

## Synthesize of bio-based encapsulated nano urea modified hydroxyapatite for controlling release of nitrogen and enhancing green bean yield

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### Abstract

The massive rise in the world population requires increasing food production, and the world needs to decrease agricultural inputs like agrochemicals to preserve natural resources. The low nutrient use efficiency of conventional fertilizers has always been a concern because of their impact on the environment, and they are considered a waste of natural resources, which is against sustainability goals. Their low efficiency is attributed to their high solubility and fast release into the soil. Controlled-release fertilizers (CRFs) can reduce nutrient loss, which increases their efficiency and controls environmental pollution. In this study, single- and double-layers coating of biopolymers were applied to encapsulate nano urea-modified hydroxyapatite to control nitrogen release in soil. Hydroxyapatite was synthesized using the wet chemical precipitation method and two different rodlike and mesoporous hydroxyapatites were obtained. Nano-hydroxyapatite that had been synthesized was mixed with urea in two different amounts: 4:1 and 8:1. Biopolymers were then added on top. The current CRF synthesis strategy focuses on using low-cost, widespread biorefinery materials to decrease the manufacturing cost of CRFs. The nitrogen release rate of the synthesized CRFs and commercial urea in water and soil was studied. In field experiments, the impact of CRFs on green bean growth and yield was studied. The results showed that both single and double-coated CRFs reduced the N release rate in the soil and increased the fertilizer's longevity to 24 days, compared to 6 days for conventional urea. The total yield of green beans increased by 48%-120% by applying 75% of the recommended dose compared with that obtained with the full dose of conventional urea (control). Also, applying double-coated CRFs at N level of 25% of the recommended dose gives a green bean yield equal to the control. The recommended treatment is SC-CRF prepared with C-HA applied at N rate of 75% to match the future increase in the required amount of food.

**Keywords:** alginate; bio-coating; lignin; mesoporous hydroxyapatite; nano fertilizer; nitrogen uptake; snap bean

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## Introduction

Increasing the world population is one of the most serious global concerns regarding the future capacity to produce sufficient agricultural products to sustain livelihoods and meet the ever-growing population's needs (Calicioglu *et al.*, 2019). Population growth will force the agriculture sector to increase food production by increasing the cultivated area or enhancing crop yield productivity to meet demand and cover the food gap in the whole world (Beig *et al.*, 2022). This requires using huge quantities of chemical fertilizers, which will make it a challenge to increase manufacturing to meet production demand (Feregrino *et al.*, 2018).

Although fertilizers are necessary to improve crop yields, due to their higher solubility, the nutrients released from conventional fertilizers are unable to match the sequential needs of crops (Meyer *et al.*, 2018). It has also been mentioned that plants only use about 50% of the nitrogen and phosphorus that are applied by conventional fertilizers (Chinta *et al.*, 2020). This means that between 50 and 80% of the fertilizers that are used are lost through volatilization and leaching (N) or through soil fixation as phosphorus (Ditta and Arshad, 2016; Zhang *et al.*, 2021). These nutrient losses affect not only crop yield, but also the environment (causing both water and air pollution) and human health.

In contrast, nano fertilizers which are novel controlled-release fertilizers (CRFs) are considered integral to precision farming because of their ability to provide controlled and site-specific delivery of nutrients, thereby improving nutrient use efficiency (NUE) (Chhipa and Joshi, 2016). Such that it facilitates the uptake of nutrients matching the crop requirements without any associated ill effects of customized fertilizer inputs. It also potentially reduces the toxicity of seeds and seedlings (salt burn), leaf burn, greenhouse gas emissions, environmental pollution, and the total amount of fertilizers used (Grant *et al.*, 2012; Zhang *et al.*, 2018). For that, Nano fertilizers are expected to be far more effective than even polymer-coated conventional slow-release fertilizers (De Rosa *et al.*, 2010; Kah *et al.*, 2018). Especially, some nanomaterials showed excellent ability to react as vehicles carrying nutrients such as biochar, chitosan, zeolite, bentonite, and other types of clay minerals (Liu and Lal, 2015; Subramanian *et al.*, 2015; Abdel-Aziz *et al.*, 2016; Lateef *et al.*, 2016; Yuvaraj and Subramanian, 2018; Zhang *et al.*, 2020). In addition, some nanomaterials not only react as vehicles but also, as sources of nutrients, such as hydroxyapatite which contains calcium and phosphorus in its composition.

Due to its excellent biocompatibility and bioactivity, hydroxyapatite is the focus of many current studies (Cao *et al.*, 2010; Zhu *et al.*, 2010), but its potential agricultural applications have not received extensive study. Several research groups (Wang *et al.*, 2016; Xiao *et al.*, 2017; Huang *et al.*, 2018) have been pursuing the use of renewable and biodegradable biopolymers as an alternative to petrochemicals, which have been the primary coating materials for the last few decades (Tomaszewska and Jarosiewicz, 2002; Ma *et al.*, 2013). For petrochemicals and other expensive biopolymers, lignin is a good alternative because it is cheap, has antimicrobial properties, does not dissolve in water, and breaks down naturally (Sipponen *et al.*, 2018; Yang *et al.*, 2018), and there are lots of sources of it. The papermaking industry's wastes and possibly a sugar-based biorefinery process can yield this second most abundant aromatic biopolymer on Earth (Chen *et al.*, 2016).

According to some previous literatures, nano Fertilizer showed a magnificent impact on improving the total yield and the release of nutrients as reported by Ramírez-Rodríguez *et al.* (2020), who found that urea loaded on nano calcium phosphate reduced release by 10 times in the first hour compared to conventional urea and it remained for 12 days against 4 days for conventional urea. Also, Helal *et al.* (2023) reported that using nano urea-modified bentonite-controlled release fertilizer significantly increased the total tomato yield and achieved the same yield using 25% of the recommended dose.

The aim of this study is to develop bio-based single and double-layer coated controlled release fertilizers derived from renewable, biodegradable, inexpensive, and biocompatible materials. Nano hydroxyapatite was synthesized using the wet chemical precipitation method, then modified with urea. The product composite

was encapsulated with two coating layers; the inner one is a hydrophobic layer of alginate, and the outer one is lignin. The performance of the synthesized CRFs was tested either in lab experiments to study the nitrogen release in water and soil, and in cultivation experiments to study its efficiency on the growth and yield of green beans.

The bottom-to-up synthesis method of nano hydroxyapatite will give us the ability to control its characteristics, such as shape, crystallinity, and particle size, which will help in increasing the nitrogen percentages in the CRFs and slowing the N release rate. Also, use of bio-based coating material will decrease CRF manufacturing costs and open new horizons in using paper manufacturing waste (Lignin) in another industry instead of burning it causing huge hazards to the environment.

