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ORIGINAL RESEARCH

Crab shell biowaste hydroxyapatite as inert material for gradual releaser of crop nutrients for sustainable food production

Yusuf Wibisono[1*], Vibi Rafianto[2], Dikianur Alvianto[1], Gunomo Djoyowasito[2], Bayu Dwi Apri Nugroho[3], Chusnul Arif [4]

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Abstract

Purpose Aggressive use of crop fertilizer during food production caused an overburden in the environment. Gradual release of crop nutrients from the fertilizer could decrease the massive utilization of fertilizer. The advantages are two folds, cheaper cost, and environmentally friendly crop production.

Method Slow-release fertilizer was prepared by encapsulating hydroxyapatite (HA) with a single fertilizer. The HA which derived from crab shell biowaste was synthesized by the wet precipitation method. The nitrogen release test was carried out every 5 minutes for 1 hour using the percolation method, then the percolates were tested for the total nitrogen content. Fertilizer was applied to see its effect on the vegetative and generative growth of tomato plants. Five treatments were applied: without fertilizer as control, ammonium sulfate (AS) fertilizer, hybrid AS-HA fertilizer, urea (U) fertilizer, and U-HA fertilizer.

Results AS-HA released nitrogen at 4.45% or three times slower than AS which released 13.51%. U-HA released nitrogen as much as 3.96% or 4.5 times slower than urea which released nitrogen as much as 18.66% in one hour. AS-HA fertilizer provided the best results for overall parameters, with an average height of 102.1 cm for plant height, 7 mm for stem diameter, 82 strands for number of leaves, 4 produced fruits, and 63.5 grams for the fruit weight per plant.

Conclusion Slow-release fertilizer with a mixture of hydroxyapatite was able to release nitrogen gradually. Korsmeyer-Peppas model was the best-fitted model for nitrogen release.

Keywords Crab shell biowaste, Crop nutrients, Food production, Gradual releaser, Hydroxyapatite, Slow-release fertilizer

Introduction

Blue swimming crabs (*Portunus pelagicus*) are abundantly found in shallow coastal and estuarine waters of tropical and temperate regions in the Indo-West Pacific, within salinity ranges from about 30 to 40 ppt with sandy or muddy bottom at seagrass and algal areas depth around 50-65 m depth (Madduppa et al. 2021). As a food resource, crab meat is widely consumed in the human diet (Ervik et al. 2020). However, the crab-shell waste becomes

✉ Yusuf Wibisono Y_Wibisono@ub.ac.id

1 Department of Bioprocess Engineering, Faculty of Agricultural Technology, Universitas Brawijaya, Malang 65141, Indonesia

2 Department of Agricultural and Biosystems Engineering, Faculty of Agricultural Technology, Universitas Brawijaya, Malang 65141, Indonesia

3 Department of Agricultural and Biosystems Engineering, Faculty of Agricultural Technology, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

4 Department of Civil and Environmental Engineering, Faculty of Agricultural Technology, IPB University, Bogor 16680, Indonesia

enormous and affects the environment (Caruso et al. 2020). Conversion into valuable bioproducts was proposed (Maschmeyer et al. 2020). Crab shell biowaste contains 15.60-23.90% protein, 53.70-78.40% calcium carbonate, and 18.70-32.20% chitin, which also depends on the type of crab and living place (Aklog et al. 2016; Jun et al. 2019). The high calcium content in the crab shell can be used as the main component for hydroxyapatite (HA) compound (Sarkar and Das 2022; Wibisono et al. 2018).

Hydroxyapatite (Ca_{10} $(PO_4)_6$ $(OH)_2$) is a biocompatible material commonly used for hard tissue biomaterials such as material for bone and dental implants, by maintaining a Ca/P ratio about 1.67 (Fiume et al. 2021; Ulfyana et al. 2018). While CaO-rich HA compound is potentially used for porous bioceramic membranes, among others (Wibisono et al. 2021). As phosphate-rich compound, HA also could be used as source of nutrients for crop production (Maghsoodi et al. 2020). As HA morphological structure has high porosity and tortuosity, depending on the raw materials and synthesis methods (Sadat-Shojai et al. 2013), HA material could be coupled with another N-rich materials as matrixes for adsorbent and gradual releaser of nutrients (Kottegoda et al. 2017; Tang and Fei 2021).

Based on data obtained from the Indonesian Fertilizer Producers Association (APPI), the consumption of urea fertilizer from January to December 2019 grew up to 5.425 million tons, while the consumption of AS fertilizer was 1.017 million tons. Inorganic fertilizers are fertilizers that dissolve easily when interacting with water, the nitrate content that is easily soluble in water in fertilizers causes more nitrogen to be wasted through surface runoff, volatilization, and leaching, before being properly absorbed by plants (Kottegoda et al. 2017). Excessive use of chemical fertilizers will change the physical and chemical properties of the soil because it can reduce soil organic content. In addition, excess nutrients will be dissolved and cause a buildup of dissolved organic matter, thus polluting and reducing the quality of groundwater (Agegnehu et al. 2016; Oladele et al. 2019; Wibisono et al. 2020).

Slow-Release Fertilizer (SRF) has the advantage of increasing nutrient absorption by plants than inorganic fertilizers (Behin and Sadeghi 2016; DeRosa et al. 2010). SRF is considered a solution to increase the efficiency of nutrient absorption by plants due to the slow release of nutrients, thereby reducing the risk of soil contamination and irrigation flow. SRF can be made by binding nutrients to conventional fertilizers with materials that are difficult to dissolve with water so that the process of releasing nutrients can be inhibited. Generally, the materials used are biopolymers such as cellulose or starch, but subsequent research has shown that the use of nanoparticles such as HA is considered more effective (Madusanka et al. 2017).

In this study, HA particles were synthesized by using wet precipitation methods from crab shell biowaste. HA particles were then encapsulated by two N-rich fertilizers, i.e., ammonium sulfate (AS) and urea (U). The hybrid compounds were then used as fertilizer for tomato (*Solanum lycopersicum*) plants, along with individual fertilizer, i.e., AS and U, respectively, and compared with un-fertilized plants. The tomato plant growth parameters were observed for 80 days, e.g., plant height, stem diameter, number of leaves, number of fruits, and fruit per plant weight. Finally, the performance of HA-based fertilizer on tomato plant growth was analyzed based on the kinetic release of nitrogen in water environment.

