added to each pot once in three days.

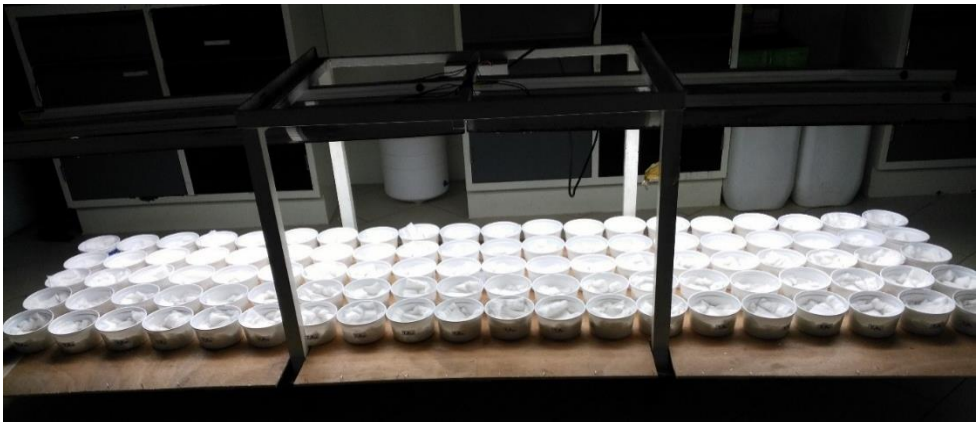

Figure 2. Experimental setup of the seed germination study.

Selected plants were removed from the experimental setup and conducted a destructive analysis after 14 and 21 days. Four plants from each treatment were analyzed per week for 35 days (5 weeks). The following parameters were obtained,

1. Average wet weight/ biomass.
2. Average dry matter weight.

Plant materials were dried in an oven at 60 °C until the weight of the sample became constant during two consecutive weighings, within two-hour intervals.

3. Average length of roots.

The length of each root was measured and obtained the average length of the roots for each treatment

4. Average plant height.

The length from the seed to the tip of the longest leaf was obtained as the plant height.

5. Average stem height.

The length of the stem was measured as the length between the seed and the point where leaves start to emerge.

6. Average number of leaves.

The number of leaves was taken in each treatment.

7. Average number of roots.
8. Average maximum width of the leaf.

The width of the leaf which is having the highest width, was obtained for each treatment.

9. SPAD measurement.

SPAD measurements were obtained in three different positions of the third leaf of the plant. The average SPAD value was obtained for each treatment.

2.2.6. Nutrient analysis

Plant samples were oven-dried separately at 72°C to a constant weight. Then, the N and C contents of the finely powdered plant samples were analyzed in triplicates using Perkin-Elmer 2400 Series II CHNS/O Analyzer.

3. Results

Characterization techniques including FT-IR, PXRD (Figure 3), and SEM (Figure 4) were carried out for the HA and HA-urea nanohybrids confirming that the formed composites were in good agreement with previously reported data (Kottegoda et al., 2017).

According to FTIR results (Figure 3 I), the characteristic peaks for the N-H stretching frequency of pure urea lies in the range of 3430-3340 cm^{-1} as two peaks. In HA-urea nanohybrid, N-H stretching frequency has shifted to a lower wavenumber around 3300 cm^{-1}. That can be attributed to the strong interactions between the NH_2 groups of urea and the OH groups of HA nanoparticles to form H-bonding [Figure 3 I (a)]. Further, the carbonyl

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stretching frequency of pure urea, which lies in the wavenumber of 1676 cm^{-1} has shifted to 1664 cm^{-1} in HA-urea nanohybrid indicating the H-bonding via carbonyl group [Figure 3 I (b)]. This phenomenon can be further confirmed by the shift of NCN stretching frequency [Figure 3 I (c)] of pure urea which lies in the wave number of 1462 cm^{-1} to 1450 cm^{-1} in HA-urea nanohybrid. PXRD patterns of synthesized HA nanoparticles (Figure 3 II) show all the characteristic peaks in the range of 2θ, 15-60° for (002), (211), (300), and (202) planes of HA, confirming the formation of HA nanoparticles. The absence of any other peaks in the PXRD pattern of HA confirms that the HA is in pure form. PXRD patterns elaborated in Figure 3 II depict that urea macromolecules have successfully modified HA nanoparticles to form HA-urea nanohybrid in all the synthesized composites.

