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

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Abstract

The term of nanotechnology has emerged recently in several fields of interest that refers to the research 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 SiO2 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 SiO2 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 Zn2 > Zn1 > Mg2 > SiO2 > 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, 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 complete 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 H2S, 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 plumping 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−1), whereas when the vegetation were exposed to the same concentration of Ca(H2PO4)2 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−1 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 scientests 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 were 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 hezacanazole 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, nanofoibers, 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 Mm3/year of treated wastewaters used, 75 percent in Israel for agriculture and generally 500 Mm3/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$_2$, 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 and 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$_2$H$_5$OH) and ammonium hydroxide solution (NH$_4$OH) that was purchased from Merck Chemicals Co., Darmstadt, Germany.

2.1.2. Preparation of MgO, SiO$_2$, and ZnO NPs

The formation of MgO, SiO$_2$, 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$_2$, 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$^{-1}$ 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$_2$, and ZnO NPs

For preparing MgO, SiO$_2$, and ZnO NPs, we have added 0.5 mol L$^{-1}$ 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$^{-1}$ to maintain the following pH values 9.7, 11.58, and 6.95 for MgO, SiO$_2$, 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$_2$ 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$_2$, 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-Ka radiation of a 2θ 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].
| 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\(^{-1}\)) | 1.57                               |
| Silt (%)                 | 11.80                   |                  |                                    |
| Clay (%)                 |                         |                  |                                    |
| Texture class            | Loamy sand              | Cation and anion (mg dm\(^{-3}\)) | 3.93                               |
| Ca\(^{++}\)              |                         |                  |                                    |
| Mg\(^{++}\)              |                         |                  |                                    |
| Na\(^{+}\)               |                         |                  |                                    |
| K\(^{+}\)                |                         |                  |                                    |
| CaCO\(_3\) (%)           | 9.78                    | HCO\(_3\)^{−}    | 8.03                               |
| OM (%)                   | 2.81                    | CO\(_3\)^{−−}    | 1.31                               |
| CEC (meq 100g\(^{-1}\)) | 20.70                   | Cl\(^{−}\)       | 11.41                              |
| pH (1:2.5)               | 8.01                    | SO\(_4\)^{−−}    | 3.60                               |
| EC (dS m\(^{-1}\))      | 2.78                    |                  |                                    |
| Total content of heavy metal (mg kg\(^{-1}\)) | 28742 6.92 | Heavy metal (mg kg\(^{-1}\)) | 0.04 0.03 |
| Fe                       |                         |                  |                                    |
| Cu                       |                         |                  |                                    |
| Chemically extractable heavy metals (mg kg\(^{-1}\)) | 13.24 4.55 |                  |                                    |
| Fe                       |                         |                  |                                    |
| 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\(_2\), and ZnO nanoparticles as adsorbent material with an initial concentration of 50 mg L\(^{-1}\) for both Cu and Fe. The solid to liquid ratio 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\(^{-1}\). 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\(_2\), 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\(^{-1}\)) of each pollutant (Fe and Cu) and (0, 150, and 300 mg kg\(^{-1}\)) of each MgO, SiO\(_2\), 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\(^3\) 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\(_2\)SO\(_4\)–H\(_2\)O\(_2\) 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, SiO₂, and ZnO NPs:

\[ D = \frac{K\lambda}{\beta\cos \theta} \]  

where \( D \) is the crystal volume, \( \lambda \) is the wavelength of the X-ray radiation (\( \lambda = 0.15406 \text{ nm} \) for CuKa; \( K \) 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 \( 2\theta = 28.72^\circ \) (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. SiO₂ 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 SiO₂ 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), \( 2\theta = 56.9^\circ \) (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 graphic carbon diffraction peaks found. Because graphic 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, SiO₂, 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, SiO₂, 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⁻¹, 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⁻¹. The bending vibration of the OH group was attributed to a wide broad peak about 1717 cm⁻¹, 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⁻¹, 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⁻¹ in the FTIR spectrum. The O-H stretch shows as a very broad band in the spectra, spanning 3700 cm⁻¹ [35, 36]. The saturated main alcohol C=O was found to have an absorption peak at 1092 cm⁻¹. The substituent of flavonoids is represented by the band seen at 1456 cm⁻¹. 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].

Glycine 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⁻¹ [37, 38]. Prior to the calcination of the intermediate product to ZnO nanoparticles, biomolecules were responsible for the conversion of ZnSO₄ to Zn(OH)₂.