Materials and methods

Materials

The crab shell (*Portunus pelagicus*) biowaste as calcium precursor was obtained from the marine industry in the north coastal line of Pasuruan, East Java, Indonesia. Some chemicals were used in this research, e.g., diammonium phosphate $(NH_4)_2HPO_4$, hydrochloric acid HCl 37%, phosphoric acid H_3PO_4 85%, ammonia NH_3 25%, and ethanol 96% are purchased from Merck KGaA (Darmstadt, Germany).

Methods

HA synthesis by wet chemical precipitation

The wet chemical precipitation method was selected for the HA synthesis. The crab shell biowaste was washed, cleaned from impurities, and then dried under open sun drying for 12 hours, followed by 4 hours of drying in the electric oven until reach 9.5 ± 0.12% wb. The dried crab shell was ground into a fine powder using a pilot-size tubular ball mill. The rotation speed of 84.6 rpm was used, and 1:10 crab-shells and stainless-steel balls ratio was utilized, with running time of 4 hours. The milled powder was then sieved using a woven wire 325 mesh sieve and crab shell powder of 44 µm was produced. Further milling was done utilizing a custom-made Planetary Ball Mill. The mill has double 500 mL stainless steel vials, while the rotation speed was 450 rpm. The second milling produced powder in 4.6 µm particle size. The powder was then calcinated at a temperature of 1000°C for 5 hours to produce calcium oxide (CaO) powder. The CaO powder was then synthesized into HA materials (Wibisono et al. 2021).

CaO powder of 22 grams was dissolved in demineralized water and mixed with diluted H_3PO_4 85%, by using a magnetic stirrer with an agitation speed of 700 rpm at 60°C. The H_3PO_4 was added by titration process with a drop rate of 3 mL/minute. NH_3 was then added to the suspension until it reached pH 10. The suspension was then sonicated with an ultrasonic bath (Branson 3510, USA) for 1 hour at 42 kHz. The suspension was then placed at room temperature for 24 hours. The obtained sediment was washed with demineralized water and filtered using filter paper. The sediment was dried in an oven (Binder Red-Line, Germany) for 15 hours at 90°C and calcinated at 1000°C for 6 hours. (Wibisono et al. 2021).

FTIR spectroscopy

The chemical bonds of HA and HA-based slow-release fertilizers were analyzed using FTIR to see whether nitrogen was bound by the hydroxyapatite material used. FTIR testing was carried out with a Fourier Transform Infra-Red Spectroscopy (Shimadzu 8400S, Kyoto, Japan), within the wavelength range of 4000 cm^{-1} – 400 cm^{-1}.

XRF observation

X-Ray Fluorencence (PANalytical Minipal 4, Malvern, UK), was used to determine the types of elements contained in the material and determine the concentration of elements in the material. Hydroxyapatite samples were analyzed using XRF to determine the elements contained in the sample and the concentration of each element.

HA encapsulation

A combination ratio of 6:1 fertilizer with HA was used. In the manufacturing process, fertilizer (AS and Urea) and HA were weighed using analytical scales, then HA powder was added to distilled water with a ratio of HA to distilled water of 1:20 w/v. The fertilizer and HA suspension were mixed using a magnetic stirrer for 1 hour at room temperature. Furthermore, the hybrid AS+HA and U+HA suspensions were dried using an oven. The drying process used a temperature of 50°C for 24 hours.

Percolation

The nitrogen release test was carried out by the percolation method at the specified time susceptibility, which was every 5 minutes for 1 hour. The mass of fertilizer used for the experiment was 1 gram. Furthermore, the surface of the fertilizer was dripped with distilled water at a flow rate of 3 mL/minute and the total nitrogen content from percolates every time it was observed was measured using the Kjeldahl method.

Nitrogen release

The cumulative release results of nitrogen were linked using the zero-order, first-order, Higuchi, and Korsmeyer-Peppas equations to determine the release kinetics. The nitrogen release kinetics of ZA, AS+HA, urea, and U+HA were studied to determine the nitrogen release kinetics of each fertilizer using a linear curve and the results were compared to obtain the best release kinetic model. The value of R^2 was used as a reference for the level of conformity of the equation used with the percentage of the dependent variable described by the independent variable with a value between 0 - 1. The best model in explaining the kinetics of nitrogen release in slow-release fertilizers was then obtained.

Statistical analysis

The data was processed using One Way ANOVA with the hypothesis tested if the P-Value> 0.05 then there is an effect of treatment on plant growth and if the P-Value <0.05 then there is no effect. Furthermore, to determine the effect between each treatment, a further test of the least significant difference (LSD) was carried out.

Results and discussion

Overview of overall assessment

Fig. 1 shows an overview of the processes during assessment of HA-based slow-release fertilizer: from dried crab shell biowaste, ground and converted into hydroxyapatite particles, then encapsulated with AS and urea, and finally applied in tomato plants grown up to 80 days after planting.

