

# Green Synthesis of Different Nanoparticles and its Effect on Irrigation Water and Soil Properties and Origanum Majorana Productivity

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## Research Article

**Keywords:** Nanotechnology, Agriculture, Water Treatment, Heavy Metals, Plant Productivity.

**Posted Date:** January 14th, 2022

**DOI:** <https://doi.org/10.21203/rs.3.rs-1230728/v1>

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## Abstract

The term of nanotechnology has emerged recently in several fields of interest that refers to the researches and innovations that are concerned with making materials on a very small size close to the scale of atoms and molecules. In the present work, the effects of green synthesis of different nanoparticles on the quality of irrigation water, the availability of some heavy metals content in soil and the plant, and the productivity of Marjoram were studied in detail. The obtained results showed that the addition of nanoparticles (NPs) materials has resulted in noticeable variations in the removal percentages of Cu and Fe from aqueous solution. The maximum values obtained for adsorption of Cu (II) on ZnO, MgO, and SiO<sub>2</sub> NPs, within pH (3–5) were 89.9%, 83.3%, and 68.36%, respectively. Whereas, the maximum adsorption values of Fe (III) at pH 3.3 were 82%, 80%, and 65% for ZnO, MgO, and SiO<sub>2</sub> NPs, respectively. It was clearly seen that the effective of NPs application on reduction of the available Cu in the studied soil samples. The order of sequence for the effects of NPs application was found to take the following order Zn<sub>2</sub> > Zn<sub>1</sub> > Mg<sub>2</sub> > Si<sub>2</sub> > Mg<sub>1</sub> > Si<sub>1</sub> > C (control). The highest values of the available Cu were observed in the control treatment, whereas the lowest values were obtained when Zn<sub>2</sub> was added, and the same tendency was observed with the substantial concentrations of Fe. The addition of NPs to the soil samples had positively affected the Cu uptake via plant. The effects of NPs and the additions of Cu and Fe on the availability of NPK in the soil system were very completed and osculated from one treatment to another. The same tendency was observed with the total concentration of NPK in the plant.

## 1. Introduction

The term of nanotechnology has emerged recently in several fields of interest that refers to the research and improvement that is interested with making materials on a very little size close to the scale of molecules and atoms. Generally, one nanometer is calculated as one billionth of meter which is considered approximately ten times in size diameter compared to the hydrogen atom. It was informed that at nanometre sizes the chemistry and physics regulations of materials are no extended be appropriate including reactivity, strength, color, and conductivity that will substantially differ among the dimension of nano and the large-scales [1, 2].

In the farming division, the nanotechnology has been exploited as a potential solution for reshaping farming construction which could be carried out via replacing traditional materials that is used for farming construction like pesticides, herbicides and fertilizers, with nano-permitted counterparts. Such nano scale-enabled counterparts have been informed on several agricultural practices including soil foliar applications, grain, and leafy plants [3]. Researchers are adopting green technologies for the preparation of different nanoparticles for medicinal uses in response to the increased demand for environmentally friendly nanoparticles [4]. Chemical synthesis processes such as chemical vapour deposition, micelle, sol-gel, chemical precipitation, pyrolysis, hydrothermal method, and others frequently result in the existence of poisonous chemical types adsorbed on the surface, which might have negative consequences in medical applications. Some reactions necessitate a high temperature and/or high pressure to start, while others necessitate an inert atmosphere and/or the use of toxic substances such as H<sub>2</sub>S, toxic template and stabilizer, and metallic precursors [5]. Chemicals utilized in the formation and stabilization of nanoparticles is hazardous and produce non-ecofriendly byproducts [6]. Biological processes including microbes and plants, as well as plant extracts, have been proposed as viable alternatives to chemical procedures for metal nanoparticles. Nanoparticles have been synthesised using a variety of biological systems, comprising bacteria, fungus, and yeast [7]. Microorganism-supported nanoparticle manufacturing entails a complex process involving cell culture maintenance, intracellular synthesis, and numerous purification processes. In this regard, because standard chemical procedures are costly and necessitate the utilize of chemical mix/organic solutions which act as plummeting agents, adopting "green" approaches in the manufacture of zinc oxide nanoparticles has develop into a growing area of interest [8]. There are several materials that have been utilized as fertilizer which are considered nanomaterials including nano-CaO, nano-urea, nano-hydroxiapatite (nano-HAP), Mg nanoparticles, and MgO nanoparticles. These supplies have been considered as the most widespread macronutrients reported for improving biomass construction and plant expansion. Researches that used nano-HAP and nano-Mg have reported an raising in seed yield production for Soybean (*Glycine max*) and Cowpea (*Vigna unguiculata*) [3]. The study of Liu and Lal, 2005 [9] reported an augment in the growth of Soybean vegetation (32.6%), and yield (20.4%) when soils were modified with nano-HAP (21.8 mg L<sup>-1</sup>), whereas when the vegetation were exposed to the same concentration of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> to provide the vegetation with the main source of phosphorous the obtained results were moderately small. The study presented by Aziz *et al.*, 2016 [10] shows that the synthesized of composites with different concentrations of NPK such as 50, 60, and 400 mg kg<sup>-1</sup> when compared to fertilizing with regular nutrients, that contained in the form of polymer (chitosan) has minimized the life cycle of nano-fertilized wheat plants. Wheat (*Triticum aestivum*) plants fertilized with chitosan nanoparticles containing the three major elements (NPK) via foliar application shortened the harvesting duration to 130 days after planting, compared to 170 days after planting if normal fertiliser containing NPK was used. Several scientists have described the benefits of engineered nanomaterials formulations that possessed pesticide properties [11, 12]. The study carried out by Chhipa, 2017 [12] shows that the pesticide properties that are contained silver nanoparticles within the major component have presented a noticeable influence against numerous fungi species. Whereas, when Cu NPs have been utilized, the efficiency of applications alongside bacteria and fungi has been remarkably improved. Other several materials like hezaconazole and nanosulfur have also presented high efficiency as fungicides. The only constraint of using such nanomaterials for the agricultural purpose as a pesticide is the ecological impacts that are considered not well understood yet [12]. Adisa *et al.*, 2019 [11] studied polymer-support nanopesticides such as nanogels, nanospheres, nanofibers, and nanocapsules have classified as antimicrobials materials that possessed different environmental persistence. In general, nanospheres can store the active component that is dispersed throughout the nanomatrix, however the active ingredient is encased in the polymeric matrix [11].

The water problem has recently become a global issue, and the water reuse scenario could be one of the alternatives for reducing the strain on already available water resources [13]. The reported causes of domesticated water reprocess were establish to be osculated from one region to another (e.g. 32 percent in Asia, 51 percent in northern Europe for environmental purposes, 46 percent in California for agriculture, 7 percent in Japan for agriculture, 44 percent in Florida, 25 percent in Tunisia, 4 percent in Australia for total consumption, 25 percent in Spain for agriculture and generally 500 Mm<sup>3</sup>/year of treated wastewaters used, 75 percent in Israel for agriculture and generally 500 Mm<sup>3</sup>/year of treated wastewaters used Mexico and China have also practised direct wastewater reuse without treatment [14–16]. Inorganic contaminants may accumulate in irrigation water or soils as a result of this.

The main aim of the present work is to study the effect of green synthesis of different nanoparticles on the quality of irrigation water, the availability of some heavy metals content in soil and plant, and the productivity of Marjoram.

## 2. Material And Methods

### 2.1. Materials

The materials that have been used for the green synthesis of different nanoparticles were lemon (*Citruslimon*) [17] peel extract mediated MgO, SiO<sub>2</sub>, and ZnO nanoparticles (NPs). The magnesium nitrate possessed high purity  $\geq 98\%$ , zinc sulfate possessed high purity  $\geq 98\%$ , and sodium metasilicate possessed high purity  $\geq 98\%$ . All materials were purchased from Merck chemicals Ltd, whereas fresh peels of lemons were collected from different lemons farms in Egypt. The fresh peels were first washed with distilled water and afterward soaked in ethanol (C<sub>2</sub>H<sub>5</sub>OH) and ammonium hydroxide solution (NH<sub>4</sub>OH) that was purchased from Merck Chemicals Co., Darmstadt, Germany.

#### 2.1.2. Preparation of MgO, SiO<sub>2</sub>, and ZnO NPs

The formation of MgO, SiO<sub>2</sub>, and ZnO NPs was carried out based on two main steps including 1) the formation of lemon (*Citruslimon*) peel extract, 2) synthesis of MgO, SiO<sub>2</sub>, and ZnO NPs.

##### 2.1.2.1. Preparation of lemon peel extract

The lemon peels (*Citrus limon*) were washed with distilled water several times to remove any dust that exist on the surface, afterward, the lemon peels were dried at 60°C inside a furnace and lasted for 48 h. The dried lemon peels were ground, crushed, and sieved into suitable size. Extraction of the lemon peels was made with a concentration of 250 g L<sup>-1</sup> at 25 °C for 24 h with steady shaking, afterward, the extract was filtered using filter paper.

##### 2.1.2.2. Synthesis of MgO, SiO<sub>2</sub>, and ZnO NPs

For preparing MgO, SiO<sub>2</sub>, and ZnO NPs, we have added 0.5 mol L<sup>-1</sup> of magnesium nitrate, sodium metasilicate, and zinc sulfate aqueous solutions to the lemon peel that has been separated previously from the extraction solution and then boiled to 70 °C. Afterward, the mixture solution was boiled for 1 h until being reduced into a white-colored solution. This color change is considered a remarkable of formation of soluble fractions from the peel extract. It was demonstrated that the ethanol lemon peel extract contains hesperidin flavanol that discharges aglycone that may be used as a reducing agent [18, 19]. The pH of each NPs mixture was adjusted via adding ammonium hydroxide solution 0.1 M mol L<sup>-1</sup> to maintain the following pH values 9.7, 11.58, and 6.95 for MgO, SiO<sub>2</sub>, and ZnO NPs, respectively. Afterward, the precipitates were washed several times with deionized water, centrifuged, and collected in a clayey crucible and heated in a muffle at 600°C for 3 h for both MgO, and ZnO NPs, whereas it was heated to 700°C for SiO<sub>2</sub> NPs formation. The elevating temperature in muffle was mandatory to vanish any organic residuals. Finally, a white precipitate for each NPs was obtained and packed carefully for further characterizations.

##### 2.1.2.3. Characterization of prepared nanoparticles

MgO, SiO<sub>2</sub>, and ZnO NPs were characterized using the following procedure. A powder of NPs was analyzed using X-ray diffraction spectrum (XRD) (PAN Analytical X'perttop Score plus Diffractometer) operated at 40 kV with a current of 30 mA under Cu-K $\alpha$  radiation of a 2 $\theta$  range of 10–80°. The surface morphology of nanoparticles was observed with an Elevated-Resolution Transmission Electron Microscopy (JEOL JEM-1400 UHR, operated at 80 KV). The chemical structures of the prepared NPs were investigated by (FTIR) Infrared Spectra (using Nicolet Avatar 230 Spectrometer).

