



Research article

A comparison of microwave and ultrasound routes to prepare nano-hydroxyapatite fertilizer improving morphological and physiological properties of maize (*Zea mays* L.)Homa Sajadina^a, Dadkhoda Ghazanfari^{a,*}, Kazem Naghavii^b, Hormozd Naghavi^c, Batool Tahamipur^a^a Department of Chemistry, Islamic Azad University Kerman, Kerman, Iran^b Department of Physics, Islamic Azad University Kerman, Kerman, Iran^c Department of Agriculture, Islamic Azad University Kerman, Kerman, Iran

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ABSTRACT

Hydroxyapatite nanoparticles have a remarkable potential to be used as nano-fertilizers with great effects on improving the yield of plants. These nano-compounds were synthesized using microwave and ultrasound methods, which decrease the particle size distribution of the products. To investigate the effects of two types of simple and triple superphosphate fertilizers on some properties of maize plant (*Zea mays* L.), a factorial experiment was conducted based on a completely randomized block design. The fertilizer treatments included in this study were simple superphosphate, triple superphosphate, microwave nano-hydroxyapatite, and ultrasound nano-hydroxyapatite and examined at five concentration levels. The results showed that the application of nano-hydroxyapatite phosphate fertilizers improved the growth and physiological properties of maize plant. This would raise better results in comparison to the simple and triple superphosphate fertilizers. Considering the positive effects of nano-hydroxyapatite fertilizers and high production levels, the results of this experiment revealed that the synthetic nano-hydroxyapatite methods prevent phosphorus loss; therefore, it is recommended to use nano-phosphate fertilizers in food resource management to achieve a favorable quantitative yield. Moreover, they can be regarded as a favorable solution to deal with the environmental problems.

1. Introduction

Today, nanotechnology has provided new opportunities to design and fabricate nano-fertilizers to improve nutrient-use efficiency and minimize the cost of environmental protection [1].

Nanotechnology can contribute to the fabrication, modification, and stability of individual nanoparticles and prepare the self-assembled nanostructures, which alter the properties of prepared structures by optionally changing the size and shape of some the nanoparticles [2]. The application of nanotechnology has been expanding in different fields such as agriculture. In this regard, one of the main applications of nanotechnology in various aspects of agriculture is in water, soil, and plant nutrition sectors [1].

Fertilizer particles can be coated by nanoscale membranes, which facilitate the slow and sustained release of the nutrients. Furthermore, when fertilizer particles are bound with nano- and subnano-composites,

they manage to regulate the release of nutrients from the fertilizer capsules [3]. These nanoparticles benefit from a high surface area, high activity, better catalytic surface, and rapid chemical reaction.

The nutrient nano-formulated elements hold great promise for application in plant nourishment because of the size-dependent qualities, high surface area, and unique optical properties [4]. Such a high surface area increases the percentage of atoms on the surface, which can serve both as a useful food source and as a bio-protective source [5, 6].

Accordingly, a thorough understanding of the main reaction pathways in the formation of these substances in soil is of paramount importance for the application of more sustainable and safe nanoparticles in agriculture [7, 8].

In general, the effective use of nano-fertilizers promotes the efficiency of crop nutrient, reduces soil toxicity, minimizes the negative effects of excessive application of the fertilizer, and reduces the number of times fertilizers. With utilizing the nano-fertilizers, the release time and speed

* Corresponding author.

E-mail address: dadkhodaghbk@yahoo.com (D. Ghazanfari).

of the elements would be in line with the plant's nutritional requirements. Accordingly, the plant could absorb the highest amount of nutrients and, consequently, reduces the leaching of the elements and increases the crop yield [9, 10, 11, 12].

Chemical fertilizers are materials required in all seasons for the growth of plants [13]. Fertilizers are the fundamental factor for agriculture production both in quality and quantity. With an increasing world population and diminishing arable land, it is necessary to employ larger quantities of chemical fertilizers, especially nitrogen (N), phosphorus (P), and potassium (K), to meet the global food demands [14, 15].

One of the most important fertilizers is phosphorus fertilizer, whose role is critical in providing necessary nutrients for plants. Phosphorus is an essential mineral with cellular structures in many vital activities, including the storage and transfer of chemical energy. Increased phosphorus uptake can ultimately enhance the harvest index of phosphorus in plants, which is a vital parameter to improve the plant yield [16].

Generally, hydroxyapatite nanoparticles as a new type of phosphorus fertilizers increase crop yields and reduce the atrophic risks of water [17, 18]. In this regard, phosphate nano-fertilizers reduce fertilizer consumption and improve the plant growth and yield [19].

Regarding the agricultural crops, maize (*Zea mays* L.) is one of the strategic crops due to its high significance in human and animals' nutrition and its wide adaptation to different temperatures and tropical climates [20, 21, 22, 23, 24]. Global demand for maize and wheat is growing at a rapid pace as such there has been an increase in lands under the cultivation during the last decades and compression of crop cultivation systems along with the high demand for the nutrients, which have consequently enhanced the consumption of chemical inputs and raised the production costs and the environmental hazards [25, 26, 27, 28, 29].

Although various developments have been made in agricultural productions, the unbalanced and excessive consumption of chemical fertilizers has unfortunately led to ecological damages and endangered human health [30]. Furthermore, the excessive application of the chemical fertilizers reduces the amount of organic materials in the agricultural fields and converts soil into hard and undesirable textures [31].

Nanotechnology, as one of the promising techniques to increase the food production, is increasingly growing in a world with diminishing resources and an ever-increasing global population [32].

Nano-fertilizers are one of the main samples for the applications of nanotechnology in different agricultural fields and in water and soil sections [33, 34, 35].

Moreover, the use of nano-fertilizers can also increase the nutrients' efficiency, reduce soil toxicity, minimize the negative effects of excessive application of fertilizer, and reduce the number of used fertilizers [10, 11, 36].

The ultrasonic and microwave methods are novel synthesis methods for different nanostructures. These methods have advantages including high-speed production, low cost and eco-friendliness. In these methods, products with a variety of structures and different physico-chemical properties can be produced [37, 38]. To the best of our knowledge, no study has been conducted on the synthesis of Nano-fertilizers using ultrasonic and microwave method.

With increasing environmental awareness and diminishing energy sources, studies have focused on the chemical synthesis via microwave irradiation (MW) because it offers the advantages of simplicity, reactivity, high efficiency, low energy consumption, pollution reduction and rapid bulk heating capability over conventional thermal heating methods [39].

Due to the great significance of nano-fertilizers in agriculture and the necessity of optimizing the use of chemical fertilizers in crop systems, the present study aimed to investigate two different synthetic hydroxyapatite nanoparticle methods. Furthermore, the effects of nanoparticles on maize growth were compared with two types of phosphorus fertilizers (namely simple superphosphate and triple superphosphate).

2. Experimental section

2.1. Materials and methods

In this study, Calcium nitrate tetrahydrate (Mw: 236.15 g/mol, 99.0%), Ammonium hydrogen phosphate (Mw: 132.05 g/mol), and Glycine (Mw: 75.06 g/mol, 99.8%) were purchased from Merck Company. Acrylic acid (Mw: 72.06 g/mol, 99%), Sodium hydroxide (Mw: 39.997 g/mol, 96%), Acetone (Mw: 58.08 g/mol, 80%), and Nitric acid (Mw: 63.01, 65%) were also purchased from Sigma Company. Double-distilled water was used to prepare all the solutions. All the materials in this study were used as received, with no further purification.

The effect of nano-hydroxyapatite particles (nano-hydroxyapatite synthesized by ultrasound and microwave methods) and two types of phosphorus fertilizers (namely simple superphosphate and triple superphosphate) on some morphological and physiological properties of maize were investigated in the laboratory and greenhouse of Kerman Agricultural Jihad Research Center during 2018–2019.

To this end, the experiment was carried out in a completely randomized block with a factorial design in three replications. Fertilizer treatments included SSP (simple superphosphate), TSP (triple superphosphate), NHA⁺ (microwave synthesized nanohydroxyapatite), and NHA⁻ (ultrasound synthesized nanohydroxyapatite).

2.2. Material characterization

The presence of nanoparticles in the final structures were confirmed by energy disperse spectroscopy (EDX, XL30). The morphological properties of the as-synthesized nanostructures were examined by using Scanning Electron Microscopy (SEM) and the Au/Pd application of a Hitachi S-4700, Japan, operating at 12 keV. X-ray diffraction (XRD) patterns were obtained in reflection mode using a powder X-ray diffractometer (X'Pert MPD, Pananalytical, Cu K α radiation, $k = 0.15406$ nm) between 2 $^{\circ}$ and 90 $^{\circ}$ (2-Theta) with a step width of 0.01 $^{\circ}$.