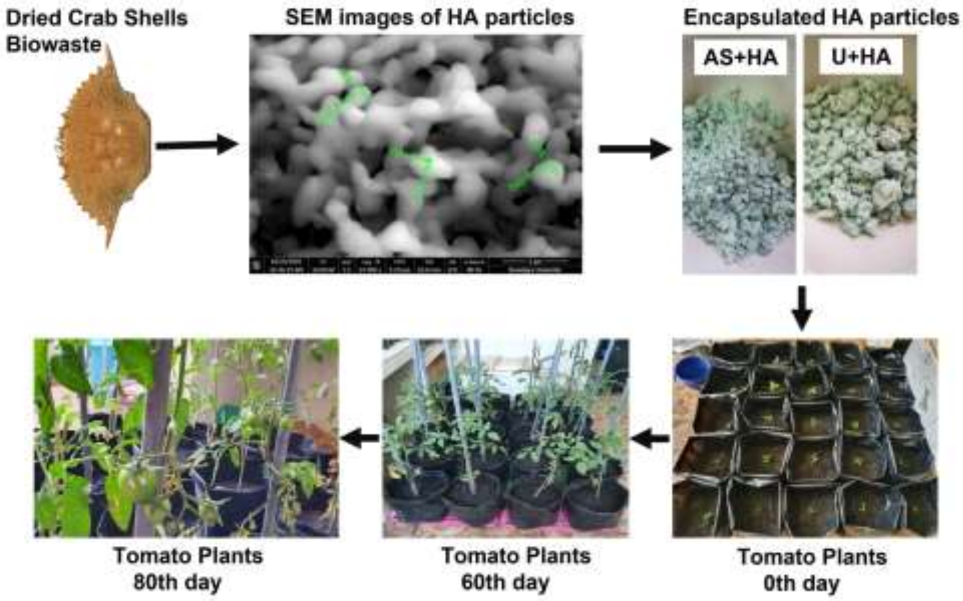

Fig. 1 An overview of the assessments in this study

During HA preparation, calcium hydroxide and phosphoric acid were used as precursors in the synthesis process with a byproduct of the synthesis process in the form of water. The rate at which phosphate was added and the temperature used during the reaction can affect the size, shape, and surface of the hydroxyapatite particles. As shown in scanning electron microscope (SEM) images, HA particles have an irregular shape, which tend to form an oval shape below 1 μm in size (Wibisono et al. 2021). The rate of addition of phosphate affects the final pH obtained, the stability of the suspension, and the size of the crystallite. While the temperature of the reaction determines the type of crystal produced (Sadat-Shojai et al. 2013).

Characterization of hydroxyapatite fertilizer

Fourier-transform infrared spectroscopy (FTIR)

Fig. 2 shows the FTIR spectra of individual crab shell-based HA particles, AS, Urea, and hybrid AS-HA and U-HA particles. As shown, observed peaks of 567.8 cm^{-1}, 604.44 cm^{-1}, 1092.4 cm^{-1}, 1038.39 cm^{-1}, and 965.10 cm^{-1} indicate the phosphate group. The absorption of the hydroxyl group was observed at a wavelength of 3451.18 cm^{-1}. The carbonate group was also observed at a wavelength of 1458.85 cm^{-1}.

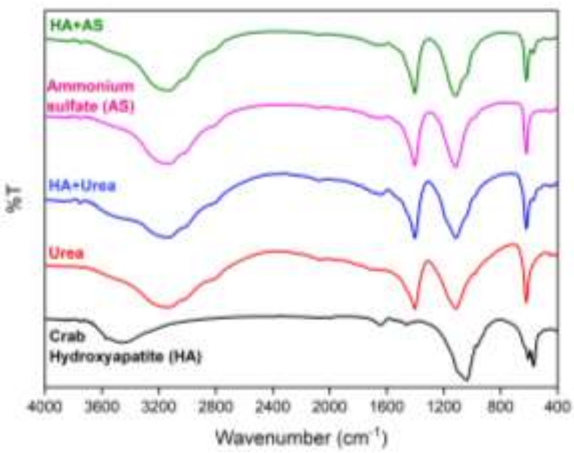

Fig. 2 FTIR spectra of crab shell HA, AS, urea, and hybrid AS-HA and U-HA particles

As for the hybrid AS-HA particles, the peaks were observed in the wavelength range of 3132.94 cm^{-1}, whereas the peak of individual AS particles was observed at a wavelength of 3131.02 cm^{-1} and hydroxyapatite showed the peak absorption point at a wavelength of 3451.18 cm^{-1}. This shift in wavelength shows that there was an interaction between the strain of the amine group in the AS fertilizer and the hydroxyl group on hydroxyapatite.

For the U-HA particles, it shows that the peaks were observed at a wavelength range of 3131.02 cm^{-1}, whereas for urea, the peak was observed at a wavelength of 3156.09 cm^{-1}, and the peak for HA was observed at a wavelength of 3451.18 cm^{-1}. The peak shift occurred due to the interaction between the strain of the amine group from the urea and the hydroxyl group of the HA. The peak shift is lower, which indicates a weak bond. However, at a wavelength of 571.65 cm^{-1} a peak was observed, which is a stretch of the HA phosphate group against the amine group in urea. The shift in peak absorption from pure urea at 1698 cm^{-1} to 1649.79 cm^{-1}, with an intensity of 65.084% and 70.463%, respectively, indicates a hydrogen bond between the N-H bond group from urea a with stronger O-H bond group from HA nanoparticles.

X-ray fluorescence (XRF)

Table 1 shows the elemental analysis of HA by using XRF.

Table 1 Elemental analysis of crab shell-based HA particles

Crab shell HA	Elements (wt.%)
Ca	77.79
P	17.8
Ti	0.071
Mn	0.29
Fe	1.06
Cu	0.057
Sr	2.2
Zr	0.2
Yb	0.31
S	0.12
Ca/P	**4.37**

As shown in Table 1, HA particles have an elemental composition that is dominated by 77.79% calcium and 17.8% phosphorus. Other elements found in the sample such as S, Ti, Mn, Fe, Cu, Sr, Zr, Eu, and Yb have very small percentage values ranging from 0.071% to 2.2%. The HA produced in this study has a higher Ca/P ratio compared to stoichiometry HA, because it was extracted from the natural resource of marine-derived bio-waste, i.e., crab shell. The presence of trace elements responsible for the non-stoichiometric HA, including the existence of CaO in the HA produced (Wibisono et al. 2021).

Release of Nitrogen

Fig. 3 shows the cumulative release of nitrogen from percolation test.