## Materials and Methods

Except for black liquor, lignin, and urea, all reagents and chemicals used in this study were analytical grade and purchased from the LOBA CHEMIE Mumbai. The black liquor was provided by the local company, “Misr-Edfu Company for Paper and Printing”, Egypt. Lignin was prepared in our lab and the commercial urea  $(\text{NH}_2)_2\text{CO}$  was purchased from the agro-market.

### *Preparation and synthesis of research materials*

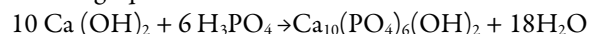
#### Preparation of lignin

Lignin was extracted from black liquor which is a bio-refinery residue from paper manufacturing. The black liquor was extracted from bagasse using the Kraft method (Figueiredo *et al.*, 2018), in which bagasse was treated with 1.5 M NaOH, at a ratio of 1:10 (bagasse: NaOH solution) at 170 °C for 120 min, then lignin was extracted in the form of black liquor. We treated the alkaline black liquor with sulfuric acid until the pH dropped to 5, precipitating lignin. We then filtered the supernatant, washed the precipitate several times, and dried it at room temperature.

The product lignin was characterized using Fourier transform Infrared spectroscopy (FTIR).

#### Synthesis of nano hydroxyapatite (HA)

The nano hydroxyapatite was synthesized using the wet chemical precipitation method described by Kottegoda *et al.* (2011), with some modifications. Calcium hydroxide  $[\text{Ca}(\text{OH})_2]$  was used as a source of calcium and orthophosphoric acid ( $\text{H}_3\text{PO}_4$ , 85%) as a phosphorous source at a Ca: P molar ratio of 1.67. Firstly, a solution of  $\text{H}_3\text{PO}_4$  (500 ml, 0.6 M) was added drop-wise into a suspension of calcium hydroxide (500 ml, 1 M) and a 3% (V/V) of ethanolamine as a dispersant to prevent the products from aggregating during the synthesis process while stirring vigorously under mechanical agitation (1000 rpm) at 50 °C. After adding the entire amount of orthophosphoric acid solution, we adjusted the pH to 10 using sodium hydroxide solution, stirred for 2 hours, and aged the mixture at room temperature for 12 hours. The reaction takes place according to the following equation:



The resulting HA nanoparticles were washed several times with deionized water before drying at 70 °C for 24 h. Half of the resulting HA nanoparticles amount were calcinated on muffle at 700 °C for an hour. The products were characterized using X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Brunauer–Emmett–Teller (BET), and FTIR.

#### Synthesis of single-coated nanohybrid urea-HA (SC-CRFs)

From the two types of synthesized HA nanoparticles, 25 g were dispersed in 100 ml distilled water under ultrasonic mixing (30 kHz for 30 min). A saturated urea solution was added to the HA suspension at two different ratios of 1:4 and 1:8 (HA: Urea) and kept stirring at room temperature for 12 h to let urea molecules

attach to the whole hydroxyapatite's surfaces. The previous 2 ratios used were determined according to our previous studies, which found that the minimum ratio that should be used is 1: 4 to produce a CRF with a suitable N percent (Helal *et al.* (2023); Fathy *et al.* (2024)). Also, the ratio of 1: 8 was expected to be more effective because of the huge surface area of the synthesized HA. The mixtures were heated on a hot plate at 80 °C before adding Na-alginate solutions of 2% and 4% (w/v) for the two urea-HA ratios, respectively. Then it was stirred until a gel was formed. The formed gel was placed in a refrigerator for 24 hrs for stabilization. The gel was stirred to be homogenized before slowly dropping into a calcium chloride solution (4% w/v) using a syringe to form beads. The formed beads were left in the calcium chloride solution for 20 min. to achieve cross-linking, then all beads were collected and dried at 60 °C (Flores-Cespedes *et al.*, 2015; Zhang *et al.*, 2020). Before adding the alginate, we characterized the urea-modified HA product using FTIR

#### Preparation of double-coated CRF beads (DC-CRFs)

Fifty grams of the homogeneous SC-CRFs beads were placed into a rotary drum (20 rpm) and covered with 20 ml of a mixture of lignin solution prepared by dissolving 3.5 g lignin in 100 ml 1M NaOH solution and carboxymethyl cellulose solution (0.5% w/v) at a ratio of 8:2, respectively. The distance between the spray nozzle and the center of the rotary drum was 25 cm and the mixture was sprayed at regular intervals. The double coated CRFs beads were continuously dried in the rotary drum by a hot air stream (60 °C) (Figure 1).



**Figure 1.** Visual images of (A) SC-CRFs (1:4), (B) DC-CRFs (1:4), (C) SC-CRFs (1:8), and (D) DC-CRFs (1:8)

#### *Characterization of the research materials.*

FTIR analysis was performed from the 400 to 4000  $\text{cm}^{-1}$  regions using FTIR spectrophotometer 4100 JASCO–Japan, and operating in the transmittance mode with a resolution of 4  $\text{cm}^{-1}$  and an accumulation of 16 scans for HA nanoparticles and urea modified hydroxyapatite. The FTIR analysis was carried out to explore the surface chemical bonds, and trace the changes in surface groups as a result of binding between urea and hydroxyapatite. The XRD patterns of HA samples were recorded using a diffractometer (Bruker D8 Discover-Germany) X-ray powder diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1546 \text{ nm}$ ) over a  $2\theta$  range of 5-80° with a step size of 0.01° and a step time of 1 s. The TEM analysis (JEOL JEM 2100 electron microscope–Japan) was operated at 200 keV to measure the sizes of the nanoparticles and explore their morphology. The sample was dispersed in ethanol using ultrasonication for 15 min, then the suspended nanoparticles were filtered and loaded on a carbon-coated copper grid (300 mesh), then left to dry prior to inspection. Both imaging and selected area diffraction patterns were recorded. The BET analysis was performed for the two types of HA by using Quantachrome TouchWin 1.2-USA, to explore the calcination effect on the surface characteristics of HA NPs. The samples subjected to examination were dried at 150 °C, then degassed at 573 K prior to the analysis.

*The release pattern of N from CRFs beads.*

Solubility of CRFs and nitrogen release in water

The solubility of CRFs and the release of N in water were studied for all prepared CRFs and commercial urea. An accurate weight (0.2 g weight to the nearest 4 digits) of all CRFs types, and commercial urea were placed in falcon tubes, then portions of deionized water (20 ml) were added to the beads and left for varied equilibrium periods, 24, 96, 168, 240, and 312 hrs. At the end of each equilibrium period, the clear solutions were collected and kept for the determination of N content using Kjeldahl method (Fertahi *et al.*, 2019).