2.3. Synthesis of nano-hydroxyapatite particles

2.3.1. Microwave method

In a typical synthesis, 50 mL solution of (Ca (NO₃)₂ · 4H₂O) with a concentration of 0.05 M was prepared. In the next step, 3.75 g Glycine (NH₂-CH₂COOH) was added to the previous solution. Afterwards, 3.6 g Acrylic acid (CH₂ = CH-COOH) was added, and an alkaline medium was prepared. Then 50 mL diammonium hydrogenphosphate ((NH₄)₂HPO₄) solution with a concentration of 0.03 M was added to make a milky solution. The resulting solution was stirred for 20 h with a magnetic stirrer. Finally, the solution was placed in a 200-W microwave reactor at 100 $^{\circ}$ C and 1atm pressure for 10 min.

2.3.2. Ultrasound method

First, 100 mL Ca (NO₃)₂ · 4H₂O with a concentration of 0.05 M was prepared and placed under a magnetic stirrer. At the same time, 7.5 g of Glycine was added to the solution. Then 7.5 g Acrylic acid was added. Afterwards, 100 mL of (NH₄)₂HPO₄ with a 0.03-M concentration was added to make a milky solution. The resulting solution was stirred for 20 h using a magnetic stirrer. The solution was then placed in an ultrasound bath for 1h (power: 160 W, frequency: 20 kHz). The resulting precipitate was separated by centrifugation and dried and calcined after washing.

2.3.3. Wet method

For the synthesis of the products using the wet method, 100 mL (Ca (NO₃)₂ · 4H₂O) with a concentration of 0.05 M was prepared and placed under a magnetic stirrer. At the same time, 7.5 g of Glycine was added to the solution. Then, 7.5 g Acrylic acid was added. In the next step, 100 mL of (NH₄)₂HPO₄ with a concentration of 0.03 M was added to make a milky solution. The resulting solution was stirred for 20 h using a

magnetic stirrer. The resulting precipitate was separated by centrifugation and dried and calcined after washing.

2.4. Greenhouse experiment

The plants were cultivated in the greenhouse of Kerman Agricultural Jihad Research Center (four separate fertilizer treatments). The treatments included simple superphosphate fertilizer (SSP), triple superphosphate (TSP), nanohydroxyapatite (NHA⁺) synthesized by a microwave, and NHA⁻ synthesized by an ultrasound method. The amount of fertilizer was measured by a soil test, and it was sprayed before soil sowing. To this end, five maize seeds were planted in each pot. The levels of treatments (five concentrations considered for each fertilizer) were applied in accordance with the soil test and the amount of phosphorus in the soil.

2.4.1. Determining the fertilizer concentration

In this pre-fertilization experiment, sampling was done in 0–30 cm depth of the soil to determine the physical and chemical properties of the soil. The samples were transferred to the soil laboratory, and the required parameters were measured (Table 1).

In this experiment, five different concentrations were considered for each fertilizer treatment to determine the desirable concentrations (Table 2). For this reason, a control treatment (with no fertilizer treatment) was considered for each replication, and the plant irrigation was controlled by a weight method.

2.4.2. Measuring plant height

After placing the seedlings in the pots, the plant height was weekly measured at 6 stages. To measure Relative Water Content (RWC) in Eq. (1) and 0.1 g leaf of the seedlings was weighed using a digital scale (FW). Then each sample was placed in a Petri dish, and 10 mL of distilled water was added to the samples and placed in a dark place for 24 h to allow saturation. The samples were extracted from the distilled water, and their saturation weight (SW) was measured.

Afterwards, the samples were dried in an oven at 75 °C for 24 h and weighed (DW). The RWC of the leaf was measured based on the following Equation [40] (Eq. (1)).

$$RWC = \frac{FW - DW}{(SW - DW)} \times 100 \quad (1)$$

2.4.3. Measuring photosynthetic pigments

In this experiment, 0.1 g leaf was carefully weighed and crushed in a mortar using liquid nitrogen. Then 10 ml acetone (80%) was added to the above mixture, and the solution was centrifuged at 6,000 rpm for 10 min. The extract isolated from the centrifuge was poured into the test tube.

The absorbance of the solution was measured using a spectrophotometer at the wavelengths of 470, 647, and 663 nm. Acetone (80%) was used as a control solution to adjust zero in optical absorption spectrophotometer (Eqs. (2) and (3)).

$$Chla = 11.75 A_{663} - 2.79 A_{647} \quad (2)$$

$$Chlb = 21.5A_{647} - 5.7 A_{663} \quad (3)$$

$$C(X + C) : \frac{(1000 A_{470} - 1.82Chla - 85.02 Chlb)}{198} \quad (4)$$

In the above equations (Eq. (2) and Eq. (3)), Chl *a* is chlorophyll *a*, Chl

b is chlorophyll *b*, C (*x* + *c*) is the amount of carotenoids, and A is the amount of absorbance at different wavelengths.

2.4.4. Measuring plant phosphorus (leaf)

After drying, the samples were crushed and passed through a 0.5 mm sieve to have a uniform product. Then 0.5 g of the plant samples were weighed and transferred to the digestion tubes. The solid residue after evaporation was digested with 2 mL of H₂SO₄ and 2 mL of H₂O₂. One sample was prepared as the control sample, in which there was only Sulfuric acid with no dry material. Then samples were kept at 60° C for 3 h. The temperature was raised to 110 ° C, and the samples were kept at this temperature for 6 h to complete the digestion process. The tubes were then put in a place to be cooled down, and some distilled water was added to the contents inside the tubes. The samples were transferred to a graded cylinder after filtering. This procedure was repeated several times, and the concentrations of the elements were finally measured using atomic absorption spectrometry [41].

2.4.5. Measuring fresh and dry weights of shoots

When the plants' heights were 70 cm, they were calcined, and their fresh weights were measured using a 0.001 digital scale. The samples were then placed in a paper bag and transferred to the oven and kept at 60 ° C for 48 h. The samples were then taken out of the oven and weighed using digital scales.

2.5. Statistical analysis

The collected data was analyzed using SAS software version 9.4, and the means were compared by LSD test at 5% using MSTAT-C software.

3. Results and discussion

3.1. Characterization of hydroxyapatite nanostructures

EDX analysis enables the semi-quantitative characterization of the nano-hydroxyapatite sample synthesized by wet, ultrasound and microwave methods (Figure 1). This analysis shows the presence of relevant elements in the final structures, which confirm the synthesis procedures for the sample.

The SEM images of the hydroxyapatite nanostructures synthesized by wet, ultrasound, and microwave methods are presented in Figures 2 and 3. Evidently, in the microwave and ultrasound methods, the samples revealed nano-ranged particle size distribution, and no evidence of agglomeration in the structures was observed. However, in the wet method, the particles agglomerated in some areas caused the structure instability. Although the samples in both microwave and ultrasonic methods indicated nano-ranged particle size distribution, the distribution of the particles in the microwave method was less (35 nm in the microwave method compared to 41nm in the ultrasound method). Accordingly, the microwave method was selected as the more optimal method (Figure 3A). In the microwave method, the samples with homogeneous morphology and small size distribution could be provided. More importantly, the microwave synthesis route can facilitate the performance of the reactions and produce Hydroxiapatite under mild conditions than conventional methods. As a result, this microwave assisted method is simple, rapid, low-cost, pro-environmental, and safe method, which can be employed for the acceleration of the procedures. Furthermore, compared to the ultrasound method, microwave can be synthesized Hydroxyapatite nanostructures with narrow size

Table 1. Physical and chemical analysis of soil at depth of 0–30 cm.

Soil pattern	K	O. N	P	O.C	EC	pH
Sandy Loam	305 _{ppm}	0.04	8 _{ppm}	0.4	0.63 _{ms}	7.3

Table 2. Concentration levels used for fertilizers based on the soil test.

Fertilizer type	1/2 of soil test (g)	1/5 of soil test (g)	1/10 of soil test (g)	Equal soil test (g)	Twice soil test (g)
SSP	0.25	0.1	0.050	0.501	1.002
TSP	0.087	0.034	0.017	0.174	0.348
NHA ⁺	42.28	16.912	8.456	84.56	169.12
NHA ⁻	42.28	16.912	8.456	84.56	169.12

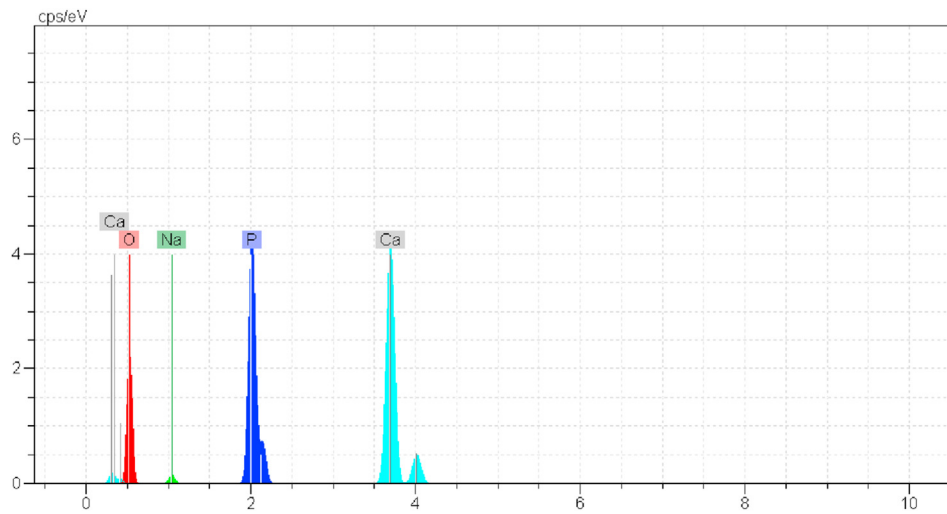


Figure 1. EDX analysis for nano-hydroxyapatite samples synthesized by wet, ultrasound and microwave methods.