Figure 3 shows the FT-IR spectra of the produced SiO₂ nanoparticles. Si–O has a band around 790 cm⁻¹, and the symmetric stretching and bending vibrations of Si–O–Si have bands around 477 and 619 cm⁻¹ [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⁻¹. The 3555 cm⁻¹ linked to specific 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\(^{-1}\) and 1 to 3.5, respectively. The initial concentrations of either Cu or Fe were close to 100 mg L\(^{-1}\) as is shown in Figure. 4. The pH values that exceed 5 mg kg\(^{-1}\) 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 68.3% were achieved for ZnO, MgO, and SiO\(_2\) NPs, respectively. Whereas the removal percentages were 82%, 80%, and 65% for the adsorption of Fe on ZnO, MgO, and SiO\(_2\) 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\(_2\) 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:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e 
\]

(2)

The Freundlich isotherm coefficients \(K_F\) and \(n\) are calculated first from intercept and slope of a chart of \(\log q_e\) vs \(\log C_e\) 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 \((K_F)\), showing that, the adsorption mechanism is endothermic.

#### Table 2

| Metal ions | Temperature | ZnO | SiO\(_2\) | MgO |
|------------|-------------|-----|-----------|-----|
| Cu\(^{2+}\) | 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\(^{3+}\) | 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:

\[
\frac{C_e}{q_i} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_L} 
\]

(3)

where \(K_L\) is the Langmuir constant related to the energy of adsorption and \(q_{\text{max}}\) is the maximum adsorption capacity (mg g\(^{-1}\)) [45]. The slope and intercept of plots of \(C_e/q_i\) versus \(C_e\) at different temperatures, were used to calculate \(q_{\text{max}}\) and \(K_L\) as is shown in Fig. 6. Langmuir isotherm parameter fits for Cu and Fe adsorption on ZnO, MgO, and SiO\(_2\) 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\(_2\) NPs at room temperature (297 K) were found to be 135, 66, and 58 mg g\(^{-1}\) for Cu\(^{2+}\) and 104, 100, and 94 mg g\(^{-1}\), respectively.
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 mg g\(^{-1}\)[46], whereas the adsorption of hematite reached 4.94 mg g\(^{-1}\)[47].

| Metal ions | Temperature | ZnO | SiO\(_2\) | MgO |
|------------|-------------|-----|----------|-----|
| Cu         |             |     |          |     |
|            | 298         | 135.13 | 0.98 | 13.68 | 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 mg kg\(^{-1}\) and 10 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 exit values by 5 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 to the artificially polluted soils with Cu (5 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 exit values of Cu by 10 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 mg kg\(^{-1}\), and 10 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 mg kg\(^{-1}\), and an experiment carried out with the addition of 10 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 (Zn1, Si2, and Mg1). Increasing the additives of Cu pollutants to the soil by adding 10 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].
The effects of Fe additives as two concentrations of 5 mg kg\(^{-1}\) and 10 mg kg\(^{-1}\) 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 > Si2 > Si1 > Mg1 > Zn1. Increasing the additives of Fe pollutants to the soil via adding 10 mg kg\(^{-1}\) resulted in changing the order of effects of NPs to the following order Zn2 > Zn1 > Si2 > Mg2 > Mg1 > Zn1 > Mg1 > C (control)\([49, 53]\). 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\(^{-1}\), 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 > Mg1 > C (control)\([49, 53]\) that was 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\(^{-1}\)) 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\(^{-1}\) 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\(^{-1}\), and 10 mg kg\(^{-1}\) 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 > Si2 > Mg1 > C (control)\([49, 53]\). 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\(^{-1}\), the order of sequences of NPs application was as follows; C (control) > Si1 > Mg1 > Zn2 > Mg2 > Mg1 > 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\(^{-1}\) 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