## 2.2. Methods

### 2.2.1. Soil sampling and analysis

The soil samples were collected from a constant depth of 0-30 cm from El-Gabal El-Asfer area, Egypt. Some soil and water properties are listed in Table 1. The soil samples were air-dried, crushed, and sieved through a 2-mm sieve to ensure the removal of gravel and organic waste. The determination of soil texture was carried out via following the International Pipette Method. The other properties of soil samples including organic matter content, pH, and EC were carried out according to published literature [19–21]. The heavy metals content were determined using Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICAP 6500 Duo, Thermo Scientific, England). N, P and K were determined in acid digested solution, which was prepared according to [22]. Available nitrogen in soil samples was extracted by 2M potassium chloride solution and determined according to [23]. Available potassium and phosphorous were extracted by DTPA + ammonium bicarbonate solution and measurement according to the method described by Soltanpour [24].

Table 1  
Some physical and chemical properties of El-Gabal El-Asfer soil samples and irrigation water.

Soil properties	El-Gabal El-Asfer soil	Water properties	El-Gabal El-Asfer irrigation water
Particle size distribution (%)	80.30	pH	8.42
Sand (%)	7.90	EC(dS m <sup>-1</sup> )	1.57
Silt (%)	11.80		
Clay (%)			
Texture class	Loamy sand	Cation and anion (mg dm <sup>-3</sup> )	3.93
		Ca <sup>++</sup>	3.25
		Mg <sup>++</sup>	16.81
		Na <sup>+</sup>	0.36
		K <sup>+</sup>	
CaCO <sub>3</sub> (%)	9.78	HCO <sub>3</sub> <sup>-</sup>	8.03
OM (%)	2.81	CO <sub>3</sub> <sup>--</sup>	1.31
CEC (meq 100g <sup>-1</sup> )	20.70	Cl <sup>-</sup>	11.41
pH (1:2.5)	8.01	SO <sub>4</sub> <sup>--</sup>	3.60
EC (dS m <sup>-1</sup> )	2.78		
Total content of heavy metal (mg kg <sup>-1</sup> )	28742	Heavy metal (mg kg <sup>-1</sup> )	0.04
Fe	6.92	Fe	0.03
Cu		Cu	
Chemically extractable heavy metals (mg kg <sup>-1</sup> )	13.24	-	-
Fe	4.55	-	-
Cu			

## 2.2.2. Adsorption experiments

A series of experiments were carried out to investigate the effects of different levels of pH on the removal of Cu and Fe ions using MgO, SiO<sub>2</sub>, and ZnO nanoparticles as adsorbent material with an initial concentration of 50 mg L<sup>-1</sup> for both Cu and Fe. The solid to liquid ratio was 10 g L<sup>-1</sup>, however, the shaking rate was 175 rpm, and finally, temperature was adjusted to 25 °C. Solutions with different pH values were prepared and pH was adjusted by adding nitric acid 0.1 M mol. After the prevailing 24 h of adsorption, the concentrations of remaining Cu and Fe ions in each solution were detected via using Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICAP 6500 Duo, Thermo Scientific, England).

The adsorption isotherm of Cu and Fe ions was carried out via using the prepared NPs as adsorbents, in which a series of concentrations of Cu and Fe were prepared via dissolving copper sulfate and iron chloride with an initial concentration of copper and iron ranging from 20 to 500 mg L<sup>-1</sup>. The initial pH values for Cu and Fe solutions were 5.2 and 3.2, respectively. In general, 50 ml of each solution and 0.5 g of adsorbent were mixed in a 100 ml sealed conical flask that was shaken at a constant speed of 175 rpm in a thermostatic water bath at 25 °C. After 24 h of adsorption, the remaining Cu and Fe concentrations in each solution were determined.

## 2.2.3. Pot experiments

Pot experiments were carried out during the cropping season 2020–2021 to investigate the effect of the MgO, SiO<sub>2</sub>, and ZnO NPs on yield and the availability of some heavy metal contents in both soil and Marjoram (*Majorana Hortensis L.*) [25] that was polluted with three levels from either Fe or Cu. The Marjoram (*Majorana Hortensis L.*) was planted in the pots containing 18 kg soil after approximately 30 days from seed germination. The fertilizers doses were added to all treatments (as ammonium sulphate, calcium superphosphate, potassium sulphate, and biofertilizers). The experimental design was performed in factorial design with three replicates at three levels (0, 5, and 10 mg kg<sup>-1</sup>) of each pollutant (Fe and Cu) and (0, 150, and 300 mg kg<sup>-1</sup>) of each MgO, SiO<sub>2</sub>, and ZnO NPs. A sum of 35 treatments was performed after 30 and 60 days from the transplanting date (21 April and 23 May). The plants were irrigated twice a month with 55 cm<sup>3</sup> of each treatment. After 97 days from the planting, the Marjoram (*Majorana Hortensis L.*) plants were cut at the soil surface and washed with deionized water. The plants were oven-dried at 70 °C for 48 h, weighed for dry matter yield, and grounded. The plants and soil samples of different treatments were digested using H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> according to [26]. The heavy metals content was detected via using ICAP.

## 2.2.4. Statistical analysis

Data that was obtained in the present work has been statistically analyzed and the differences between means of different treatments were considered a significant when they were more than the values of the least significant differences (LSD) at the 5% level via using Statistix program version No. 9, in which all treatments were used in a factorial design.

### 3. Results And Discussion

#### 3.1 Characterizations of NPs

The XRD procedure is a widely used method for determining particle size and nanoparticle structure. The X-ray diffraction of different NPs produced with lemon peel extract is shown in Figure 1. The following is how Debye–equation Scherrer's was used to determine the dimension of MgO, SiO<sub>2</sub>, and ZnO NPs:

$$D = K\lambda / (\beta \cos\theta) \dots\dots\dots (1)$$

where D is the crystal volume;  $\lambda$  is the wavelength of the X-ray radiation ( $\lambda = 0.15406$  nm) for CuK $\alpha$ ; K is frequently taken as 0.9, and  $\beta$ ; is the line width at half-maximum height.

Peaks of MgO NPs matching to the plane (JCPDS card No.89–7102) and found at  $2\theta = 36.72^\circ$  (111),  $2\theta = 42.80^\circ$  (200),  $2\theta = 62.38^\circ$  (202),  $2\theta = 74.5^\circ$  (311),  $2\theta = 78.5^\circ$  (312). (222). MgO NPs produced with lemon peel extract were found to be crystallized face-centered cubed (fcc) phase of magnesium oxide, according to the XRD spectrum [27]. Using Scherrer's formula, the crystal size was predicted to be around 16.77 nm. SiO<sub>2</sub> NPs have been shown to have peaks that correspond to the planes  $2\theta = 28.4^\circ$  (040),  $2\theta = 31.5^\circ$  (200),  $2\theta = 36.06^\circ$  (130),  $2\theta = 48.4^\circ$  (330), and  $2\theta = 56.9^\circ$  (330) [28]. The XRD spectrum indicates that the SiO<sub>2</sub> NPs made from lemon peels were crystalline. Using Scherrer's formula, the crystal diameters calculated were around 42.6 nm. In addition, the patterns produced by ZnO NPs demonstrate. ZnO NP patterns also suggest that the planes were approximately  $2\theta = 31.8^\circ$  (100),  $2\theta = 34.4^\circ$  (100), (002)  $2\theta = 36.3^\circ$  (101),  $2\theta = 47.5^\circ$  (102)  $2\theta = 56.6^\circ$  (110),  $2\theta = 56.69^\circ$  (110),  $2\theta = 62.8^\circ$  (103),  $2\theta = 67.98^\circ$  (200), and  $2\theta = 69.1^\circ$  (200), (201). These findings are in line with those of other researchers who have shown ZnO diffractograms [10, 29]. As indicated in Figure. 1, no contaminant diffraction peaks were identified. These findings revealed that the produced ZnO was extremely pure. There was no usual graphitic carbon diffraction peaks found. Because graphitic carbon is amorphous in nature, its existence cannot be ruled out. The sample's highly crystalline nature is indicated by the crisp and high diffraction peaks [30]. High heat treatment is likely to provide sufficient kinetic energy for rearranging of atomic groupings and hence the development of nanoparticle crystal structure [31]. ZnO was synthesised in this process at a sufficiently high temperature of around 500°C, resulting in a crystalline structure product. Using Scherrer's formula, the crystallite size of the ZnO nanocrystallite was around 60.5 nm.

TEM images provide a more detailed insight of the interior structure of nanoparticles. Figure 2 shows a TEM image of MgO, SiO<sub>2</sub>, and ZnO nanoparticles generated by lemon peel extract. The circular structures are built of the unique individuals of distinct manufactured nanoparticles, according to the increased two-dimensional picture of the nanoparticles. Each produced nanoparticle has a size about less than 100 nm as measured by TEM imaging. This size corresponds to the size calculated from the XRD pattern. In order to determine the probable chemical bonds in the lemon peel extract and the produced nanoparticles, the FTIR technique was used. The FTIR spectra of MgO, SiO<sub>2</sub>, and ZnO nanoparticles, as well as lemon peel extract, are shown in Fig. 3. The spectrum of lemon peel extract had a strong peak in the area of 3200–3700 cm<sup>-1</sup>, which may be attributed to the stretching mode of the hydroxyl of phenolic, which also coincided with the N-H of the amines, which could be attributable to the various bioactive chemicals found in lemon [32, 33]. The symmetrical and asymmetrical C–H of the aliphatic groups has been assigned to two minor intensity peaks about 2925 cm<sup>-1</sup>. The bending vibration of the OH group was attributed to a wide broad peak about 1717 cm<sup>-1</sup>, which could be due to chemisorbed and/or physisorbed moisture. on the surface of nanoparticles [34]. The occurrence of C–O symmetric stretching of alcoholic and C–H vibrating of the –CH=CH of the ethylene structure can be seen in the bands at 1019 and 616 cm<sup>-1</sup>, respectively. When these peaks are compared to the spectra of MgO NPs, a decrease in peak position of MgO NPs is observed. Magnesium oxide NPs absorb at 450–850 cm<sup>-1</sup> in the FTIR spectrum. The O-H stretch shows as a very broad band in the spectra, spanning 3700 cm<sup>-1</sup>[35, 36]. The saturated main alcohol C=O was found to have an absorption peak at 1092 cm<sup>-1</sup>. The substituent of flavonoids is represented by the band seen at 1456 cm<sup>-1</sup>. Our FTIR research indicates that phenolic compounds in flavonoids have a higher affinity for metal, implying that phenolic groups may produce metal nanoparticles to avoid agglomeration and therefore stabilize a media. This shows that biological molecules may have a dual role in the formation and stabilization of magnesium oxide NPs in water [34].

Glycone steroids may have played a key role in the stabilization and capping of magnesium oxide nanoparticles in our research [19, 32, 33]. When these peaks are compared to the spectra of ZnO NPs, the peak broadening of ZnO NPs is reduced. The typical Zn-O stretching vibration of ZnO NPs causes a significant peak about 450 cm<sup>-1</sup> [37, 38]. Prior to the calcination of the intermediate product to ZnO nanoparticles, biomolecules were responsible for the conversion of ZnSO<sub>4</sub> to Zn(OH)<sub>2</sub>.

