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Green synthesis of manganese zinc ferrite nanoparticles and their application as nanofertilizers for *Cucurbita pepo* L.

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Abstract

This study aims to synthesize manganese zinc ferrite nanoparticles ($Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs) using a green chemistry synthesis technique and investigate their efficiency as nanofertilizers for squash plant (*Cucurbita pepo* L). In this work, $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs were successfully prepared at different temperatures via simple template-free microwave-assisted hydrothermal route and used as foliar nanofertilizers for squash plant. The physicochemical characteristics of the as-prepared ferrites were investigated using X-ray diffraction (XRD), N_2 adsorption-desorption isotherm, field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM) techniques. The prepared nanoferrites showed type IV adsorption isotherm characteristic for mesoporous materials. FE-SEM and HR-TEM imaging proves the production cubic shaped nanoparticles with average particle size 10-12 nm. Also the impact of using different concentrations of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on vegetative growth, minerals content and the yield of squash plant were investigated. The result showed that the highest

vegetative growth for squash appeared with plants supplied by $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs synthesized at 180°C. On the contrary, the yield of squash recorded the best with 160°C. As for the use of different concentrations of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs, it was found that the use of the lowest concentrations gave the highest values of vegetative growth and yield characters. The chemical content of the squash plant differs from the components of proximate value and the elements according to the temperature used in the composition of the compound $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs and its concentrations. Accordingly, these nanoferrites can be considered as good candidates for *Cucurbita pepo* L fertilization.

Keywords

Nano manganese zinc ferrite; Physicochemical characterization; Green synthesis; Squash (*Cucurbita pepo* L.) plant; Nanofertilizer.

Abbreviations

FE-SEM: Field emission scanning electron microscopy.

HR-TEM: High resolution transmission electron microscopy.

LSD: Least significant differences.

XRD: X-ray diffraction

Introduction

The agriculture process all around the world suffers from poor efficiency of current fertilizers. Traditional fertilizers, owing to their low thermal stability, high solubility and small molecular weight, tend to migrate into the air and water through volatilization, runoff and leaching; causing severe environmental pollution such as acid rain, eutrophication and worsening global warming [1]. Nowadays, nanotechnology started to be used in the plant nutrition production aiming to improve the efficiency of current fertilizers, either by improving the fertilizers bioavailability or by limiting losses of such nutrients to the surrounding environment **[2]**.

Moreover, nanofertilizers can be introduced in the agriculture process in different ways. The nutrition can be encapsulated inside an inert nanomaterial **[3]**, or inside polymeric membrane **[4]**. In addition, the essential nutrition can be delivered as nanoparticles **[5]**.

Spinel ferrites are widely used magnetic materials **[6, 7]**. The magnetic properties as well as thermal and chemical stability of such materials made it a good candidate in many applications including, gas sensing **[8]**, magnetic recording device manufacture **[7]**, and even as drug carrier for targeting drug delivery **[9, 10]**. On the other hand, the applications of such materials in the agriculture process are so limited. As far as we know this could be the first study using such materials as nanofertilizer.

Squash (*Cucurbita pepo* L.) is one of the most essential crops of the family *Cucurbitaceae*, and also highly polymorphic vegetable grown during the summer in the tropical and semi-subtropical condition **[11].** The squash is harvested when the fruit is immature. Its importance is not only due to its use as human food but also as a medical plant**.** In Egypt, it is an annual crop, planted for its fruits only and which is edible part of the plants after cooking and processing. The quantity and quality of the crops are affected by several factors. Among which fertilization techniques are the most important one. Instead of using the traditional fertilizers there are other sources like nanofertilizers. The use of nanofertilizer is very essential for economical production because nanoparticles (NPs) can interact with plants causing a lot of morphological and physiological changes, depending on the properties of NPs. The NPs are effectively determined by their chemical composition, size, surface covering, reactivity, and most significantly the amount **[12].**

The micronutrients, including iron, manganese, zinc, copper, boron and molybdenum, are those elements that the plant needs in small amounts about 0.1 g/kg of dry matter **[13].** Micronutrients fertilizers as a foliar application can enhance plants. Foliar application is a valuable practice for some micronutrients, because it uses small rates and the micronutrient does not straight contact the soil, avoiding losses during fixation **[14].** The application of micronutrients to growing crop leaves will get better crop yield, which in turn may increase the yield **[15]**. The micronutrient spray was just as effective or more effective as soil application **[16].**

Zinc plays an essential function in carbohydrate and proteins metabolism; in addition, it controls plant growth hormone **[17].** It is necessary for the synthesis of tryptophan which is a precursor of Indol Acetic Acid. Furthermore, it has an active function in the production of important growth hormone auxin **[18]**. Whereas, manganese is an essential plant micronutrient with an indispensable function as a catalyst in the oxygen-evolving complex of photosystem, respiration and nitrogen assimilation. It is required by plants in the second greatest quantity compared to iron. So, manganese competes with the micronutrients (Fe, Zn, Cu, Mg and Ca) for uptake by the plant **[19].** As for iron is a constituent of a number of enzymes and some pigments and assists in nitrate and sulfate reduction and energy production in the plant. Even though iron is not used in the synthesis of chlorophyll, it is necessary for its formation **[20]**.

Sheykhbaglou et al. **[21]** found that mineral elements (Fe, Mg, Ca and P) and chlorophyll contents as well as lipid and protein levels were increased by increasing the concentration of ferrous oxide NPs, which used as a foliar application on a soybean plant. While these biochemical contents were reduced with increasing the ferrous oxide NPs concentration over 0.75g/l. Researchers from their findings suggested that plant growth and development, and the impact of engineered NPs on plants depends on the composition, concentration, size, and physical and chemical properties of NPs as well as plant species. Efficacy of NPs depends on their concentration and varies from plants to plants. In addition, Amorós Ortiz-Villajos et al. **[22]** showed that Fe, Zn, Cu and Ni are preferentially accumulated in roots; Mn and Mg are accumulated in leaves; Mo, Ca, and S in roots and leaves; and K in roots, leaves and stems/sheaths. There were positive correlations between changes in the concentrations of mineral pairs Fe-Mn, K-S, Fe-Ni, Cu-Mg, Mn-Ni, S-Mo, Mn-Ca, and Mn-Mg throughout the reproductive development of rice in the above ground organs.

Furthermore, Microwave-assisted hydrothermal synthesis technique has been chosen for the preparation of the nanofertilizers in this study. It is a widely used technique in many areas of chemistry **[12]**, especially in metal oxide NPs synthesis **[23]**. This method is facile, fast, secure, controllable and energy-saving process **[24].** It can dramatically decrease the synthesis process form days and hours to few minutes. It also provides an effective way to control particle size distribution and macroscopic morphology during the synthesis process **[10, 25]**.

The aim of this study is to produce manganese zinc ferrite ($Mn_{0.5}Zn_{0.5}Fe_2O_4$) NPs, via template-free microwave-assisted hydrothermal synthesis route, as an efficient nanofertilizer containing the essential nutrients required for the growth of squash.

Methods/Experimental

Materials

All the used chemicals were of analytical grade and used without any further purification. $Fe(NO_3)_3.9H_2O$ was of 99% purity and purchased from Winlab, UK. $Mn(NO_3)_2.4H_2O$ was a product of Sigma-aldrich and of a purity ≥97%. In addition, $Zn(NO_3)_2.6H_2O$, 96% pure, was

S.D.fine-chem ltd, India. Finally, NaOH flakes was GPR 99% grade and purchased from Alpha chemicals, Egypt.

Preparation of manganese zinc ferrite nanoparticles ($Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs)

The nanoferrite samples were prepared using a green microwave-assisted hydrothermal method. The desired amounts of $Zn(NO_3)_2.6H_2O$, $Mn(NO_3)_2.4H_2O$, and $Fe(NO_3)_3.9H_2O$ were dissolved in water. The Zn:Mn:Fe ratio was 0.5:0.5:2 to produce the target ferrite $Mn_{0.5}Zn_{0.5}Fe_2O_4$. The pH of this solution was adjusted to 10 using NaOH solution and then transferred to 100 mL Teflon autoclave vessel. The vessel was then transferred to a 750 w advanced microwave synthesis labstation (Milestone MicroSYNTH). The microwave was adjusted to reach the desired temperature in 3 min and then the temperature was hold constant for more 10 min. Five ferrite samples were prepared at different holding temperatures, 100, 120, 140, 160, and 180 °C to obtained nanoferrite samples T-100, T-120, T140, T-160 and T-180, respectively. The obtained nanoferrite was then washed 3 times with water, dried at 100 °C for about 6 hours, grinded, and then stored in a desiccator for further characterizations and studies.

Characterization of nanoferrites

The prepared five nanoferrite fertilizer samples were fully characterized using X-ray diffraction (XRD) to confirm the formation of the ferrite spinel structure. A PHILIPS® X'Pert diffractometer, which has the Bragg-Brentano geometry and copper tube, was used to collect the XRD patterns for the different samples. The operating voltage was kept at 40 kV and the current at 30 mA. The divergence-slit angle = 0.5°, the receiving slit = 0.1°, the step scan size = 0.03° and the scan step time = 2 seconds. The K_β radiation was eliminated using the secondary monochromator at the diffracted beam. Adsorption–desorption isotherm of purified N_2 at 77 K was carried out using BELSORP-mini apparatus (BEL Japan, Inc.) that allowed prior outgassing to a residual pressure of 10^{-5}Torr at 100^{o}C overnight to remove all moisture adsorbed on sample surface and pores. The calculation of pore size distribution was carried out using Barrett-Joyner-Halenda (BJH) method.

The morphology and particles size and shape of such samples were studied using the Scanning Electron Microscope (SEM), Model Quanta 250, high-resolution field emission gun (HRFEG, Czech), and High-Resolution Transmission Electron Microscope (HR-TEM), model: JEM2100, Japan.

Agriculture process.

This study aims to assess the effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs, which were prepared at different temperatures with different concentrations, as foliar application on the growth, and the yield as well as the quality of squash plants. Seeds of squash (cv. Eskandarani F1) were provided from Agricultural Research Centre, Ministry of Agricultural and Land Reclamation, Egypt. Seeds were sown on March 1st in clay soil in Shebin El-kom, El-Monifia governorate, Egypt during two seasons 2017 &2018, and then sown at rate of one seed per hill and 50 cm distance between hills on one side of a ridge.