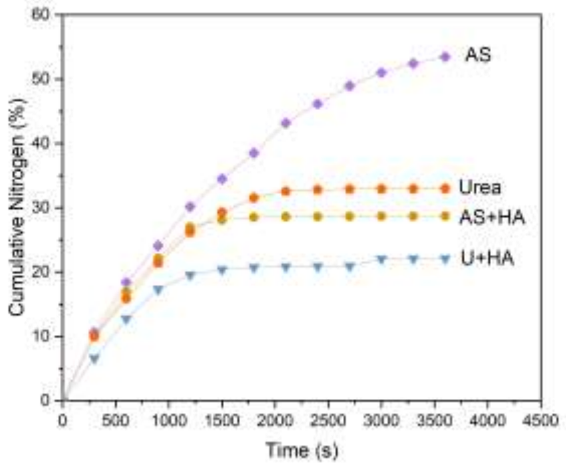

Fig. 3 Cumulative nitrogen release of AS, urea, AS+HA and U+HA particles

Based on the results of the percolation test, within 1 hour, the total nitrogen released by the AS was 53.46% of the total content or about 13.51%. Whereas for the AS-HA fertilizer, the nitrogen released slowly with an amount of nitrogen released as much as 28.73% of the total nitrogen content in the AS-HA fertilizer or only 4.45%. As for the urea, the total nitrogen released was 32.98% of the total nitrogen content in the urea or around 18.66 %. Whereas for the U-HA fertilizer, nitrogen released slowly with an amount of nitrogen released as much as 22.11% of the total nitrogen content in AS-HA fertilizer or only 3.96%. The AS-HA particles released nitrogen 3-fold slower than that of the AS, and the U-HA released nitrogen 4.5-fold slower than that of the urea.

Release Kinetics

Fig. 4 shows the fitting of cumulative nitrogen release in the zero-order model. In zero-order fitting, the line equation for the AS-HA fertilizer is y = 0.0062x + 12.339 with an R^2 value of 0.6621, and for the AS fertilizer, the line equation is y = 0.0142x +9.1576 with an R^2 value of 0.9347. Whereas for the urea, the line equation is y = 0.0079x + 11.249 with an R^2 value of 0.7446 and in U-HA the line equation is y = 0.0048x +8.7928 with an R^2 value of 0.66.

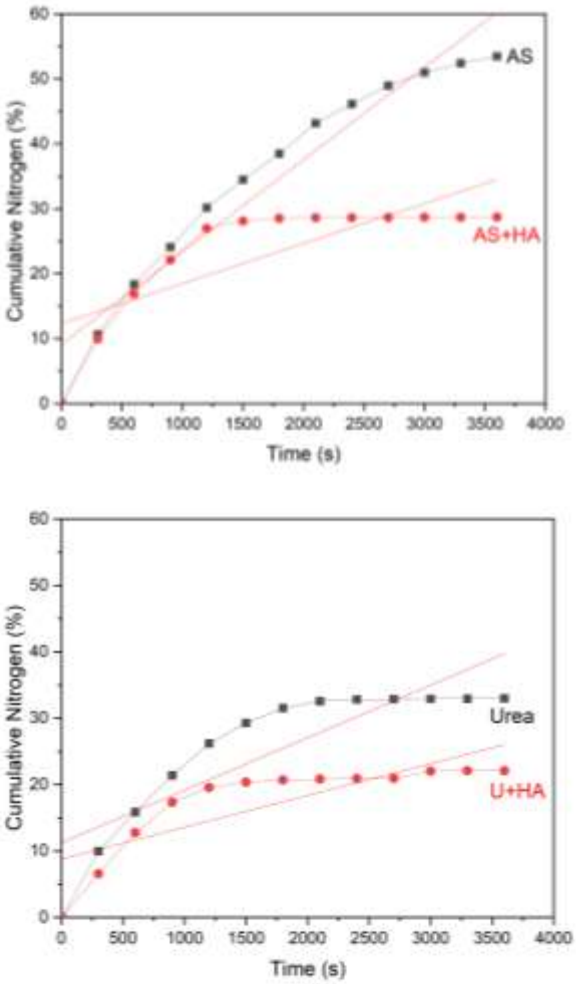

Fig. 4 The zero-order model of the cumulative nitrogen release of: AS and AS+HA (top); Urea and U+HA (bottom)

Fig. 5 shows the fitting of the cumulative nitrogen release using the Higuchi model. By using the Higuchi model, the line equation for the AS-HA fertilizer is y = 0.4809x +4.6918 with an R^2 value of 0.846, and for the AS fertilizer, the line equation is y = 0.9774x-3.3678 with an R^2 value of 0.9885. Whereas for the U-HA, the line equation is y = 0.3676x + 3.0767 with an R^2 value of 0.8706, and for the urea, the line equation is y = 0.5886x + 2.5515 with an R^2 value of 0.9205.

Fig. 6 shows the fitting of cumulative nitrogen release using the first-order model. In the first order, the equation for the AS-HA fertilizer line is y = 0.0002x + 0.8733 with R^2 of 0.4207, and for the AS fertilizer, the line equation is y = 0.0003x +0.8566 and R^2 is 0.5906. Whereas for the U-HA fertilizer, the line equation is y = 0.0002x + 0.7653 with R^2 of 0.4584, and in the urea, the line equation is y = 0.0003x +0.8546 with an R^2 value of 0.4841.

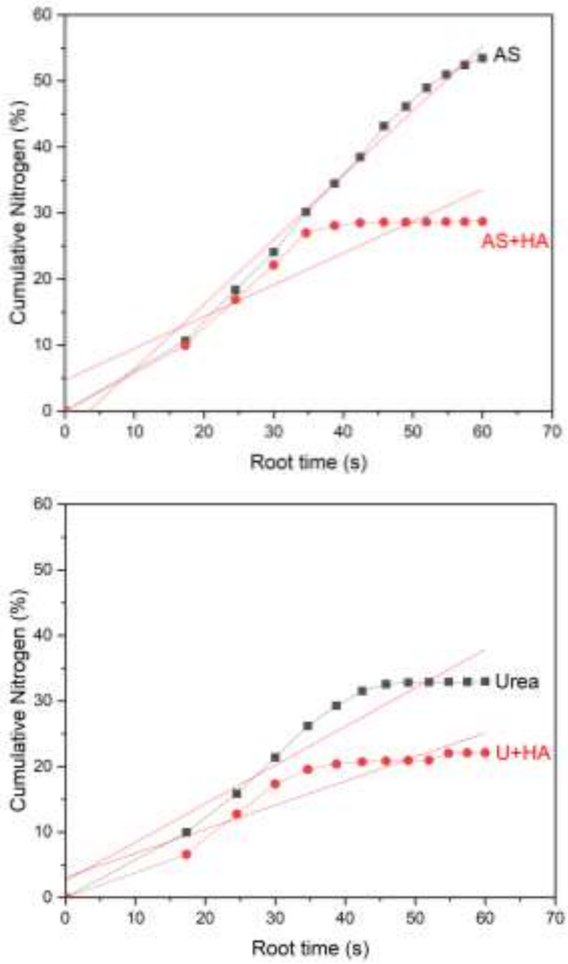

Fig. 5 The Higuchi model of the cumulative nitrogen release of: AS and AS+HA (top); Urea and U+HA (bottom)