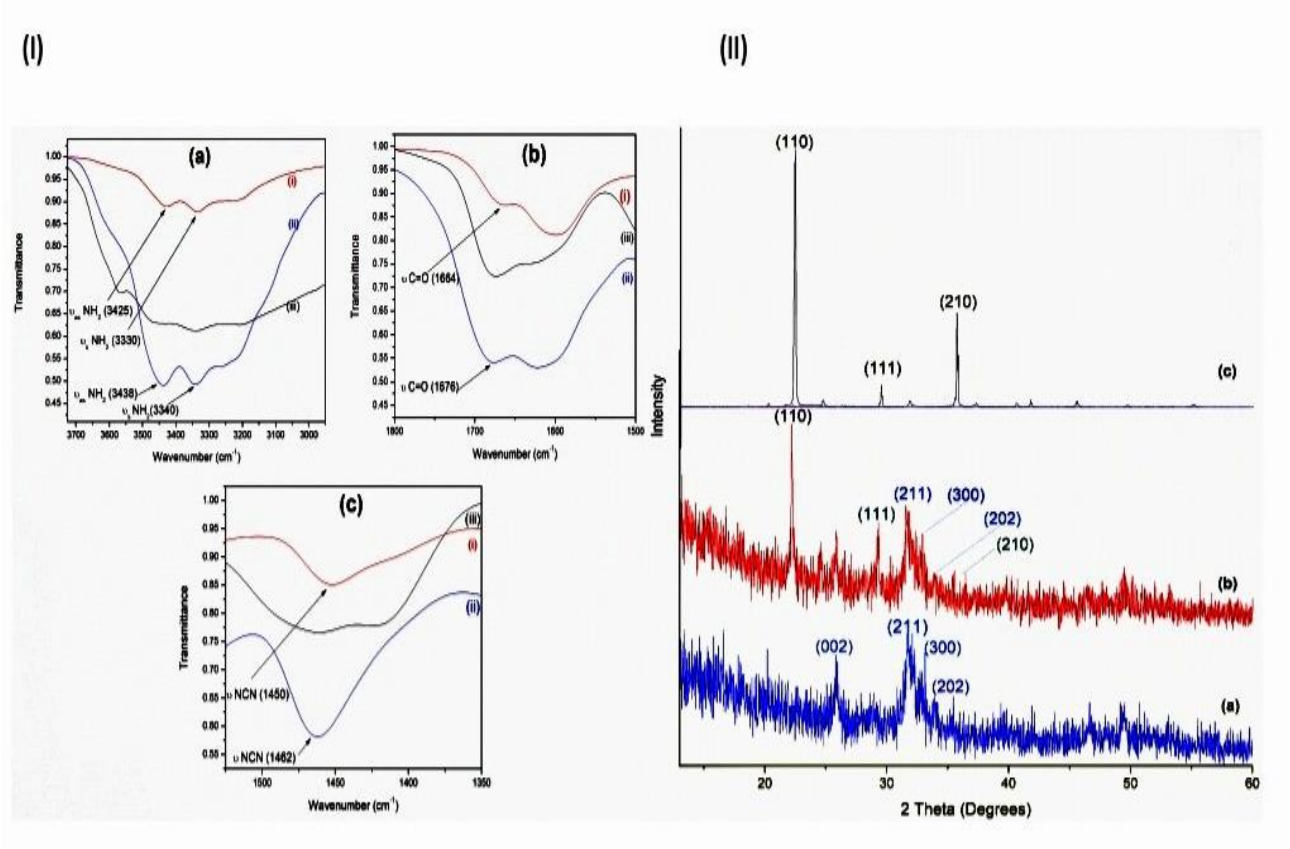

Figure 3. (I) FTIR spectra of (a) NH_2 (b) CO (c) NCN regions of (i) HA-urea (ii) Urea and (iii) HA (II) PXRD patterns of (a) HA nanoparticles (b) HA-urea nanohybrid and (c) pure urea.

