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Microwave Synthesis of Fe_2O_3 and ZnO Nanoparticles and Evaluation Its Application on Grain Iron and Zinc Concentrations of Wheat (Triticum aestivum L.) and their Relationships to Grain Yield

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ABSTRACT

Fe_2O_3 and ZnO nanoparticles were synthesized by a fast microwave method. Nanostructures were characterized by X-ray diffraction and scanning electron microscopy. The goal of bio-fortification is to develop plants that have an increased content of bioavailable nutrients in their edible parts. The micronutrients magnesium (Mg), manganese (Mn) and copper (Cu), boron (B) and calcium (Ca) are essential for plants and the humans and animals that consume plants. Increasing the micronutrient density of staple crops, will greatly improve human nutrition on a global scale. In order to investigate the effect of Iron and Zinc on nutrient uptake of two line of wheat. The experimental design used for this research was a factorial experiment under complete randomized block design with three replications and two variety of wheat including Roshan back cross (V1) and C-78-14 line (V2), three levels of Iron from Fe-EDDHA (Sequestrene 138) including no application (F0), Fe sulphate (F1) and Nano Fe_2O_3 (F2) and three Levels of Zinc as zinc sulphate ($ZnSO_4$) including no application (Z0), 25 kg/ha-1 (Z1) and 50 kg/ha-1 (Z2) were used. The result is showed that application of nanoparticles increased the study of parameters such as magnesium, manganese, copper, boron and calcium. Highest levels of grain yield with 5.13 ton/ha^{-1} was obtained in C-78-14 variety.

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INTRODUCTION

High growth rate of population in developing countries has increased demands for food supplies. Food shortage and malnutrition problems have placed numerous stresses on the human health and environment [1]. During the recent decade global food production has generally followed a positive growth rate, still on a per capita basis. Nonetheless, the number of constantly undernourished has further grown. The strange increase of hunger during the recent food crisis in 2007-2008 occurred in spite of a record cereal harvest in 2008 [2-4]. Number and percentage of undernourished person in the word was

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925 million in 2010 [5]. Moreover most of the world's hungry people live in developing countries [6]. There are many methods to overcome these problems include population control, sustainable agricultural development and increasing potential yield per plants. In numerous developing countries, Wheat is consumed as a main source of protein in the human food and contains high levels of vitamin and minerals [4]. Developing countries have been importers of cereals and specially wheat [7]. Wheat (*Triticum aestivum* L.) is the world's most widely adapted crop, supplying one-third of the world population with more than half of their calories, and nearly half of their protein [8,9].

In 2013, world production of wheat was 713 million tons, making it the third most-produced cereal after maize (1,016 million tons) and rice (745 million tons) [10]. Wheat was the second most-produced cereal in 2009; world production in that year was 682 million tons, after maize (817 million tons), and with rice as a close third (679 million tons) [11].

This grain is grown on more land area than any other commercial food. World trade in wheat is greater than for all other crops combined [12,13]. Globally, wheat is the leading source of vegetable protein in human food, having a higher protein content than other major cereals, maize (corn) or rice [14]. In terms of total production tonnages used for food, it is currently second to rice as the main human food crop and ahead of maize, after allowing for maize's more extensive use in animal feeds. The archaeological record suggests that this first occurred in the regions known as the Fertile Crescent. Producing nutritious and safe foods sufficiently and sustainably are the ultimate goal of modern agriculture. Past efforts have been focused on increasing grain yields, but enhancing the concentrations of mineral microelements have become an urgent task because about of the world population suffers from the malnutrition of iron, zinc, copper, calcium and magnesium. Microelements deficiencies affect a large proportion of the world population [15]. Microelements deficiencies affect primarily children and pregnant women in low-income, vulnerable populations, whose diets often rely on a few starchy staple crops. Bio-fortification by the breeding of staples with increased microelements content is a sustainable approach to reduce microelements malnutrition in these populations [16].

Deficiencies of the mineral micronutrients iron (Fe), zinc (Zn), selenium (Se), and iodine (I) affect more than half of the world population [17]. Other minerals, such as calcium (Ca), magnesium (Mg), and copper (Cu), can also be deficient in the diets of some Countries [18].