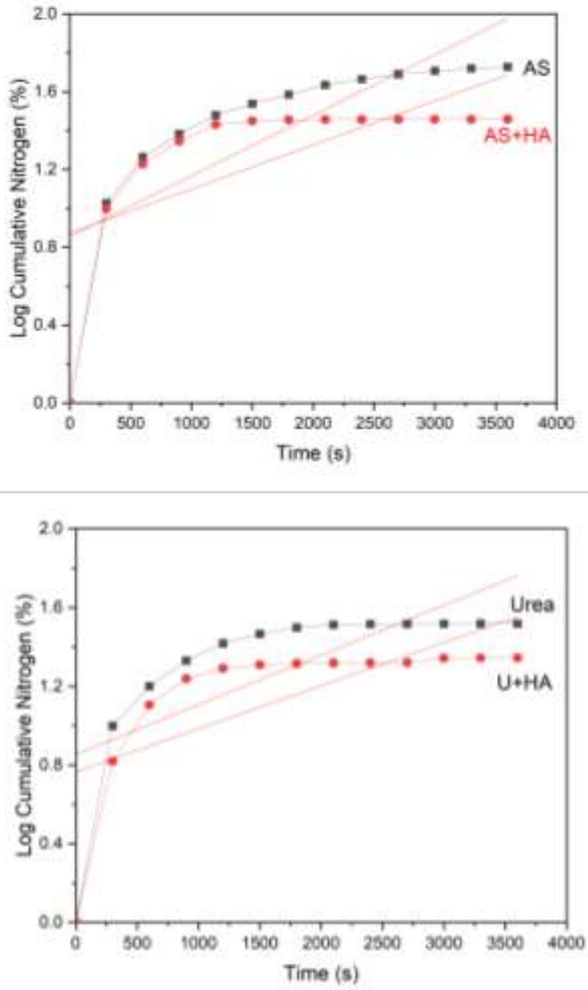

Fig. 6 The first-order model of the cumulative nitrogen release of: AS and AS+HA (top); Urea and U+HA (bottom). AS, urea, AS+HA and U+HA

Fig. 7 shows the fitting of the cumulative nitrogen release using the Korsmeyer-Peppas model. In the Korsmeyer-Peppas model, AS fertilizer has a function of y = 0.024x + 0.450 with R^2 of 0.8372, and for the AS-HA fertilizer, the line equation of is y = 0.0194x + 0.5223 with R^2 0.694. Whereas for the U-HA fertilizer, the line equation is y = 0.01847x + 0.43959 with R^2 of 0.7284, and for the urea, the line equation is y = 0.002105x + 0.4884 with R^2 0.7524.

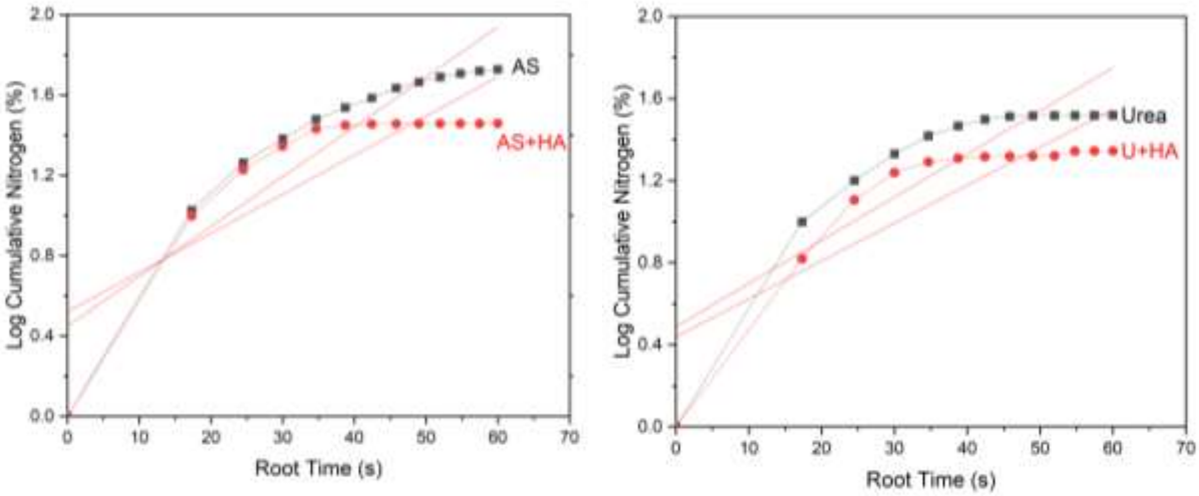

Fig. 7 The Korsmeyer-Peppas model of the cumulative nitrogen release of: AS and AS+HA (left); Urea and U+HA (right)

Vegetative growth of tomato plants

Vegetative observations were made to determine the effect of fertilizer treatment on the generative growth period of plants. Fig. 8 shows the tomato plant height for 80 days supplied with AS, urea, AS+HA, and U+HA fertilizers, compared to the plant growth without fertilizer.