Figure 3 shows the FT-IR spectra of the produced SiO<sub>2</sub> nanoparticles. Si-O has a band around 790 cm<sup>-1</sup>, and the symmetric stretching and bending vibrations of Si-O-Si have bands around 477 and 619 cm<sup>-1</sup>[38]. Bending vibration occurs when oxygen moves at a perfect angle to the Si-Si bands in the Si-O-Si plane [39, 40]. The stretching vibration of the Si-O-Si band, wherein the bridging oxygen atom shifts parallel to the Si-Si lines in the reverse direction of their Si neighbors, corresponds to the band approximately 1072 cm<sup>-1</sup>. The 3555 cm<sup>-1</sup> linked to specific to Si-OH stretching mode that are hydrogen-bonded [40].

#### 3.2. Batch adsorption experiments

##### 3.2.1. Effect of initial pH on adsorption efficiency

The pH of any solution is considered one of the most important parameters that basically influence the adsorption of ions such as Cu and Fe that have been studied in the present work. To evaluate the effect of pH on the removal efficiency of Cu and Fe a set of experiments were performed in pH ranging between 1 to 5 mg kg<sup>-1</sup> and 1 to 3.5, respectively. The initial concentrations of either Cu or Fe were close to 100 mg L<sup>-1</sup> as is shown in Figure. 4. The pH values that exceed 5 mg kg<sup>-1</sup> and less than 3.5 for Cu and Fe ions did not study to avoid the natural phenomenon of Cu and Fe precipitation in hydroxide forms. It can be seen that the variations in the removal percentages with different pH values were approximately constant and maximum values were obtained within the pH ranging of 3–5 for Cu in which removal percentages 89.9%, 83.3%, and 68.36% were achieved for ZnO, MgO, and SiO<sub>2</sub> NPs, respectively. Whereas the removal percentages were 82%, 80%, and 65% for the adsorption of Fe on ZnO, MgO, and SiO<sub>2</sub> NPs, respectively at pH 3.3. In general, at the lower levels of pH it as noticed the reduction in adsorption percentages. This is may be because of the reduced number of a negative sites in addition to the competition between the positive copper, iron, and hydrogen ions on these negative adsorption sites [41]. By increasing the pH of the media, more adsorptive sites can be created and the adsorption capacity will be increased. However, with continued increases in pH values, the formation of a precipitate of Cu and Fe hydroxide will be increased. Accordingly, it was preferable to carry out adsorption experiments at pH value of 5.2 for Cu and 3.3 for Fe.

### 3.2.2. Adsorption isotherm models

An adsorption isotherm has been used to easily describe the adsorption of different fraction of sorbets molecules that are partitioned between liquid and solid phases at equilibrium. Generally, the adsorption of Cu and Fe ions on ZnO, MgO and SiO<sub>2</sub> NPs was modeled using two adsorption isotherms as follows:

#### 3.2.2.1. Freundlich isotherm

The Freundlich isotherm is a model that is used to represent monolayer (chemisorption) and multilayer (physisorption) adsorption, and it is founded on the supposition that the adsorbed molecules adsorbs onto the uneven surface of an adsorbent [42]. Freundlich's equation is written in linear form as follows:

$$\text{Log } q_e = \log k_F + 1/n \log C_e \dots\dots\dots (2)$$

The Freundlich isotherm coefficients K<sub>F</sub> and n are calculated first from intercept and slope of a chart of log q<sub>e</sub> vs log C<sub>e</sub> as shown in Fig. 5. In this investigation, n values greater than unity were discovered, indicating chemisorptions as shown in Table 2 [43]. L-type isotherms with n > 1 suggest a high affinity between the adsorbate and the adsorbent and are suggestive of chemisorption [44]. With increasing in temperature, the Freundlich constant (K<sub>F</sub>), showing that, the adsorption mechanism is endothermic.

Table 2  
Freundlich isotherm model parameters and correlation coefficients for the adsorption of Cu and Fe ions on ZnO, SiO<sub>2</sub>, and MgO NPs.

Freundlich isotherm model parameters										
Metal ions	Temperature	ZnO			SiO <sub>2</sub>			MgO		
		n	K <sub>F</sub>	R <sup>2</sup>	n	K <sub>F</sub>	R <sup>2</sup>	n	K <sub>F</sub>	R <sup>2</sup>
Cu <sup>2+</sup>	298	2.85	2.88	0.95	5.26	1.05	0.63	2.85	2.34	0.96
	313	3.35	8.12	0.94	2.00	1.13	0.96	2.94	6.45	0.88
	338	3.35	9.54	0.94	1.88	1.11	0.97	3.33	8.31	0.95
Fe <sup>3+</sup>	298	2.94	2.15	0.95	2.11	0.70	0.92	2.92	1.62	0.78
	313	1.88	2.42	0.96	1.74	1.10	0.99	2.08	2.51	0.90
	338	1.97	3.81	0.92	1.53	1.17	0.98	2.38	2.70	0.99

#### 3.2.2.2. Langmuir isotherm

The Langmuir isotherm assumes the adsorption of monolayer on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \dots\dots\dots (3)$$

where K<sub>L</sub> is the Langmuir constant related to the energy of adsorption and q<sub>max</sub> is the maximum adsorption capacity (mg g<sup>-1</sup>) [45]. The slope and intercept of plots of C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub>, at different temperatures, were used to calculate q<sub>max</sub> and K<sub>L</sub> as is shown in Fig. 6. Langmuir isotherm parameter fits for Cu and Fe adsorption on ZnO, MgO, and SiO<sub>2</sub> NPs and yielded isotherms that were in good agreement with observed behavior as presented in Table 3. The Cu and Fe adsorption capacities on ZnO, MgO, and SiO<sub>2</sub> NPs at room temperature (297 K) were found to be 135, 66, and 58 mg g<sup>-1</sup> for Cu<sup>2+</sup> and 104, 100, and 94 mg g<sup>-1</sup>,

respectively for Fe as shown in Table 3. This is much higher than the adsorption capacity of other adsorbents reported in other relevant literature in which the activated carbon reached  $3.37 \text{ mg g}^{-1}$ [46], whereas the adsorption of hematite reached  $4.94 \text{ mg g}^{-1}$ [47].

Table 3  
Langmuir isotherm model parameters and correlation coefficients for the adsorption of Cu and Fe on ZnO, SiO<sub>2</sub>, and MgO NPs.

Langmuir isotherm model parameters										
Metal ions	Temperature	ZnO			SiO <sub>2</sub>			MgO		
Cu		$q_{\max}$	$K_L$	$R^2$	$q_{\max}$	$K_L$	$R^2$	$q_{\max}$	$K_L$	$R^2$
		( $\text{mg g}^{-1}$ )	( $\text{Lmg}^{-1}$ )		( $\text{mg g}^{-1}$ )	( $\text{Lmg}^{-1}$ )		( $\text{mg g}^{-1}$ )	( $\text{Lmg}^{-1}$ )	
	298	135.13	9.54	0.98	58.82	2.00	0.94	66.22	0.01	0.94
	313	370.37	1.61	0.97	150.57	9.12	0.94	305.81	1.38	0.99
338	403.22	1.42	0.95	333.33	6.30	0.92	370.37	1.51	0.97	
Fe	298	104.16	4.50	0.98	93.45	5.10	0.98	100.00	12.02	0.99
	313	333.33	3.98	0.99	294.11	1.41	0.97	285.71	5.12	0.97
	338	454.54	2.63	0.94	416.66	3.60	0.92	666.66	3.34	0.92

### 3.3 Effect of NPs and Cu and Fe additives on the availability of Cu and Fe in soil and plant

#### 3.3.1 Effect of NPs and Cu additives on the available concentrations of Cu in soil and plant

Data listed in Table 4 shows the effects of Cu additives with two concentrations of  $5 \text{ mg kg}^{-1}$  and  $10 \text{ mg kg}^{-1}$ , respectively simultaneously with different treatments of NPs. It was clearly seen that the effect of NPs application on the availability of substantial concentrations of Cu without any pollutants additives resulted in a reduction of the available Cu in the studied soil samples. The order of sequence for the effects of NPs application was found to take the following order Zn2 > Zn1 > Mg2 > Si2 > Mg1 > Si1 > C (control). The highest values of the available Cu were observed in the control treatment, whereas the lowest values were obtained when Zn2 was added [48]. There was significant difference between all treatments except for the treatments of (Si2 and Mg2) and (Si1 and Mg1). When Cu was added to the soil as an external pollutant to increase the original exist values by  $5 \text{ mg kg}^{-1}$ , the effects of NPs application on the availability of Cu that was extracted via using DTPA were took the following order Zn2 > Zn1 > Si2 > Mg2 > Si1 > Mg1 > C (control). The highest value of the effects of adding NPs on the artificially polluted soils with Cu ( $5 \text{ mg kg}^{-1}$ ) was found when Zn2 was added to the soil, whereas the lowest effect was found when Mg1 was added[49]. There was a significant difference between all treatments except for the treatments of (Si2 and Mg2) and (Si1 and Mg1) similar to what was observed in control experiments. Increasing the values of original exist values of Cu by  $10 \text{ mg kg}^{-1}$  resulted in changing the order of effects of NPs to the following to take the following order Zn2 > Zn1 > Mg2 > Si2 > Mg1 > Si1 > C (control). There was a significant difference between all treatments except for the treatments of (Si2 and Mg1). It was clearly seen that the highest effect of reduction on available Cu in the three trials that were studied including control,  $5 \text{ mg kg}^{-1}$ , and  $10 \text{ mg kg}^{-1}$  was relevant to the additives of Zn2. The sum of values of means for each trial of NPs in the control experiment, an experiment carried out with the addition of  $5 \text{ mg kg}^{-1}$ , and an experiment carried out with the addition of  $10 \text{ mg kg}^{-1}$  have presented a significant differences among values except for (Si1 and Mg1). Data presented in Table 4 also explores the effects of NPs on Cu uptake via the plant that was osculated among the higher and lower values compared with the control experiments. The order of sequences for increasing Cu uptake via the plants without addition of Cu was found to take the following order Si1 > Zn2 > Si2 > Zn1 > Mg1 > C (control) > Mg2. There was a significant difference between all treatments except for the treatments of (Si2 and Zn2) and (C control and Mg1). When Cu was added to the soil at constant concentrations of  $5 \text{ mg kg}^{-1}$ , the order of sequence of NPs application was as follows; C (control) > Si1 > Si2 > Mg1 > Zn1 > Zn2 > Mg2 which indicates that the addition of NPs to the soil system had decreased Cu uptake via plant. There was a significant difference between all treatments except for the treatments of (Zn1, Si2, and Mg1). Increasing the additives of Cu pollutants to the soil by adding  $10 \text{ mg kg}^{-1}$  changed the sequence of effects of NPs to the following order C (control) > Mg1 > Mg2 > Zn2 > Si1 > Zn1 > Si2. There was a significant difference between all treatment except for the treatments of (Zn1, and Mg2). The application of NPs minimized the Cu levels in Marjoram because of the antagonistic impacts of metals the trend of these results agreed with those reported by Saifullah *et al.*, [50], Hussain *et al.*, [51], Wang *et al.*, [52].