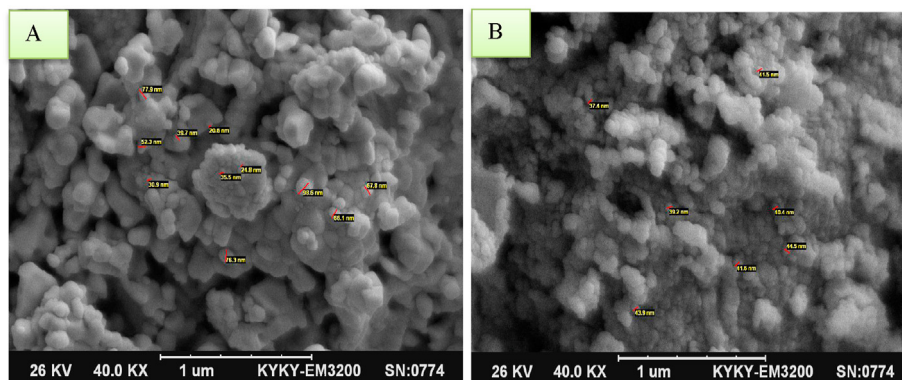


Figure 2. SEM images of hydroxyapatite nanostructures synthesized by wet (A) and ultrasound methods (B).

distribution. This capability may be affected the application of the product in different area [42].

Figure 3B showed the TEM image of synthesized in optimal condition (microwave method). According to this Figure, the products have a

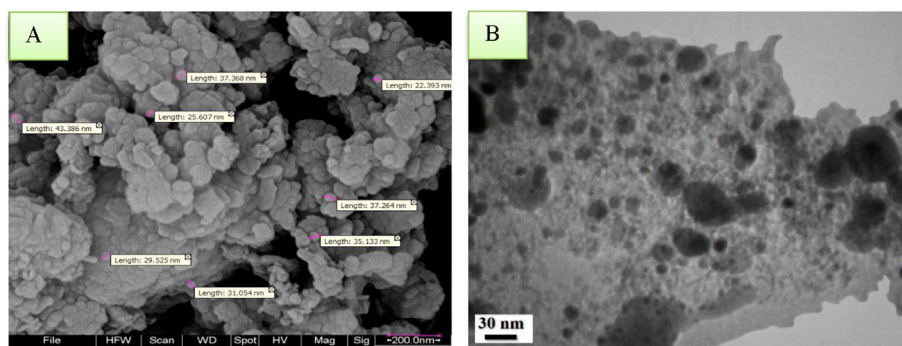


Figure 3. SEM (A) and TEM images (B) of hydroxyapatite nanostructures synthesized by optimal method (microwave).

homogenous morphology with narrow particle size distribution which confirmed the SEM results obtained from microwave method. Furthermore, TEM image confirmed the crystallinity nature for Hydroxyapatite nanostructures.

Figure 4 presents the XRD patterns of the synthesis of the Hydroxyapatite nanostructure samples by the microwave and ultrasound methods. According to the results obtained from these patterns, although the average crystal size of both samples is in the nanometric range based on Debye-Scherrer method, the sample synthesized by the microwave method has a smaller size to have broad peaks (22 nm in the microwave method compared to 31 nm in the ultrasound method). In both methods, the diffraction patterns at the different angles are excellent consistent with all of the peaks may be indexed to the orthorhombic crystal system. Except for the difference in the widening rate of the peaks, which changes the size of crystals, other crystallographic data of the Hydroxyapatite nanostructure samples synthesized by both methods are similar, as reported in Table 3.

3.2. Plant height

Plant height was measured at six stages (once every seven days). The analysis of variance results showed that the effects of the fertilizer and concentration on plant height were significant at all the six stages at $p = 0.01$. However, the interaction effects of the fertilizer and concentration

on plant height were significant at the first three stages but not at the last three stages (Table 4).

The results of the interaction effect on concentration in the first three measurement stages revealed a significant difference between the fertilizer treatments and different concentrations; hence, the largest plant height in all the three stages was reported for the nano-hydroxyapatite fertilizers.

However, it should be noted that there was a statistically significant difference between the syntheses of the two nano-hydroxyapatite methods; hence, the largest plant height was obtained for the nano-hydroxyapatite synthesized by the microwave method at concentrations equal to soil test and twice soil test (Figure 5, a-c).

Moreover, the main effects of the fertilizer and concentrations in the last three stages of height measurement showed a statistically significant difference between the fertilizer levels and the concentration levels. Regarding the fertilizer levels, the largest plant height was obtained for the nano-hydroxyapatite fertilizer synthesized by the microwave method. According to the concentration levels, the concentration level equal to the soil test showed the largest plant height (Table 5).

In all the stages of the plant height measurement, the smallest plant height was obtained for the control sample, followed by the simple superphosphate fertilizer (Figure 5 & Table 5). The lower height of the control plant can be related to the positive effect of the fertilizer treatments, especially nano-hydroxyapatite fertilizers. Furthermore, since there was no significant difference between the levels of concentration

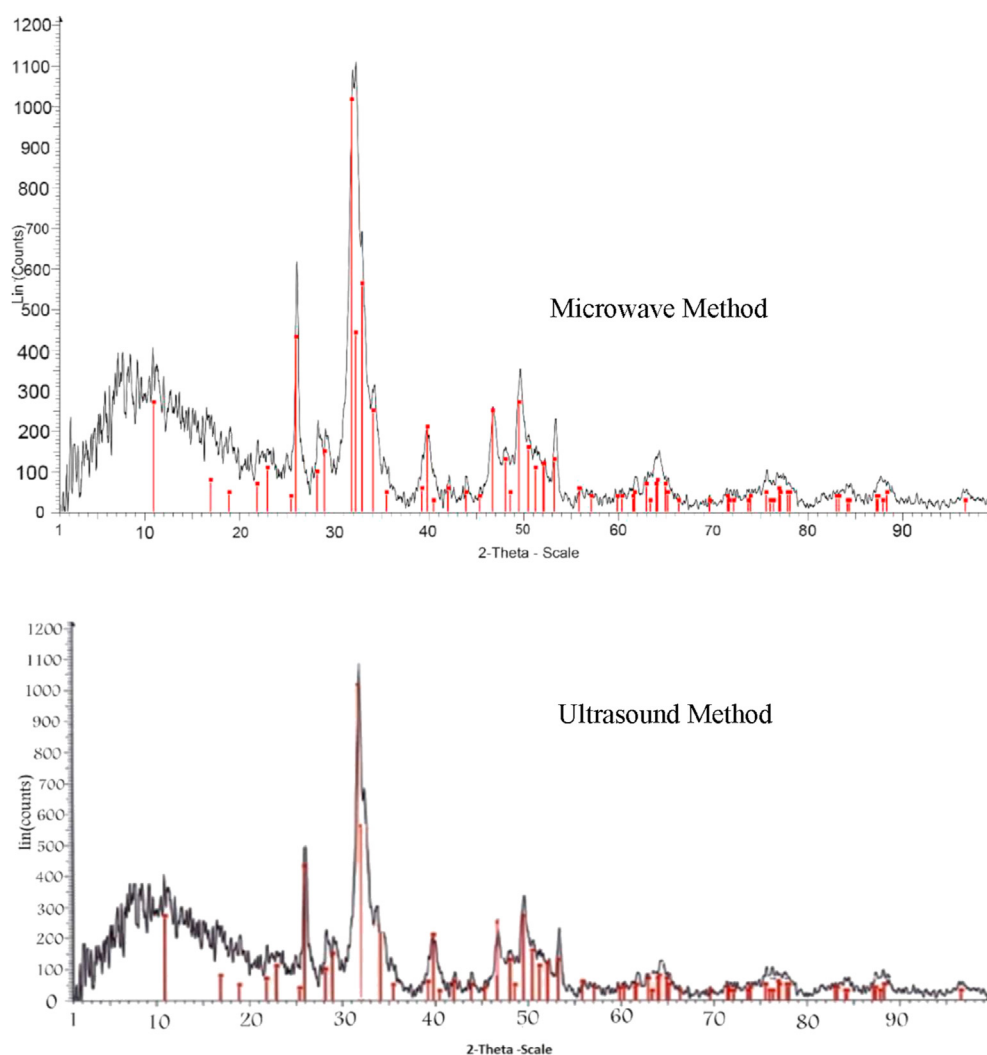


Figure 4. XRD patterns of samples synthesized by ultrasound and microwave methods.

Table 3. Crystallographic data of Hydroxyapatite nanostructures samples.