SEM images of the coated seeds confirmed that the composite had successfully coated the seed surface with an average thickness ranging from 50-100 µm as depicted in Figure 4. The images further corroborated the excellent compatibility of the seed coating with the seed surface without cracking. From the results obtained by the Kjeldahl experiment (Table 1), it can be shown that nitrogen content per gram of seeds has been increased; hence, the existence of the HA-urea nanohybrid encapsulated in the coating composite can be proved.

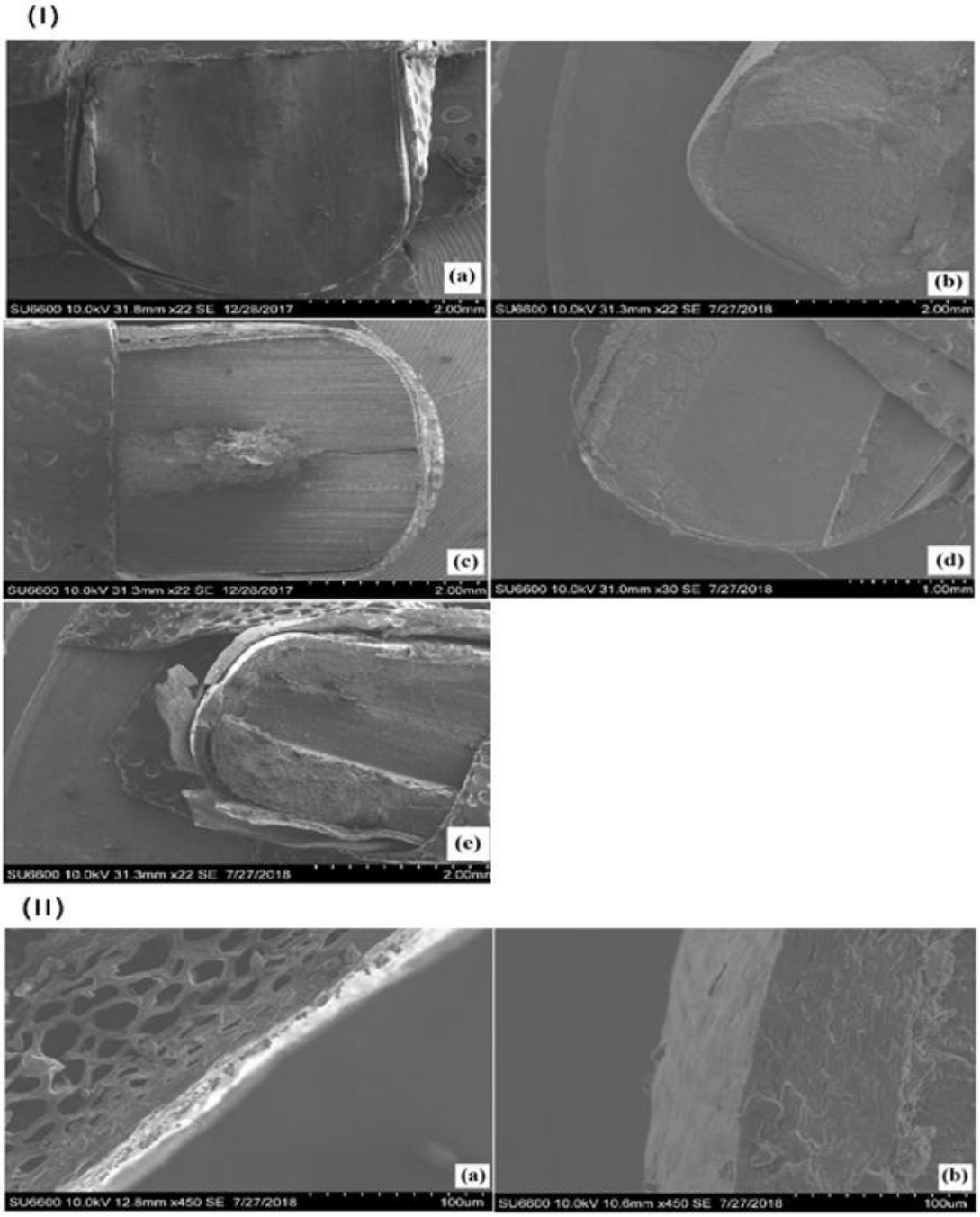

Figure 4. Cross sectional SEM images of (I) (a) Non-coated (b) HA-urea (1:0.3) coated (c) HA-urea (1:0.6) coated (d) HA-urea (1:1) coated, and (e) HA