Experiments treatments:

The plants of squash were sprayed with $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs which prepared at different temperatures (T-100, T-120, T-140, T-160 and T-180) with a concentration of 0, 10, 20 and 30 ppm. The experiment was arranged as split plot design with three replications. Main plots concluded the temperature treatments while the concentrations were arranged randomly within the sub-plots. Squash plants were sprayed with the treatments after 20 days from the seeds sowing. The fertilization, irrigation and resistance to weeds and diseases of squash plants were carried out according to the recommendations of the Ministry of Agriculture.

Data recorded

Five plants of squash plants were randomly taken from each experimental plot after 35 days from planting the seeds for measuring the vegetative growth parameters as expressed as plant length, number of leaves per plant, leave area/plant, as well as a fresh and dry weight of the whole plant. The plants were harvested to determine the fruit length, fruit diameter, and yield per plant and ton/hectare after 40 days from sowing. The fruits of the squash plants were collected for a month

Chemical analyses:

Fresh samples of squash (leaves and fruits) were dried in an oven at 60 °C till constant weight, and then the dried sample was taken for the following chemical analyses.

Proximate analysis:

Organic matter, carbohydrates, protein, lipids, ash and fiber were determined according to **AOAC [26].** The energy value was calculated using the atwater factor method [(9x fat) + (4 x carbohydrate) + (4 x protein)] as described by **Nwabueze [27]**.

Minerals determination:

Plant samples were ground and digested with H_2SO_4-H_2O_2. The concentration of phosphorus was determined by spectrophotometer, whereas zinc, copper, iron and manganese in the digested solutions were determined by atomic absorption. Potassium was determined by flam spectrophotometer. While the nitrogen, in the digested solutions, was determined by the Kjeldahl method [28]

Statistical analysis:

All data were subjected to analysis of variance (ANOVA) according to the procedures reported by Kobata et al. **[29]** and the data were analyzed for statistical significant differences using LSD test at 5% level.

Results and discussion

The nanofertilizers characterization

Ferrite phase and crystal parameters investigation

The crystal structure of the ferrite samples was investigated using X-ray diffractions (XRD). All the samples showed the diffraction patterns corresponding to the cubic spinel crystal structure such as (220), (311), and (400) corresponding to 2θ around 30, 36 and 43, respectively [30], as shown in **Fig. 1.** On the other hand, samples prepared at higher microwave holding temperature, T-140, T-160, and T-180, showed XRD patterns at 2θ around 24° and 33° which was interpreted as α-Fe_2O_3 ones [31].

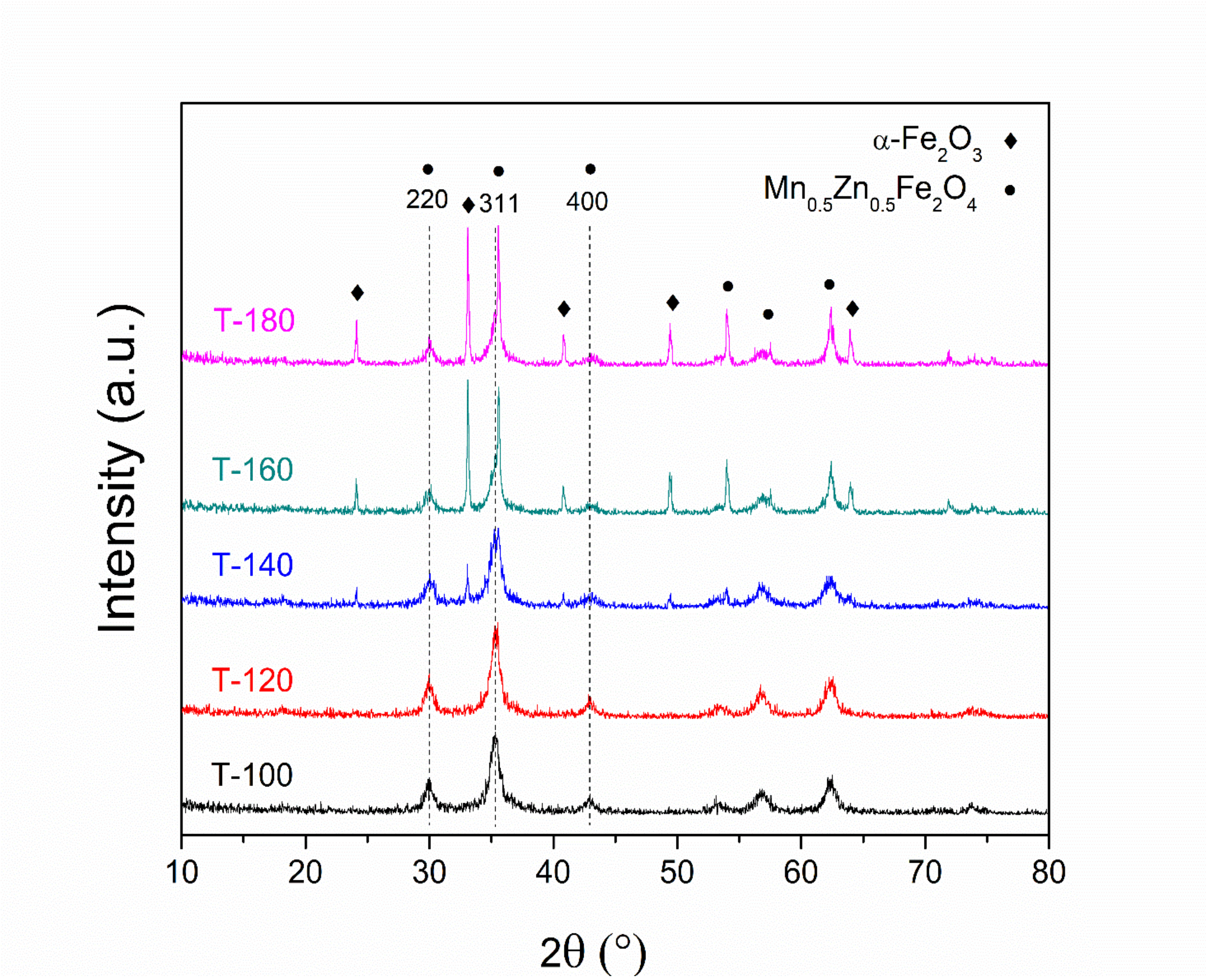


Fig.1: XRD patterns of the prepared ferrite samples

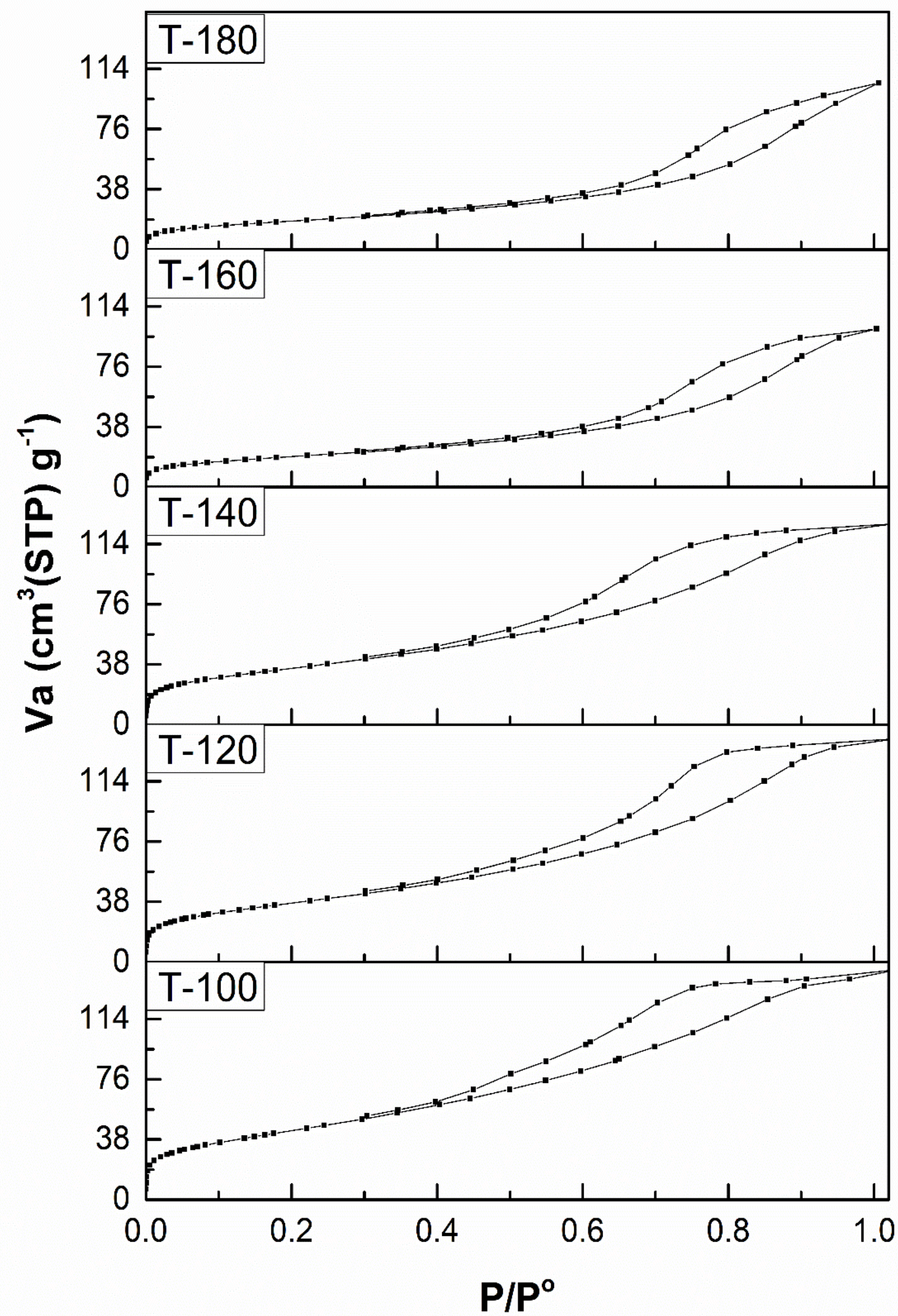
Surface area and pore structure analysis