Parameter	Results
Crystal system	Orthorhombic
Space group	Pmm2
Space group No	25
a (Å)	43.9970
b (Å)	3.8940
c (Å)	6.2090
Alpha (°)	90.0000
Beta (°)	90.0000
Gamma (°)	90.0000
density (g/cm ³)	8.28
Volume of cell (Å ³)	1063.75
Z	12
RIR	6.53
Radiation	Cuka
Temperature (K)	293
Wavelength (Å)	1.54178

equal to soil test and twice soil test, the application of fertilizer treatment equal to soil test was regarded as the most optimal case, resulting in the favorable growth of the plant.

As a result, this process not only increases the profits of the farmers but also reduces the negative consequences of excessive use of the chemicals on the environment. The previous studies have suggested that the use of nanoparticles stimulated reactive oxygen ions such as superoxide and hydroxide, eventually increases the permeability of the seed and facilitates the entry of water and oxygen into the cell.

Accordingly, they would enhance the metabolism and germination of the seed and thus enable the plant to be settled faster and better in comparison to the conditions where no nanoparticle is used (control conditions) [43].

The nature of nanostructures is unique, particularly in the microwave method as it is affected by a range of inherent properties of the particles, including color, strength, heat resistance, and penetration of moist gases. The nanoscale particle size also increases the surface area of the material enormously and ultimately improves the efficiency of the nanoparticles [44].

Ref. [45], reported that magnesium and iron nanoparticles significantly increased some traits such as stem height in bean plants in comparison to the control treatment. They concluded that the application of nanoparticles increased the yield of the pods. They also confirmed the significant effect of magnesium oxide and conventional iron nanoparticles on promoting the growth traits and yield of Cowpea.

Ref. [46], reported that the use of phosphorus fertilizers increased the plant growth and height of sunflower bushes due to the increased root development. Increasing plant height as a result of an increase in available phosphorus by the plant is due to the positive effects of phosphorus element on promoting root system development, absorption of water and

essential nutrients, especially nitrogen, which improves the shoot height [47, 48].

The results of this experiment showed that nano-hydroxyapatite synthetic methods prevented phosphorus loss and made it available for the plant usage. The distinctive properties of nanotechnology can be explained by this issue that smaller particles cause new chemical phenomena and lead to new size-dependent behaviors; hence, the nutrients are gradually released in the fertilizer. As a result, the fertilizer efficiencies are improved, and this could be a reason for the higher growth and ultimately higher yield of the plants under the conditions of using nano-fertilizers.

3.3. RWC

The variance analysis of the results showed that, with regard to the studied treatments, the main effect of fertilizer and concentration on relative water content was significant at $p = 1\%$; however, the interaction effect of the fertilizer and concentration on this trait was not significant (Table 4).

Comparing the means for the main effects of the fertilizer showed that a statistically significant difference between the fertilizer treatments; hence, the highest and lowest RWC levels were obtained for NHA⁺ (nano-hydroxyapatite phosphate fertilizer synthesized by microwave method) and the control treatments, respectively (Table 5). The results also revealed significant differences among the concentrations levels. Regarding the considered levels, the highest RWC was equal and twice the soil test. Moreover, the lowest RWC was obtained for the control treatment (Table 5).

Ref. [49], reported that, due to the use of the nanoparticles, the rate of water uptake and retention in the plant increased and led to the better germination of the plant. In addition, nanoparticle-treated plants retained more water in their tissues, and this can be a reason for the high RWC of the plants under such conditions.

As mentioned before, nano-phosphate fertilizers gradually released the phosphorus element in the plant, thereby improved the uptake of nutrients in the plant [50]. Accordingly, when the plant nutrition system improved under the influence of nano-phosphate fertilizers, the plant root system improved as well [50]. This may explain an increase in RWC in comparison to the conditions where no nano-fertilizer was used (i.e., control condition).

In this study, the plant under the conditions using nano phosphate fertilizers in both microwave and ultrasound methods showed more lateral growth and expansion than the control condition and simple and triple super phosphate fertilizers. Since the plants under nano-phosphate fertilization conditions had higher growth, this behavior was a better developed root system.

According to the studied traits, the results could differentiate the fertilizer treatments and showed that the plants had a higher RWC in the case of using nano-phosphate fertilizers. In other word, the amount of leaf water loss under these conditions was less in comparison to the control condition and two levels of phosphate fertilizer (namely simple superphosphate and triple phosphate).

Table 4. Analysis of variance results for Plant Height (in six stages) Affected by Four Types of Fertilizers. SSP stands for (simple superphosphate), TSP (triple superphosphate), NHA⁺ (microwave synthesis of nano-hydroxyapatite) and NHA⁻ (Ultrasound synthesis of nano-hydroxyapatite). 1 (1/2 concentration of soil test), 2 (1/5 concentration of soil test), 3 (1/10 concentration of soil test), 4 (concentration equal to soil test) and 5 (concentration twice soil test). Columns with at least one letter in common have no statistically significant difference based on the 5% probability level.

S.O.V	DF	H1	H2	H3	H4	H5	H6
Fertilizer	3	619.02**	933.99**	1075.01**	1483.43**	1969.16**	2484.97**
Consistency	4	22.51**	35.41**	58.77**	68.94**	80.95**	103.73**
Fertilizer × Consistency	12	1.54**	2.18**	1.63*	1.94 ns	1.13 ns	1.68 ns
Error	42	0.22	0.45	0.87	1.7	2.65	2.69
CV		2.08	2.41	2.89	3.65	3.94	3.42

ns, * and ** show non-significance, significance at the 5% and 1% probability levels respectively.

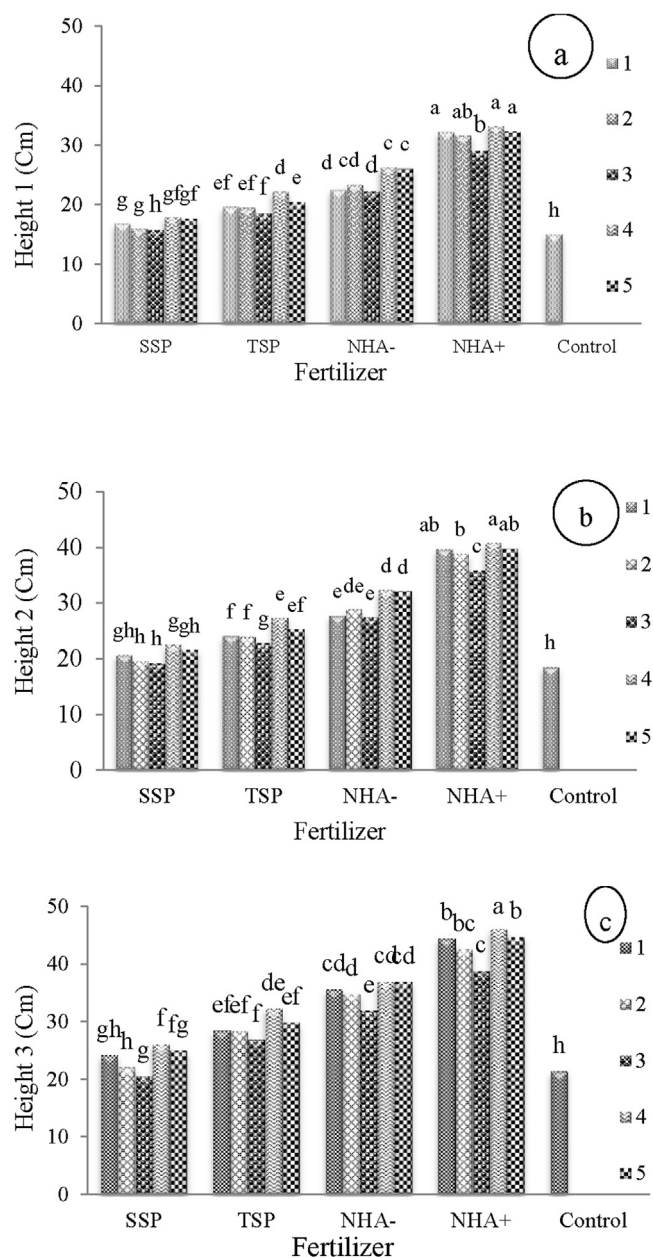


Figure 5. a) Interaction effect of fertilizer at concentration on plant height at the first stage of measurement, b) second stage of measurement. c) Third stage of measurement. SSP stands for (simple superphosphate), TSP (triple superphosphate), NHA⁺ (microwave synthesis of nano-hydroxyapatite) and NHA⁻ (ultrasound synthesis of nano-hydroxyapatite). 1 (1/2 concentration of soil test), 2 (1/5 concentration of soil test), 3 (1/10 concentration of soil test), 4 (concentration equal to soil test) and 5 (concentration twice soil test). Columns with at least one letter in common have no statistically significant difference based on the 5% probability level.

3.4. Chlorophyll *a* and *b*

The variance analysis showed significant effects of the fertilizer and concentration on chlorophyll *a* and *b* levels at $p = 0.01$. For both of the traits, the interaction effects of the fertilizer on concentration was significant at $p = 0.05$ (Table 6). The interaction effect of fertilizer at different concentration levels was a significant difference between the fertilizer treatments and concentration levels in both chlorophyll *a* and *b* traits. On the other hand, there was no significant difference between the two nano-hydroxy phosphate fertilizer treatments using the two microwave and ultrasound synthesis methods.