Release of N from CRFs in soil

The release of N from all synthesized CRFs and commercial urea was studied in clay loam soil. The soil was air-dried for one week before it was sieved through a 2 mm sieve. The fine soil was placed in glass columns to a height of 20 cm, then saturated with a portion of distilled water equal to the water holding capacity of the soil. Certain weights (0.5 g) of the fertilizer's beads were buried in the surface of the soil, then the soil was leachate out with 20 ml of deionized water at different periods, 3,6,12, 18, and 24 days. The leachate water was collected, then subjected for determine of nitrogen release content.

*Efficiency of CRFs on growth and yield of green beans*

A field experiment was carried out at the Experimental Station of the Faculty of Agriculture, Cairo University, Giza, Egypt (30°01'32.5 "N and 31°11'33.0 "E) to study the efficiency of CRFs on the growth and yield of green bean plants. Seeds of sv1541GA cultivar supplied by Bayer Company, Cairo, Egypt, were sown on 10<sup>th</sup> of March, 2022, in clay loam soil. The main properties of the soil were; pH (7.52), Electrical Conductivity (EC) 2.8 dSm<sup>-1</sup>, organic matter (1.69%), and the texture was clay loam with a composition of 4.4, 31, 27.3, and 37.3% for coarse sand, fine sand, silt, and clay. The randomized complete block design (RCBD) with three replicates was used for this study. Four types of nano CRFs with three rates of N (75, 50, and 25% of the recommended dose) were added to green bean plants in 3 portions (50, 25, and 25%) of the total added amount. Commercial urea was added at a rate of 100% of the recommended dose as a control treatment. Four treatments of single coated CRFs synthesize at a ratio of 1:4 of non-calcinated HA: urea (T1) and calcinated HA: urea (T2); and double-coated CRFs synthesize at a ratio of 1:8 of non-calcinated HA: urea (T3) and calcinated HA: urea (T4). All plants received 130 kg ha<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> as triple super phosphate was added before transplanting and potassium fertilizer was applied at a rate of 65 kg ha<sup>-1</sup> K<sub>2</sub>O in the form of potassium sulfate in three portions 33, 16, and 16 kg ha<sup>-1</sup> at 15, 40 and 60 days, respectively after transplanting. Also, a total content of 130 kg ha<sup>-1</sup> N (recommended dose) was applied for control treatment in three portions. Irrigation water with 7.25 (pH) and 0.42 dSm<sup>-1</sup> (EC) was applied regularly to maintain soil moisture at 75% of the field capacity.

*Data recorded*

Vegetative growth parameters and yield

After 75 days of planting, six plants were taken randomly from each replicate to determine plant length, number of branches per plant, fresh weight, and dry weight. Dry weight was calculated after drying the plants in the oven at 70 °C until they reach a constant weight. Pods were harvested during the harvesting season (3 harvestings), when pods reached 14 cm in length to calculate yield/plant.

Analytical procedures

Total N content in CRFs beads, water, soil leachate, and plants, was determined using Kjeldahl method without catalyst, in which urea and leaf tissues were digested using concentrated H<sub>2</sub>SO<sub>4</sub> (98% w/v) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) (Estefan *et al.*, 2013; Purificación *et al.*, 2013). The N concentration was measured in the acid digestion extract using the ammonia distilling unit of Kjeldahl (KJELDAHL DISTILLERS, DNP series DNP-1500-MP, Raypa, Spain). Potassium concentration in plant leaves was

determined in the digestion solution using Flame Emission Spectrophotometry (Corning 4100, Corning 4100, UK). Using the concentrations of N and K in the acid digestion extract, the total N content in CRFs, N released in water and soil, and N and K uptake by green beans were calculated. The basic properties of irrigation water and the cultivation soil are; The pH was directly measured in irrigation water and in 1:2.5 soil: water suspension using a pH meter (Accumet AR.20, Fisher Scientific, USA). The EC was measured in irrigation water and in the filtrate of the suspension of 1:2.5 soil: water ratio, using an EC meter (JENWAY, UK, 4510). The total organic matter (OM) of the experimental soil was determined using Walkley and Black method (Dewis and Freitas, 1970). Mechanical analysis was performed according to the pipette method (Gee and Bauder, 1986), and the class was obtained from the Texture Triangle.

#### *Statistical analysis*

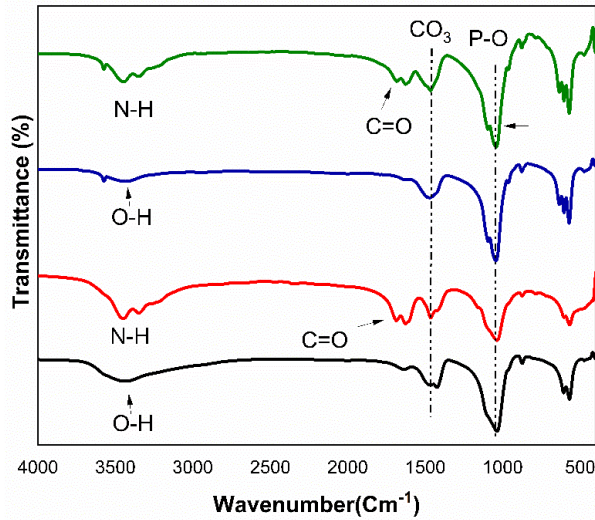
Data were analyzed using MSTAT-C (version 2.1 Michigan State University, East Lansing, MI, USA), and the Duncan's multiple range test was used to compare the means between treatments.

## **Results and Discussion**

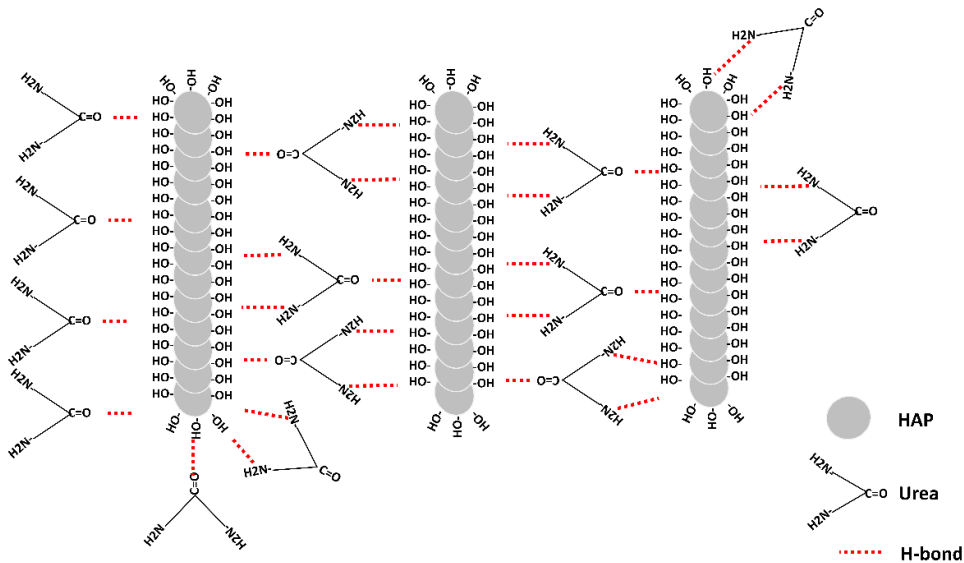
### *Characterization of hydroxyapatite nanoparticles*