The main surface and pore structure characteristics of the synthesized nanoferrites at different synthesis temperatures were studied using nitrogen gas adsorption at liquid nitrogen temperature (77 K) and the results are summarized in **Table 1**. The adsorption-desorption isotherms for all samples exhibit irreversible type IV according to the classification of Brunauer–Deming–Deming–Teller [32], as shown in **Fig. 2**, characteristic for mesoporous structure. Increasing the synthesis temperature going from sample T-100 to T-180 can cause sintering which is confirmed in terms of reduction in surface area **(Table 1)**. Evidently, there is a considerable change in the pore structure as the synthesis temperature increases. The adsorption-desorption isotherms of samples T-100, T-120, T-140 show an H2 type of hysteresis [32, 33] which indicated the presence of constricted "ink bottle" pores. The ink bottle type of pores is hinted by **Kraemer [34]**, developed by **McBain [35]** and others [36]. It consists of a wider body with a narrow entrance "neck". One can observe from the shape of the hysteresis loops of these three samples that the solids had experienced a sort of bottle-neck widening as the synthesis temperature increases, as indicated from the narrowing of the hysteresis loops going from sample T-100 to T-140. Further increase in the synthesis temperature, samples T-160 and T-180, causes a drastic change in the porous structure which is confirmed by the presence of an H3 hysteresis loops for both samples. This type of hysteresis originates from aggregates (assemblage of loosely coherent particles) of plate like form producing slit shaped pores, proving the occurrence of deformation as a result of increasing the synthesis temperature.

Besides, the closure of the hysteresis loops at $p/p^{\circ} < 0.4$ especially for samples T-100, T-120 and T-140 indicates the presence of some micropores [37], which is confirmed from the BJH pore size distribution curves **(Fig. 3)**. Additionally, the broadness of the pore size distribution curves decreases as the synthesis temperature increases; indicating the influence of the temperature in narrowing the pore sizes scattering. This result is in accordance with the decreasing in the hysteresis loops when the synthesis temperature increases **(Fig. 2)**. It is worthy to mention that later in sections 3.2.1 and 3.2.2.2, the most efficient sample regarding the squash yield (ton/ha) and total energy resulted from the proximate components of squash fruit (kcal/g) is sample T-160 at optimum concentrations of 10 and 20 ppm, respectively. This sample is of the narrower pore radius distribution among all other samples as shown in **Fig. 3**. This result confirms the correlation between pore size distribution and the fertilizing efficiency of the material.

Table 1 The surface characteristics of the prepared ferrites

Sample	Surface area (m^2 g^{-1})	Mean pore radius (nm)	Total pore volume (cm^3 g^{-1})
T-100	162.44	2.69	0.2187
T-120	135.62	3.15	0.2140
T-140	130.02	2.96	0.1927
T-160	69.98	4.34	0.1521
T-180	65.35	4.79	0.1567



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232 Fig. 2: Adsorption-desorption isotherms of N_2 at 77 K on ferrite samples

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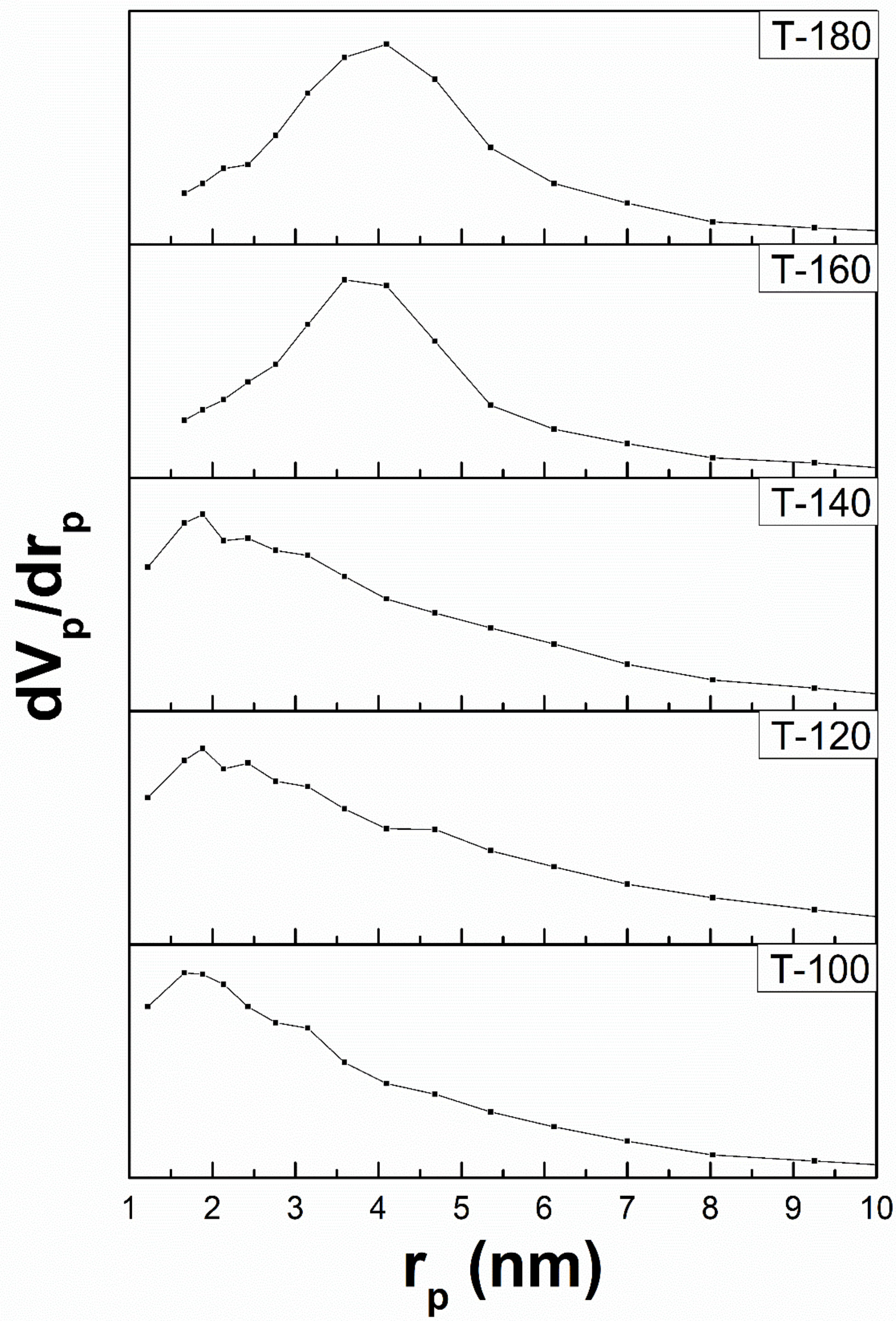

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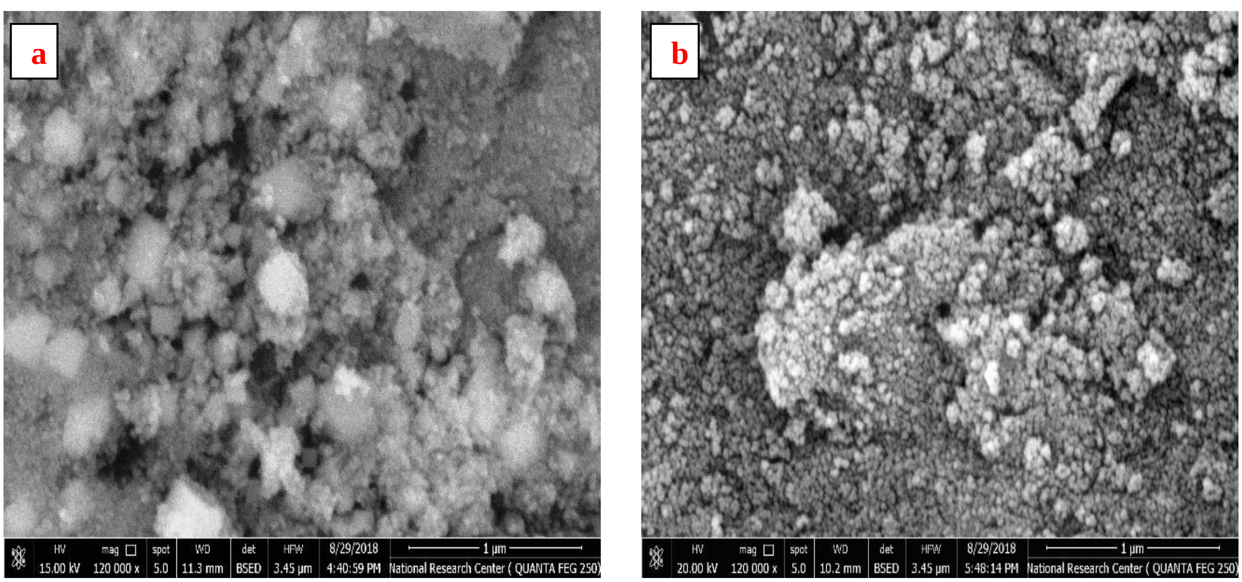
Fig. 3: Pore size distribution curves for ferrite samples

Ferrite morphology and textural analysis

The morphology as well as particles shape and size of the prepared ferrites were studied using SEM and HR-TEM as shown in **Fig. 4 and 5**, respectively. All the prepared ferrite particles showed cubic shape whose crystallinity and regularity are enhanced as holding synthesis temperature increases. This agreed with the obtained cubic spinel XRD patterns (**Fig. 1**).

According to SEM images, the particles constituting the material surface become closely packed together as the synthesis temperature increases, forming –eventually- large cubic morphological structure as shown in Fig. 4e for sample T-180. This results in an increment in the intermediate pore size as indicated earlier in the previous section.