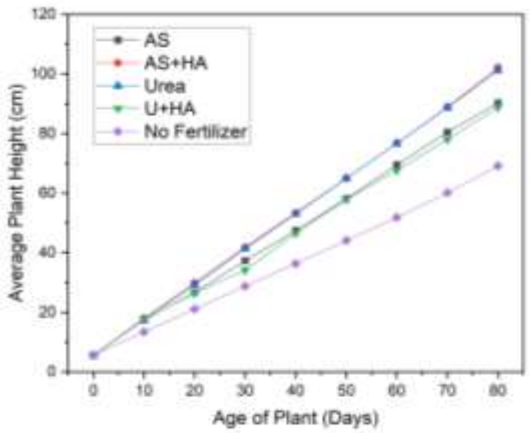

Fig. 8 Tomato plant height for 80 days with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer

Least significant difference (LSD) analysis was carried out for the effect of AS+HA and U+HA treatment on tomato plant height. The best results were obtained in the treatment using AS+HA fertilizer, but there was no significant difference between the two on plant heights. The application of hydroxyapatite fertilizer gave significant results when compared with the single and control fertilizer treatments.

Furthermore, comparing the single AS and urea treatments, the best results shown by using a single AS fertilizer, and there were significant differences between the two.

The best results were obtained in the following order of height: AS+HA 102.1 cm, U+HA 101.17 cm, AS 90.23 cm, urea 88.83 cm and without fertilizer 69.17 cm.

Fig. 9 shows the tomato plant stem diameter for 80 days with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer.

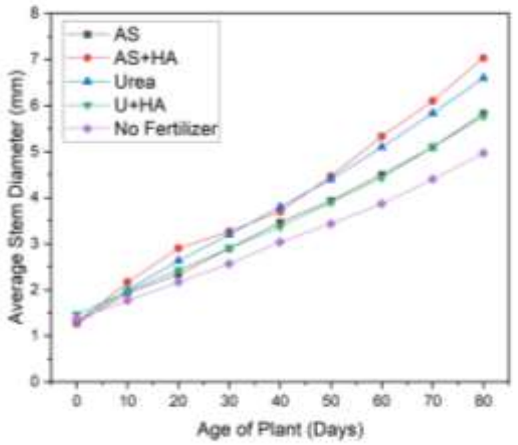

Fig. 9 Tomato plant stem diameter for 80 days with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer

The stem diameters show that the AS+HA and U+HA treatments obtained the best results in the treatment using AS-HA fertilizer, by showing a significant difference between the two of the plant stem diameters. The application of hydroxyapatite fertilizers of both AS+HA and U+HA gave significantly different results compared to the single and control fertilizer treatments. Furthermore, comparing the single AS and urea treatments, the best results was obtained using a single AS fertilizer, yet there was no significant difference between the two, as measured by LSD analysis shown in Table 2.

Table 2 Least Significance Different (LSD) analysis

Treatment	Plant height (cm)	LSD (5%)
No Fertilizer	36.714[a]	0.64874
U	46.970[b]	0.64847
AS	48.092[c]	0.64847
U+HA	53.111[d]	0.64847
AS+HA	53.459[d]	0.64847

Fig. 10 shows the tomato plant number of leaves for 80 days with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer.

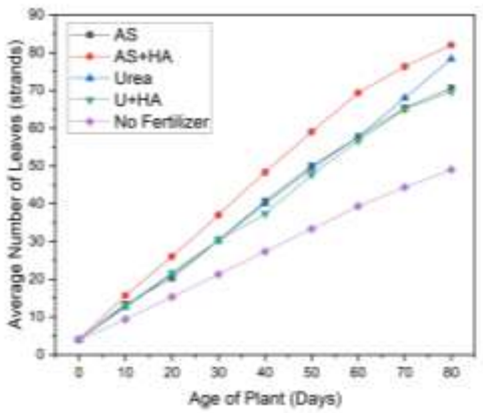

Fig. 10 Tomato plant number of leaves for 80 days with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer

In observing the number of leaves, the AS+HA and U+HA treatments obtained the best results in the treatment using AS+HA fertilizer, by showing a significant difference between the two on the number of plant leaves.

The application of both AS+HA and U+HA fertilizers gave significant results compared to the single and control fertilizer treatments. Furthermore, comparing the single AS and urea treatments, the best results by using a single AS fertilizer, yet there was no significant difference between the two.

Generative growth of tomato plants

Observations on generative growth of tomato plants were made to determine the effect of fertilizer treatment on the generative growth period of plants. Fig. 11 shows the average tomato fruits harvested on the 80th day with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer.

Least significant difference (LSD) analysis on the number of fruit, shown that in the treatment using U+HA fertilizer, there was no significant difference between the two on the number of fruits.

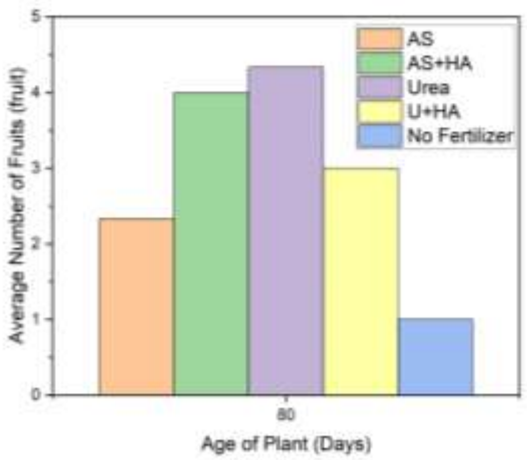

Fig. 11 Tomato fruits harvested on the 80th day with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer

The application of both AS+HA and U+HA hydroxyapatite fertilizers gave significant results compared to single and control fertilizer treatments. Furthermore, the single AS and urea fertilizers obtained the best results using a single AS fertilizer with significant differences between the two.

Fig. 12 shows the average weight of tomato fruits per plant harvested on the 80th day with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer.