#### Fourier transformer infrared spectroscopy (FTIR)

The FTIR analysis was carried out for the two types of synthesized hydroxyapatite before and after the modification with urea, as shown in Figure 2 to determine the chemical composition of hydroxyapatite, the effect of the calcination process on its composition, and to confirm the modification of HA with urea. It was observed that in the two types of hydroxyapatites the same peak referring to  $\text{PO}_4^{3-}$  appears at 567, 605, 632, 964, and  $1040\text{ cm}^{-1}$  (Liu *et al.*, 2003; Kannan *et al.*, 2006). Additionally, previous works observed  $\text{CO}_3$  bands at 875, 1424, and  $1470\text{ cm}^{-1}$  (Okazaki *et al.*, 2005; Montazeri *et al.*, 2011). The appearance of the carbonate group in the spectrum might be due to the adsorption of atmospheric carbon dioxide during the synthesis process. The band observed at  $3400\text{-}3570\text{ cm}^{-1}$  in both graphs refers to the OH group. As shown from the calcinated Hydroxyapatite (C-HA) spectra the peaks of OH and  $\text{CO}_3$  groups have a lower intensity than their peaks in the non-calcinated one (NC-HA). That leads us to believe that the calcination process improved the purity of HA by eliminating or decreasing carbonate from the composition. After treating HA with urea, it showed 4 other peaks; these peaks belong to NH bands observed at  $3345\text{-}3450\text{ cm}^{-1}$  (Kottegoda *et al.*, 2011) and the carbonyl group band at 1626, 1685 (Madhurambal *et al.*, 2010; Fertahi *et al.*, 2020). This indicates significant hydrogen bonding formed between O-H groups of HA nanoparticles and both C=O and N-H groups of urea (Kottegoda *et al.*, 2011; Fathy *et al.*, 2024), as presented in Figure 3 which approved the modification of HA with urea.



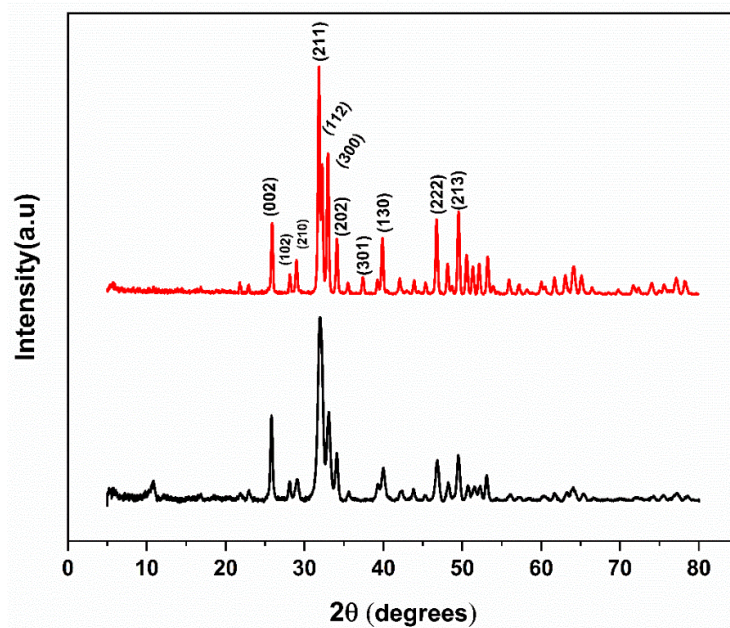
**Figure 2.** FTIR spectra of; NC-HA (black line), urea modified NC- HA (red line), C-HA (blue line), and urea modified C-HA (green line)



**Figure 3.** Schematic representation of the model for urea-modified HA nanoparticle

X-ray Diffraction (XRD) analysis

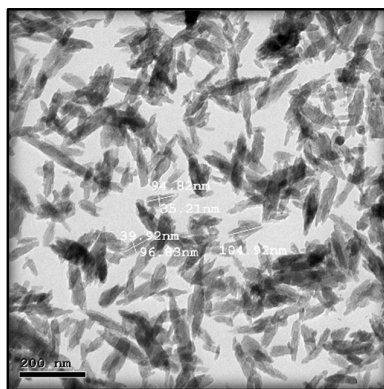
The XRD patterns of the two synthesized samples are illustrated in Figure 4. They were identified as hydroxyapatite both non-calcinated and calcinated HA typically matched the X-ray diffraction patterns of the reference cards COD 9001233 and COD 9002214, respectively. The phase analysis showed that the predominant phase was determined as HA with no impurities of any other calcium phosphate component and/or carbonate with a tangible amount. The hydroxyapatite feature peaks were observed between 30 and 35 appearing at 31.8, 32.2, 32.9, and 34.1, respectively, referring to the peaks (211), (112), (300), and (202). Furthermore, the (002) reflection of HA resulted in an isolated peak centered at 25.9. The calcinated HA shows obviously more intensity and sharper peaks, which indicates higher crystallinity than the non-calcinated one. The average crystallite size calculated using Scherer’s equation was found to be ~19 nm for non-calcinated hydroxyapatite and ~31 nm for calcinated one.



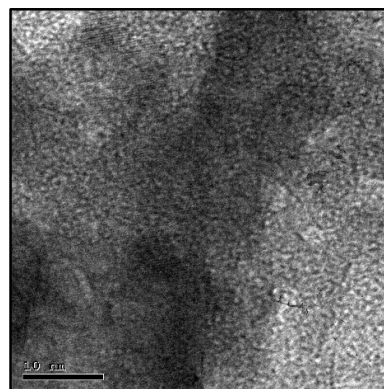
**Figure 4.** XRD patterns of; NC-HA (Black line), and C-HA (Red line)