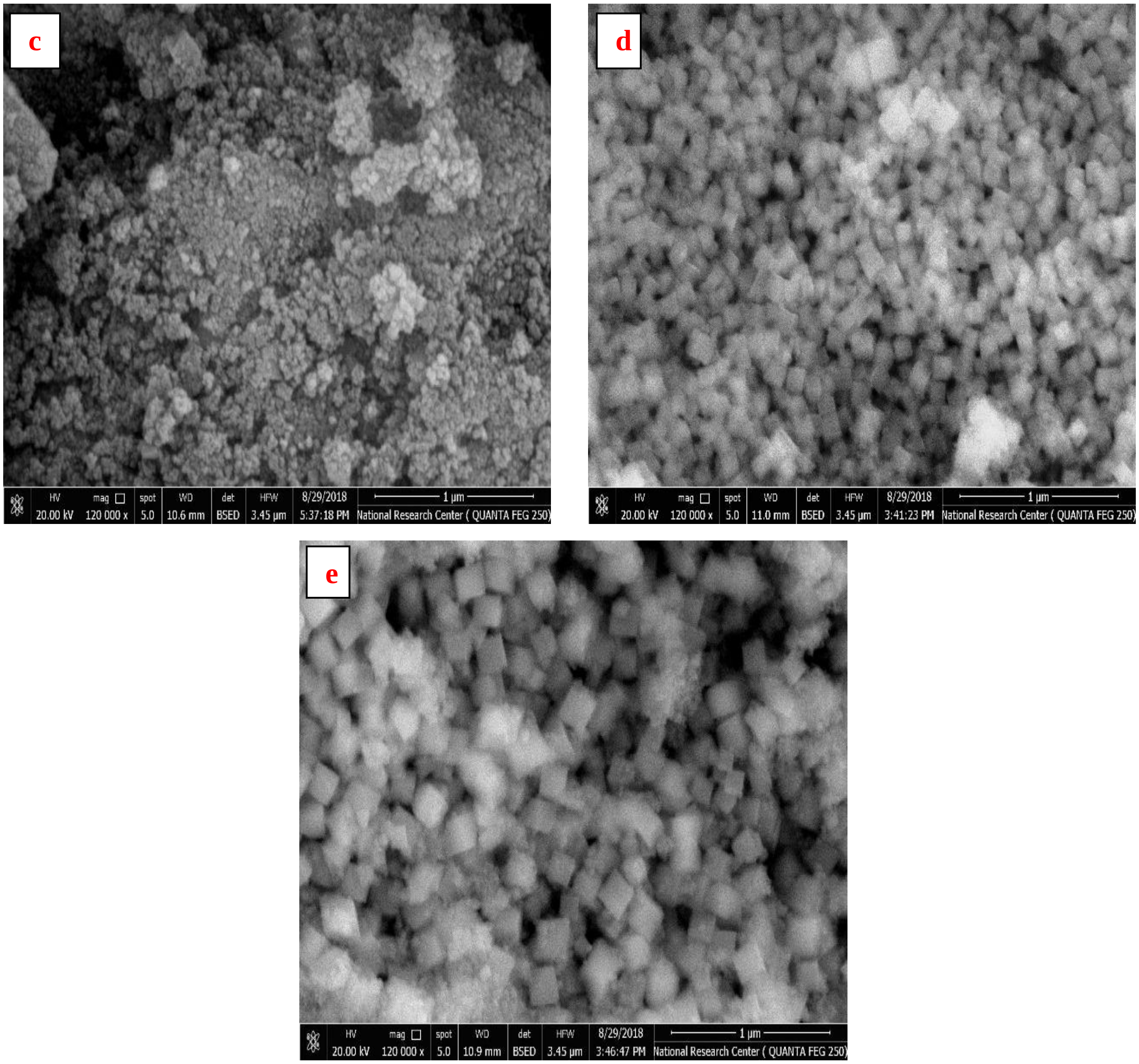
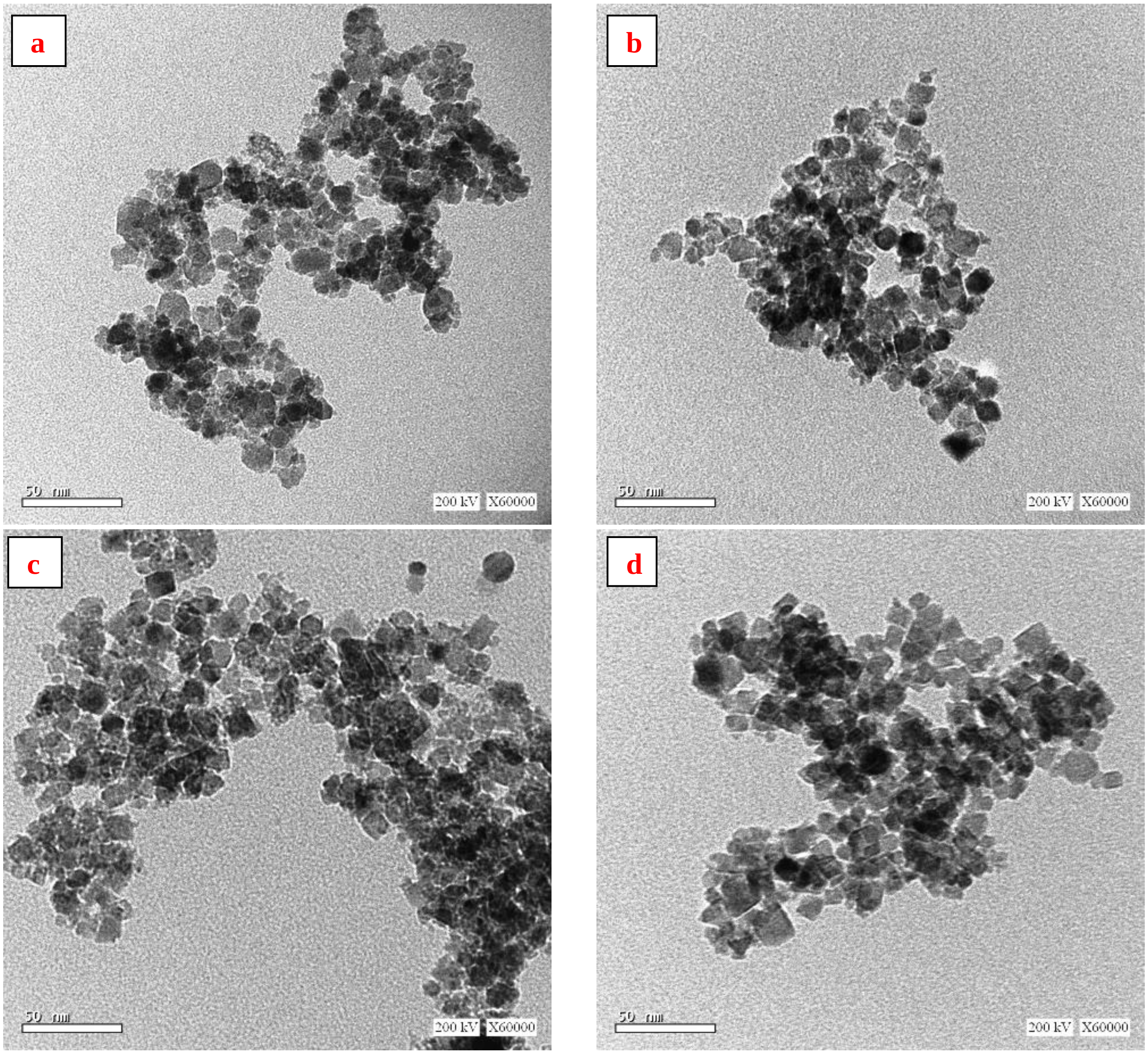


Fig. 4: SEM images of ferrite samples (a) T-100, (b) T-120, (c) T-140, (d) T-160, and (e) T-180

Regarding TEM images, the particle size of the prepared ferrites exhibited slight increase with the increase of the microwave holding temperature. The average particles size of the prepared samples was estimated from TEM graphs. At least 100 particles were used to calculate the average particle size and the standard deviation for each sample. It was obtained from **Fig. 5** that the average particles size increased with increasing the temperature of the preparation of ferrite, since the average particles sizes were 10.0 ± 2.1, 10.7 ± 2.3, 11.0 ± 2.4, 11.1 ± 1.9, 11.5 ±

2.4 for samples T-100, T-120, T-140, T-160, and T-180, respectively. This proves the successfulness of such green synthesis route in producing nanoparticles even without template.



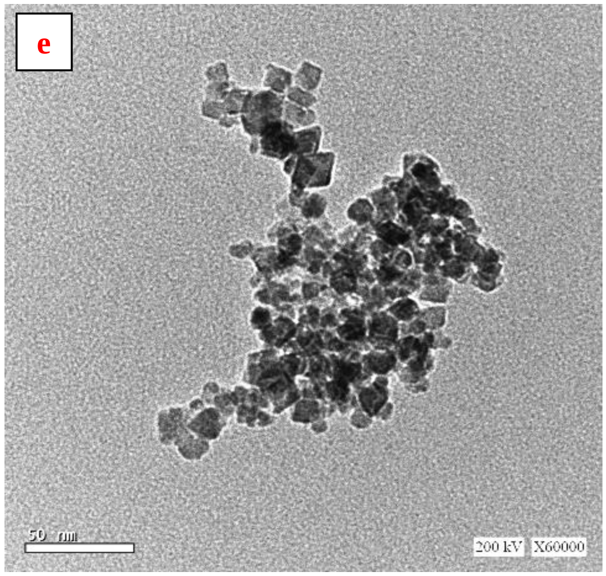


Fig.5: TEM images of ferrite samples (a) T-100, (b) T-120, (c) T-140, (d) T-160, and (e) T-180

The squash planting process

Effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on squash growth and yield.