Table 4  
Effect of NPs and Cu and Fe additives on the availability of Cu and Fe in soil and plant

Cu additives								
Nano Exp.	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean
	Cu-DTPA				Cu-plant			
C	4.60F	5.31E	9.37A	<b>6.42A</b>	6.89J	14.30E	17.69B	<b>12.96B</b>
Zn1	1.42I	2.45H	3.40G	<b>2.42E</b>	8.59I	13.34G	8.16I	<b>10.03E</b>
Zn2	0.42J	1.66I	1.58I	<b>1.22F</b>	11.11H	7.39J	14.96D	<b>11.16D</b>
Si1	3.55G	4.11F	8.37B	<b>5.34B</b>	35.71A	13.94EF	11.44H	<b>20.36A</b>
Si2	2.60H	3.37G	7.84C	<b>4.60C</b>	10.96H	13.54FG	2.49M	<b>9.00F</b>
Mg1	3.36G	4.53F	7.98BC	<b>5.29B</b>	7.01J	13.48FG	15.29D	<b>11.93C</b>
Mg2	2.57H	3.42G	6.47D	<b>4.16D</b>	5.31K	3.31L	16.21C	<b>8.28G</b>
<b>Mean</b>	<b>2.64C</b>	<b>3.55B</b>	<b>6.43A</b>		<b>12.23A</b>	<b>11.33B</b>	<b>12.32A</b>	
LSD at 5%	P=0.197	N= 0.301	P*N= 0.522		P= 0.220	N=0.336	P*N=0.582	
Fe additives								
Nano Exp.	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean
	Fe-DTPA				Fe-plant			
C	12.89G	20.43B	29.56A	<b>20.96A</b>	2087.0L	4404.8B	6277.8A	<b>4256.5A</b>
Zn1	8.61K	10.20J	9.177JK	<b>9.33E</b>	1664.5Q	1534.2S	4199.8D	<b>2466.2C</b>
Zn2	5.88L	8.45K	6.75L	<b>7.03F</b>	1629.8R	1779.1P	3025.9H	<b>2144.9G</b>
Si1	11.93GH	19.18BC	19.18BC	<b>16.93B</b>	19698L	3305.9F	4387.3C	<b>3221.0B</b>
Si2	12.88G	14.62F	14.62F	<b>15.23C</b>	2584.8J	1315.2T	2934.8I	<b>2278.3F</b>
Mg1	11.61GH	19.86B	19.86B	<b>15.88C</b>	1899.8M	1863.9O	3347.7E	<b>2370.5E</b>
Mg2	10.64HI	17.29DE	17.29DE	<b>14.16D</b>	24955K	1534.8S	3164.8G	<b>2398.4D</b>
<b>Mean</b>	<b>10.63C</b>	<b>16.71A</b>	<b>16.71A</b>		<b>2047.3C</b>	<b>2248.3B</b>	<b>3905.4A</b>	
LSD at 5%	P=0.520	N=0.794	P*N=1.376		P=0.8067	N=1.232	P*N=2.134	

### 3.3.2 Effect of NPs and Fe additives on the available concentrations of Fe in soil and plant

The effects of Fe additives as two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> with different treatment of NPs are listed in Table 4. It was clearly seen that the effect of NPs application on the availability of substantial concentrations of Fe without any pollutants additives resulted in the reduction of the available Fe in the soil samples. The order of sequence for the effects of NPs application on reduction of the available Fe was found to take the following sequence Zn2 > Zn1 > Mg2 > Mg1 > Si1 > Si2 > C (control)[48]. The highest values of the available Fe were observed in the control, whereas the lowest values were obtained when Zn2 was added. There was a significant difference between all treatments except for the treatments of (Si1 and Mg1). When Fe was added to the soil as an external source of pollutants to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs additions on the availability of Fe that was extracted via using DTPA were found to take the following order Zn2 > Zn1 > Si2 > Mg2 > Si1 > Mg1 > C (control) that is considered similar to what was observed with the same treatment of Cu. The highest values of the effects of NPs addition on the artificially polluted soils with Fe (5 mg kg<sup>-1</sup>) were found when Zn2 was added to the soil, whereas the lowest effects were found when Mg1 was added. There was a significant difference between all treatments except for the treatments of Mg1 and control. Increasing the values of polluted Fe to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs to the following order Zn2 > Zn1 > Si2 > Mg2 > Si1 > Mg1 > C (control). There was a significant difference between all treatments. It was clearly seen that the highest effect in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> was relevant to the additives of Zn2[49, 53]. Data presented in Table 4 also explores the effects of NPs on Fe uptake via the plants that were osculated among the higher and lower values compared with the control experiments. The order of sequences of NPs for increasing Fe uptake via the plants was found to take the following order Si2 > Mg2 > C (control) > Si1 > Mg2 > Zn1 > Zn2. There was a significant difference between all treatments except for the treatments of (control and Si1). When Fe was added to the soil at constant concentrations of 5 mg kg<sup>-1</sup>, the order of sequence of NPs application was as follows; C (control) > Si1 > Mg1 > Zn2 > Mg2 > Zn1 > Si2 that indicates that the addition of NPs to the soil system had positive effects of the Cu uptake via the plant. There was a significant difference between all treatments except for the treatments of (Mg2 and Zn1). Increasing the additives of Fe pollutants to the soil via adding 10 mg kg<sup>-1</sup> changed the sequence of effects of NPs on increasing Fe concentrations inside the plant tissue to the following order C (control) > Si1 > Zn1 > Mg1 > Mg2 > Zn2 > Si2[49, 53]. There was a significant difference between all treatments. At the root surface, NPs can compete with Fe as both the metals are being transported by common transporters in the roots [54]. The higher Zn concentrations in the roots may inhibit the Fe uptake by Marjoram plants. The trend of these results agreed with those reported by Ali *et al.*, [55] who suggested that the improved Zn nutritional status with the foliar applied ZnO NPs may suppress the expression of Zn transporters in roots, decreasing the Cd



accumulation by roots. This variation in metal accumulation by plants under NP treatments might be due to variation in size and shape of NPs as well as crop species and mode of application of NPs.

## Effect of Cu, Fe additives and NPs treatment on the availability and accumulation of N, P, and K in the treated soils and plants

### 3.3.3 Effect of Cu additives and NPs treatment on the availability of N, P, and K in soils

The effects of Cu additives with two concentrations of  $5 \text{ mg kg}^{-1}$  and  $10 \text{ mg kg}^{-1}$  simultaneously with different treatment of NPs are listed in Table 5. It was clearly seen that the effects of NPs application on the availability of substantial concentrations of N without any pollutants additives resulted in an oscillating in the reduction or increment of the available N in the soil system. The order of sequence for the effects of NPs application on reducing available N was found to take the following sequence  $\text{Mg2} > \text{Mg1} > \text{C (control)} > \text{Si2} > \text{Zn2} > \text{Zn1} > \text{Si1}$ . The highest values that were affected the reduction of the available N were observed with Mg2, whereas the lowest values were obtained when Si1 was added. There was a significant difference between all treatments except for the treatments of (control and Mg1) [49, 53]. When Cu was added to the soil as an external pollutant to increase the original exit values by  $5 \text{ mg kg}^{-1}$ , the effects of NPs application on the availability of N were found to take the following order  $\text{Mg2} > \text{Zn2} > \text{Si2} > \text{Si1} > \text{Mg2} > \text{Si2} > \text{C (control)} > \text{Zn1}$ . The highest value of the effects of adding NPs on the artificially polluted soils with Cu ( $5 \text{ mg kg}^{-1}$ ) to reduce the availability of N was found when Mg2 was added to the soil, whereas the lowest effect was found when Zn1 was added. There was a significant difference between all treatments except for the treatments of (control and Si2) and (Z2 and Si1). Increasing the values of polluted Cu to  $10 \text{ mg kg}^{-1}$  resulted in changing the order of effects of NPs on the availability of N to the following order  $\text{Si2} > \text{Mg1} = \text{Mg2} = \text{Si1} = \text{Zn2} > \text{C (control)} > \text{Zn1}$ . There was a significant difference between all treatments except for the following treatments Mg1, Mg2, Si1, and Zn2. It was clearly seen that the highest effects in the three trials that were studied in the present work including control,  $5 \text{ mg kg}^{-1}$ , and  $10 \text{ mg kg}^{-1}$  were oscillated among Mg2 and Si2. The effects of Cu additives as two concentrations of  $5 \text{ mg kg}^{-1}$  and  $10 \text{ mg kg}^{-1}$  simultaneously with different treatment of NPs on available phosphorous (P) are listed in Table 5. It was clearly seen that the effect of NPs application on the availability of substantial concentrations of P without any pollutants additives resulted in an oscillating of the reduction or increment of the available P in the soil system. The order of sequence for the effects of NPs application on reducing available P was found to take the following sequence  $\text{Zn2} > \text{C (control)} > \text{Mg2} > \text{Mg1} > \text{Zn1} > \text{Si1} > \text{Si2}$ . The highest values that affected the reduction of the available P were observed with Zn2, whereas the lowest values were obtained when Si2 was added. There was a significant difference between all treatments except for the treatments of (control and Zn2). When Cu was added to the soil as an external pollutant to increase the original exit values by  $5 \text{ mg kg}^{-1}$ , the effects of NPs application on reducing the availability of P was found to take the following order  $\text{Mg2} > \text{Si2} > \text{Mg1} > \text{Zn1} > \text{C (control)} > \text{Si1} > \text{Zn2}$ , [49, 53]. The highest value of the effects of adding NPs on the artificially polluted soils with Cu ( $5 \text{ mg kg}^{-1}$ ) to reduce the availability of P was found when Mg2 was added to the soil, whereas the lowest effect was found when Zn2 was added. There was a significant difference between all treatments except for the treatments of (Si2 and Mg2). Increasing the values of an external pollution of Cu to  $10 \text{ mg kg}^{-1}$  resulted in changing the order of effects of NPs on the availability of P to the following order  $\text{C (control)} > \text{Zn1} > \text{Mg2} > \text{Si1} = \text{Si2} > \text{Mg1} > \text{Zn2}$ . There was a significant difference between all treatments except for the following treatments (Si1 and Si2). It was clearly seen that the highest effects in the three trials that were studied in the present work including control,  $5 \text{ mg kg}^{-1}$ , and  $10 \text{ mg kg}^{-1}$  were oscillated among Zn2, Mg2, and control. The effects of Cu additives with two concentrations of  $5 \text{ mg kg}^{-1}$  and  $10 \text{ mg kg}^{-1}$  simultaneously with different treatment of NPs on the availability of K are also listed in Table 5. It was clearly seen that the effect of NPs application on the availability of substantial concentrations of K without any pollutants additives resulted in an oscillation in the reduction or increment of the available concentrations of available K in the soil system. The order of sequence for the effects of NPs application on reducing the available concentrations of K was found to take the following sequence  $\text{Mg2} > \text{Si2} > \text{Mg1} > \text{C (control)} > \text{Si1} > \text{Zn1} > \text{Zn2}$ . The highest values affected the reduction of the available K were observed with Mg2, whereas the lowest value was obtained when Zn2 was added. There was a significant difference between all treatments except for the treatments of (Si2 and Mg1). When Cu was added to the soil as an external pollutant to increase the original exit values by  $5 \text{ mg kg}^{-1}$ , the effects of NPs application on the availability of K were found to take the following order  $\text{Si1} > \text{Mg1} > \text{Zn2} > \text{C (control)} > \text{Mg2} > \text{Zn1} > \text{Si2}$ . The highest value of the effect of adding NPs on the artificially polluted soils with Cu ( $5 \text{ mg kg}^{-1}$ ) to reduce the availability of K was found when Si1 was added to the soil, whereas the lowest effect was found when Si2 was added. Generally, there was a significant difference between all treatments. Increasing the values of an external polluted Cu to  $10 \text{ mg kg}^{-1}$  resulted in changing the order of effects of NPs on the availability of K to the following order  $\text{Si2} > \text{Si1} > \text{Mg2} > \text{Zn2} > \text{Mg1} = \text{Zn1} > \text{C (control)}$ . There was a significant difference between all treatments. It was clearly seen that the highest effects in the three trials that were studied in the present work including control,  $5 \text{ mg kg}^{-1}$ , and  $10 \text{ mg kg}^{-1}$  on K availability were oscillated among Mg2, Si1, and Si2. On the other hand, the lowest effects were attributed to the Zn2 in the control experiment, whereas in the experiments that have been carried out with the addition of Cu ( $5 \text{ mg kg}^{-1}$  and  $10 \text{ mg kg}^{-1}$ ), the effects of Si2 and control were more dominant. The highest values of available K were found with the control experiment followed by the experiments that were carried out with the addition of an external Cu with concentrations of  $5 \text{ mg kg}^{-1}$  and  $10 \text{ mg kg}^{-1}$ , respectively.