#### Transmission electron microscopic (TEM)

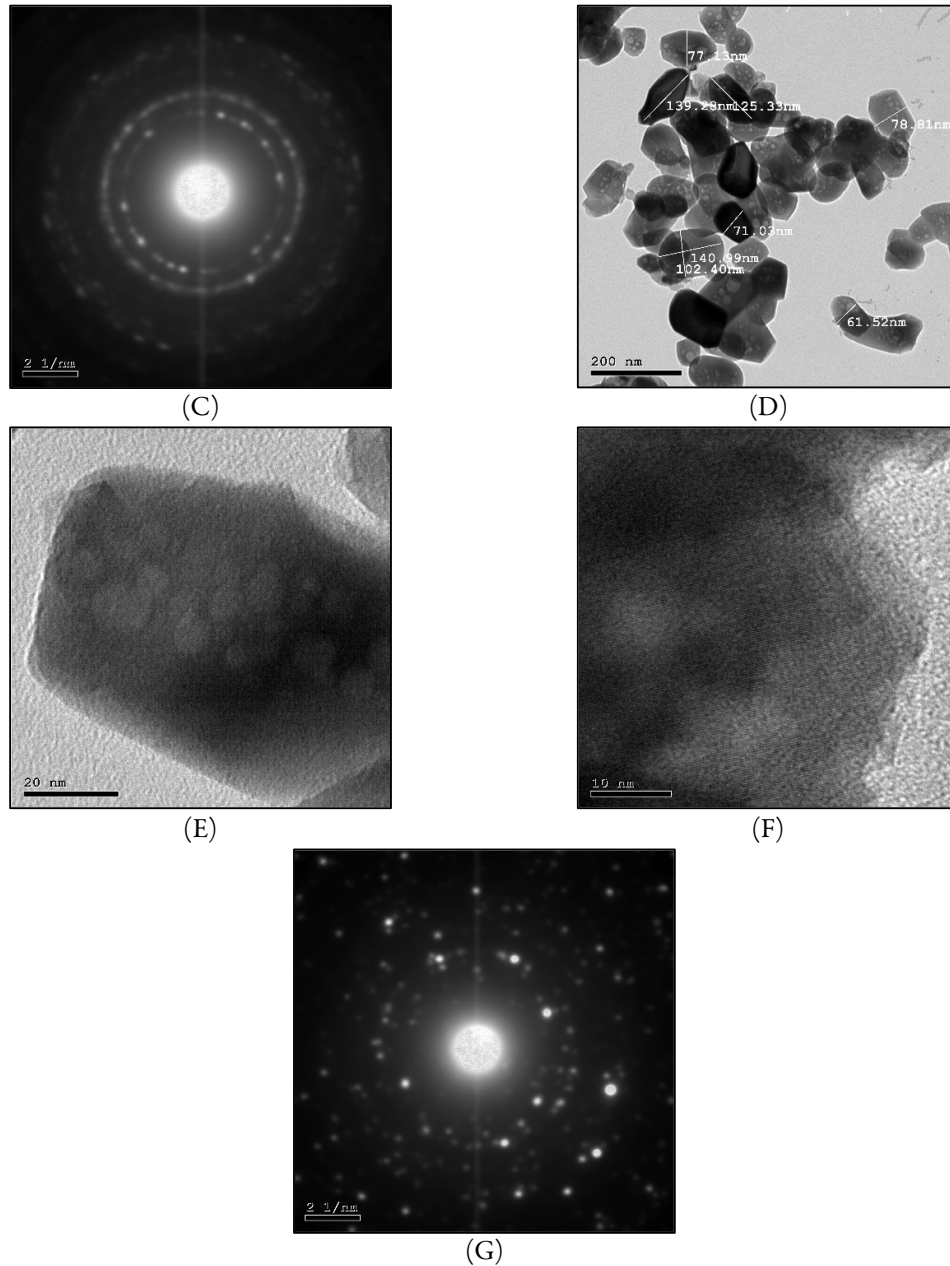
Figure 5 illustrates the nano size of the synthesized HA. The TEM images of NC-HA (Figure 5A) showed rod-like NPs with average diameters of 30 nm and lengths ranging from 90 to 105 nm. Whereas the C-HA images (Figure 5D) showed wide rodlike shape NPs with average diameters of 60 nm and lengths ranging from 60 to 140 nm. Also, when the image was amplified to a scale of 20 nm (Figure 5E), it clearly showed mesoporous HA and the particles were full of different sized pores. It seems that the calcination process not only affected the shape, size, and formation of the pores but also, affected the crystallinity, as appears from the electron diffraction pattern (Figure 5C, G), which shows the broader and lower intensity of NC-HA diffraction peaks than C-HA in the XRD pattern, and from the orientation of the crystal lattice planes (Figure 5 B, F). Despite the polycrystalline nature of the two types of NPHA, the calcinated HA exhibited higher crystallinity and perfectly aligned crystal lattice planes.



(A)



(B)



**Figure 5.** HRTEM image of (A) NC-HA., (B) lattice fringes of NC-HA nanoparticles., (C) Electron diffraction patterns of NC-HA., (D) C-HA., (E) Nanopores C-HA., (F) lattice fringes of C-HA nanoparticles., and (G) Electron diffraction patterns of C-HA

Brunauer–Emmett–Teller (BET) analysis

The BET analysis was carried out for the two types of HA to explore the effect of the calcination process and trace the changes in the surface characteristics of NPHA. The N<sub>2</sub> adsorption–desorption analysis was made to study the pore size, pore volume, and the specific surface area of the samples. As shown in Table 1, N<sub>2</sub> adsorption–desorption isotherms of the NC- and C-HA NPs revealed a BET surface area of 245.6 and 293 m<sup>2</sup>g<sup>-1</sup>, respectively. Despite the fact that the particle size of C-HA is bigger than the NC-HA, the specific surface area of the former is higher than that of the latter. The fact that the specific surface area of C-HA could be attributed to the total pore volume of C-HA was higher than that of NC-HA.

**Table 1.** Surface properties of calcinated and non-calcinated HA

Sample type	BET Surface area (m <sup>2</sup> /g)	Langmuir surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
NC-HA	245.64	361.68	0.56	4.57
C-HA	293	434.15	0.67	4.60

*Total nitrogen contents in controlled release urea fertilizers (CRFs)*

The total nitrogen content of all synthesized CRFs is listed in Table 2. The results showed that the total nitrogen content ranged from 22: 36%. Except for urea (46%), the N content in CRFs was higher than that in all other commercial nitrogenous fertilizers, e.g. ammonium sulfate (21%), nitric acid (14%), potassium nitrate (13%), and ammonium nitrate (33%). The variation in the total N content in CRFs could be attributed to, the varied ratios adopted between hydroxyapatite and urea, using different types of hydroxyapatites with different characteristics, and the coating type. As shown in Table 1. the CRFs synthesized using mesoporous NPHA had a higher nitrogen content because it had a higher surface area than NC-NPHA, besides the pores in their surface exposed inner surfaces, which allowed pores-urea penetration. The N percentages in DC-CRFs were slightly lower than those of SC-CRFs which could be attributed to the increase in the mass of the coating layer. The results showed that using HA: urea at a ratio of 1:8 led to similar N content for the two types of HA, which means the added urea at this ratio was higher than the surface adsorption capacity, and a portion of the urea molecules may exist in a soluble, no bonded form in the alginate layer. The release rate of this portion of urea molecules is faster than that of urea molecules bonded with HA. This portion will supply N to the growing plants at their first growth stage, helping them to develop faster, which will help them to pass through any difficulties and stress that might exist.