### 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\(^{-1}\) | 10 mg kg\(^{-1}\) | Mean | C 5 mg kg\(^{-1}\) | 10 mg kg\(^{-1}\) | Mean |
|--------------|-----------|-------------------|-----------------|------|-------------------|-----------------|------|
| Cu-DTPA      | C         | 4.60F             | 5.31E           | 9.37A| 6.42A             | 6.89J           | 14.30E| 17.69B| 12.96B|
| Zn1          | 1.42I     | 2.45H             | 3.40G           | 2.42E| 8.59I             | 13.34G          | 8.16I| 10.03E|
| Zn2          | 0.42J     | 1.66I             | 1.58I           | 1.22F| 11.11H            | 7.39J           | 14.96D| 11.16D|
| Si1          | 3.55G     | 4.11F             | 8.37B           | 5.34B| 35.71A            | 13.94EF         | 11.44H| 20.36A|
| Si2          | 2.60H     | 3.37G             | 7.84C           | 4.60C| 10.96H            | 13.54FG         | 2.49M| 9.00F  |
| Mg1          | 3.36G     | 4.53F             | 7.98BC          | 5.29B| 7.01J             | 13.48FG         | 15.29D| 11.93C|
| Mg2          | 2.57H     | 3.42G             | 6.47D           | 4.16D| 5.31K             | 3.31L           | 16.21C| 8.28G  |
| Mean         | 2.64C     | 3.55B             | 6.43A           | 12.23A| 11.39B            | 12.32A         |

| LSD at 5%    | P=0.197   | N=0.301           | P*N=0.522       |

| Fe additives | Nano Exp. | C 5 mg kg\(^{-1}\) | 10 mg kg\(^{-1}\) | Mean | C 5 mg kg\(^{-1}\) | 10 mg kg\(^{-1}\) | Mean |
|--------------|-----------|-------------------|-----------------|------|-------------------|-----------------|------|
| Fe-DTPA      | C         | 12.89G            | 20.43B          | 29.56A| 20.96A            | 2087.0L         | 4404.8B| 6277.8A| 4256.5A|
| Zn1          | 8.61K     | 10.20J            | 9.177K          | 9.33E| 1664.5Q           | 1534.2S         | 4199.8D| 2466.2C|
| Zn2          | 5.88L     | 8.45K             | 6.75L           | 7.03F| 1629.8R           | 1779.1P         | 3025.9H| 2144.9G|
| Si1          | 11.93G    | 19.18BC           | 19.18BC         | 16.93B| 1969.8L           | 3305.9F         | 4387.3C| 3221.0B|
| Si2          | 12.88G    | 14.62F            | 14.62F          | 15.23C| 2584.8J           | 1315.2T         | 2934.81| 2278.3F|
| Mg1          | 11.61G    | 19.86B            | 19.86B          | 15.88C| 1899.8M           | 1863.9O         | 3347.7E| 2370.5E|
| Mg2          | 10.64H    | 17.29DE           | 17.29DE         | 14.16D| 2495.5K           | 1534.8S         | 3164.8G| 2398.4D|
| Mean         | 10.63C    | 16.71A            | 16.71A          | 2047.3C| 2248.3B           | 3905.4A         |

| LSD at 5%    | P=0.520   | N=0.794           | P*N=1.376       |

\(P=0.220\) \(N=0.336\) \(P*N=0.582\)

### 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\(^{-1}\) and 10 mg kg\(^{-1}\) with different treatment of NPs were found to take the following sequence Zn2 > Zn1 > Mg2 > Mg1 > Si2 > Si1 > Mg1 > 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\(^{-1}\), 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 > Mg1 > C (control)\([48]\). 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