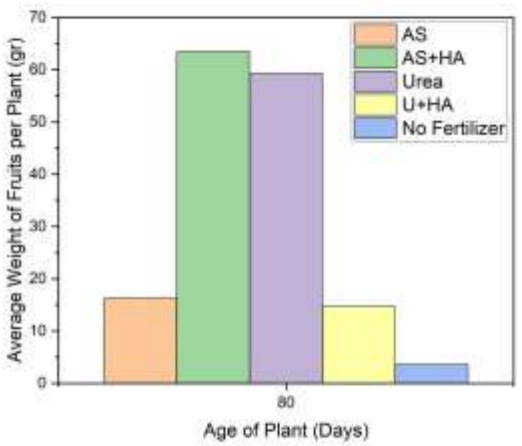

Fig. 12 Weight of tomato fruits per plant harvested on the 80th day with supplies of AS, urea, AS+HA and U+HA fertilizers, compared to the plant growth without fertilizer

For the weight of produced fruit per plant treated using AS+HA fertilizer, there was a significant difference between the two on fruit per plant weight. The application of both AS+HA and U+HA hydroxyapatite fertilizers gave significant results compared to the single and control fertilizer treatments with fruit per plant weight in the AS+HA treatment of 63.5 grams. Furthermore, comparing the single AS and urea treatments, the best results obtained by using a single AS fertilizer without significant differences between the two. Where the AS fruit per plant weight 16.3 grams and 14.7 grams of urea.

Effect of soil acidity

In the soil acidity test, it was observed that the AS and AS+HA treatments had significant differences in their effect on soil acidity. For the AS fertilizer, the acidity value obtained was 6.5 while for the AS+HA, the average value was 6.67, which shows that AS fertilizer treatment reducesd the soil acidity more than AS+HA. In the treatment of urea and U+HA, no significant differences between the two were shown. The acidity value obtained in urea was 6.83 and in U+HA was 6.8. Meanwhile, the control treatment obtained an acidity value of 7. The decrease in acidity which is not too significant in AS+HA fertilizer was imposed by the presence of calcium content in HA which had the potential to increase soil acidity.

Hydroxyapatite particles characterization

For the hydroxyapatite sample that was synthesized using the wet chemical deposition method, based on the results of XRF analysis, it contained 77.79% Ca and 17.8% phosphorus. Furthermore, the FTIR analysis of the sample showed that there was an absorption peak of the $PO4^{3-}$ group which occurred at the wavelengths of 567.8 cm^{-1}, 604.4 cm^{-1}, 627.58 cm^{-1}, 1092.4 cm^{-1}, 1038.39 cm^{-1}, and 965.10 cm^{-1}. The HA showed a phosphate group uptake at the wavelengths of 567 – 572 cm^{-1}, 600 – 605 cm^{-1}, 960 – 967 cm^{-1}, 1086 – 1101 cm^{-1}, and the OH absorption was seen in the wavelengths range of 1629 - 1641 cm^{-1} and 3421 - 3500 cm^{-1}(Yelten-Yilmaz and Yilmaz 2018). The presence of phosphate groups at a wavelength of 963 cm^{-1} is in accordance with the vibration of v1 ion PO_4^{3-} and in the range of 1059 cm^{-1} until 1100 cm^{-1} due to the vibration of v3 ion $PO4^{3-}$. The peak at the wavelength of 1459 cm^{-1} is a vibration of v3 CO_3^- due to contact with air (CO_2) during the synthesis process (Wibisono et al. 2021). As Ca element and PO_4^{3-} dan OH^- observed, it can be concluded that the particles are HA.

Hybrid AS+HA and U+HA fertilizers

Based on the FTIR analysis carried out on the AS fertilizer, the absorption peaks of the NH_4^+ at the wavelengths of 1400.99 cm^{-1}, 1659.43 cm^{-1}, and 3131.02 cm^{-1}, and SO_4^{2-} absorption at the wavelengths of 452.07 cm^{-1}, 619.87 cm^{-1}, 986.32 cm^{-1}, 1113.61 cm^{-1} were observed. Whereas for the AS+HA, the NH_4^+ absorption was obtained at the wavelengths of 1400.99 cm^{-1}, 1647.86 cm^{-1}, 3132.94 cm^{-1}, and SO_4^{2-} absorption at a wavelength of 454 cm^{-1}, 569.72 cm^{-1} , 617.94 cm^{-1}, 1115.54 cm^{-1}. Similarly found, where the NH_4^+ group can be found at the wavelength of 1200 - 1510 cm^{-1} with an absorption peak of around 1400 cm^{-1} and in the range of 2600 - 3300 cm^{-1} with the absorption peaks at 2800, 2900, and 3200 cm^{-1} (Özen et al. 2019). Meanwhile, the SO_4^{2-} absorption can be found at 450 - 650 cm^{-1} with the absorption peak at 610 cm^{-1} and at 650 - 1200 cm^{-1} at 1030 cm^{-1}.

The FTIR results of the AS+HA show that the peak absorption occurred in the wavelength range of 3132.94 cm^{-1} whereas in the AS without hydroxyapatite, the peak absorption occurs at the wavelength of 3131.02 cm^{-1}, and the hydroxyapatite showed the peak absorption point at the wavelength of 3451.18 cm^{-1}. The shift in the wavelength was due to an interaction between the strain of the amine group in the AS fertilizer and the hydroxyl group on hydroxyapatite. The peak at the wavelength of about 3500 cm^{-1} showed the presence of a hydroxyl group. The shift of the peak absorption from pure AS at 3131.02 cm^{-1} to 3132.94 cm^{-1} with a higher absorption intensity in AS+HA shows a strong bond that occurs due to the interaction between the N-H bond groups of the AS and the O-H group of the hydroxyapatites. Shift of the absorption wavelength from 3426 cm^{-1} to 3432 cm^{-1} indicates a strong bond between the NH urea and OH hydroxyapatite groups (Elhassani et al. 2019). The change in the stretching frequency of pure AS carbonyl from 1659.43 cm^{-1} to 1647.86 cm^{-1} shows that the C = O electron bond was influenced by the N-H bond of the HAp and AS.