**Table 2.** Total nitrogen content (%) in single and double coated CRFs

HA Type	HA: urea	SC-CRFs	DC-CRFs
NC-HA	1:4	24	22.5
NC-HA	1:8	36.5	36
C-HA	1:4	27.5	26
C-HA	1:8	36.5	36

*The pattern of N release from CRFs in water.*

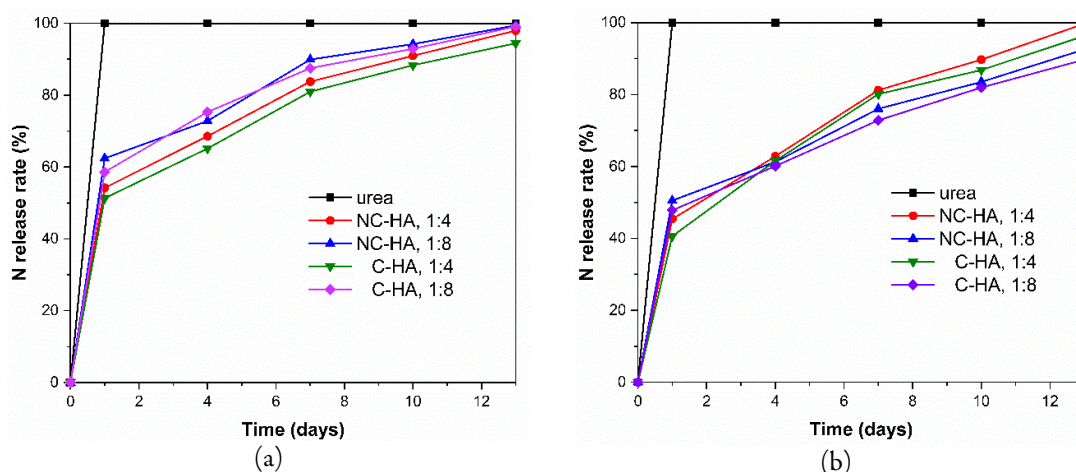
The solubility and rate of N release from all synthesized CRFs in water compared with conventional urea are shown in Figure 6. The result showed that commercial urea had a rapid release rate. It was completely dissolved, and the total content of N released in the first portion of the added water. However, for 13 days over 5 portions of added water, all synthesized CRFs maintained a slow-release rate. The slow release of N from CRFs could be attributed to the fact of that the added urea was loaded on the hydroxyapatite's surface and bonded through hydrogen bonds formed between C=O and N-H groups of urea and OH ones of HA as illustrated in Figure 3. Also, the hydrophobic coating (lignin one) decreased the direct contact between water molecules and the modified HA.

The single-coated controlled-release fertilizers (SC-CRFs) showed a significant slow-release rate of N, as shown in Figure 6a. Although the release rates of N from SC-CRFs were almost convergent for all synthesized CRFs, the slowest release rates were recorded for those prepared at lower ratios (1:4) of HA: urea compared with those of 1:8 ones, which were slightly faster, which could be attributed to the easy release of the free urea molecules unbounded by the HA surface. In contrast, the double-coated controlled release fertilizers (DC-CRFs) prepared at the higher ratio (1:8) of HA: urea showed release rates of N slower than those prepared at the lower ratio, as shown in Figure 6b. Despite the fact that the total contents of N in both single- and double-coated CRFs were completely released in a period of 13 days, the portions of N released from double-coated CRFs were markedly lower, particularly at the early leachates, and found to represent 79-84, 80-94, 83-99, 88-

98, and 88-100% of those recorded for single coated ones, at the first, second, third, fourth, and fifth leachates, respectively.

As the portions of N released in the early stages decreased, the loss of N decreased and the residence time increased, which is a sign of increasing plant utilization. Although, at the first portion of added water, the release of N from DC-CRFs synthesized with the higher ratio of HA: urea (1:8) was slightly higher than that of 1:4 ones, it decreased sooner and became lower in the subsequent water portions. The initial higher release of N could be attributed to the free urea molecules unbounded by the HA surface at the higher ratio. The efficiency of the lignin layer in preventing water molecules from penetrating the alginate layer stems from its hydrophobic characteristic. Also, both SC-CRFs and the DC-CRFs synthesized using calcinated HA (C-HA) showed slightly slower N release rates for the two HA: urea ratios compared with the non-calcinated ones (NC-HA), which could be attributed to the higher surface area of the former than the latter ones, and to the ability of urea molecules to be attached to the inner surfaces provided by mesoporous C-HA.

The HA calcination process had varying effects. It worked well with SC-CRFs at lower ratios of 1:4, however, in the case of DC-CRFs, it worked well with the higher ones (1:8). Similar results were reported by Zhang *et al.* (2020), who found that conventional urea fertilizer was dissolved in water immediately, in contrast, all synthesized slow-release fertilizers (SRFs) coated with alginate and lignin–clay nano hybrid had a slow-release capability. Comparable outcomes were also observed for the release of nitrogen (N) into water from CRF, which was produced by coating urea with biopolymers. It was discovered that the N release was maintained for ten days. (Zhang *et al.* 2016).