Table 5  
Effect of Cu and Fe additives and NPs treatment on the availability and accumulation of N, P, and K in the treated soils

Cu additives												
Nano Exp.	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	
	N				P				K			
C	50.73G	121.80C	84.60E	<b>85.71D</b>	25.11G	29.00D	15.52J	<b>23.21D</b>	140.80F	133.74F	178.90D	
Zn1	135.33B	135.33B	135.33B	<b>135.33A</b>	28.85D	22.23H	17.06I	<b>22.72D</b>	188.27C	209.32B	119.60G	
Zn2	118.40C	84.60E	67.67F	<b>90.22C</b>	24.78G	32.56AB	32.29AB	<b>29.88A</b>	203.20B	107.91IJ	116.30GH	
Si1	203.00A	88.00E	67.67F	<b>119.56B</b>	31.61BC	30.81C	26.74E	<b>29.72A</b>	149.80E	87.82K	58.90L	
Si2	88.00E	118.40C	50.73G	<b>85.71D</b>	33.09A	14.10K	26.74E	<b>24.64B</b>	114.03GHI	221.75A	40.97M	
Mg1	50.73G	50.73G	67.67F	<b>56.38E</b>	26.47EF	16.26IJ	28.97D	<b>23.90C</b>	115.17GHI	102.75J	119.60G	
Mg2	10.53D	101.53D	67.67F	<b>90.24C</b>	25.64FG	13.71K	26.50EF	<b>21.95E</b>	109.07HIJ	155.74E	109.63HIJ	
Mean	<b>106.82A</b>	<b>100.06B</b>	<b>77.33C</b>		<b>27.93B</b>	<b>22.67C</b>	<b>24.83B</b>		<b>145.76A</b>	<b>145.58A</b>	<b>106.27B</b>	
LSD at 5%	P=2.5823	N=3.9446	P*N=6.8322		P=0.3989	N=0.6093	P*N=1.0554		P=3.1479	N=4.8085	P*N=8.3287	
Fe additives												
Nano Exp.	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	
	N				P				K			
C	50.73G	101.50D	84.60E	<b>78.94E</b>	25.11F	29.09C	18.08G	<b>24.09A</b>	140.80IJ	145.60HI	150.37GH	
Zn1	135.33B	118.40C	67.67F	<b>107.13C</b>	28.85C	26.94D	16.38H	<b>24.06A</b>	188.27D	179.09E	197.83BC	
Zn2	118.40C	67.67F	84.58E	<b>90.22D</b>	24.78F	15.49H	16.32H	<b>18.86C</b>	203.20AB	135.27J	168.57F	
Si1	203.00A	101.53D	50.73G	<b>118.42A</b>	31.61B	13.71JK	8.87L	<b>18.06D</b>	149.80H	201.67B	207.60A	
Si2	88.00E	84.60E	67.67F	<b>80.09E</b>	33.09A	15.28HI	16.23H	<b>21.53B</b>	114.03KL	140.23IJ	199.94B	
Mg1	50.73G	101.53D	84.60E	<b>78.96E</b>	26.47DE	14.19IJ	12.61K	<b>17.76D</b>	115.17K	194.03C	198.22BC	
Mg2	101.53D	101.50D	135.33B	<b>112.79B</b>	25.64EF	13.62JK	16.08H	<b>18.45CD</b>	109.07L	155.93G	173.70EF	
Mean	<b>106.82A</b>	<b>96.68B</b>	<b>82.17C</b>		<b>27.93A</b>	<b>18.33B</b>	<b>14.94C</b>		<b>145.76C</b>	<b>164.55B</b>	<b>185.18A</b>	
LSD at 5%	P=2.3657	N=3.6137	P*N=6.2591		P=0.4541	N=0.6937	P*N=1.2014		P=2.1487	N=3.2822	P*N=5.6849	

### 3.3.4 Effect of Fe additives and NPs treatment on the availability of N, P, and K in the treated soils

The effects of Fe additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> simultaneously with different treatment of NPs are listed in Table 6. It was clearly seen that the effect of NPs application on the availability of substantial concentrations of N without any an external Fe additives resulted in an oscillating in the reduction or increment of the available N in the soil system. The order of sequence for the effects of NPs application on reducing the available N was found to take the following sequence C (control) = Mg1 > Si1 > Mg2 > Zn2 > Zn1 > Si1. The highest values that affected the reduction of the available N were observed with both control and Mg1, whereas the lowest values were obtained when Si1 was added. There was a significant difference between all treatments except for the treatments of (control and Mg1). When Fe was added to the soil as an external pollutant to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the reduction of available N were found to take the following order Zn2 > Si2 > Mg2= C (control) > Si1= Mg1 > Zn1. The highest value of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg<sup>-1</sup>) to reduce the availability of N was found when Zn2 was added to the soil, whereas the lowest effect was found when Zn1 was added. There was a significant difference between all treatments except for the treatments of (control, Si1, Mg1, and Mg2), [49, 53]. Increasing the values of an external addition of Fe to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on reducing the availability of N to the following order Si1 > Zn1 = Si2 = Zn2 > C (control) > Mg1 > Mg2. There was a significant difference between all treatments except for the following treatments (control and Zn2), (Zn2 and Mg1), and (Zn1 and Si2). It was clearly seen that the highest effect in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> was oscillated among Mg1, control, Zn2, and Si1. On the other hand, the lowest effects were attributed to the Si1 in the control experiment, whereas in the experiments that have been carried out with the addition of Fe with concentrations of 5 mg kg<sup>-1</sup> 10 mg kg<sup>-1</sup>, the effects of Zn1 and Mg2 were more dominant. The highest values of available N were found with the control experiment followed by experiments that were carried out with the addition of Fe at concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup>. The effects of Fe additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> with different treatment of NPs on the reduction of available P are listed in Table 6. It was clearly seen that the effect of NPs application on the availability of substantial concentrations of P in soil without any pollutants additives resulted in an oscillating in the reduction or increment values of the available P in the soil system. The order of sequence for the effects of NPs application on reducing the

available P was found to take the following sequence Zn2 > C (control) > Mg2 > Mg1 > Zn1 > Si1 > Si2. The highest values affected the reduction of the available P were observed with Zn2, whereas the lowest values were obtained when Si2 was added. There was a significant difference between all treatments [53]. When Fe was added to the soil as an external pollutant to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the availability of P were found to take the following order Mg2 > Si2 > Mg1 > Si2 > Zn2 > Zn1 > C (control). The highest value of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg<sup>-1</sup>) to reduce the availability of P was found when Mg2 was added to the soil, whereas the lowest effect was found when Zn1 was added. There was a significant difference between all treatments except for the treatments of (Si1 and Mg2). Increasing the values of an external addition of Fe to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on the availability of P to the following order Si1 > Mg1 > Mg2 > Si2 > Zn2 > Zn1 > C (control). There was a significant difference between all treatments except for the following treatments (Zn1, Zn2, Si2, and Mg2).

Table 6  
Effect of Cu and Fe additives and NPs treatment on the availability and accumulation of N, P, and K in plant.

Nano Exp.	Cu additives											
	C				5 mg kg <sup>-1</sup>				10 mg kg <sup>-1</sup>			
	N	P	K	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	
C	2.783E	3.750C	3.750C	<b>3.428B</b>	0.236DE	0.213GH	0.155K	<b>0.201D</b>	1.003EF	0.903HI	1.100D	
Zn1	1.453G	2.900E	3.146D	<b>2.500G</b>	0.227EF	0.250B	0.178J	<b>0.218B</b>	0.320L	1.377 C	1.077 D	
Zn2	3.266D	2.783E	3.266D	<b>3.106C</b>	0.215GH	0.196I	0.065P	<b>0.159F</b>	1.673 B	1.367 C	0.983EFG	
Si1	2.056F	2.173F	3.866BC	<b>2.699F</b>	0.271A	0.206H	0.220FG	<b>0.238A</b>	0.817J	1.043 DE	0.907 HI	
Si2	2.880E	3.866BC	4.233A	<b>3.660A</b>	0.246BC	0.240CD	0.134MN	<b>0.206C</b>	0.850IJ	1.8500 A	0.970FG	
Mg1	2.173F	3.146D	3.266D	<b>2.862E</b>	0.245BC	0.140LM	0.127N	<b>0.171E</b>	0.990 EFG	0.827 J	0.950FGH	
Mg2	3.993B	2.900E	2.173F	<b>3.022D</b>	0.142LM	0.143L	0.113O	<b>0.133G</b>	0.937 GH	1.070D	0.743K	
Mean	<b>2.658C</b>	<b>3.074B</b>	<b>3.386A</b>		<b>0.226A</b>	<b>0.198B</b>	<b>0.142C</b>		<b>0.941B</b>	<b>1.205 A</b>	<b>0.961B</b>	
LSD at 5%	P=0.0496	N=0.0758	P*N=0.1313		P=0.0033	N=.00508	P*N=0.0088		P=0.0233	N=0.0356	P*N=0.0616	
Nano Exp.	Fe additives											
	C				5 mg kg <sup>-1</sup>				10 mg kg <sup>-1</sup>			
	N	P	K	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	
C	2.783EF	3.506B	3.146D	<b>3.145A</b>	0.236C	0.147J	0.174H	<b>0.186c</b>	1.003E	0.630HIJ	0.643HI	
Zn1	1.453I	2.900E	2.783EF	<b>2.379D</b>	0.227D	0.142J	0.265A	<b>0.212A</b>	0.320M	2.350A	0.560IJ	
Zn2	3.266CD	2.660FG	2.056H	<b>2.661C</b>	0.215E	0.162I	0.216E	<b>0.197B</b>	1.673B	0.830G	0.666H	
Si1	2.056H	3.866A	0.606J	<b>2.177E</b>	0.271A	0.188G	0.077K	<b>0.178D</b>	0.816G	1.260D	0.450KL	
Si2	2.880E	3.266CD	2.513G	<b>2.887B</b>	0.246B	0.203F	0.190G	<b>0.213A</b>	0.850FG	0.536JK	0.846FG	
Mg1	2.173H	3.386BC	2.900E	<b>2.820B</b>	0.245B	0.163I	0.232CD	<b>0.213A</b>	0.990E	0.606HIJ	0.363LM	
Mg2	3.993A	2.660FG	0.363K	<b>2.338D</b>	0.142J	0.170HI	0.077K	<b>0.129E</b>	0.936EF	1.526C	0.203N	
Mean	<b>2.658B</b>	<b>3.178A</b>	<b>2.053C</b>		<b>0.226A</b>	<b>0.168C</b>	<b>0.176B</b>		<b>0.941B</b>	<b>1.105A</b>	<b>0.533C</b>	
LSD at 5%	P=0.0632	N=0.0965	P*N=0.1671		P=0.0032	N=0.0049	P*N=0.0086		P=0.0358	N=0.0547	P*N=0.0947	