The shift in the absorption peak that occured in the U+HA fertilizer in this wavelength range was due to the interaction between the strain of the amine group from the urea and the hydroxyl group of the hydroxyapatites, but the shift in the wavelength peak decreased, indicating it was a weak bond. However, the peak absorption at the wavelength of 571.65 cm^{-1} was a stretch of the hydroxyapatite phosphate group against the amine group in urea. The NH bond stretching band occurred in the wavelength range of 1613 cm^{-1} to 3432 cm^{-1}. The C-O stretch occurred at the peak of the wavelength of about 1673 cm^{-1} and the peak of the C-N stretch at a wavelength of about 1457 cm^{-1} (Elhassani et al. 2019). Meanwhile, the peak at the wavelength of about 3500 cm^{-1} showed the presence of a hydroxyl group, the shift in peak absorption from pure urea at 1698 cm^{-1} with an intensity of 65.084% to 1649.79 cm^{-1} with an intensity of 70.463% in U+HA showed that hydrogen bonding occurred between the NH bond group from urea and the OH bond group from the stronger HA nanoparticles. The change in stretching frequency of pure urea carbonyl from 1588 cm^{-1} to 1613 cm^{-1} shows a strong bond to the hydroxyl of hydroxyapatite with the amine bond of urea (Elhassani et al. 2019). So that it can be concluded from the results of FTIR testing showing that urea is adsorbed on the surface of the hydroxyapatite nanoparticles with several types of bonds.

Kinetics of Nitrogen release

Based on Figs 4-7, it can indicate that there was not much nitrogen dissolved or washed in the experiment using hydroxyapatite because its release time was slower than a single fertilizer. Whereas in the experiment using a single fertilizer AS and urea, there was nitrogen content in the percolate for up to one hour, which means that the dissolved nitrogen content was more than the hydroxyapatite fertilizer. Based on its chemical bonds, urea contains NH_3 while AS contains NH_4. NH_4^+ elements with a positive charge were bound by colloids in the soil so that they were not easily subjected to the washing process and easily utilized by plants through the ion exchange process. A graph with zero-order kinetics shows a function of time to the cumulative percentage of nitrogen released (Kottegoda et al. 2017). Time is shown in seconds while the cumulative percentage of nitrogen release is in grams. Order 1 kinetics shows a graph of the decimal logarithm of the amount of substance released with respect to linear time. The first-order kinetic model is usually applied to the water solute profile of porous materials (Jose et al. 2013). The Higuchi model defines the linear dependence of the active fraction released per unit (Q) from the square root of time (Jose et al. 2013). Meanwhile, the Korsmeyer-Peppas model describes the release of nutrients from polymeric materials (Lisik and Musiał 2019). In this study, the R^2 value that is the closest to 1 for each fertilizer was obtained using the Higuchi model. Hence, the release of nitrogen from the fertilizers can be described by the amount of nutrients released from the root of the time square based on Fick's law. Based on the R^2 value obtained, the nitrogen release kinetics of each fertilizer has a high level of compatibility with the Korsmeyer-Peppas model. The AS fertilizer (R^2 value of 0.9861) shows that 98% of the log cumulative nitrogen release was influenced by the log time function,. Then, for AS+HA ferilizers, the value obtained was 0.979 or close to 98%, for urea with a value of 0.9869 or about 98%, and in U-HA by 0.9723 or 97%, respectively. Based on the percentage values, the kinetics of nitrogen release using the Korsmeyer-Peppas model only remains about 3%. Based on these data, the best nitrogen release kinetics for each fertilizer was in accordance with the Korsmeyer-Peppas model.

HA as slow-release fertilizer

The application of fertilizers to plants is intended to meet the nutritional needs of plants during the vegetative and generative growth period. Using inorganic fertilizer shows great results on the dry weight per plant, fruit number per plant, average fruit weight and fruit yield. The rapid release of elements can reduce the efficiency of absorption of these elements by plants due to the possibility of leaching and nutrients dissolving by water before being absorbed by plants. In this study, the treatment of hydroxyapatite fertilizer showed better results because the release of nutrients was slow, thereby increasing the efficiency of nutrient absorption by plants (Zhu et al. 2020). The insignificant decrease in pH in the AS+HA fertilizer can be caused by the presence of calcium in hydroxyapatite which has the potential to increase soil acidity. The amount of calcium in the soil caused an increase in pH, with research on various types of soil and it was found that the higher the calcium content, the higher the soil acidity (Sowers et al. 2018). During the watering process, there was a reaction between AS and urea fertilizers with water molecules. For the urea, the reaction that occurred was $NH_2CONH_2 + H_2O \Rightarrow 2NH_3 + CO_2$ while for the AS fertilizer the reaction that occurred was $(NH_4)_2SO_4 + H_2O \Rightarrow 2NH_4OH + H_2SO_4$. The presence of H_2SO_4 in the AS indicates that the acidity level was higher than urea, which when applied to the soil, it caused a decrease in the pH value to become more acidic. The nature of hydroxyapatite which tends to dissolve easily in acid caused the release of nitrogen from the AS+HA fertilizer to be higher than that of U+HA fertilizer. The use of hydroxyapatite fertilizers worked better in the acidic soil conditions and could potentially be used as P fertilizer (Xiong et al. 2018).

Conclusion

The HA derived from crab shell waste was synthesized by the wet precipitation method. The nitrogen release test was carried out every 5 minutes for 1 hour using the percolation method, then the percolates were tested for the total nitrogen content. It was found that the slow-release fertilizer with a mixture of hydroxyapatite was able to release nitrogen gradually. The AS-HA released nitrogen 4.45% or three times slower than the AS which released 13.51%. The U-HA released nitrogen at 3.96% or 4.5 times slower than the urea which released nitrogen at 18.66% in one hour. Considering the release kinetics model, the Korsmeyer-Peppas model was the best-fitted model for nitrogen release.

Fertilizer was applied to determine its effect on the vegetative and generative growth of tomato plants. Five treatments were applied: without fertilizer as control, ammonium sulfate (AS) fertilizer, hybrid AS+HA fertilizer, urea (U) fertilizer, and U+HA fertilizer. The growth parameters were plant height, stem diameter, number of leaves, number of fruits, and fruit per plant weight which were measured every 10 days for 80 days for the vegetative growth, while the generative growth was observed on the 80th day. The use of the AS-HA fertilizer provided the best results for overall parameters, among others, with an average height of 102.1 cm for plant height, 7 mm for stem diameter, 82 strands for number of leaves, 4 produced fruits and 63.5 grams for the fruit weight per plant. Optimization of dominant parameters affecting the plant growth should be conducted in the future, using response surface methodology or Taguchi method.

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Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

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