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accretion by roots. This variation in metal accretion 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 mg kg\(^{-1}\) and 10 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 Mg\(_2\) > Mg\(_1\) > control > Si\(_2\) > Zn\(_2\) > Zn\(_1\) > Si\(_1\). The highest values that were affected the reduction of the available N were observed with Mg\(_2\), whereas the lowest values were obtained when Si\(_1\) was added. There was a significant difference between all treatments except for the treatments of control and Mg\(_1\) [49, 53]. When Cu was added to the soil as an external pollutant to increase the original exit values by 5 mg kg\(^{-1}\), the effects of NPs application on the availability of N were found to take the following order Mg\(_2\) > Zn\(_2\) > Si\(_2\) > Si\(_1\) > Mg\(_2\) > Si\(_2\) > C (control) > Zn\(_1\). The highest value of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg\(^{-1}\)) to reduce the availability of N was found when Mg\(_2\) was added to the soil, whereas the lowest effect was found when Zn\(_1\) was added. There was a significant difference between all treatments except for the treatments of (control and Si\(_2\)) and (Z\(_2\) and Si\(_1\)). Increasing the values of polluted Cu to 10 mg kg\(^{-1}\) resulted in changing the order of effects of NPs on the availability of N to the following order Si\(_2\) > Mg\(_1\) = Mg\(_2\) = Si\(_1\) = Zn\(_2\) > C (control) > Zn\(_1\). There was a significant difference between all treatments except for the following treatments Mg\(_1\), Mg\(_2\), Si\(_1\), and Zn\(_2\). It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg\(^{-1}\), and 10 mg kg\(^{-1}\) were osculated among Mg\(_2\) and Si\(_2\). The effects of Cu additives as two concentrations of 5 mg kg\(^{-1}\) and 10 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 osculating 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 Zn\(_2\) > C (control) > Mg\(_2\) > Mg\(_1\) > Zn\(_1\) > Si\(_1\) > Si\(_2\). The highest values that affected the reduction of the available P were observed with Zn\(_2\), whereas the lowest values were obtained when Si\(_2\) was added. There was a significant difference between all treatments except for the treatments of (control and Zn\(_2\)). When Cu was added to the soil as an external pollutant to increase the original exit values by 5 mg kg\(^{-1}\), the effects of NPs application on reducing the availability of P was found to take the following order Mg\(_2\) > Si\(_2\) > Mg\(_1\) > Zn\(_1\) > C (control) > Si\(_1\) > Zn\(_2\). [49, 53]. The highest value of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg\(^{-1}\)) to reduce the availability of P was found when Mg\(_2\) was added to the soil, whereas the lowest effect was found when Zn\(_2\) was added. There was a significant difference between all treatments except for the treatments of (Si\(_2\) and Mg\(_2\)). Increasing the values of external pollution of Cu to 10 mg kg\(^{-1}\) resulted in changing the order of effects of NPs on the availability of P to the following order C (control) > Zn\(_1\) > Mg\(_2\) > Si\(_1\) = Si\(_2\) > Mg\(_1\) > Zn\(_2\). There was a significant difference between all treatments except for the following treatments (Si\(_1\) and Si\(_2\)). It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg\(^{-1}\), and 10 mg kg\(^{-1}\) were osculated among Zn\(_2\), Mg\(_2\), and control. The effects of Cu additives with two concentrations of 5 mg kg\(^{-1}\) and 10 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 osculating 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 Mg\(_2\) > Si\(_2\) > Mg\(_1\) > Zn\(_1\) > C (control) > Si\(_1\) > Zn\(_2\). When Cu was added to the soil as an external pollutant to increase the original exit values by 5 mg kg\(^{-1}\), the effects of NPs application on reducing the availability of K was found to take the following order Si\(_2\) > Si\(_1\) > Mg\(_2\) > Mg\(_1\) > C (control) > Zn\(_2\). [49, 53]. The highest value of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg\(^{-1}\)) to reduce the availability of K was found when Mg\(_2\) was added to the soil, whereas the lowest effect was found when Zn\(_2\) was added. Generally, there was a significant difference between all treatments. Increasing the values of external polluted Cu to 10 mg kg\(^{-1}\) resulted in changing the order of effects of NPs on the availability of K to the following order Si\(_2\) > Si\(_1\) > Mg\(_2\) > Zn\(_2\) > Mg\(_1\) = Zn\(_1\) > 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 mg kg\(^{-1}\), and 10 mg kg\(^{-1}\) on K availability were osculated among Mg\(_2\), Si\(_1\), and Si\(_2\). On the other hand, the lowest effects were attributed to the Zn\(_2\) in the control experiment, whereas in the experiments that have been carried out with the addition of Cu (5 mg kg\(^{-1}\) and 10 mg kg\(^{-1}\)), the effects of Si\(_2\) 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 mg kg\(^{-1}\) and 10 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

| Nano Exp. | C | 5 mg kg⁻¹ | 10 mg kg⁻¹ | Mean | N | 5 mg kg⁻¹ | 10 mg kg⁻¹ | Mean | K |
|-----------|---|------------|-------------|------|---|------------|-------------|------|---|
|           |   |            |             |      |   |            |             |      |   |
| C         | 50.73G | 121.80C | 84.60E | 85.71D | 25.11G | 29.09D | 18.08G | 24.09A | 140.80IJ | 145.60HI | 150.37GH |
| Zn1       | 135.33B | 135.33B | 135.33B | 135.33A | 28.85D | 22.32H | 17.06I | 22.72D | 188.27C | 209.32B | 119.60G |
| Zn2       | 118.40C | 84.60E | 67.67F | 90.22C | 24.78G | 32.56AB | 32.29AB | 29.88A | 203.20B | 107.91I | 116.30GH |
| Si1       | 203.00A | 88.00E | 67.67F | 119.56B | 31.61BC | 30.81C | 26.74E | 29.72A | 149.80E | 87.82K | 58.90L |
| Si2       | 88.00E | 118.40C | 50.73G | 85.71D | 33.09A | 14.10K | 26.74E | 24.64B | 114.03GHI | 221.75A | 40.97M |
| Mg1       | 50.73G | 50.73G | 67.67F | 56.38E | 26.47E | 16.26L | 28.97D | 23.90C | 115.17GHI | 102.75J | 119.60G |
| Mg2       | 10.53D | 101.53D | 67.67F | 90.24C | 25.64FG | 13.71K | 26.50EF | 21.95E | 109.07HIJ | 155.74E | 109.63HJJ |
| Mean      | 106.82A | 100.06B | 77.33C | 27.93B | 22.67C | 24.83B | 145.76A | 145.58A | 106.27B |