The highest amounts of chlorophyll *a* and *b* were obtained from nano-hydroxyapatite phosphate fertilizer treatments using the microwave and ultrasound methods at equal and twice concentration levels of soil test, respectively. In addition, the lowest amount of controlled treatment was obtained in both traits (Figure 6b).

Since chlorophylls play a major role in accelerating photosynthetic reactions and affect the vegetative and reproductive yield of plants, an increase in the amount of photosynthetic pigments under the nano-fertilizer application conditions can explain the higher vegetative yield of plants (with wet and dry weights). Increasing the amount of chlorophyll *a* and *b* under the fertilizer conditions can be due to the positive effects of fertilizers, especially nano-fertilizers, on the availability of more water and nutrients for the plant, in comparison to the conditions where no fertilizer was used [51]. According to the results of this experiment, it can be concluded that the control conditions decreased the amount of chlorophyll *a* and *b*.

On the other hand, the modification of soil physical properties, due to the application of nano-fertilizers, increased chlorophyll *a* and *b* levels in comparison to the non-application of fertilizers. In other words, the application of nanotechnology released the nutrients in these fertilizers, and this ultimately led to better plant growth and greening. This parameter may be one reason explaining the increase in photosynthetic pigments of chlorophyll *a* and *b* under these conditions [52].

3.5. Carotenoid

The comparison of the means in the variance analysis showed that the significant effects of fertilizer, concentration, and interaction effect on carotenoid level at $p = 0.01$ (Table 6).

Moreover, comparing the mean interaction effect of the fertilizer and concentration confirmed the significant difference between the concentration levels and fertilizer treatments. Additionally, no statistically significant difference was observed between triple superphosphate fertilizer at the concentration level of 1/10 soil test and the simple super phosphate fertilizer at concentration levels of 1/10 and 1/5 soil test (Figure 7). The lowest amount of carotenoids was observed for the nano-hydroxyapatite fertilizer treatment synthesized by the microwave method at concentration levels equal and twice the soil test. This finding showed no significant difference with nano-hydroxyapatite fertilizer treatment synthesized by the ultrasound method at the concentration levels equal and twice the soil test.

Ref. [52], reported that plants benefit from the protective effect of carotenoids when they are exposed to harsh conditions increasing the amount of oxygen free radicals. As a result, carotenoid levels increase under adverse environmental conditions. In this study, considering the control condition where no fertilizer treatment was used, the plant condition was more severe rather than the conditions; therefore, the amount of carotenoids under these conditions would be higher than the conditions using fertilizers.

Moreover, in this study, the carotenoid content of the protective pigment was higher in the controlled treatment and simple superphosphate fertilizers. It is thus expected that the plant production would be higher under the above conditions. On the other hand, since the plant had lower chlorophyll *a* and *b* under these conditions, compared to the conditions used for super phosphate triple fertilizers and nano-fertilizers; hence, the plant production did not increase under these conditions. Regarding the positive relationship between the amount of chlorophyll in the plant and the photosynthetic rate, it can be concluded that the plant consumed more energy to tolerate the adverse environmental conditions and survived under these conditions with an increase in the carotenoid protective pigment.

On the other hand, due to the lower chlorophyll *a* and *b* levels, it can be concluded that the degradation of the chlorophyll molecule under the control and simple superphosphate conditions was higher, and this led to lower vegetative growth, organogenesis and yield, compared to nano-fertilizer conditions.

Table 5. Analysis of variance results for Main Effects of Plant Height (in the second three stages) under four types of fertilizers. SSP stands for (simple superphosphate), TSP (triple superphosphate), NHA⁺ (microwave synthesis of nano-hydroxyapatite) and NHA⁻ (Ultrasound synthesis of nano-hydroxyapatite). 1 (1/2 concentration of soil test), 2 (1/5 concentration of soil test), 3 (1/10 concentration of soil test), 4 (concentration equal to soil test) and 5 (concentration twice soil test). Columns with at least one letter in common have no statistically significant difference based on the 5% probability level.

Fertilizer	Height 4(Cm)	Height 5(Cm)	Height 6(Cm)	Dry Weight(g)	RWC %
SSP	25 d	31.07 d	34.81 d	9.45 c	57.35 d
TSP	32 c	35.65 c	41.8 c	9.33 c	60.45 c
NHA ⁻	40.04 b	45.44 b	52.93 b	16.94 a	63.08 b
NHA ⁺	47.99 a	56.09 a	64.16 a	12.16 b	65.65 a
Control	25.17 d	30.03 e	36.3 d	8.29 d	53.65 e
Consistency					
1	32.62 b	42.04 bc	48.68 b	12.05ab	61.69 b
2	35.3 c	40.54 c	47.01 c	11.8 ab	60.17 c
3	32.75 d	38.22 d	44.35 d	11.37 b	58.42 b
4	39.09 a	45.09 a	52.1 a	12.69 a	64.62 a
5	37.52 b	43.12 b	49.98 b	12.59 a	63.26 a
Control	25.17 e	31.78 e	36.36 e	8.29 c	53.65 e

ns, * and ** show non-significance, significance at the 5% and 1% probability levels respectively.

Generally, under the conditions using nano-phosphate fertilizers, as the soil physical properties improved and the release of phosphorus fertilizer occurred gradually, the effects of environmental stress decreased; therefore, the plant consumed less energy to produce carotenoid, as a protective pigment. Hence, this could explain the lower plant carotenoids under the condition using nano-phosphate fertilizer. There have been some reports in line with the results of this experiment, according to which the effects of nanoparticles on chlorophyll *a* and *b* content in maize and bean plants has been examined, and it was concluded that nanoparticles increased chlorophyll content and decreased carotenoid content [53].

3.6. Phosphorus (leaf)

The variance analysis of the results at $p = 0.01$ confirmed that the significant effect of fertilizer, concentration, and interaction effect of fertilizer and concentration on plant phosphorus concentration (Table 6). All the fertilizer treatments increased plant phosphorus, compared to the control condition (i.e., no fertilizer application). Regarding the treated fertilizers, the highest phosphorus content was obtained from the nano-hydroxyapatite treatment.

It should be noted that there was a significant statistical difference between nano-hydroxyapatite fertilizers so that the highest amount of phosphorus was obtained from the nano-hydroxyapatite fertilizer treatment synthesized by the microwave synthetic method at the concentration level equal to the soil test. Furthermore, the lowest amount of plant phosphorus was obtained from the controlled level, indicating the positive effects of the fertilizer on the plant phosphorus content (Figure 8). Although it was also found that the total amount of phosphorus in the soil was relatively high [54, 55].

According to the findings, it can be stated that the nano-hydroxyapatite fertilizer prevents the loss of phosphorus and also facilitates the plant availability. In addition, the findings showed that the application of nano-fertilizers functionalized by phosphate nano-fertilizers was more effective, in comparison to simple superphosphate fertilizers and triple superphosphate fertilizers. These findings were consistent with those reported by Bansiwai et al. (2006) [56].

Nano-hydroxy phosphate fertilizers benefit from high phosphorus uptake and the slow release of this element into soil. Accordingly, they enable nano-phosphate fertilizers to compete with commercial super phosphate and super phosphate fertilizers; hence, the nano-fertilizers in the present study, in addition to supplying the plant with nutrients during the growth period, prevented the entry of excessive amounts of these compounds into the groundwater resources [56].

3.7. Plant fresh weight

The results showed a statistically significant difference between fertilizer levels and concentration levels. These results showed that phosphorus fertilizers and nano-phosphate fertilizers increased plant fresh weight in comparison to the controlled treatment. In addition, it was found that the plants treated with both types of nano-phosphate fertilizers exhibited higher fresh weight. Comparing the means showed that the highest fresh weight of the plant was obtained from the nano-hydroxyapatite phosphate fertilizer treatment using ultrasound synthetic method at the concentration equal to the soil test. However, no statistically significant difference was observed between these two fertilizers with concentrations twice, 1/2, and 1/5 of the soil test (Figure 9). The results of this experiment indicated that the different sources of phosphorus fertilizers had a statistically significant effect on the fresh weight of the plant. Since the plant showed the highest level of nano-

Table 6. Analysis of variance for Chlorophyll *a*, *b*, Carotenoid, Relative Water Content, Fresh Weight, Dry Weight and amount of Plant Phosphorus affected by Four Types of Fertilizers. SSP stands for (simple superphosphate), TSP (triple superphosphate), NHA⁺ (microwave synthesis of nano-hydroxyapatite) and NHA⁻ (Ultrasound synthesis of nano-hydroxyapatite). 1 (1/2 concentration of soil test), 2 (1/5 concentration of soil test), 3 (1/10 concentration of soil test), 4 (concentration equal to soil test) and 5 (concentration twice soil test). Columns with at least one letter in common have no statistically significant difference based on the 5% probability level.