It was clearly seen that the highest effect in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> was observed among Zn2, Mg2, and Si1. The effects of Fe additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> simultaneously with different treatment of NPs on the reduction of available K are listed in Table 6. It was clearly seen that the effect of NPs application on the availability of substantial concentrations of K in soil without any pollutants additives resulted in an oscillating in the reduction or increment of the available concentrations of K in the soil system. The order of sequence for the effects of NPs application on reducing the available concentrations of K was found to take the following sequence Mg2 > Si2 > Mg1 > C (control) > Zn1 > Si1 > Zn2. The highest values affected the reduction of available K were observed with Mg2, whereas the lowest values were obtained when Zn2 was added [49, 53]. There was a significant difference between all treatments. When Fe was added to the soil as an external pollutant to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the availability of K was found to take the following order Zn2 > Si2 > C (control) > Mg2 >

Zn1 > Mg1 > Si1. The highest value of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg<sup>-1</sup>) to reduce the availability of K was found when Zn2 was added to the soil, whereas the lowest effect was found when Si1 was added. There was a significant difference between all treatments except for (Mg1 and Mg2). Increasing the values of an external addition of Fe to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on the availability of K to the following order C (control) > Zn2 > Mg2 > Zn1 > Mg1 > Si2 > Si1. There was a significant difference between all treatments except for (Z1 and Mg1), [53]. It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> on K availability were osculated among Mg2, Zn2, and control.

### 3.3.5 Effect of Cu additives and NPs treatment on the accumulation of N, P, and K in the plant

The effects of Cu additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> simultaneously with different treatment of NPs on increasing the total amounts of N in the plant are listed in Table 6. It was clearly seen that the effect of NPs application on increasing the total concentrations of N without any Cu additives resulted in an osculation in the reduction or increment of N in the plant,[53]. The order of sequence for the effects of NPs application on the increasing the total N was found to take the following sequence Mg2 > Zn2 > Si2 > Si1 > C (control) > Zn2 > Zn1 > Si1. The highest values affected the increases of the available N in the plant were observed with Mg2, whereas the lowest values were obtained when Si1 was added. There was a significant difference between all treatments except for the treatments of (control and Si2) and (Si1 and Mg1). When Cu was added to the soil as an external pollutant to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the increment of total N were found to take the following order Si2 > C (control) > Mg1 > Zn1 = Mg2 > Zn2 > Si1. The highest value of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg<sup>-1</sup>) to increase the total concentrations of N in the plant was found when Si2 was added to the soil, whereas the lowest effect was found when Si1 was added,[53]. There was a significant difference between all treatments except for the treatments of (control and Si2) and (Z1 and Mg2). Increasing the values of an external addition of Cu to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on increase the total concentrations of N in the plant to the following order Si2 > Si1 > C (control) > Zn2 = Mg1 > Zn1 > Mg2. There was a significant difference between all treatments except for the following treatments (control and Si1) and (Zn1, Zn2, and Mg1). It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> were osculated among Mg2, Si2, and Si2, respectively. The effects of Cu additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> simultaneously with different treatment of NPs on increasing the total amounts of P in the plant are listed in Table 6. It was clearly seen that the effect of NPs application on increasing the total concentrations of P without any pollutants additives resulted in an osculating in the reduction or increment of P in the plant. The order of sequence for the effects of NPs application on the increasing the total P was found to take the following sequence Si1 > Si2 > Mg1 > C (control) > Zn1 > Zn2 > Mg2. The highest values affected the increases of the available P were observed with Si1, whereas the lowest values were obtained when Mg2 was added. There was a significant difference between all treatment except for the treatments of (Si2 and Mg1). When Cu was added to the soil as a pollutant to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the increment of total P were found to take the following order Zn1 > Si2 > C (control) > Si1 > Zn2 > Mg2 > Mg1, [53]. The highest value of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg<sup>-1</sup>) to increase the total concentrations of P in the plant was found when Zn1 was added to the soil, whereas the lowest effect was found when Mg1 was added. There was a significant difference between all treatments. Increasing the values of an external addition of Cu to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on increase the total concentrations of P in the plant to the following order Si1 > Zn1 > C (control) > Si2 > Mg1 > Mg2 > Zn2. There was a significant difference between all treatments. It was clearly seen that the highest effects in the three trials that were studied in the present work including the control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> were osculated among Si1, Zn1, and Si1, respectively. The effects of Cu additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> simultaneous with different treatments of NPs on increasing the total amounts of K in the plant are listed in Table 6. It was clearly seen that the effect of NPs applications on increasing the total concentrations of K without any Cu additives were resulted in an osculating in the reduction or increment of total K in the plant. The order of sequence for the effects of NPs application on increasing the total K was found to take the following sequence Zn2 > C (control) > Mg1 > Mg2 > Si2 > Si1 > Zn1. The highest values affected the increases of the total N were observed with Zn2, whereas the lowest values were obtained when Zn1 was added. There was a significant difference between all treatments. When Cu was added to the soil as an external pollutant to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the increment of total K were found to take the following order Si2 > Zn1 > Zn2 > Mg2 > Si1 > C (control) > Mg1. The highest values of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg<sup>-1</sup>) to increase the total concentrations of K in the plant were found when Si2 was added to the soil, whereas the lowest effect was found when Mg1 was added. There was a significant difference between all treatments except for the treatments of (Z1 and Zn2). Increasing the values of Cu to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on increase the total concentrations of K in the plant to the following order C (control) > Zn1 > Zn2 > Si2 > Mg1 > Si1 > Mg2[49, 53]. There was a significant difference between all treatments except for the following treatments (control and Zn1). It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> were osculated among Zn2, Si2, and control, respectively.

### 3.3.6 Effect of Fe additives and NPs treatment on the accumulation of N, P, and K in the plant

The effects of Fe additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> simultaneously with different treatment of NPs on increasing the total amounts of N in the plant are listed in Table 6. It was clearly seen that the effect of NPs application on increasing the total concentrations of N without any pollutants additives resulted in an osculating in the reduction or increment of N in the plant. The order of sequence for the effects of NPs application on the increasing the total N was found to take the following sequence Mg2 > Zn2 > Si2 > C (control) > Mg1 > Si1 > Zn1. The highest values affected the increases of the total N were observed with Mg2, whereas the lowest values were obtained when Zn1 was added. There was a significant difference between all treatment except for the treatments of (Si1 and Mg1). When Fe was added to the soil as an external addition to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the increment of total N were found to take the following order Si1 > C (control) > Mg1 > Si1 > Zn1 > Zn2 = Mg2. The highest value of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg<sup>-1</sup>) to increase the total concentrations of N in the plant was found when Si1 was added to the soil, whereas the lowest effect was found when Mg2 was added. There was a significant difference between all treatments except for the treatments of (Zn2 and Mg2). Increasing the values of polluted Fe to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on increase the total concentrations of N in

the plant to the following order C (control) > Mg1 > Zn1 > Si2 > Zn2 > Si1 > Mg2. There was a significant difference between all treatments. It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> were osculated among Mg2, Si1, and control, respectively. The effects of Fe additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> simultaneously with different treatment of NPs on increasing the total amounts of P in the plant are listed in Table 6. It was clearly seen that the effect of NPs application on increasing the total concentrations of P without any pollutants additives resulted in an osculating in the reduction or increment of P in the plant[49]. The order of sequence for the effects of NPs application on the increasing the total P was found to take the following sequence Si1 > Si2 > Mg1 > C (control) > Zn1 > Zn2 > Mg2 which is similar to what was observed with Cu additives at the same concentrations. The highest values affected the increases of the total P were observed with Si1, whereas the lowest values were obtained when Mg2 was added. There was a significant difference between all treatments except for the treatments of (Si2 and Mg1). When Fe was added to the soil as pollutant to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the increment of total P were found to take the following order Si2 > Si1 > Mg2 > Mg1 > Zn2 > C (control) > Si1 = Mg2. The highest values of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg<sup>-1</sup>) to increase the total concentrations of P in the plant were found when Si2 was added to the soil, whereas the lowest effects were found when Mg2 were added. There was a significant difference between all treatments except for (control and Zn1) and (Zn2 and Mg1). Increasing the values of an external addition of Fe to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on increasing the total concentrations of P in the plant to the following order Zn1 > Mg1 > Zn2 > Si2 > C (control) > Si1 = Mg2, [53]. There was a significant difference between all treatments. It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> were osculated among Si1, Si2, and Zn1, respectively. The effects of Fe additives with two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> simultaneously with different treatment of NPs on increasing the total amounts of K in the plant are listed in Table 6. It was clearly seen that the effect of NPs application on increasing the total concentrations of K without any pollutants additives resulted in an osculating in the reduction or increment of K in the plant. The order of sequence for the effects of NPs application on increasing the total K was found to take the following sequence Zn2 > C (control) > Mg1 > Mg2 > Si2 > Si1 > Zn1 which is similar to what was observed during Cu additives at the same concentrations. The highest values affected the increases of the total K were observed with Zn2, whereas the lowest values were obtained when Zn1 was added. There was a significant difference between all treatments except for (control and Mg1). When Fe was added to the soil as an external addition to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on the increment of total K were found to take the following order Zn1 Mg2 > Si1 > Zn2 > C (control) > Mg1 > Si2. The highest value of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg<sup>-1</sup>) to increase the total concentrations of K in the plant was found when Zn1 was added to the soil, whereas the lowest effect was found when Si2 was added. There was a significant difference between all treatments except for the treatments of (control and Mg1), [49]. Increasing the values of an external addition of Fe to 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on increase the total concentrations of K in the plant to the following order Si2 > Zn2 > C (control) > Zn1 > Si1 > Mg1 > Mg2. There was a significant difference between all treatments. It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> were osculated among Zn2, Zn1, and Si2, respectively. The trend of these results agreed with those reported by Ali, *etal.*,[51]and Hegabet *al.*,[55, 56].