The application of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs as a foliar fertilizer significantly improved the growth and fruit characters of the squash plant during two successive seasons 2017-2018 **Tables** (**2&3**). These characters were increased with concentration and the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs as foliar nutrition. The highest values of plant height and number of leaves/plant were obtained with the T-180 (**Table 2)**. But, the leaves area/plant significantly increased with enhancement the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs T-100. The highest values of fresh and dry weight of squash plant were obtained with T-160. This effect reflected that T-160 was enough and suitable to improve the characters of growth. While, nanoferrite prepared at T-140 had a significant effect on length and diameter of squash fruit. The fruit yield of squash (kg/plant and ton/ha) increased with the temperature treatment T-160. These results showed that the growth characters were related to the temperature of preparation of nanoparticles. However, the size of ion was effective; also the NPs interact with plants causing various morphological and physiological changes, depending on the properties of NPs. The efficacy of NPs was determined by their chemical structure, size, surface covering, reactivity, and most significantly the dose at which they are useful. In addition, the change in the reaction temperature will certainly affect the morphological and structure of the nanomaterials, since the particle morphology is highly dependent on the super-saturation which in turn is dependent upon the solution temperature [38].

Concerning the concentration of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs, the foliar application of nanoferrite significantly increased both vegetative and fruit growth characters of the squash plant (**Table 2&3)**. The concentration 20 ppm gave the best values of plant height and number of leaves/plant, which were related to dry weight of plant. While, concentrate 10 ppm was more effective on fresh weight that was related to length and diameter of fruit, as well as the fruit yield kg/plant and ton/hectare. In the same trend found by Zheng et al. [39], the concentration of nanoparticles affects processes such as germination and development of the plant. As well as, Amorós Ortiz-Villajos et al. [22] showed that Fe, Zn, Cu and Ni are preferentially accumulated in roots; Mn and Mg are accumulated in leaves; Mo, Ca, and S in roots and leaves; and K in roots, leaves and stems/sheaths. There were positive correlations between changes in the concentrations of mineral pairs Fe-Mn, K-S, Fe-Ni, Cu-Mg, Mn-Ni, S-Mo, Mn-Ca, and Mn-Mg throughout the reproductive development of rice in the above-ground organs.

The interaction between the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs and the concentration had a significant effect on improving growth and yield of squash plant. The characters were enhanced with increasing the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs as well as the concentration of NPs. Growth characters, plant height was improved with T-180 and 30 ppm interaction, while number of leaves per plant enhanced with T-180 and 20 ppm interaction and dry weight was the highest with T-160 and 30 ppm concentrate interaction. On the contrary, the leave area/plant was recorded the best value with T-120 and 10 ppm interaction that was related to fresh weight /plant. Length and diameter of fruit increase were related to T-140 and 30 ppm and T-140 and 20 ppm concentrate interaction. On the contrary, fruit yield of squash per kg/plant and per ton/hectare enhanced with plants treated with T-160 and 10 ppm concentration.

Table 2 Effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on plant growth characters of squash plant. (During two successive seasons 2017-2018)

Types of copper	**Concentrations**	**Plant height (cm)**		**No. of leaves/plant**		**Leave area/plant (m^2)**		**Plant weight (g/plant)**			
								Fresh		**Dry**	
		1st	**2nd**	**1st**	**2nd**	**1st**	**2nd**	**1st**	**2nd**	**1st**	**2nd**
T-100	**0 ppm**	44.2	44.1	17.7	17.3	0.58	0.63	222.6	225.3	27.5	27.1
	10 ppm	51.8	51.3	25.0	25.0	1.15	1.18	378.8	376.7	32.6	32.4
	20 ppm	55.6	55.2	21.3	20.3	1.28	1.28	409.8	405.0	26.9	26.9
	30 ppm	56.0	55.8	19.3	19.7	1.03	1.05	404.6	407.0	35.5	35.3
Mean		**51.9**	**51.6**	**20.8**	**20.6**	**1.01**	**1.04**	**354.0**	**353.5**	**30.6**	**30.4**
T-120	**0ppm**	44.2	44.1	17.7	17.3	0.58	0.63	222.6	225.3	27.5	27.1
	10 ppm	58.2	58.0	20.7	21.3	1.49	1.44	469.5	463.5	35.4	35.4
	20 ppm	52.8	52.7	23.3	22.7	1.08	1.08	372.1	367.3	34.2	34.1
	30 ppm	47.0	46.3	17.0	18.0	0.80	0.87	251.9	261.3	29.9	30.3
Mean		**50.5**	**50.3**	**19.7**	**19.8**	**0.99**	**1.01**	**329.0**	**329.4**	**31.8**	**31.7**
T-140	**0ppm**	44.2	44.1	17.7	17.3	0.58	0.63	222.6	225.3	27.5	27.1
	10 ppm	51.1	51.2	25.0	24.3	0.80	0.79	335.6	331.6	24.9	25.2
	20 ppm	55.2	55.4	19.3	20.0	0.93	0.97	345.4	340.6	30.9	30.7
	30 ppm	46.2	46.5	19.0	19.7	0.73	0.74	263.5	271.7	24.0	24.1
Mean		**49.2**	**49.3**	**20.3**	**20.3**	**0.76**	**0.78**	**291.8**	**292.3**	**26.8**	**26.8**
T-160	**0ppm**	44.2	44.1	17.7	17.3	0.58	0.63	222.6	225.3	27.5	27.1
	10 ppm	55.8	56.0	25.3	25.7	1.29	1.26	417.4	417.4	33.2	33.4
	20 ppm	54.0	53.5	30.3	29.7	0.98	0.99	414.5	406.9	34.7	34.8
	30 ppm	55.0	54.7	18.7	19.3	1.13	1.13	433.8	425.8	40.0	39.8
Mean		**52.3**	**52.1**	**23.0**	**23.0**	**0.99**	**1.00**	**372.1**	**368.8**	**33.8**	**33.8**
	0ppm	44.2	44.1	17.7	17.3	0.58	0.63	222.6	225.3	27.5	27.1

T-180	**10 ppm**	54.7	54.0	25.0	25.0	0.87	0.86	359.2	361.0	33.3	33.3
	20 ppm	55.3	56.0	33.7	32.7	0.88	0.88	390.5	392.0	35.6	35.6
	30 ppm	58.2	58.9	24.3	25.0	0.99	1.00	344.4	345.9	30.9	30.9
Mean		**53.1**	**53.2**	**25.2**	**25.0**	**0.83**	**0.84**	**329.2**	**331.0**	**31.8**	**31.7**
Average	**0ppm**	44.2	44.1	17.7	17.3	0.58	0.63	222.6	225.3	27.5	27.1
	10 ppm	54.3	54.1	24.2	24.3	1.12	1.11	392.1	390.0	31.9	31.9
	20 ppm	54.6	54.6	25.6	25.1	1.03	1.04	386.5	382.4	32.4	32.4
	30 ppm	52.5	52.4	19.7	20.3	0.94	0.96	339.7	342.3	32.1	32.1
LSD at 5%	**Effect of temp.**	**2.16**	**1.81**	**2.40**	**1.93**	**N.S.**	**0.19**	**32.11**	**26.76**	**3.39**	**3.31**
	Concentrations	**1.74**	**1.68**	**2.91**	**2.44**	**0.11**	**0.10**	**34.17**	**33.87**	**4.16**	**4.23**
	Interaction	**3.47**	**3.35**	**5.82**	**4.88**	**0.23**	**0.21**	**68.35**	**67.73**	**N.S.**	**N.S.**

N.S = Not Significant ($p < 0.05$).

Table 3 Effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on the characters and the yield of squash fruit plant. (During two successive seasons 2017-2018)

Types of copper	**Concentrations**	**Fruit Length (cm)**		**Fruit Diameter (cm)**		**Yield kg/plant**		**Yield Ton/ha**	
		1st	**2nd**	**1st**	**2nd**	**1st**	**2nd**	**1st**	**2nd**
T-100	**0ppm**	11.1	11.3	4.7	4.6	0.92	0.90	36.7	36.1
	10 ppm	13.5	13.4	6.0	5.9	1.06	1.07	42.5	42.7
	20 ppm	12.5	12.6	5.7	5.7	1.16	1.16	46.5	46.5
	30 ppm	11.3	11.4	5.2	5.1	0.94	0.97	37.6	38.7
Mean		**12.1**	**12.2**	**5.4**	**5.3**	**1.02**	**1.03**	**40.8**	**41.0**
T-120	**0ppm**	11.1	11.3	4.7	4.6	0.92	0.90	36.7	36.1
	10 ppm	11.7	11.9	5.3	5.2	1.30	1.31	52.1	52.3
	20 ppm	11.3	11.3	5.3	5.2	1.08	1.12	43.1	44.9
	30 ppm	11.3	11.5	5.2	5.1	1.14	1.15	45.7	46.0
Mean		**11.4**	**11.5**	**5.1**	**5.0**	**1.11**	**1.12**	**44.4**	**44.8**
T-140	**0ppm**	11.1	11.3	4.7	4.6	0.92	0.90	36.7	36.1
	10 ppm	12.3	12.5	5.6	5.6	1.19	1.18	47.6	47.1
	20 ppm	13.5	13.6	6.1	6.0	1.20	1.23	48.0	49.3
	30 ppm	13.3	13.4	5.8	5.9	1.31	1.31	52.5	52.5
Mean		**12.6**	**12.7**	**5.5**	**5.5**	**1.15**	**1.16**	**46.2**	**46.3**
T-160	**0ppm**	11.1	11.3	4.7	4.6	0.92	0.90	36.7	36.1
	10 ppm	11.5	11.7	5.2	5.3	1.37	1.38	54.8	55.2
	20 ppm	11.4	11.5	4.6	4.7	1.20	1.22	48.1	48.9

	30 ppm	10.5	10.6	4.2	4.3	1.32	1.32	52.8	52.8
Mean		**11.1**	**11.3**	**4.7**	**4.7**	**1.20**	**1.21**	**48.1**	**48.3**
T-180	**0ppm**	11.1	11.3	4.7	4.6	0.92	0.90	36.7	36.1
	10 ppm	12.2	12.1	5.9	5.9	1.24	1.26	49.6	50.3
	20 ppm	11.9	11.8	5.6	5.7	1.17	1.17	46.8	46.8
	30 ppm	12.1	12.2	5.5	5.6	1.20	1.21	48.1	48.4
Mean		**11.8**	**11.8**	**5.4**	**5.5**	**1.13**	**1.14**	**45.3**	**45.4**
Average	**0ppm**	11.1	11.3	4.7	4.6	0.92	0.90	36.7	36.1
	10 ppm	12.3	12.3	5.6	5.6	1.23	1.24	49.3	49.5
	20 ppm	12.1	12.2	5.5	5.5	1.16	1.18	46.5	47.3
	30 ppm	11.7	11.8	5.2	5.2	1.18	1.19	47.3	47.7
LSD at 5%	**Effect of temp.**	**0.27**	**0.25**	**0.19**	**0.22**	**0.04**	**0.04**	**1.6**	**1.6**
	Concentrations	**0.56**	**0.59**	**0.31**	**0.31**	**0.05**	**0.06**	**2.1**	**2.3**
	Interaction	**1.13**	**1.18**	**0.62**	**0.62**	**0.11**	**0.11**	**4.3**	**4.6**

Effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on proximate components of squash leave and fruit.