S.O.V	df	Chl <i>a</i> g.g.FW ⁻¹	Chl <i>b</i> mg.g.FW ⁻¹	Car mg.g.FW ⁻¹	RWC %	Wet Weight g	Dry weight g	phosphor
Fertilizer	3	16.77**	12.47**	7.06**	189.96**	196.24**	192.24**	0.009**
Consistency	4	10.92**	9.59*	24.41**	72.05**	7.94**	3.65**	0.0006**
Fertilizer × Consistency	12	0.46*	0.36*	0.26**	2.52 ns	2.45**	1.17 ns	0.0005**
Error	42	0.26	0.18	0.09	2.04	0.54	0.78	0.0001
CV		5.11	4.7	3.92	2.33	4.56	7.41	6.37

ns, * and ** show non-significance, significance at the 5% and 1% probability levels respectively.

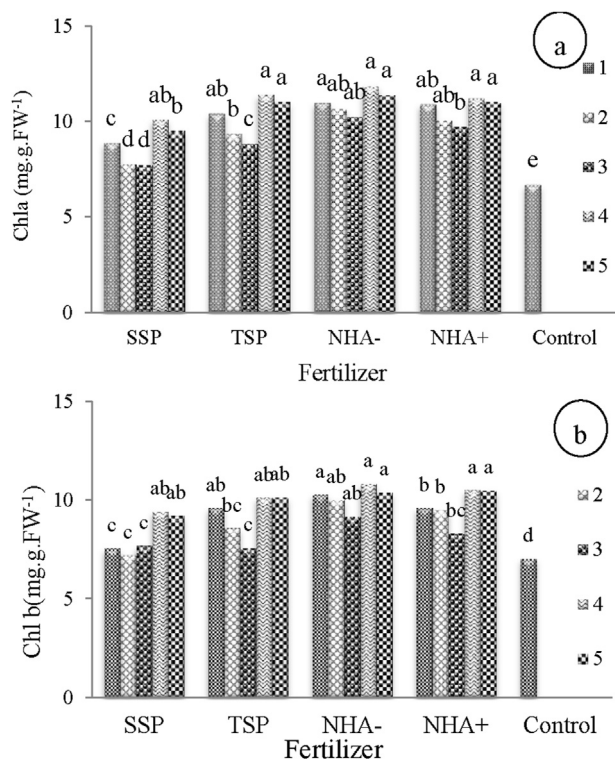


Figure 6. Interaction effect of fertilizer at concentration on chlorophyll a (Figure a) and b (Figure b). SSP stands for (simple superphosphate), TSP (triple superphosphate), NHA⁺ (microwave synthesis of nano-hydroxyapatite) and NHA⁻ (Ultrasound synthesis of nano-hydroxyapatite). 1 (1/2 concentration of soil test), 2 (1/5 concentration of soil test), 3 (1/10 concentration of soil test), 4 (concentration equal to soil test) and 5 (concentration twice soil test). Columns with at least one letter in common have no statistically significant difference based on the 5% probability level.

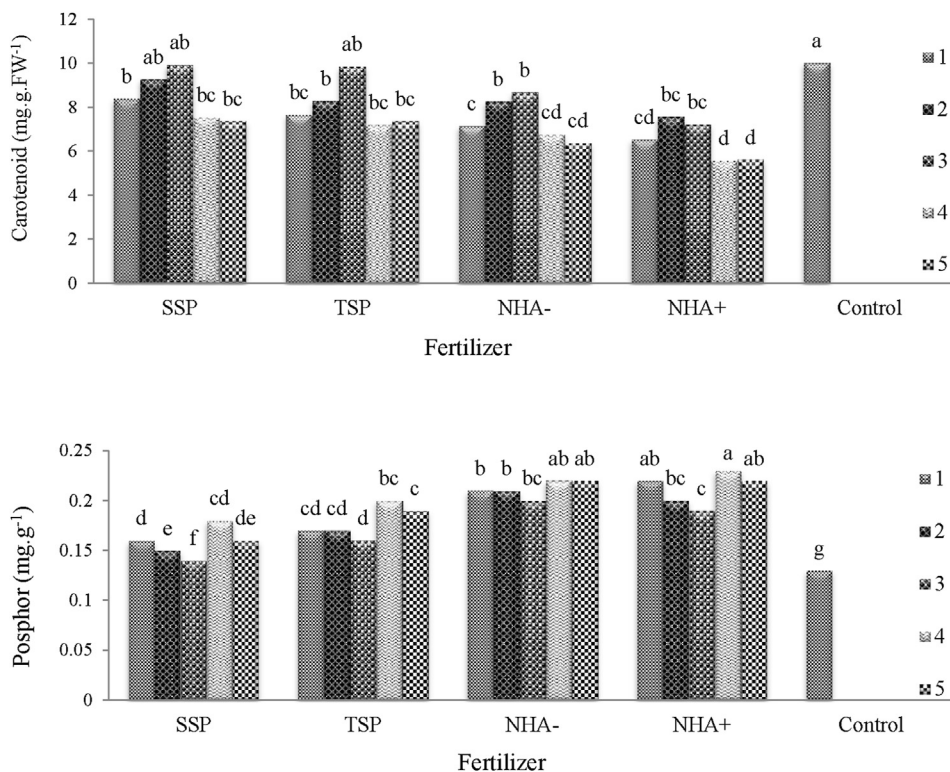


Figure 7. Interaction Effect of Fertilizer at Concentration on Carotenoid. SSP stands for (simple superphosphate), TSP (triple superphosphate), NHA⁺ (microwave synthesis of nano-hydroxyapatite) and NHA⁻ (Ultrasound synthesis of nano-hydroxyapatite). 1 (1/2 concentration of soil test), 2 (1/5 concentration of soil test), 3 (1/10 concentration of soil test), 4 (concentration equal to soil test) and 5 (concentration twice soil test). Columns with at least one letter in common have no statistically significant difference based on the 5% probability level.

Figure 8. Interaction Effect of Fertilizer with concentration on the amount of Plant Phosphorus in mg/g. SSP stands for (simple superphosphate), TSP (triple superphosphate), NHA⁺ (microwave synthesis of nano-hydroxyapatite) and NHA⁻ (Ultrasound synthesis of nano-hydroxyapatite). 1 (1/2 concentration of soil test), 2 (1/5 concentration of soil test), 3 (1/10 concentration of soil test), 4 (concentration equal to soil test) and 5 (concentration twice soil test). Columns with at least one letter in common have no statistically significant difference based on the 5% probability level.

phosphate fertilizer in all measured traits, the accumulation of nutrients and consequently vegetative yield of the plant (fresh and dry weights) were not unexpected. This element was easily stabilized in the soil and is out of the plant's access. It seems that the nanofosphate fertilizers improve soil structure and stabilize the nutrients [57].

The gradual release of the elements increases the plant's ability to consume the elements and ultimately enhances vegetative and reproductive yield of the plant [58]. Previous studies have confirmed that the application of phosphorus fertilizers improves root capacity to absorb phosphorus and transfer it to the aerial part of the plant, thereby enhancing the vegetative and reproductive yield of the treated plant [59].

3.8. Plant dry weight

The highest and lowest plant dry weights (aerial organ dry weight) were obtained from the nano-hydroxyapatite phosphate treatment synthesized by ultrasound method and control plant, respectively (Table 6). Although there was no statistically significant difference between the concentration levels of 1/2 and 1/5 of the soil test, the results revealed that the control plants had lower dry weights, in comparison to the treated plants (Table 6). Nano-phosphate fertilizers released the required phosphorus effectively and gradually, which improved the quantitative or vegetative yield of the maize.

Ref. [17] investigated the effect of nano-hydroxyapatite as phosphorus fertilizer on *Matricaria chamomilla* plant. The results showed that the application of the nanoparticles can increase the growth of *Matricaria chamomilla* [59], also studied the effects of nano-hydroxyapatite fertilizer on soybean. Their findings showed that the use of this fertilizer increased the uptake of phosphorus and enhanced the vegetative and reproductive yield of the plant. Although there are fewer reports examining the effects of nano-fertilizers on the crop growth, the positive effect of nanonutrients on maize growth has been reported by Moaveni et al. [60]. Nano-fertilizers are likely to increase the fertilizer efficiency. Moreover, they can release their nutrients optimally due to the slow and controlled release of the elements present in the fertilizers. Accordingly, an increase

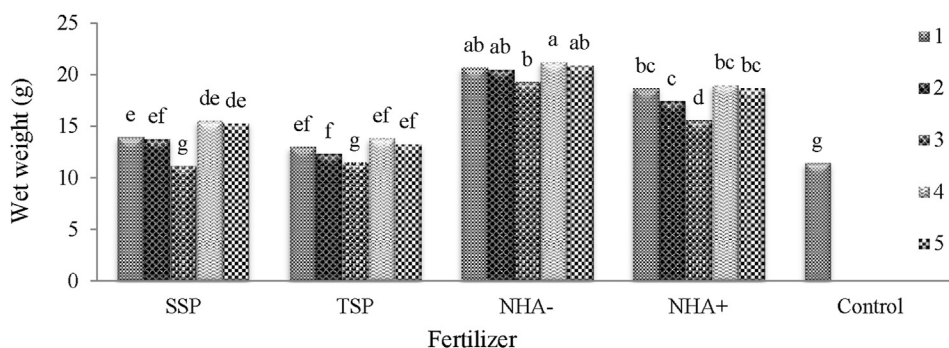


Figure 9. Interaction Effect of Fertilizer with Concentration on Fresh Plant Weight (g). SSP stands for (simple superphosphate), TSP (triple superphosphate), NHA+ (microwave synthesis of nano-hydroxyapatite) and NHA - (Ultrasound synthesis of nano-hydroxyapatite). 1 (1/2 concentration of soil test), 2 (1/5 concentration of soil test), 3 (1/10 concentration of soil test), 4 (concentration equal to soil test) and 5 (concentration twice soil test). Columns with at least one letter in common have no statistically significant difference based on the 5% probability level.

in the plant photosynthetic period improved the carbohydrate production and ultimately the plant yield [61].