### 3.4 Effect of NPs treatments and Cu and Fe additives on dry and wet weights of Marjoram plant.

#### 3.4.1. Effect of NPs treatments and Cu additives on dry and wet weights of Marjoram plant.

The effects of Cu additives with different NPs treatments on dry and wet weights of Marjoram are presented in Table 7. The effects of two concentrations (5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup>) of Cu additives have been investigated. It was clearly seen that the effect of NPs application presented a negative effect on Marjoram dry weight in the experiments that have been carried out without Cu additives. The order of sequence for the effects of NPs application on increasing the dry weight was found to take the following order control > Si2 = Mg1 > Si1 > Zn1 > Mg2 > Zn2. The highest values of means for dry weight were observed in the control treatment, whereas the lowest values were obtained when Zn2 was added. There was a significant difference between all treatments except for the treatments of (Si2 and Mg2)[53]. When Cu was added to the soil as an external addition to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on Marjoram dry weight took the following order Zn2 > Mg2 > Si2 > C (control) > Zn1 > Si1 > Mg1. The highest value of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg<sup>-1</sup>) was found when Zn2 was added to the soil, whereas the lowest effect was found when Mg1 was added. There was a significant difference between all treatments except for the treatments of (control, Zn1, and Si2) and (Si1 and Mg1). Increasing the values of original exist values of Cu by 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on Marjoram dry weight to the following order Zn1 > Zn2 > Mg2 > Si2 > C (control) > Si1 Mg1. There was a significant difference between all treatments except for the treatments of (control, Si1, Si2 and Mg1) and (Zn2, Mg2). It was clearly seen that the highest effect in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> was relevant to the additives of control, Zn2, and Zn1, respectively. It was clearly seen that the effect of NPs application presented a negative effect on Marjoram wet weight in the experiments that have been carried out without Cu additives. The order of sequence for the effects of NPs application on increasing the wet weight was found to take the following order control > Si2 = Mg1 > Si1 > Mg2 > Zn1 > Zn2. The highest values of means for wet weight were observed in the control treatment, whereas the lowest values were obtained when Zn2 was added which is similar to data that has been observed in dry weight. There was a significant difference between all treatments except for the treatments of Si2 and Mg1. When Cu was added to the soil as an external pollutant to increase the original exiting values by 5 mg kg<sup>-1</sup>, the effects of NPs application on Marjoram wet weight took the following order Zn2 > Si1 = Mg2 > Zn1 = Mg1 > C (control) > Si2. The highest value of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg<sup>-1</sup>) was found when Zn2 was added to the soil, whereas the lowest effect was found when Si2 was added. There was a significant difference between all treatments except for the treatments of control, Zn1, Si1, Mg1, and Mg2. Increasing the values of original exist values of Cu addition by 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on Marjoram wet weight to the following order Zn1 > Zn2 > C (control) > Mg1 > Si2 = Mg2 > Si1. There was a significant difference between all treatments except for the

treatments of (control and Zn<sub>2</sub>) and (Si<sub>2</sub>, Mg<sub>1</sub>, and Mg<sub>2</sub>). It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg<sup>-1</sup>, and 10 mg kg<sup>-1</sup> were relevant to the additives of control, Zn<sub>2</sub>, and Zn<sub>1</sub>, respectively similar to what was observed in dry weight. The fresh and dry weights were affected by the use of Zn, Si, Mg NPs and may be the lower biomass in the control plants might be due to the higher Fe and Cu levels in these plants. These elements mediated reduction in plant growth might be associated with the disturbance of several mechanisms in plants such as chlorophyll biosynthesis, water deficit, and ultra structural alteration in plant [57]. These results are in close conformity with Venkatachalam *et al.*, [58].

Table 7  
Effect of NPs treatments and pollutants additives on dry and wet weights of Marjoram plant.

Cu additives								
NPs Treatments	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean
Dry weight				Wet weight				
C	36.96A	15.30DEF	14.96DEF	<b>22.41A</b>	51.66A	25.33DEF	25.66DEF	<b>34.22A</b>
Zn <sub>1</sub>	17.96CDE	14.30DEF	18.96CD	<b>17.07BC</b>	22.66EF	25.66DEF	36.66B	<b>28.33B</b>
Zn <sub>2</sub>	11.96F	17.96CDE	16.96CDE	<b>15.63C</b>	20.33F	32.66BC	26.66DEF	<b>26.55B</b>
Si <sub>1</sub>	20.96BC	13.63EF	14.30DEF	<b>16.41BC</b>	30.66BCD	26.00DEF	20.66F	<b>25.77B</b>
Si <sub>2</sub>	23.96B	15.96DEF	15.63DEF	<b>18.52B</b>	32.66BC	22.00EF	22.66EF	<b>25.77B</b>
Mg <sub>1</sub>	23.96B	13.63EF	14.30DEF	<b>17.30BC</b>	32.66BC	25.66DEF	23.33EF	<b>27.22B</b>
Mg <sub>2</sub>	17.96CDE	17.30CDE	16.96CDE	<b>17.41BC</b>	27.66CD	26.00DEF	22.66EF	<b>25.44B</b>
<b>Mean</b>	<b>21.96A</b>	<b>15.49B</b>	<b>16.01B</b>		<b>31.19A</b>	<b>26.19B</b>	<b>25.47B</b>	
LSD at 5%	P=1.82	N=2.78	P*N=4.83		P=2.41	N=3.68	P*N=6.38	
Fe additives								
NPs Treatments	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean	C	5 mg kg <sup>-1</sup>	10 mg kg <sup>-1</sup>	Mean
Dry weight				Wet weight				
C	36.96B	19.96EF	19.96EF	<b>25.63B</b>	51.66B	32.66EF	38.66D	<b>41.00B</b>
Zn <sub>1</sub>	17.96FG	16.96G	16.96G	<b>17.30D</b>	22.66IJ	22.66IJ	26.00HI	<b>23.77E</b>
Zn <sub>2</sub>	11.96H	19.96EF	19.96EF	<b>17.30D</b>	20.33J	32.66EF	32.66EF	<b>28.55D</b>
Si <sub>1</sub>	20.96DE	22.96CD	15.30G	<b>19.74C</b>	30.66FG	35.66DE	22.00IJ	<b>29.44D</b>
Si <sub>2</sub>	23.96C	15.63G	34.96B	<b>24.85B</b>	32.66EF	28.00GH	52.66B	<b>37.77C</b>
Mg <sub>1</sub>	23.96C	23.96C	65.96A	<b>37.96A</b>	32.66EF	43.66C	94.66A	<b>57.00A</b>
Mg <sub>2</sub>	17.96G	15.96G	19.96EF	<b>17.96D</b>	27.66GH	21.66J	32.66EF	<b>27.33D</b>
<b>Mean</b>	<b>21.96B</b>	<b>19.34C</b>	<b>27.58A</b>		<b>31.19B</b>	<b>31.00B</b>	<b>42.76A</b>	
LSD at 5%	P=1.09	N=1.67	P*N=2.90		P=1.62	N=2.48	P*N=4.29	

### 3.4.2. Effect of NPs treatments and Fe additives on dry and wet weights of Marjoram plant.

The effects of Fe additives with different NPs treatments on dry and wet weights of Marjoram are presented in Table 7. The effects of two concentrations of 5 mg kg<sup>-1</sup> and 10 mg kg<sup>-1</sup> of Fe on dry and wet weights of Marjoram plant have been investigated. It was clearly seen that the effect of NPs application presented a negative effect on Marjoram dry weight in the experiments that have been carried out without Fe additives. The order of sequence for the effects of NPs application was found to take the following order C (control) > Si<sub>2</sub> = Mg<sub>1</sub> > Si<sub>1</sub> > Zn<sub>1</sub> > Mg<sub>2</sub> > Zn<sub>2</sub>. The highest values of means for dry weight were observed in the control treatment, whereas the lowest values were obtained when Zn<sub>2</sub> was added. There was a significant difference between all treatments except for the treatments of Si<sub>2</sub> and Mg<sub>1</sub>. When Fe was added to the soil as an external addition to increase the original exit values by 5 mg kg<sup>-1</sup>, the effects of NPs application on Marjoram dry weight took the following order Mg<sub>1</sub> > Si<sub>1</sub> > C (control) = Zn<sub>2</sub> > Zn<sub>1</sub> > Mg<sub>2</sub> > Si<sub>2</sub>. The highest value of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg<sup>-1</sup>) was found when Mg<sub>1</sub> was added to the soil, whereas the lowest effect was found when Si<sub>2</sub> was added. There was a significant difference between all treatments except for the treatments of (control and Zn<sub>2</sub>) and (Zn<sub>1</sub>, Si<sub>2</sub>, and Mg<sub>2</sub>) [49, 53]. Increasing the values of original exist values of Fe by 10 mg kg<sup>-1</sup> resulted in changing the order of effects of NPs on Marjoram dry weight to the following

order  $Mg1 > Si2 > C$  (control) =  $Zn2 = Mg2 > Zn1 > Si1$ . There was a significant difference between all treatment except for the treatments of (control, Zn2, and Mg2) and (Zn1 and Si1). It was clearly seen that the highest effects in the three trials that were studied in the present work including control,  $5 \text{ mg kg}^{-1}$ , and  $10 \text{ mg kg}^{-1}$  were relevant to the additives of control, Mg1, and Mg1, respectively. It was clearly seen that the effect of NPs application presented a negative effect on Marjoram wet weight in the experiments that have been carried out without Fe additives. The order of sequence for the effects of NPs application was found to take the following order  $C$  (control)  $> Si2 = Mg1 > Si1 > Mg2 > Zn1 > Zn2$ . The highest values of means for wet weight were observed in the control treatment, whereas the lowest values were obtained when Zn2 was added. There was a significant difference between all treatments except for the treatments of (Si2 and Mg1). When Fe was added to the soil as an external addition to increase the original exit values by  $5 \text{ mg kg}^{-1}$ , the effects of NPs application on Marjoram wet weight took the following order  $Mg1 > Si1 > control = Zn2 > Si2 > Zn1 > Mg2$ . The highest values of the effects of adding NPs on the artificially polluted soils with Fe ( $5 \text{ mg kg}^{-1}$ ) were found when Mg1 was added to the soil, whereas the lowest effect was found when Mg2 was added. There was a significant difference between all treatments except for the treatments of control and Zn2. Increasing the values of original exist values of Fe by  $10 \text{ mg kg}^{-1}$  resulted in changing the order of effects of NPs on Marjoram wet weight to the following order  $Mg1 > Si2 > C$  (control)  $> Zn2 > Mg2 > Zn1 > Si1$ . There was a significant difference between all treatment except for the treatments of (Zn2 and Mg2). It was clearly seen that the highest effect in the three trials that were studied in the present work including control,  $5 \text{ mg kg}^{-1}$ , and  $10 \text{ mg kg}^{-1}$  was relevant to the additives of control, Mg1, and Si2, respectively. These results are in close conformity with Tripathiet al.,[59] who reported that Supply of SiO<sub>2</sub> NPs enhanced the photosynthetic pigments in Cr-stressed pea leaves