Past efforts have concentrated on increasing seed yields but there is evidence that seed yield increment over the last four decades has been accomplished by the decrease in micronutrients concentrations in seed [19,20]. Bio-fortification, which aims to increase mineral concentrations in the plants through breeding or the use of biotechnology, is considered to be a cost-effective way to reducing micronutrient malnutrition in the developing countries where the problem is most prevalent [21,22].

Nutrient-rich seeds will not only be advantageous for combating malnutrition in humans, but can also improve food security by increasing seed vigor and thereby crop productivity. Low levels of micronutrients in seeds can negatively affect seed vigor and seedling vitality. Reduced vitality is primarily observed when nutrient-deficient seeds are grown in nutrient-poor soils [23]. One of the major goals of this study is enhancement microelements by select of suitable varieties with different sources of fertilizers. Attempts to improve seed yield and quality by developing new genotypes and agronomic practices are underway throughout the world. Breeding Zn-resistant plant species and varieties and applying Zn-containing fertilizers to correct Zn deficiencies are two approaches to the improvement of Zn concentration in seeds. To obtain genotypes resistant to Zn deficiency through plant breeding requires a long period of Time. However, increases in yield and in the level of Zn in seeds are possible and relatively easy with Zn fertilization. A few studies have investigated the response of wheat to Zn fertilization. It would be adaptable to the climatic and land conditions. The mono-cultural management of Thrace has caused the increase of phosphorus in soil. Phosphorus fertilizer in large amounts leads to iron deficiency. In addition, iron absorb of the plant falls when pH increases in the land [24-29]. The microwave heating involves two main mechanisms, dipolar polarization and ionic conduction. During the microwave heating, polar molecules like glycol molecules try to orientate with the rapidly changing alternating electric field; thus heat is generated by the rotation, friction, and collision of molecules. In the case of ions, any ions present in solution will move through the solution based on the orientation of the electric field, and because this is in constant fluctuation, the ion is moving in constantly changing directions through the solution, causing a local temperature rise due to friction and collision [30-33].

During the past few years, a variety of synthesis strategies for Fe_2O_3 nanostructure materials have been described. Recently, microwave method as a simple, effective and novel route has been developed to prepare nanostructures. Microwave method is one of the fastest methods operated under ambient conditions. In this work, various morphologies of Fe_2O_3 nanoparticles were synthesized by microwave-assisted Chemical method.

MATERIALS AND METHODS

Materials and characterization

In order to study the effects of Zinc and Iron on yield and yield components of two variety of Wheat, a field study was conducted at the Markazi province (Iran) in 2014-15.

A factorial experiment was arranged in randomized complete block design with three replications. Two variety of wheat including Roshan back cross (V1) and C-78-14 line (V2), three levels of Iron from Fe-EDDHA (**Sequestrene 138**) including no application (F0), Fe sulphate (F1) and Nano Fe_2o_3 (F2) and three Levels of Zinc, no application (Z0), zinc sulphate (ZnSO4) as (Z1) and Nano ZnO (Z2) were used.

Theses cultivars have a high growth potential. Theses cultivars have been recommended for cold and temperate regions in Iran.

The cultivation rows were 25 cm apart in each plot. Weeds were removed by hand and plots were irrigated as required through the growing seasons. Harvest was done manually.

Ca, Mg, B, Mn and Cu were determined after wet digestion in a H_2SO_4-salicylic acid mixture. Ca, Mg, B, Mn, and Cu analysis were done by atomic absorption spectrometry [29].

Statistical analysis was done with SAS statistical software (SAS 2004). Duncan method was used for means comparison.

$Fe(NO_3)_3$ $9H_2O$, Zinc acetate, and NH_3 were purchased from Merck Company. All the chemicals were used as received without further purifications. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered $CuK_{\acute{a}}$ radiation. A multi-wave ultrasonic generator (Bandeline MS 73) equipped with a converter/transducer and titanium oscillator operating at 20 kHz with a maximum power output of 100 W was used for the ultrasonic irradiation. Scanning electron microscopy (SEM) images were obtained using a LEO instrument (Model 1455VP). Prior to taking images, the samples were coated by a very thin layer of Pt (BAL-TEC SCD 005 sputter coater) to make the sample surface conducting obtain better contrast and prevent charge accumulation.