Effect on squash leave.

It was found that the temperature of preparation $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs had a significant effect on proximate components of the squash leaves during two seasons 2017 and 2018 (**Table 4**). $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs, which prepared at 180 ºC (T-180), gave the best values of organic matter and carbohydrate content that were related to total energy. While, the highest values of protein and ash percentage were obtained with T-160 as well as lipids percentage with T-140. On the other hand, the highest value of fiber percentage was more affected by T-100. The results showed that the change in the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs had a role on photosynthesis processes of leave squash; this may be due to the change of the size and the shape of the prepared nanoferrite (**Fig. 2& 3**). The trends of these results are supported by that of **Guozhong [38].**

In addition, the concentration of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs had a significant effect on proximate components of squash leave as shown in **Table 4**. The maximum percentage of organic matter, carbohydrate and total energy showed with control compared other concentrations. Increasing the content percentages of protein were related to increasing the concentration of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs, sine, the highest concentration (30 ppm) gave the best values of both protein content in the squash leaves. While, the highest fiber and lipid content percentage was related to 20 ppm concentration. In addition, 10 ppm concentration was more effective on ash percentage. This effect might be due to the role of the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs in the metabolic processes and penetration to the plant cell.

The interaction between the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs and their concentration had a significant effect on proximate components of squash leave (**Table** 4). The increasing of temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs and the concentration (T-180 and 30 ppm) led to enhance organic matter %, carbohydrate % and total energy (kcal/g). In this trend, protein percentage increase was significantly related to T-140 and 30 ppm concentration interaction. Also, the fiber concentration and lipids percentages were affected with the temperature treatment (T-140) and 20 ppm concentration interaction compared with the control. Moreover, ash percentage increase was related to temperature treatment (T-160) and 10 ppm concentration. This effect might be related to increase the translocation, penetration and the accumulation in the plant cell.

Table 4 Effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on proximate components of squash leaves. (During two successive seasons 2017-2018)

Types of copper	Concentrations	Organic matter (%)		Protein (%)		Fiber (%)		Lipids (%)		Carbohydrate (%)		Ash (%)		Total Energy (kcal/g)	
		1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
T-100	**0 ppm**	69.5	68.9	21.4	21.3	9.7	9.6	1.7	1.6	36.6	36.3	30.5	31.1	247.7	245.2
	10 ppm	66.7	66.1	21.7	21.5	13.5	13.4	1.0	1.0	30.5	30.2	33.3	33.9	218.1	216.0
	20 ppm	68.1	67.4	20.4	20.3	12.7	12.6	1.4	1.3	33.6	33.3	31.9	32.6	228.3	225.7
	30 ppm	66.5	66.0	23.4	23.2	13.6	13.6	1.4	1.4	28.1	27.8	33.5	34.0	218.7	216.6
Mean		**67.7**	**67.1**	**21.7**	**21.5**	**12.4**	**12.3**	**1.4**	**1.3**	**32.2**	**31.9**	**32.3**	**32.9**	**228.2**	**225.9**
T-120	**0ppm**	69.5	68.9	21.4	21.3	9.7	9.6	1.7	1.6	36.6	36.3	30.5	31.1	247.7	245.2
	10 ppm	63.8	63.0	22.0	21.6	12.2	12.1	1.2	1.2	28.5	28.1	36.2	37.0	212.7	209.7
	20 ppm	67.1	66.6	23.1	23.1	13.1	13.1	1.7	1.6	29.2	28.8	32.9	33.4	224.5	222.4
	30 ppm	66.2	65.9	20.9	20.7	13.2	13.1	1.3	1.3	30.8	30.7	33.8	34.1	218.0	217.2
Mean		**66.7**	**66.1**	**21.8**	**21.7**	**12.1**	**12.0**	**1.5**	**1.4**	**31.3**	**31.0**	**33.3**	**33.9**	**225.7**	**223.6**
T-140	**0ppm**	69.5	68.9	21.4	21.3	9.7	9.6	1.7	1.6	36.6	36.3	30.5	31.1	247.7	245.2
	10 ppm	65.4	65.1	22.0	21.9	12.4	12.3	1.7	1.8	29.3	29.2	34.7	34.9	220.5	220.1
	20 ppm	67.7	67.2	22.3	22.2	14.0	13.9	2.9	2.8	28.5	28.3	32.3	32.8	229.5	227.5
	30 ppm	64.7	64.3	24.6	24.4	13.3	13.3	2.0	2.1	24.9	24.6	35.3	35.7	215.4	214.3
Mean		**66.8**	**66.4**	**22.6**	**22.4**	**12.3**	**12.3**	**2.1**	**2.1**	**29.8**	**29.6**	**33.2**	**33.6**	**228.2**	**226.8**
T-160	**0ppm**	69.5	68.9	21.4	21.3	9.7	9.6	1.7	1.6	36.6	36.3	30.5	31.1	247.7	245.2
	10 ppm	62.5	61.2	21.8	21.6	11.4	11.3	1.5	1.5	27.8	26.8	37.5	38.8	211.7	207.1
	20 ppm	66.1	65.4	24.7	24.5	12.0	11.8	2.0	1.8	27.5	27.3	33.9	34.6	226.5	223.6
	30 ppm	66.3	65.8	24.3	24.2	11.1	11.0	1.8	1.7	29.1	28.9	33.7	34.2	230.3	227.9
Mean		**66.1**	**65.3**	**23.0**	**22.9**	**11.0**	**10.9**	**1.8**	**1.7**	**30.3**	**29.9**	**33.9**	**34.7**	**229.0**	**225.9**
T-180	**0ppm**	69.5	68.9	21.4	21.3	9.7	9.6	1.7	1.6	36.6	36.3	30.5	31.1	247.7	245.2
	10 ppm	65.5	64.9	22.4	22.3	11.9	11.9	2.2	2.1	29.0	28.6	34.5	35.1	225.4	223.0
	20 ppm	64.4	63.9	22.7	22.6	11.7	11.5	2.0	1.9	28.0	27.8	35.6	36.2	220.7	218.8
	30 ppm	73.0	72.5	23.6	23.4	10.4	10.3	1.9	1.9	37.2	37.0	27.0	27.5	260.0	258.3
Mean		**68.1**	**67.5**	**22.5**	**22.4**	**10.9**	**10.8**	**1.9**	**1.9**	**32.7**	**32.4**	**31.9**	**32.5**	**238.5**	**236.3**
Average	**0ppm**	69.5	68.9	21.4	21.3	9.7	9.6	1.7	1.6	36.6	36.3	30.5	31.1	247.7	245.2
	10 ppm	64.8	64.1	22.0	21.8	12.3	12.2	1.5	1.5	29.0	28.6	35.2	35.9	217.7	215.2
	20 ppm	66.7	66.1	22.6	22.5	12.7	12.6	2.0	1.9	29.4	29.1	33.3	33.9	225.9	223.6
	30 ppm	67.4	66.9	23.3	23.2	12.3	12.3	1.7	1.7	30.0	29.8	32.7	33.1	228.5	226.9
LSD at 5%	**Effect of temp.**	**0.68**	**N.S.**	**0.31**	**0.31**	**0.17**	**0.18**	**0.10**	**0.10**	**0.47**	**1.54**	**0.68**	**N.S.**	**2.52**	**6.90**
	Concentrations	**1.86**	**1.71**	**0.82**	**0.83**	**0.18**	**0.19**	**0.16**	**0.18**	**1.02**	**0.84**	**1.86**	**1.71**	**7.44**	**6.91**
	Interaction	**3.72**	**3.41**	**1.64**	**1.65**	**0.36**	**0.38**	**0.32**	**0.36**	**2.03**	**1.68**	**3.72**	**3.41**	**14.89**	**13.82**

Effect on squash fruits.

The results in **Table 5** showed a significant effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs as a foliar application on proximate components of the squash fruit. T-140 was significantly increased organic matter % carbohydrate % and total energy (kcal/g). While, protein and lipid percentage increases were related to T-160. However, the maximum ash % was obtained with the highest temperature of preparation nanoparticles (T-100). The difference of the proximate component response to nanoparticles temperature might be due to the size of nanoparticles and their role in physiological processes in plant cell as a stimulating or co-enzymes.

Data in **Table 5** showed a significant response of the proximate component of squash fruit with the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs concentration compared with the control. The proximate components were varied in their response to the applied different concentrations. Organic matter %, protein %, carbohydrate % and total energy were significantly increased up to NPs concentration 30 ppm while, fiber % and lipid % were significantly enhanced up to the NPs concentration 20 ppm. While, the ash % was significantly affected with the concentration 10 ppm. These results appeared that the applied concentrations were suitable for increasing the quality and quantity of squash fruit.

The results in Table 5 appeared a significant improvement in approximate components with the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs the concentration of NPs and their interactions. Protein % was more affected with the T-180 and the concentration 30 ppm, thus protein % and fiber % were significantly affected with the type of temperature and the concentration 30 and 10 ppm, respectively. The maximum carbohydrate % was obtained with T-180 in the traditional agriculture (control).While maximum organic matter, lipids and total energy was obtained by T-160 and 20 ppm concentration. Ash percentage increased with T-100 and 10 ppm concentration. These results showed that the proximate contents were varied in their response according to the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs and their concentration.