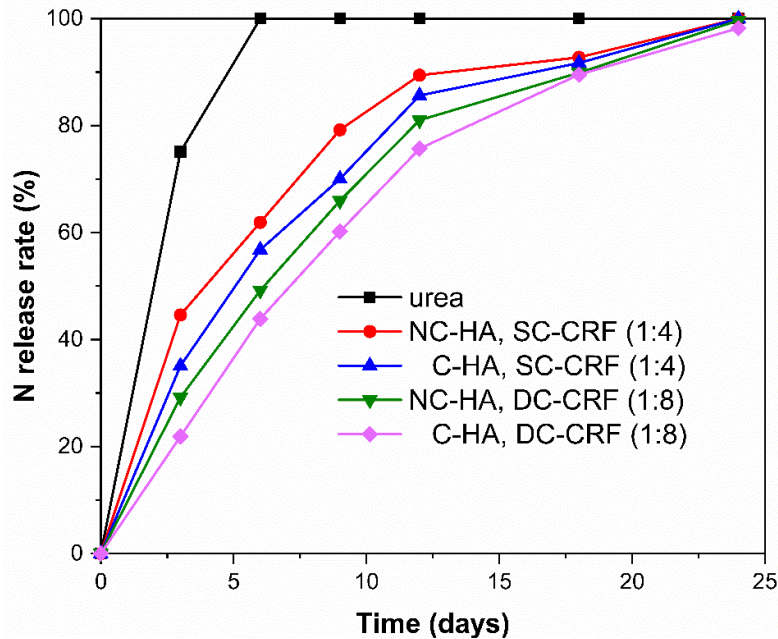


**Figure 6.** The N release pattern in water compared with conventional urea. (a) SC-CRFs; and (b) DC-CRFs

#### *The pattern of N release from CRFs in soil*

Based on the results of N release in water, four types of single and double coated CRFs were selected to study the release patterns of N in loamy clay soil. The selected CRFs were, two single-coated CRFs of the lower HA: urea ratio (1:4), and two double-coated ones of the higher ratio (1:8). The results showed that the N release rate from all types of single and double-coated CRFs was significantly slower than conventional urea (Figure 7). The N release period was extended to 24 days for all CRF types against 6 days for conventional urea. The slowest release rate was recorded for the DC-CRFs (purple and green lines) prepared at the higher ratio of HP: urea (1:8), followed by the SC-CRFs (blue and red) prepared at the lower ratio of 1: 4. Besides, for both types of single and double coated CRFs, the beads synthesized using calcinated-HA (C-HA) gave the slowest N release rate (purple and blue) compared with those synthesized using non-calcinated-HP (NC-HP, green and red lines).

These results revealed the double coating lignin layer, the characteristics of C-HA, and the high nitrogen content of DC-CRFs. The first leachate (after 3 days) released 75% of the total N content of conventional urea, while DC-CRFs synthesized using C-HA released 22% of the total N at the same period, with the remaining 75% released after 4 leachates (12 days). As a rule of thumb, as the N release period increased, soil residence time increased, plant utilization efficiency increased, and N loss decreased. In this connection, all synthesized CRFs used in our study had high efficiency to decrease N loss, and increase plant utilization efficiency. Similar to our findings, Carmona *et al.* (2022) reported that the SRF produced using amorphous calcium phosphate as a urea vehicle released urea five times slower than regular urea.



**Figure 7.** The N release pattern of CRFs in the soil compared with conventional urea

#### *The effect of CRFs on the growth and yield of green beans*

In the experiment shown in Table 3, using all three types of CRF greatly improved the vegetative growth of green beans (plant height, number of branches, fresh and dry weight), as well as their ability to take in N and K, when compared to using regular urea. As illustrated in Table 3, applying the SC-CRFs at N levels of 75% and 50% of the recommended dose for all treatments showed significant improvements in all plant's attributes compared to the full dose of conventional urea. Also, applying SCRF synthesized using NC-HA (T1) at N level of 50% of the recommended dose improved the nitrogen and potassium uptake by 66% and 70% (significantly) compared to the control treatment, while recording the almost same value of fresh weight, dry weight, plant height, and the number of branches as in the control treatment.

Also, applying the DCRF synthesized using C-HA (T4) at N level of 50% improved plant height, number of branches, fresh and dry weight and N and K uptake by 31, 33, 24, 36, 73, and 68% (significantly) compared to the control, while the SCRF synthesized using C-HA (T2) and DCRF synthesized using the NC-HA (T3) applied at the same N level improved all plant attributes without significant difference to the control treatment. Applying CRFs at 25% of N level has no significant effect on all plant attributes compared with the full dose of urea, which is a very good result because it doesn't negatively affect the plant attributes. The important finding of these results is that applying nano-controlled release fertilizers, particularly the double-coated one, at N rate of 25% of the recommended dose has a similar effect on growth parameters as the full

dose of urea fertilizer. This means that we can save 75% of the consumption of nitrogenous fertilizers, and produce the same yield as the green bean plants, by applying double-coated nano-controlled release fertilizer.

Increasing the vegetative growth parameters in CRF treatments compared to control treatments due to the high N uptake in these treatments, especially at the high rate of nitrogen (75%). Nitrogen plays an important role in the photosynthesis process as it is a key component of chlorophyll and a main component of protein (Nigatie, 2021). N uptake was correlated positively with plant fresh weight (0.738<sup>\*\*</sup>), plant dry weight (0.903<sup>\*\*</sup>), number of branches (0.609<sup>\*\*</sup>), plant height (0.539<sup>\*\*</sup>), and K uptake (0.847<sup>\*\*</sup>) as shown in Table 4.

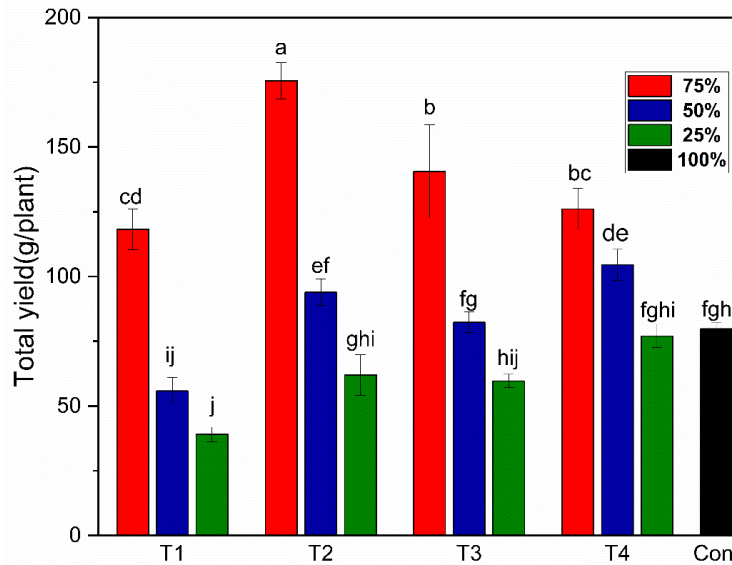
**Table 3.** Green bean growth attributes as affected by CRFs treatments