Synthesis of Fe_2O_3 nanoparticles

Firstly $Fe(NO_3)_3$ $9H_2O$ was dissolved in 50 mL of water. Then ammonia solution was then slowly added to the mentioned solution (pH was adjusted about 10) under microwave radiation (600W , 30s On, 60s Off) for 4 minutes. The red-brown precipitate is then centrifuged and rinsed with distilled water. The product was calcined at 400ºC for 2h.

Synthesis of ZnO nanoparticles

$ZnSO_4$ was dissolved in 30 mL of water. Then ammonia solution was then slowly added to the mentioned solution (pH was adjusted about 8) under microwave radiation (600W , 20s On, 60s Off) for 2 minutes. The white product was then centrifuged and rinsed with distilled water.

RESULTS AND DISCUSSION

The XRD pattern of Fe_2O_3 nanoparticles is shown in Fig. 1 and is indexed as a Rhombohedra phase (space group: 1-42b). The experimental values are very close to the literature (JCPDS No. 13-0534).

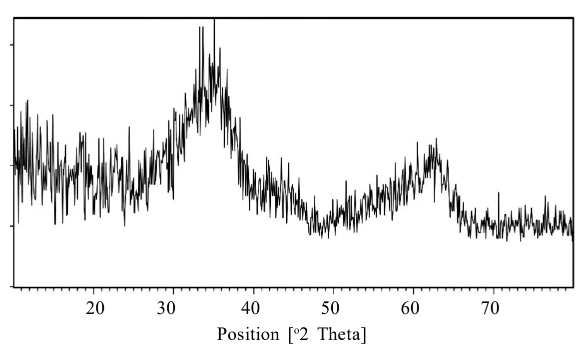

Fig. 1. XRD pattern of Fe_2O_3 nanoparticles

The XRD pattern of ZnO nanoparticles is shown in Fig. 2 and is indexed as a tetragonal phase (space group: P63mc). The experimental values are very close to the literature (JCPDS No. 79-0208) [30]. The crystallite size measurements were carried out using the Scherrer equation (Eq. 1),

$$Dc=0.9\lambda/\beta\cos\theta \quad (1)$$

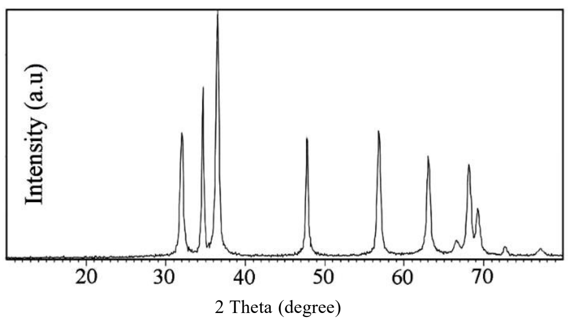

Fig. 2. XRD pattern of zinc oxide nanoparticles

Where β is the width at half maximum intensity of the observed diffraction peak, and λ is the X-ray wavelength (CuK_α radiation, 0.154 nm). The estimated crystallite size is about 24 nm.

Scanning electron microscopic images of Fe_2O_3 nanoparticles achieved at micro wave reaction are illustrated in Fig. 3. Nanoparticles with average diameter about 20 nm were synthesized.

Fig. 4 depicts SEM image of ZnO nanoparticles synthesized. The mono dispersed nanoparticles were observed and it seems nucleation stage overcomes to growth stage and smaller particles were synthesized [31-33]. Nanostructures were formed from nanoparticles with average particle size less than 50 nm.According to Simple Variance Analysis, a significant difference (P<0.01) was observed for grain yield by considering only simple effects of variety and iron treatments. As shown in Fig. 5 treatment V2 produced higher grain yield. For iron treatments F2 produced higher grain yield.