Table 5 Effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on proximate components of squash fruits. (During two successive seasons 2017-2018)

Types of copper	**Concentrations**	**Organic matter (%)**		**Protein (%)**		**Fiber (%)**		**Lipids (%)**		**Carbohydrate (%)**		**Ash (%)**		**Total Energy (kcal/g)**	
		1st	**2nd**	**1st**	**2nd**	**1st**	**2nd**	**1st**	**2nd**	**1st**	**2nd**	**1st**	**2nd**	**1st**	**2nd**
T-100	**0ppm**	76.1	75.7	27.8	27.6	16.0	16.2	1.8	1.9	30.6	30.1	23.9	24.3	249.6	247.3
	10 ppm	70.3	70.4	25.4	25.3	21.3	21.0	1.7	1.8	21.9	22.3	29.7	29.6	204.9	206.4
	20 ppm	72.9	73.2	26.3	26.2	22.3	22.3	2.9	2.7	21.5	22.0	27.1	26.8	216.9	216.9
	30 ppm	71.2	71.7	25.7	25.7	21.4	21.5	2.6	2.5	21.6	22.1	28.8	28.3	212.2	213.3
Mean		**72.6**	**72.7**	**26.3**	**26.2**	**20.2**	**20.3**	**2.2**	**2.2**	**23.9**	**24.1**	**27.4**	**27.3**	**220.9**	**221.0**
T-120	**0ppm**	76.1	75.7	27.8	27.6	16.0	16.2	1.8	1.9	30.6	30.1	23.9	24.3	249.6	247.3
	10 ppm	72.4	72.4	26.6	26.6	20.8	20.7	2.2	2.2	22.9	23.0	27.6	27.6	217.5	217.8
	20 ppm	72.0	71.8	25.1	25.0	20.1	20.1	2.8	2.7	23.9	24.0	28.1	28.2	221.6	220.1
	30 ppm	75.2	74.9	26.1	25.9	19.4	19.1	2.0	2.1	27.8	27.8	24.8	25.1	233.4	233.4
Mean		**73.9**	**73.7**	**26.4**	**26.3**	**19.1**	**19.0**	**2.2**	**2.2**	**26.3**	**26.2**	**26.1**	**26.3**	**230.5**	**229.7**
T-140	**0ppm**	76.1	75.7	27.8	27.6	16.0	16.2	1.8	1.9	30.6	30.1	23.9	24.3	249.6	247.3
	10 ppm	76.2	75.7	28.7	28.6	18.7	18.5	2.5	2.4	26.3	26.2	23.8	24.3	242.2	240.9
	20 ppm	75.4	75.2	26.1	26.3	19.8	19.6	2.2	2.2	27.3	27.2	24.6	24.8	233.3	233.4
	30 ppm	75.6	75.5	28.5	28.5	18.2	18.1	2.2	2.2	26.8	26.8	24.4	24.5	240.8	240.7
Mean		**75.8**	**75.5**	**27.8**	**27.7**	**18.2**	**18.1**	**2.2**	**2.2**	**27.8**	**27.6**	**24.2**	**24.5**	**241.5**	**240.6**
T-160	**0ppm**	76.1	75.7	27.8	27.6	16.0	16.2	1.8	1.9	30.6	30.1	23.9	24.3	249.6	247.3
	10 ppm	70.6	70.1	26.0	25.7	20.1	19.7	3.5	3.3	21.0	21.3	29.4	29.9	219.5	218.0
	20 ppm	76.6	76.3	30.0	29.7	17.7	18.0	3.6	3.4	25.2	25.2	23.4	23.7	253.6	250.3
	30 ppm	76.3	76.4	27.9	28.0	19.5	19.3	2.7	2.8	26.2	26.3	23.8	23.6	240.3	242.0
Mean		**74.9**	**74.6**	**27.9**	**27.7**	**18.3**	**18.3**	**2.9**	**2.8**	**25.8**	**25.7**	**25.1**	**25.4**	**240.7**	**239.4**
T-180	**0ppm**	76.1	75.7	27.8	27.6	16.0	16.2	1.8	1.9	30.6	30.1	23.9	24.3	249.6	247.3
	10 ppm	71.2	71.2	22.8	22.6	24.5	24.5	2.9	2.9	21.0	21.2	28.8	28.8	201.4	201.3
	20 ppm	70.9	70.4	24.1	23.9	24.3	24.1	1.9	2.0	20.6	20.5	29.1	29.6	195.6	195.1
	30 ppm	75.0	74.4	30.4	29.7	18.8	19.1	2.4	2.3	23.4	23.4	25.0	25.6	236.7	232.7
Mean		**73.3**	**72.9**	**26.3**	**25.9**	**20.9**	**21.0**	**2.3**	**2.3**	**23.9**	**23.8**	**26.7**	**27.1**	**220.8**	**219.1**
Average	**0ppm**	76.1	75.7	27.8	27.6	16.0	16.2	1.8	1.9	30.6	30.1	23.9	24.3	249.6	247.3
	10 ppm	72.1	71.9	25.9	25.7	21.1	20.9	2.6	2.5	22.6	22.8	27.9	28.1	217.1	216.9
	20 ppm	73.5	73.4	26.3	26.2	20.9	20.8	2.7	2.6	23.7	23.8	26.5	26.6	224.2	223.2
	30 ppm	74.7	74.6	27.7	27.5	19.4	19.4	2.3	2.4	25.2	25.3	25.3	25.4	232.7	232.4
LSD at 5%	**Effect of temp.**	**0.59**	**0.36**	**0.77**	**0.84**	**0.23**	**0.25**	**0.11**	**0.20**	**0.39**	**0.63**	**0.59**	**0.36**	**1.97**	**1.66**
	Concentrations	**0.49**	**0.56**	**0.32**	**0.45**	**0.13**	**0.27**	**0.07**	**0.14**	**0.44**	**0.64**	**0.49**	**0.56**	**2.18**	**2.60**

	Interaction	**0.98**	**1.11**	**0.65**	**0.91**	**0.26**	**0.53**	**0.15**	**0.28**	**0.89**	**1.28**	**0.98**	**1.11**	**4.37**	**5.20**

Effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on elements contents of squash leaves and fruits.

Effect on squash leaves.

The temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs had a significant effect on elements leaves content during two seasons 2017-2018 (**Table 6**). It was varied in their ability to penetrate the cell surface. This effect appeared in surpass in increasing N and P content by the lowest size of nanoparticles application (T-160). While, K and Fe content were more affected with T-120 as well as Zn leave content with T-100. However, Mn leaves content was enhanced by T-180. This effect might be due to the competition between the shape of NPs and their penetration the cell wall.

The results indicated that the concentrations of NPs were significantly affected on leave content of the different element contents (N, P, K, Mn, Zn and Fe) compared with the control (**Table 6)**. The leave element contents (N, Zn, Fe and Mn) were significantly increased with increasing the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs applied as a foliar fertilizer. The highest concentration 30 ppm was related to the highest value of the elements (N, Zn, Fe and Mn) content in the leaves. While, leave elements (P and K) content were significantly affected by 20 and 10 ppm concentration of applied nanoferrite.

Concerning the interaction between the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs and their concentration on leaves element contents, the results showed that the interactions had a significant increase in all elements compared with the control (**Table 6**). T-160 and concentration 20 ppm gave the highest values of the leave elements (N) content. In this regard, T-100 and concentration 20 ppm interaction led to a significant increase in P leave content. The best potassium percentage appeared with T-100 and 10 ppm concentration interaction, as well as both Zn, Fe and Mn content significantly increased by concentration 30 ppm with T-100, T-120 and T-180, respectively. It appeared from the results that the increasing of the leave element contents was mostly attributed to the temperature of preparation of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs and the concentration of the nanoparticles.

Table 6 Effect of nanoferrite on squash leaves content of the endogenous minerals. (During two successive seasons 2017-2018)