coated seeds. (II) Zoomed SEM images of (a) HA (b) HA-urea seed coatings. Seed coating is indicated using arrows.

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Table 1: Calculated initial total nitrogen percentages (N %) per 1.0 g of seeds

Treatment	N% (w/w)
Control	0.94
HA	0.93
HA-urea (1:0.3)	1.20
HA-urea (1:0.6)	1.23
HA-urea (1:1)	1.54
Urea	45.70

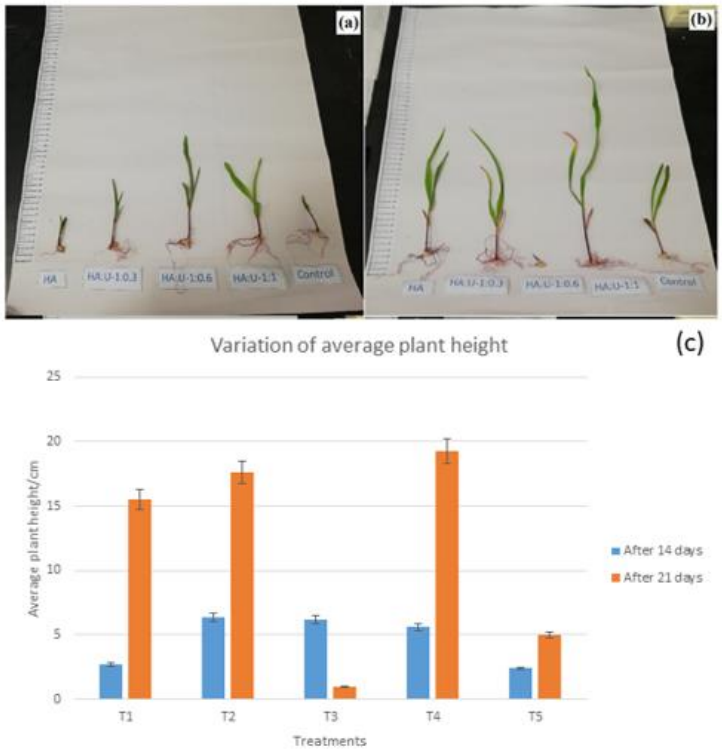

Figure 5: Images representing the growth of plants germinated from treated seeds compared to the control after (a) 14 days (b) 21 days, and (c) Variation of average plant height after 14 days and 21 days for each treatment T1 (HA), T2 (urea: HA 0.3:1 ratio), T3 (urea: HA 0.6:1 ratio), T4 (urea: HA 1:1 ratio) and T5 (control).