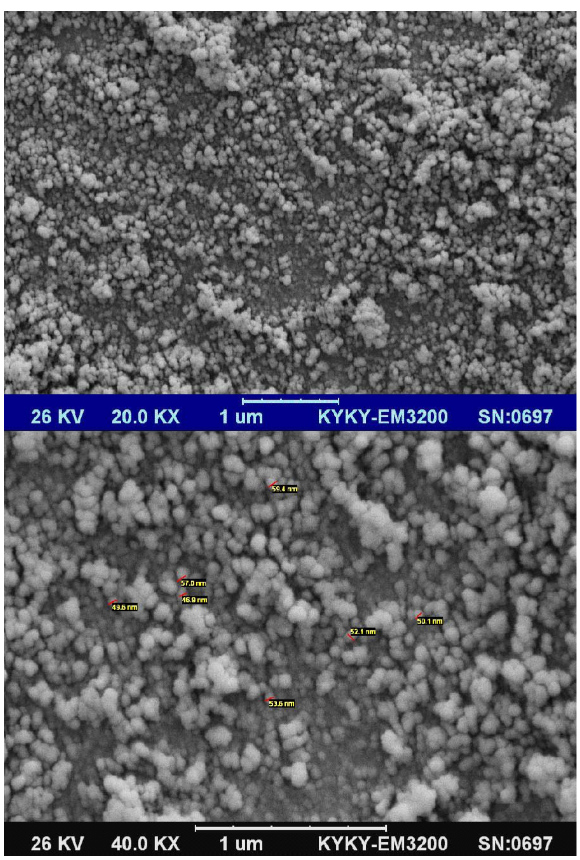

Fig. 3. SEM images of Fe_2O_3 nanoparticles

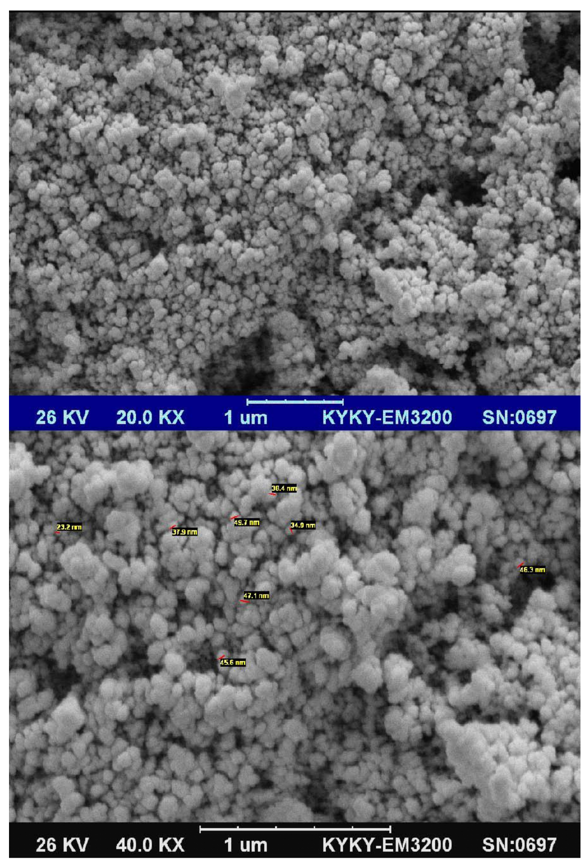

Fig. 4. SEM image of ZnO nanoparticles

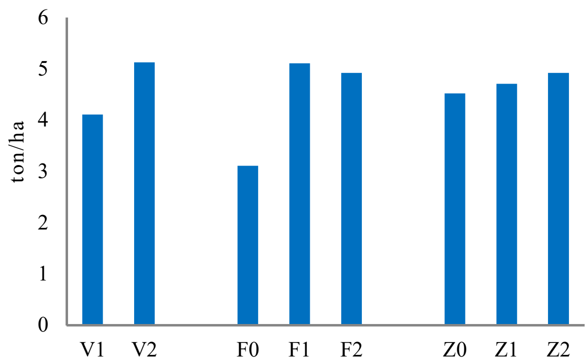

Fig. 5. Mean comparison of variety, Iron and Zinc simple effects on yield.