Treatments	Level	Fresh weight (g)	Dry weight (g)	Number of branches	Plant height (Cm)	N uptake (mg/plant)	K uptake (mg/plant)
T 1	75%	72.25 ab	19.38 ab	4.5 bc	30.5 bcd	551.4 a	139.8 ab
	50%	55.25 def	15.25 bcde	3.5 cde	28.25 bcde	428.8 bcd	128.2 bcd
	25%	42.0 g	6.12 f	3.0 e	26.5 e	126.5 g	32.3 f
T 2	75%	81.25 a	22.0 a	5.5 a	34.5 a	552.2 a	184.1 a
	50%	64.25 bcde	14.13 cde	4.0 bcde	29.0 bcde	355.9 cdef	121.4 bcde
	25%	44.25 fg	12.75 de	3.25 de	29.25 bcde	303.6 ef	88.5 cde
T 3	75%	71.5 abc	22.5 a	4.75 ab	31.75 ab	539.7 ab	150.5 ab
	50%	59.75 cde	13.13 cde	3.75 bcde	28.75 bcde	321.2 def	85.1 cde
	25%	52.25 efg	14.75 cde	4.0 bcde	28.0 cde	297.2 ef	87.5 cde
T4	75%	67.25 bcd	17.5 bc	4.25 bcd	31.75 ab	396.7 cde	135.5 bc
	50%	65.50 bcd	16.17 bcd	4.0 bcde	31.0 bc	446.9 abc	126.6 bcd
	25%	56.75 de	10.75 e	4.25 bcd	29.0 bcde	312.7 def	79.7 de
Control	100%	52.75 efg	11.88 de	3.0 e	27.25 de	257.8 f	75.0 ef

**Table 4.** Correlation coefficients amongst total yield, fresh weight, dry weight, N of branches, plant height, K and N uptake

Attributes	Yield	F.W.	D.W.	N. of branches	Plant length	K uptake
F.W.	0.760 <sup>**</sup>					
D.W.	0.679 <sup>**</sup>	0.765 <sup>**</sup>				
N. of branches	0.714 <sup>**</sup>	0.652 <sup>**</sup>	0.605 <sup>**</sup>			
Plant length	0.667 <sup>**</sup>	0.653 <sup>**</sup>	0.611 <sup>**</sup>	0.624 <sup>**</sup>		
K uptake	0.658 <sup>**</sup>	0.780 <sup>**</sup>	0.874 <sup>**</sup>	0.655 <sup>**</sup>	0.645 <sup>**</sup>	
N uptake	0.616 <sup>**</sup>	0.738 <sup>**</sup>	0.903 <sup>**</sup>	0.609 <sup>**</sup>	0.539 <sup>**</sup>	0.847 <sup>**</sup>

All types of controlled-release fertilizers, either single- or double-coated nano CRFs received N rate of 75% of the recommended dose, significantly increased the green bean yield by 48, 120, 76, and 58% for T1, T2, T3, and T4, respectively, over the control (full dose of conventional urea), as shown in Figure 8. That could be attributed to the increase in nitrogen uptake because of the slow-release rate of N from the CRFs which met the plant's needs. Applying both DC-CRFs (T4) and SC-CRFs (T2) synthesized using C-HA, at N rate of 50% of the recommended dose increased the yield of the green bean by 30% (significant) and 18% (nonsignificant), respectively, while T3 (DC-CRFs) synthesized using NC-HA, at the same level of N rate slightly increased the yield, over the full dose of conventional urea. This result matched the effect of applying CRFs on plant growth parameters mentioned above, which indicates that applying DC-CRFs (T4) at 50% of the recommended dose significantly improved all plant attributes. While applying SC-CRF (T3) at the same N level, it improved the plant growth parameters but not significantly.



**Figure 8.** Total yield/plant of; SC-CRFs prepared with NC-HA (T1), SC-CRFs prepared with C-HA (T2), DC-CRFs prepared with NC-HA (T3), DC-CRFs prepared with C-HA (T4) levels, and conventional urea (control)

The bar values indicate mean and standard error. Different letters indicate significant differences ( $p < 0.05$ )

Previous literature supported this result, as reported by Kottegoda *et al.* (2017) which used uncoated urea-modified hydroxyapatite and achieved an 8% increase in the total yield compared with urea by applying CRFs at 50% of the recommended dose. Increasing the yield through CRF treatments due to improvements in biomass and the photosynthesis process. Yield was correlated directly with plant fresh weight (0.760<sup>\*\*\*</sup>), plant dry weight (0.679<sup>\*\*\*</sup>), N. of branches (0.714<sup>\*\*\*</sup>), plant length (0.667<sup>\*\*\*</sup>), K uptake (0.658<sup>\*\*\*</sup>) and N uptake (0.616<sup>\*\*\*</sup>) as shown in Table 4. The best finding of this research is that the total yield obtained for plants of T4 that received N rate of 25% was almost equal to the full dose of conventional urea, which means that we can produce an almost full yield of green beans, while at the same time saving 75% of the current applied dose of nitrogenous fertilizers. This finding also had economically and environmentally significant effects.

## Conclusions

In this study, we synthesized single- and double-coated nano urea-modified hydroxyapatite-controlled release fertilizers (CRFs) to increase the nitrogen release period, hence increasing soil residence time and nitrogen uptake by plants, while at the same time reducing nutrient loss and environmental pollution. The double-coated CRFs prepared at a wide ratio (1:8) of hydroxyapatite: urea had the highest N release period in the soil as well as green bean yield. The lowest applied N rate (25% of the recommended dose) of both single and double-coated nano urea-controlled release fertilizers enhanced plant growth since all plant growth attributes were equal or better than control (full dose of commercial urea), beside the yield obtained from double-coated CRFs synthesized using calcinated hydroxyapatite was almost equal to that of control (full dose urea). The best finding of these results was that applying nano controlled release fertilizers, particularly the double-coated one prepared using calcinated hydroxyapatite, at N rate of 25% of the recommended dose, significantly improved plant growth parameters, and produced green bean yield almost equal to that obtained for the full dose of conventional urea. On one hand, that will help farmers to produce the same yield using only a quarter of the recommended dose of nitrogenous fertilizers. On the other hand, they can increase the total yield by 128% more than the usual yield and save 25% of the recommended dose using SC-CRFs prepared with

C-HA at N rate of 75% of the recommended dose. Based on the previous results, it can be concluded that the recommended treatment is SC-CRF prepared with C-HA applied at an N rate of 75% to match the future increase in the required amount of food.

### **Authors' Contributions**

Conceptualization, M.A.F., M.I.D.H., and H.A.K.; methodology, M.A.F., M.I.D.H., K.F.A. and; software, M.A.F., K.F.A. and M.M.E.-M.; validation, M.A.F., M.I.D.H., and K.F.A.; formal analysis, M.A.F., and K.F.A.; investigation, M.A.F., M.I.D.H. and; resources, M.A.F., M.I.D.H. and K.F.A.; data curation, M.A.F., M.M.E.-M. and K.F.A.; writing—original draft preparation, M.A.F.; writing—review and editing, M.I.D.H., K.F.A., H.A.K., M.M.E., and N.H.A.; visualization, M.A.F., and K.F.A.; supervision, M.I.D.H. H.A.K., K.F.A. N.H.A.; All authors have read and agreed to the published version of the manuscript. All authors read and approved the final manuscript.

### **Ethical approval** (for researches involving animals or humans)

Not applicable.

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### **Conflict of Interests**

The authors declare that there are no conflicts of interest related to this article.

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