According to Figure 5, HA-urea 1:0.6 and 1:1 treatments showed maximum plant height after 14 and 21 days, respectively. As Figure 6 illustrates, seed coating composed of hydroxyapatite-urea (1:0.3) treatment

revealed an increase of 124.6%, 147.6%, 100%, and 166.7% in average biomass, root length, number of roots, and maximum plant width, respectively compared to the control, after 21 days of planting.

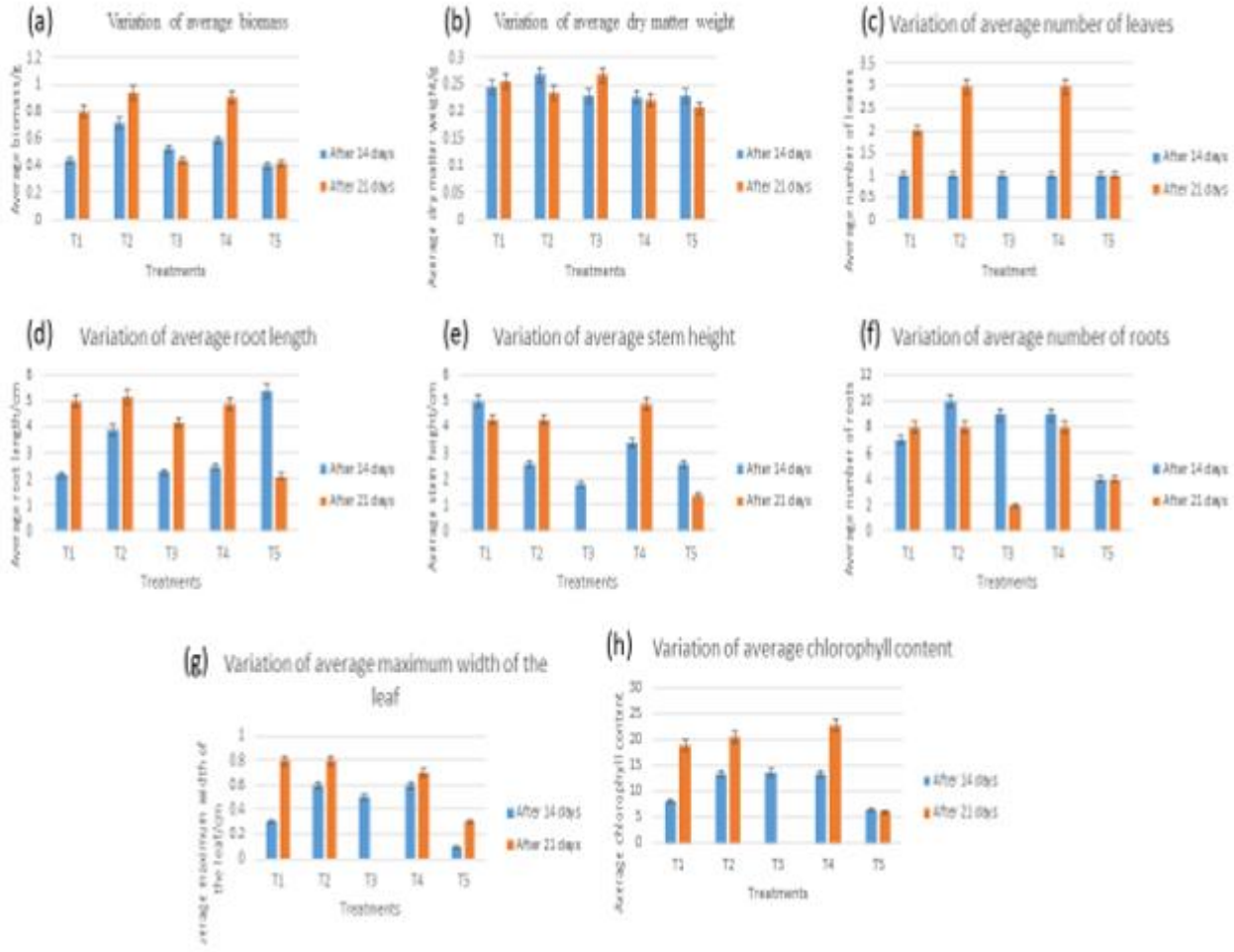