## 4. Conclusion

In the present study, we have carried out the green synthesis of different nanoparticles to investigate its effect on the quality of irrigation water, the availability of some heavy metals in soil and plant, and the productivity of Marjoram. In general, the term of nanotechnology has emerged recently in several fields of interest that refers to the research and innovation that is concerned with making materials on a very small size close to the scale of atoms and molecules. The results obtained from our experiments explored that the addition of nanoparticles (NPs) materials have resulted in noticeable variations in the removal percentages of both Cu and Fe. The maximum values obtained for adsorption of Cu on ZnO, MgO, and SiO<sub>2</sub> NPs, within pH (3–5) were 89.9%, 83.3%, and 68.36% for respectively. Whereas, the maximum adsorption values of Fe at pH 3.3 were 82%, 80%, and 65% for ZnO, MgO, and SiO<sub>2</sub> NPs, respectively. It was clearly seen that the effect of NPs application on the availability of substantial concentrations of Cu without any pollutants additives resulted in the reduction of the available Cu in the soil samples, and that same tendency was observed with the substantial concentrations of Fe exist in the soil. Adding NPs to the soil system had positive effects on Cu uptake via the plant. The effect of NPs and the addition of Cu and Fe on the availability of NPK in the soil system were very completed and osculated from one treatment to another. The same tendency was observed with the total concentration of NPK in the plant. It was clearly seen that the effects of NPs application have presented a negative effects on Marjoram dry and wet weight in the experiments that have been carried out without the additions of either Cu or Fe.

## Declarations

## Acknowledgment

The present work was funded by Desert Research Center Research No. 52OCT2020.

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## Figures

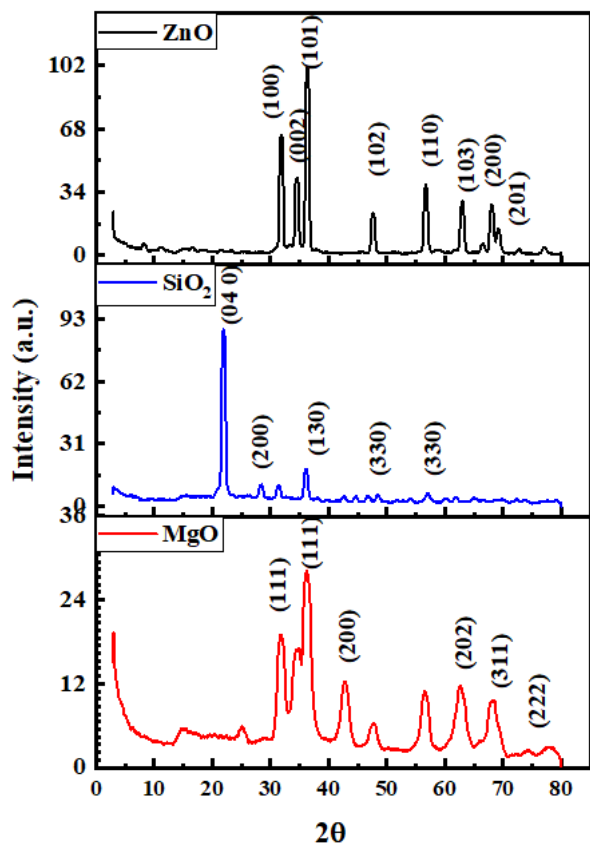
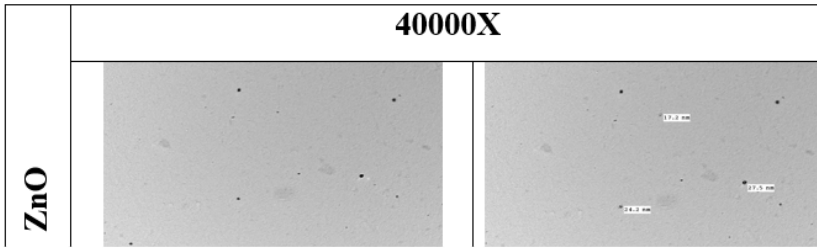


Figure 1

The X-ray diffraction profile of NPs synthesized using the lemon peel extract.



**Figure 2**

The TEM micrograph of MgO, SiO<sub>2</sub>, and ZnO nanoparticles synthesized by lemon peel extract.

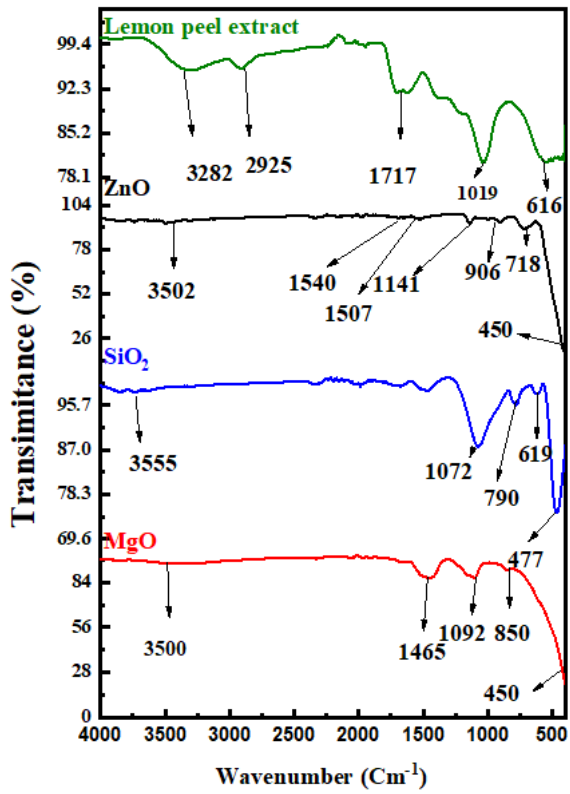


Figure 3

The FTIR spectra of the MgO, SiO<sub>2</sub>, and ZnO nanoparticles and lemon peel extract.

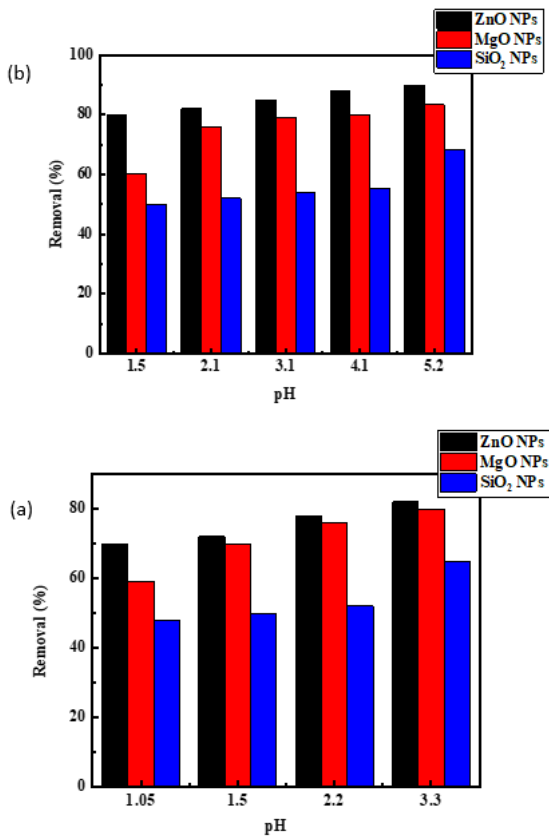


Figure 4

Effect of pH on adsorption of Cu (a) and Fe (b) ions (conditions: 10 g l<sup>-1</sup> adsorbent, 10 ml of 50 mg L<sup>-1</sup> of ions, duration of oscillation time of 24h at temperature 25°C).

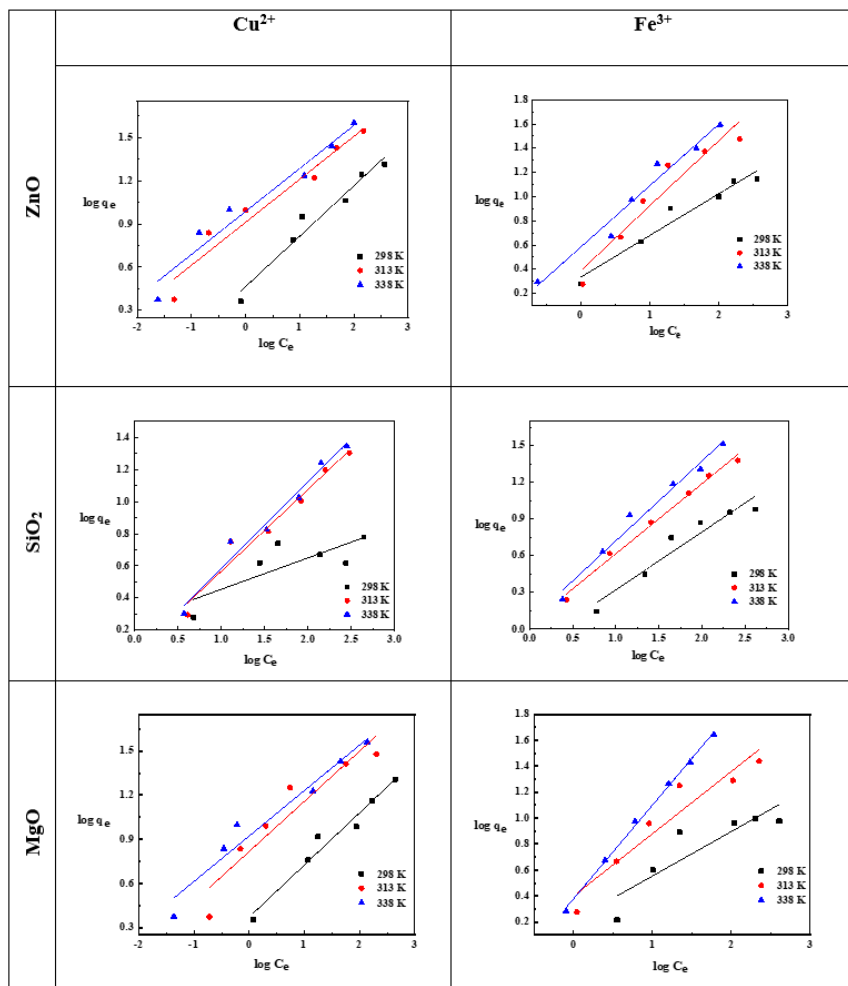


Figure 5

Linearized Freundlich isotherms for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions adsorption on ZnO, MgO, and  $\text{SiO}_2$  NPs at different temperatures.

Figure 6

Linearized Langmuir isotherms for Cu and Fe ions adsorption on ZnO, MgO, and  $\text{SiO}_2$  NPs at different temperatures.