In this study, the amount of plant's quantitative yield was lower than fertilizer levels. Under these conditions, the plant had lower chlorophyll a and b content, relative water content, and phosphorus content. Furthermore, it showed less fresh and dry weights, compared to the fertilizer treatment conditions, especially nano-phosphate fertilizers. The results indicated the positive effect of the fertilizers on the plant growth and production. In line with these findings, it has been reported that nano-fertilizers increase the plant yield by promoting the plant photosynthetic potential and providing the required photosynthetic materials [60].

As a result, in previous works, the effects of experimental parameters have been studied by the conventional methods, which could increase the number of experiments and ignore the interaction between the parameters. However, in this study, using a scientific analysis variance lead to systematic studies of the parameters.

4. Conclusion

In this study, four types of fertilizers were included while nano-phosphate fertilizers showed the highest effect on the growth properties of maize (*Zea mays* L.). The effectiveness of these fertilizers in some of the studied traits of the maize was higher, in comparison to simple and triple superphosphate commercial fertilizers. Moreover, since not many differences were observed between the two chemical synthesis methods of nano-phosphate fertilizers (i.e., microwave and ultrasound), it was concluded that both methods could increase the plant yield and production. However, the ultrasound synthesis method produced a higher yield (i.e., wet and dry weight), and it was considered more beneficial with regard to the two chemical synthesis methods. Regarding the statistical analysis, it can be concluded that higher concentration of the fertilizers (twice the soil test) should be avoided to reduce the application costs and the pollution caused by the unnecessary use of fertilizers. In this study, the level of concentration equal to the soil test is presented as an optimal level for acceptable production.

Declarations

Author contribution statement

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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References

- [1] R. Naderi, A. Abedi, Application of nanotechnology in agriculture and refinement of environmental pollutants, *J. Nanotechnol.* 11 (1) (2012) 18–26.
- [2] V.J. Mohanraj, Y. Chen, Nanoparticles - a review, *Trop. J. Pharmaceut. Res.* 5 (1) (2006) 561–573.
- [3] A. Liu, C. Hamel, R.I. Hamilton, B.L. Ma, D.L. Smith, Acquisition of Cu, Zn, Mn and Fe by mycorrhizal maize (*Zea mays* L.) grown in soil at different P and micronutrient levels, *Mycorrhiza* 9 (6) (2000) 331–336.
- [4] S. Mazaherinia, A.R. Astaraei, A. Fotovat, A. Monshi, Nano iron oxide particles efficiency on Fe, Mn, Zn and Cu concentrations in wheat plant, *World Appl. Sci. J.* 7 (1) (2010) 36–40.
- [5] M. Premanathan, K. Karthikeyan, K. Jayasubramanian, G. Manivannan, Selective toxicity of ZnO nanoparticles toward Gram-positive bacteria and cancer cells by apoptosis through lipid peroxidation, *Nanomed. Nanotechnol. Biol. Med.* 7 (2) (2011) 184–192.
- [6] S.S. Mukhopadhyay, Nanotechnology in agriculture: prospects and constraints, *Nanotechnol. Sci. Appl.* 7 (2014) 63–71.
- [7] N. Milani, M.J. McLaughlin, G.M. Hettiaratchchi, D.G. Beak, J.K. Kirby, S. Stacey, R. Gilkes, Fate of nanoparticulate zinc oxide fertilisers in soil: solubility, diffusion and solid phase speciation, *Soil Solut. Chang. World* (2010) 1–6.
- [8] C.R. Chinnamuthu, P.M. Boopathi, Nanotechnology and agroecosystem, *Madras Agric. J.* 96 (1-6) (2009) 17–31.
- [9] H. Zhu, J. Han, J.Q. Xiao, Y. Jin, Uptake, translocation and accumulation of manufactured iron oxide nanoparticles by pumpkin plants, *J. Environ. Monit.* 10 (2008) 713–717.
- [10] M.C. Derosa, C. Monreal, M. Schnitzer, R. Walsh, Y. Sultan, Nanotechnology in fertilizers, *Nat. Nanotechnol.* 5 (2) (2010) 91–92.
- [11] M.R. Naderi, A. Danesh-Shahraki, Nanofertilizers and their roles in sustainable agriculture, *Intl. J. Agric. Crop Sci.* 5 (19) (2013) 2229–2232.
- [12] R. Liu, R. Lal, Potentials of engineered nanoparticles as fertilizers for increasing agronomic productions, *Sci. Total Environ.* 514 (2015) 131–139.
- [13] B. Jabbari, S.M. Mousavi-Nik, P. Yadollahi-Dehcheshme, Effect of chemical fertilizers and plant density on yield, yield components and oil percentage of castor bean (*Ricinus communis* L.) in Sistan region, *Agric. Crop Manag.* 6 (4) (2015) 275–290.
- [14] P. Wen, Z. Wu, Y. He, B.C. Ye, Y. Han, J. Wang, X. Guan, Microwave-assisted synthesis of a semi-interpenetrating polymer network slow-release nitrogen fertilizer with water absorbency from cotton stalks, *ACS Sustain. Chem. Eng.* 4 (12) (2016) 6572–6579.
- [15] P. Wen, Z. Wu, Y. Han, G. Cravotto, J. Wang, B. Ce-Ye, Microwave-assisted synthesis of a novel biochar-based slowrelease nitrogen fertilizer with enhanced water-retention capacity, *ACS Sustain. Chem. Eng.* 5 (8) (2017) 7374–7382.
- [16] K.K. Singh, C. Srinivasarao, M. Ali, Root growth, nodulation, grain yield, and phosphorus use efficiency of lentil as influenced by phosphorus, irrigation, and inoculation, *Commun. Soil Sci. Plant Anal.* 36 (2005) 1919–1929.
- [17] A. Mikhak, A. Sohrabi, M.Z. Kassaee, M. Feizian, Synthetic nanozeolite/nanohydroxyapatite as a phosphorus fertilizer for German chamomile (*Matricaria chamomilla* L.), *Ind. Crop. Prod.* 95 (2017) 444–452.
- [18] M.M. McKnight, Z. Qu, J.K. Copeland, D.S. Guttman, V.K. Walker, A practical assessment of nano-phosphate on soybean (*Glycine max*) growth and microbiome establishment, *Sci. Rep.* 10 (1) (2020) 1–17.
- [19] M. Safari, The tendency of conventional agriculture (Intensive Agric.) Sustainable agriculture (Sustainable Agric) solutions to improve the quality of soils in semi-arid