Figure 6: Variation of (a) average biomass, (b) average dry matter weight (c) the average number of leaves, (d) average root length, (e) average stem height, (f) average number of roots, (g) average maximum width of the leaf and (h) average chlorophyll content throughout 14 days for each treatment T1 (HA), T2 (urea-HA 0.3:1 ratio), T3 (urea-HA 0.6:1 ratio) T4 (urea-HA 1:1 ratio) and T5 (control).

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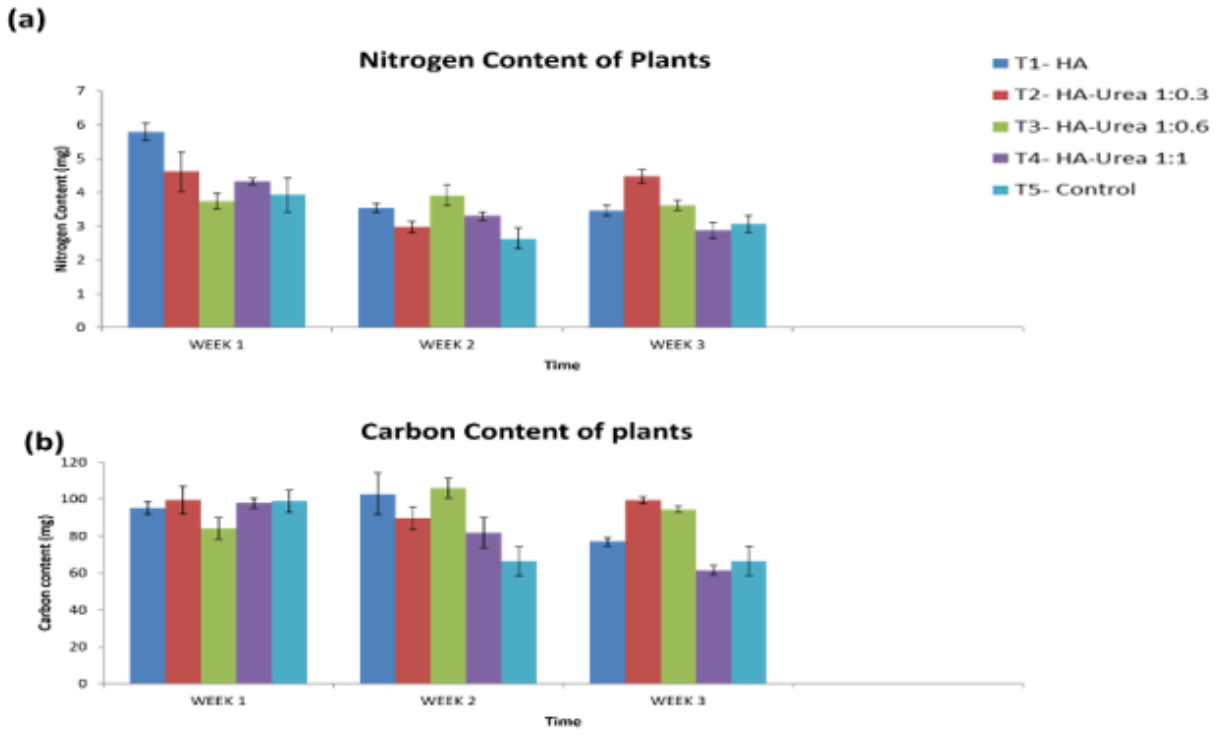

Figure 7: Variation of (a) Nitrogen content and (b) carbon content of plants over 3 weeks after planting.