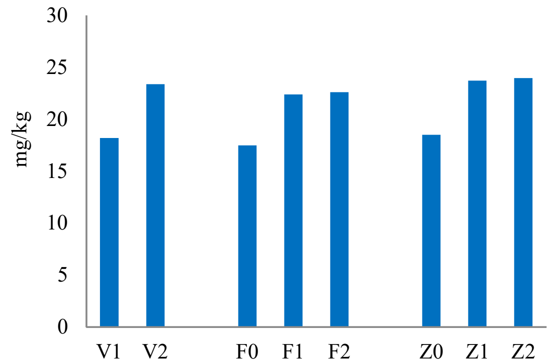

Fig. 7. Mean comparison of Variety, Iron and Zinc simple effects on Zn content

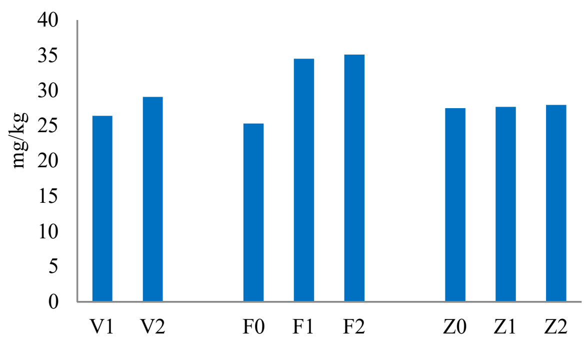

Fig. 6. Mean comparison of Variety, Iron and Zinc simple effects on Fe content

Application of micronutrients (Zn and Fe) might be due to their critical role in crop growth, involving in photosynthesis processes, respiration and other biochemical and physiological activates and thus their importance in achieving higher yields. Similar results were reported by [34-36]. Application of Zinc or Iron has been reported significant effects on growth measurements and chemical composition of wheat [34]. The reasons for differential response among crop varieties may be the genetic makeup of a variety which affects its capability to exploit soil nutrients [15]. Fageria and Rabelo (1987), Fageria et al. (2007), Nayyar et al. (1985), and Rengel and Romheld (2000) also reported an increase in wheat grain yields with Fe and Mn applications on coarse textured Fe and Mn deficient soils[16].

The result of Fe contain showed that only Fe treatment is very significant. The means comparison for simple effects of each factor is shown in Fig 6. The grain Fe concentration in Fe sulphate (F1) and Nano Fe_2o_3 (F2) was 34.5 mg/kg and 35.1 mg/kg, respectively (Fig. 7). This result demonstrated use of Fe as fertilizer had significant effects on Fe uptake.

Results indicated the significant effect of Variety, Iron and zinc on Zn content; the effect of iron was non-significant. Moreover, the interactions of Variaty × iron and zinc × iron significantly affected boron content (Fig. 7).

Significant responses of wheat varieties to Zn, Fe and Mn applications confirmed that the crop was suffering from latent deficiencies of these micronutrients and increase in grain yield with their application resulted from the increased availability of these nutrients to plants when fed through foliage in case of Fe and Mn and by basal application of Zn.

CONCLUSION

The results revealed that the magnitude of susceptibility to Fe and Zn deficiencies in different wheat varieties primarily depends on their capacity to utilize soil Fe and Zn. However, there is an inevitable need for Fe and Zn applications on severely deficient soils regardless of wheat variety. But on marginally Fe and Zn status soils, their fertilization is not advisable when efficient wheat varieties are cultivated.

From the previous results it could be concluded that: Fe and Zn application is necessary and important for Wheat plants grown on Fe and Zn deficient soils. Also our results shown the effect of Iron and Zinc nanoparticles on Wheat growth was significantly, also on Fe and Zn content. The advanced breeding lines analyzed from the Harvest Plus yield trial showed good processing quality characteristics and a significant enhancement in grain Zn and Fe concentrations.

The final releases of bio-fortified wheat varieties in the target regions will help improve the livelihoods and health of numerous resource-poor, micronutrient-deficient people, as well as offer new bio-fortified varieties acceptable by the whole wheat value chain.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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