Types of copper	Concentrations	N		P		K		Zn		Fe		Mn	
		1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
T-100	0	3.43	3.40	0.11	0.10	2.40	2.37	48.0	47.3	120.0	118.3	53.0	53.0
	10 ppm	3.47	3.44	0.31	0.31	4.30	4.23	55.0	57.7	90.0	91.3	26.0	27.0
	20 ppm	3.26	3.24	0.37	0.35	2.76	2.79	103.0	101.0	150.0	153.0	35.0	36.7
	30 ppm	3.74	3.71	0.15	0.16	3.30	3.27	240.0	238.0	290.0	291.7	44.0	45.3
Mean		**3.47**	**3.45**	**0.24**	**0.23**	**3.19**	**3.16**	**111.5**	**111.0**	**162.5**	**163.6**	**39.5**	**40.5**
T-120	0	3.43	3.40	0.11	0.10	2.40	2.37	48.0	47.3	120.0	118.3	53.0	53.0
	10 ppm	3.51	3.45	0.30	0.29	3.80	3.73	25.0	26.7	135.0	133.3	25.0	26.7
	20 ppm	3.70	3.69	0.20	0.19	3.24	3.22	63.0	63.0	150.0	151.7	26.0	28.3
	30 ppm	3.34	3.32	0.13	0.13	3.60	3.57	25.0	26.7	300.0	296.7	53.0	54.3
Mean		**3.49**	**3.47**	**0.19**	**0.18**	**3.26**	**3.22**	**40.3**	**40.9**	**176.3**	**175.0**	**39.3**	**40.6**
T-140	0	3.43	3.40	0.11	0.10	2.40	2.37	48.0	47.3	120.0	118.3	53.0	53.0
	10 ppm	3.52	3.50	0.15	0.16	3.80	3.79	13.0	16.0	150.0	148.3	18.0	20.3
	20 ppm	3.57	3.55	0.14	0.15	3.20	3.22	68.0	68.3	135.0	133.3	44.0	44.7
	30 ppm	3.93	3.90	0.15	0.16	2.00	2.10	18.0	18.0	25.0	26.7	61.0	62.0
Mean		**3.61**	**3.59**	**0.14**	**0.14**	**2.85**	**2.87**	**36.8**	**37.4**	**107.5**	**106.7**	**44.0**	**45.0**
T-160	0	3.43	3.40	0.11	0.10	2.40	2.37	48.0	47.3	120.0	118.3	53.0	53.0
	10 ppm	3.49	3.46	0.22	0.22	3.34	3.32	13.0	13.0	40.0	42.0	26.0	27.0
	20 ppm	3.94	3.91	0.32	0.30	2.00	2.07	33.0	33.0	70.0	70.7	53.0	53.7
	30 ppm	3.89	3.87	0.15	0.16	3.34	3.31	58.0	59.3	100.0	103.0	70.0	72.0
Mean		**3.69**	**3.66**	**0.20**	**0.20**	**2.77**	**2.77**	**38.0**	**38.2**	**82.5**	**83.5**	**50.5**	**51.4**
T-180	0	3.43	3.40	0.11	0.10	2.40	2.37	48.0	47.3	120.0	118.3	53.0	53.0
	10 ppm	3.59	3.57	0.24	0.24	2.00	2.17	93.0	93.7	85.0	86.7	70.0	71.0
	20 ppm	3.63	3.62	0.29	0.28	3.40	3.37	70.0	71.0	80.0	81.7	100.0	101.7
	30 ppm	3.77	3.74	0.22	0.21	3.30	3.28	88.0	86.7	125.0	126.7	118.0	118.7
Mean		**3.61**	**3.58**	**0.22**	**0.21**	**2.78**	**2.80**	**74.8**	**74.7**	**102.5**	**103.3**	**85.3**	**86.1**
Average	0	3.43	3.40	0.11	0.10	2.40	2.37	48.0	47.3	120.0	118.3	53.0	53.0
	10 ppm	3.52	3.48	0.24	0.24	3.45	3.45	39.8	41.4	100.0	100.3	33.0	34.4
	20 ppm	3.62	3.60	0.26	0.25	2.92	2.93	67.4	67.3	117.0	118.1	51.6	53.0
	30 ppm	3.73	3.71	0.16	0.16	3.11	3.11	85.80	85.73	168.0	168.9	69.20	70.47
LSD at 5%	Effect of temp.	**0.05**	**0.05**	**0.01**	**0.01**	**0.05**	**0.07**	**2.09**	**1.59**	**1.29**	**3.24**	**4.13**	**4.19**
	Concentrations	**0.13**	**0.13**	**0.01**	**0.01**	**0.06**	**0.06**	**1.99**	**2.61**	**1.32**	**2.24**	**2.18**	**2.43**
	Interaction	**0.26**	**0.26**	**0.02**	**0.02**	**0.12**	**0.13**	**3.97**	**5.22**	**2.63**	**4.48**	**4.36**	**4.87**

Effect on squash fruits.

Data in **Table 7** showed that $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs were significantly affected on the squash fruits content of the minerals. The nanoferrite T-160 was more effective on N, P, K and Mn content while, Zn content was enhanced by the T-100. In this regard, Fe content was significantly increased by the T-140. These results appeared that N, P, K and Mn content of squash fruit was more responded to the temperature of preparation $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs T-160.

Concerning the nanoparticles concentration were effects on squash fruit content of the minerals, (**Table 7)**. It appeared that the nanoparticles concentration as foliar application had a significant effect on squash fruit minerals content. The contents of K, Zn and Mn were significantly increased by the concentration 10 ppm as well as P and Fe content by concentration 30 ppm. In this trend, the mineral content of N was significantly enhanced with the traditional agriculture (control). The results stated that the minerals content responses were varied according to the ability of penetration and size. Thus, the minerals content decreased with increasing the applied nanoferrite concentration.

The interaction between the temperature of the preparation of NPs and the concentration of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs showed a significant effect on squash fruits content of the elements compared with the control as shown in **Table 7**. The contents of N and P were more affected by both the temperature of preparation $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs (T-160) and the concentration 30 ppm. While, the increment of N showed with T-160 and the concentration 30 ppm. The highest value of Zn content was obtained by T-100 and 30 ppm concentration. The Fe content increase was attributed to nanoparticles T-140 and 30 ppm concentration as well as Mn with T-160 and 30 ppm concentration interaction. These results appeared that the highest temperature of preparation the $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs, concentrations of nanoferrite and their interaction were suitable to improve the quality of squash.

Table 7 Effect of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs on squash fruits content of the endogenous minerals. (During two successive seasons 2017-2018)

Types of copper	Concentrations	N		P		K		Zn		Fe		Mn	
		1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
T-100	0	4.44	4.41	0.24	0.23	4.20	4.13	62.0	61.0	59.0	60.0	59.0	58.3
	10 ppm	4.07	4.05	0.18	0.17	5.16	5.13	85.0	83.7	63.0	64.7	62.0	61.7
	20 ppm	4.21	4.19	0.24	0.24	4.20	4.27	91.0	90.3	75.0	75.7	61.0	60.3
	30 ppm	4.11	4.11	0.24	0.23	4.87	4.93	99.0	98.0	75.0	75.7	57.3	56.7
Mean		**4.21**	**4.19**	**0.23**	**0.22**	**4.61**	**4.61**	**84.3**	**83.3**	**68.0**	**69.0**	**59.8**	**59.3**
T-120	0	4.44	4.41	0.24	0.23	4.20	4.13	62.0	61.0	59.0	60.0	59.0	58.3
	10 ppm	4.25	4.25	0.34	0.34	4.20	4.13	94.0	94.0	72.0	72.7	59.0	58.7
	20 ppm	4.02	4.00	0.26	0.25	3.60	3.66	83.0	83.7	72.0	73.0	60.0	59.7
	30 ppm	4.17	4.14	0.31	0.30	2.76	2.92	68.0	69.0	65.0	66.0	62.0	62.0
Mean		**4.22**	**4.20**	**0.29**	**0.28**	**3.69**	**3.71**	**76.8**	**76.9**	**67.0**	**67.9**	**60.0**	**59.7**
T-140	0	4.44	4.44	0.24	0.23	4.20	4.13	62.0	61.0	59.0	60.0	59.0	58.3
	10 ppm	4.59	4.57	0.28	0.28	5.76	5.70	98.0	97.0	60.0	60.7	55.0	55.3
	20 ppm	4.18	4.20	0.29	0.28	5.40	5.35	98.0	96.7	74.0	75.0	50.0	51.0
	30 ppm	4.56	4.55	0.28	0.27	3.34	3.42	60.0	61.7	82.0	81.7	41.0	42.7
Mean		**4.44**	**4.43**	**0.27**	**0.27**	**4.68**	**4.65**	**79.5**	**79.1**	**68.8**	**69.3**	**51.3**	**51.8**
T-160	0	4.44	4.41	0.24	0.23	4.20	4.13	62.0	61.0	59.0	60.0	59.0	58.3
	10 ppm	4.16	4.12	0.38	0.38	5.76	5.69	93.0	92.0	64.0	65.0	62.0	61.7
	20 ppm	4.80	4.75	0.57	0.56	6.24	6.11	88.0	88.7	75.0	74.7	60.0	59.3
	30 ppm	4.47	4.47	0.34	0.36	5.50	5.60	62.0	63.0	72.0	72.3	70.0	69.0
Mean		**4.47**	**4.44**	**0.38**	**0.38**	**5.43**	**5.38**	**76.3**	**76.2**	**67.5**	**68.0**	**62.8**	**62.1**
T-180	0	4.44	4.41	0.24	0.23	4.20	4.13	62.0	61.0	59.0	60.0	59.0	58.3
	10 ppm	3.64	3.61	0.23	0.23	6.70	6.57	83.3	82.0	60.0	61.3	57.0	57.0
	20 ppm	3.85	3.82	0.10	0.10	3.60	3.69	68.0	69.7	64.0	65.3	55.0	54.0
	30 ppm	4.87	4.75	0.42	0.41	5.50	5.56	93.0	92.0	82.0	81.3	41.3	43.3
Mean		**4.20**	**4.15**	**0.25**	**0.24**	**5.00**	**4.99**	**76.6**	**76.2**	**66.3**	**67.0**	**53.1**	**53.2**
Average	0	4.44	3.97	0.24	0.23	4.20	4.13	62.0	61.0	59.0	60.0	59.0	58.3
	10 ppm	4.14	3.67	0.28	0.28	5.52	5.44	90.7	89.7	63.8	64.9	59.0	58.9
	20 ppm	4.21	3.82	0.29	0.29	4.61	4.62	85.6	85.8	72.0	72.7	57.2	56.9
	30 ppm	4.44	3.92	0.32	0.32	4.39	4.49	76.40	76.73	75.20	75.40	54.33	54.73
LSD at 5%	**Effect of temp.**	**0.12**	**0.13**	**0.01**	**0.01**	**0.05**	**0.06**	**1.32**	**1.37**	**0.39**	**0.73**	**0.95**	**1.73**
	Concentrations	**0.05**	**0.07**	**0.01**	**0.01**	**0.06**	**0.11**	**0.94**	**1.74**	**0.44**	**0.89**	**1.11**	**1.11**

	Interaction	**0.10**	**0.15**	**0.02**	**0.02**	**0.12**	**0.21**	**1.87**	**3.49**	**0.89**	**1.79**	**2.22**	**2.22**

Conclusions

Green microwave-assisted hydrothermal synthesis method was successfully applied to prepare manganese zinc ferrites nanoparticles. The produced ferrites nanoparticles showed cubic shape whose regularity are enhanced as holding synthesis temperature increases. The as-synthesized nanoferrites displayed an irreversible type IV adsorption-desorption isotherm which could be attributed to the mesopores capillary condensation effect. It was found that the effective surface parameter in fertilization efficiency is the pore size distribution. The application of these ferrites as nanofertilizers has improved the growth and yield of squash plant. The growth characters and the yield of squash plant were increased with increasing the reaction holding temperature of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs, which used as foliar nutrition, as well as the use of lower concentrations of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ NPs achieved the highest values of the characteristics of the vegetative and yield. The results had proven the influence of the synthesis temperature of ferrite nanoparticles on the surface, pore structure, size and shape of the prepared nanoferrites, as well as the characters and the yield of squash plants.

.Declarations

Competing interests

The authors declare that they have no competing interests

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