- regions of Iran, in: The First National Conference on Sustainable Management of Soil Resources and the Environment, Martyr Bahonar University, Kerman, 2014.
- [20] M. Yazdani, M.A. Bahmanyar, H. Pirdashti, M.A. Esmaili, Effect of phosphate solubilization microorganisms (PSM) and plant growth promoting rhizobacteria (PGPR) on yield and yield components of corn (*Zea mays* L.), *World Acad. Sci. Eng. Technol.* 49 (2009) 90–92.
- [21] Z. Zalud, P. Hlavinka, K. Prokeš, D. Semerádová, J. Balek, M. Trnka, Impacts of water availability and drought on maize yield—a comparison of 16 indicators, *Agric. Water Manag.* 188 (2017) 126–135.
- [22] USDA, Circular Series on World Agricultural Supply and Demand Estimates-578, 2018. Available online: <http://usda.mannlib.cornell.edu/usda/waob/wasde//2010s/2018/wasde-06-12-2018.pdf>.
- [23] M. Khan, S.U. Afzal, K. Khan, N. Ali, M.M. Anjum, H. Usman, M.O. Iqbal, Seed yield performance of different maize (*Zea mays* L.) genotypes under agro climatic conditions of Haripur, *Int. J. Environ. Sci. Nat. Resour.* 5 (5) (2017) 97–102.
- [24] FAOSTAT, Food and Agricultural Commodities Production, 2018. Available online: <http://www.fao.org/faostat/%20en/#data/QC/visualize>.
- [25] A. Biari, A. Gholami, H.A. Rahmani, Growth promotion and enhanced nutrient uptake of maize by application of plant growth promoting rhizobacteria in arid region of Iran, *J. Biol. Sci.* 8 (2008) 1015–1020.
- [26] I.A. Khan, G. Hassan, N. Malik, R. Khan, H. Khan, S.A. Kkhan, Effect of herbicides on yield and yield components of hybrid maize (*Zea mays*), *Planta Daninha, Viçosa-MG* 34 (4) (2016) 729–736.
- [27] Ghasem Sargazi, Ahmad Khajeh Ebrahimi, Daryoush Afzali, Arastoo Badoei-dalfard, Saeid Malekabadi, Zahra Karami, Fabrication of PVA/ZnO fibrous composite polymer as a novel sorbent for arsenic removal: design and a systematic study, *Polymer Bulletin* 76 (11) (2019) 5661–5682.
- [28] L.J. Abendroth, K.P. Woli, A.J. Myers, R.W. Elmore, Yield-based corn planting date recommendation windows for Iowa, *Crop Forage Turf Grass Manag.* 3 (2017) 1–7.
- [29] B. Wang, C. Liu, D. Zhang, C. He, J. Zhang, Z. Li, Effects of maize organ-specific drought stress response on yields from transcriptome analysis, *BMC Plant Biol.* 19 (1) (2019) 335.
- [30] A. Koocheki, Potential of saltbush (*Atriplex* spp.) as a fodder shrub for the arid lands of Iran, *Fodder Shrub Dev. Arid Semiarid Zones* 1 (2000) 178–183.
- [31] R.B. Bhattacharjee, A. Singh, S.N. Mukhopadhyay, Use of nitrogen-fixing bacteria as biofertilizer for non-legumes: prospects and challenges, *Appl. Microbiol. Biotechnol.* 80 (2) (2008) 199–209.
- [32] R. Lal, Soils and India's food security, *J. Indian Soc. Soil Sci.* 56 (2008) 129–138.
- [33] A. Johnson, The Effects of FDI Inflows on Host Country Economic Growth, The Royal Institute of Technology & Centre of Excellence for studies in Science and Innovation, 2006. <http://www.infra.kth.se/cesis/research/publications/workingpapers>.
- [34] A. Johnson, Agriculture and nanotechnology, Website, <http://tahan./Charlie/na nosociety>.
- [35] D.B. Warheit, W.J. Brock, K.P. Lee, T.R. Webb, K.L. Reed, Comparative pulmonary toxicity inhalation and instillation studies with different TiO₂ particle populations: impact of surface treatments on particle toxicity, *Toxicol. Sci.* 88 (2) (2005) 514–524.
- [36] M.R. Maghsoodi, L. Ghodsad, B.A. Lajayer, Dilemma of hydroxyapatite nanoparticles as phosphorus fertilizer: potentials, challenges and effects on plants, *Environ. Technol. Innov.* 4 (2020) 100869.
- [37] F. Akbarzadeh, M. Motaghi, N.P.S. Chauhan, G. Sargazi, A novel synthesis of new antibacterial nanostructures based on Zn-MOF compound: design, characterization and a high performance application, *Heliyon* 6 (1) (2020), 03231.
- [38] F.M. Khandan, D. Afzali, G. Sargazi, M. Gordan, Novel uranyl-curcumin-MOF photocatalysts with highly performance photocatalytic activity toward the degradation of phenol red from aqueous solution: effective synthesis route, design and a controllable systematic study, *J. Mater. Sci. Mater. Electron.* 29 (21) (2018) 18600–18613.
- [39] P. Wen, Y. Han, Z. WuY. He, Y. Bang-Ce, J. Wang, Rapid synthesis of a corn-cob-based semi interpenetrating polymer network slow-release nitrogen fertilizer by microwave irradiation to control water and nutrient losses, *Arab. J. Chem.* 10 (2017) 922–934.
- [40] A. Gunes, A. Inal, M.S. Adak, E.G. Bagci, N. Cicek, F. Eraslan, Effect of drought stress implemented at pre-or post-anthesis stage on some physiological parameters as screening criteria in chickpea cultivars, *Russ. J. Plant Physiol.* 55 (1) (2008) 59–67.
- [41] I. Waling, W.V. Vark, V.J.G. Houba, J.J. Vanderlee, Soil and Plant Analysis, a Series of Syllabi. Part 7. Plant Analysis Procedures, Wageningen Agriculture University, The Netherlands, 1989.
- [42] G. Sargazi, D. Afzali, A. Mostafavi, A novel microwave assisted reverse micelle fabrication route for Th (IV)-MOFs as highly efficient adsorbent nanostructures with controllable structural properties to CO and CH₄ adsorption: design, and a systematic study, *Appl. Organomet. Chem.* 33 (4) (2019) 4816–4826.
- [43] L. Zheng, F. Hong, S. Lu, C. Liu, Effect of nano-TiO₂ on strength of naturally aged seeds and growth of spinach, *Biol. Trace Elem. Res.* 104 (1) (2005) 83–91.
- [44] M. Sharon, N. Richardson, Nanotechnology: implications for food and nutrition professionals, *J. Am. Diet Assoc.* 107 (2007) 1494–1496.
- [45] M. Dalfani, Effect of nano particle spreading of iron and magnesium on some morphological and physiological characteristics of beans (*Phaseolus vulgaris* L.), Master's Thesis in Agronomy, University Of Shahroud, 2011, pp. 170–175.
- [46] Y. Emam, M.N. Eilkaee, Effects of plant density and chlormequat chloride (CCC) on morphological characteristics and grain yield of winter oilseed rape cv. Talayeh, *Agron. Sci. J.* 1 (2002) 1–8.
- [47] C. Dordas, Dry matter, nitrogen and phosphorus accumulation: partitioning and remobilization as affected by N and P fertilization and source-sink relation, *Eur. J. Agron.* 30 (2009) 129–139.
- [48] G. NourMohammadi, S.A. Siadat, A. Kashani, Cereal Agronomy, Publication of Shahid Chamran, Ahwaz, Ahwaz, Iran, 2001, pp. 183–187.
- [49] R.F. Garcia, P.I. Arza, Influence of a stationary magnetic field on water relations in lettuce seeds, *Part I: theoretical Considerations, Bioelectromagnetics* 22 (2001) 589–595.
- [50] D. Blaise, A.N. Bonde, R.S. Chaudhary, Nutrient uptake and balance of cotton+ pigeonpea strip intercropping on rainfed Vertisols of central India, *Nutr. Cycling Agroecosyst.* 73 (2-3) (2005) 135–145.
- [51] P.K. Ghosh, K.K. Ajay, M.C. Bandyopadhyay, K.G. Manna, A.K. Mandal, K.M. Hati, Comparative effectiveness of cattle manure, poultry manure, phosphocompost and fertilizer-NPK on three cropping system in vertisols of semi-arid tropics. II. Dry matter yield, nodulation, chlorophyll content and enzyme activity, *Bioresour. Technol.* 95 (2004) 85–93.
- [52] S.K. Behera, R.K. Panda, Integrated management of irrigation water and fertilizers for wheat crop using field experiments and simulation modeling, *Agric. Water Manag.* 96 (2009) 1532–1540.
- [53] M. Hediati, H. Salama, Effect of silver nanoparticles in some crop plants, common bean (*Phaseolus vulgaris* L.) and corn (*Zea mays* L.), *Res. J. Biotechnol.* 3 (10) (2012) 190–197.
- [54] B. Kacar, V. Katkat, Bitki Besleme, 4. Baski, Nobel Yaymevi, Ankara, 2010, pp. 217–289.
- [55] D. Mahanta, R.K. Rai, S.D. Mishra, A. Raja, T.J. Purakayastha, E. Varghese, Influence of phosphorus and biofertilizers on soybean and wheat root growth and properties, *Field Crop. Res.* 166 (2014) 1–9.
- [56] N.K. Bansawal, S.S. Rayalu, N.K. Labhasetwar, A.A. Juwarkar, S. Devotta, Surfactant-modified zeolite as a slow release fertilizer for phosphorus, *J. Agric. Food Chem.* 4 (2006) 4773–4779.
- [57] J.L. Kovar, V. Barber, Phosphorus supply characteristics of 33 soils as influenced by seven rates of phosphorus addition, *Soil Sci. Soc. Am. J.* 52 (1998) 160–165.
- [58] S.C. Chapman, H.J. Barreto, Using a chlorophyll meter to estimate specific leaf nitrogen of tropical maize during vegetative growth, *Agron. J.* 89 (1997) 557–562.
- [59] L. Ruiqiang, L. Rattan, Synthesis of apatite nanoparticles as a phosphorus fertilizer for soybean (*Glycine max*), *Sci. Rep.* 4 (5686) (2014) 1–6.
- [60] P. Moaveni, T. Kheiri, November. TiO₂ nano particles affected on maize (*Zea mays* L.), in: 2nd International Conference on Agricultural and Animal Science, vol. 22, IACSIT Press, Singapore, 2011, pp. 160–163.
- [61] R. Lai, Soil Science in the Era of Hydrogen Economy and 10 Billion People, The Ohio State University, USA, 2007, pp. 1–9.