According to Figure 7, the highest nitrogen content was observed for HA-urea 1:0.3 treatment at week 3, while HA-urea 1:1 treatment represented the lowest. The carbon content of plants originating from the seeds treated with HA-urea 1:0.3 displayed the maximum value while HA-urea 1:1 treatment displayed the minimum at week 3.

4. Discussion

As illustrated in Figure 5, HA-urea showed a higher plant height compared to control up to 21 days due to the enhancement of cell division at its favorable nitrogen concentration (Samavini et al., 2018). An increment of growth with increasing nitrogen concentration with time was revealed.

As Figure 6 illustrates, HA-urea 1:0.3 showed the highest biomass up to 21 days period of time. It can be proved that this is due to the utilization of nitrogen at its optimum level for better growth, as nitrogen helps for the growth and development of the plant (Samavini et al., 2018). HA-urea 1:0.6 treatment demonstrated the highest average dry matter weight up to 21 days of planting due to optimum utilization of nitrogen-containing in the seed coating as nitrogen is said to enhance dry matter weight in grain crops (Samavini et al., 2018). HA-urea 1:0.3 ratio showed a better average root length compared to the control as nitrogen helps for root elongation by cell division. Further, the higher phosphorus content due to HA in the seed coating might affect the roots of the treated plants to grow healthier compared to the control. HA treated plants showed a higher significant increment in average stem height due to the phosphorus utilization in the seed coating by the plants for cell division, growth, and enhanced enzyme

activity (Samavini et al., 2018). Up to 14 days, the number of leaves shows no significant change between treated plants and the control. From 21 days, HA and HA-urea 1:1 treated plants showed the highest number of leaves as it is known that nitrogen helps the plants to grow their leaves healthier. HA and HA-urea treated plants showed a higher number of roots compared to the control because of the higher availability of phosphorus for the plants due to the seed coating. However, HA: urea ratio 1:0.3 showed the highest optimum root growth. HA and HA-urea 1:0.3 treated plants showed higher maximum width of leaf compared to the control because of the nitrogen and phosphorus-rich environment for the leaves to grow. Nitrogen being an element in chlorophyll, HA-urea treated plants showed a higher chlorophyll content compared to the control. 1:1 HA-urea showed the highest chlorophyll content in 21 days because of the highest available nitrogen content (FeiBo et al., 1998).

From the results obtained from the germination study, it is evident that HA-urea seed coating has been successfully effected on seed germination and seed health up to 21 days of planting. The results obtained validate the ability of the seed coating to enhance the seed quality and seed germination during the early growth stage, and the subsequent addition of the normal fertilizer cycle is recommended for the latter growth stages of the plant.

According to Figure 7 (a), the N content of plant samples originating from HA coated seeds represented the highest amount at week 1, irrespective of the amount of urea added. This may be because of the seed's incapability to utilize externally provided urea at the early germination stage. At week 2, the seed coating with HA: urea 1:0.6 illustrated the greatest proportion of N while the control had the lowest. These were observed during the germination phase, and the nutrient availability of seeds may have contributed to the values. However, at week 3, the coating comprised of HA: urea 1:0.3 displayed the maximum amount of N, suggesting that this composition is responsible for greater growth of plants along with the highest available N at the early growth stage of plants. Similarly, the C contents illustrated in Figure 7(b) show the highest content for the seed coating with HA: urea 1:0.3 while control exhibited the lowest confirming that the nutrient availability of the above seed coating is the highest at the initial development stage.

According to these observations, HA-urea 1:0.3 composite demonstrated better growth after 14 days and 21 days compared to other treatments, while HA-urea 1:0.6 and HA-urea 1:1 showed inhibited growth, which may be due to nitrogen toxicity towards the plant during the seed germination period.

4. Conclusions

The novel HA-urea encapsulated seed coating formulation introduced showed improved germination, growth and development for Zea maize with increased growth parameters measured compared to control up to 21 days which is considered the seedling stage. These results bring out the suitability of the invented seed coating to be used as a mode of efficient delivery of P and N for seed germination and seedling development.

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