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

### 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⁻¹ and 10 mg kg⁻¹ 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 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 be 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⁻¹, the effects of NPs application on the reduction of available N were found to be 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⁻¹) 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⁻¹ 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 Si1). It was clearly seen that the highest effect in the three trials that were studied in the present work including control, 5 mg kg⁻¹, and 10 mg kg⁻¹ 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⁻¹ 10 mg kg⁻¹, 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⁻¹ and 10 mg kg⁻¹. The effects of Fe additives with two concentrations of 5 mg kg⁻¹ and 10 mg kg⁻¹ 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 > Si2 > Si1. 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 [S3]. When Fe was added to the soil as an external pollutant to increase the original exit values by 5 mg kg$^{-1}$, 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$^{-1}$) 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$^{-1}$ 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).

| Nano Exp. | Cu additives | 5 mg kg$^{-1}$ | 10 mg kg$^{-1}$ | Mean | 5 mg kg$^{-1}$ | 10 mg kg$^{-1}$ | Mean | 5 mg kg$^{-1}$ | 10 mg kg$^{-1}$ |
|-----------|--------------|----------------|----------------|------|----------------|----------------|------|----------------|----------------|
| C         | 2.783E       | 3.750C         | 3.750C         | 3.428B | 0.236DE       | 0.213GH         | 0.155K | 0.201D         | 1.003EF        |
| Zn1       | 1.453G       | 2.900E         | 3.146D         | 2.500G | 0.227EF       | 0.250B          | 0.178J | 0.218B         | 0.320L         |
| Zn2       | 3.266D       | 2.783E         | 3.266D         | 3.106C | 0.215GH       | 0.196I          | 0.065P | 0.159F         | 1.673B         |
| Si1       | 2.056F       | 2.173F         | 3.866BC        | 2.699F | 0.271A        | 0.206H          | 0.220FG | 0.238A         | 0.817J         |
| Si2       | 2.880E       | 3.866BC        | 4.233A         | 3.660A | 0.246BC       | 0.240CD         | 0.134MN | 0.206C         | 0.850J         |
| Mg1       | 2.173F       | 3.146D         | 3.266D         | 2.862E | 0.245BC       | 0.140LM         | 0.127N | 0.171E         | 0.990          |
| Mg2       | 3.993B       | 2.900E         | 2.173F         | 3.022D | 0.142LM       | 0.143L          | 0.113O | 0.133G         | 0.937          |
| Mean      | 2.658C       | 3.074B         | 3.386A         | 0.226A | 0.198B        | 0.142C          |       | 0.941B         | 1.205A         |
| LSD at 5% | P=0.0496     | N=0.0758       | P'=N=0.1313    | P=0.0033 | N'=0.0058 | P'=N=0.0088    |       | P=0.0233       | N=0.0356       |

| Nano Exp. | Fe additives | 5 mg kg$^{-1}$ | 10 mg kg$^{-1}$ | Mean | 5 mg kg$^{-1}$ | 10 mg kg$^{-1}$ | Mean | 5 mg kg$^{-1}$ | 10 mg kg$^{-1}$ |
|-----------|--------------|----------------|----------------|------|----------------|----------------|------|----------------|----------------|
| C         | 2.783EF      | 3.506B         | 3.146D         | 3.145A | 0.236C       | 0.147J          | 0.174H | 0.186c         | 1.003E         |
| Zn1       | 1.453I       | 2.900E         | 2.783EF        | 2.379D | 0.227D       | 0.142J          | 0.265A | 0.212A         | 0.320M         |
| Zn2       | 3.266CD      | 2.660FG        | 2.056H         | 2.661C | 0.215E       | 0.162I          | 0.216E | 0.197B         | 1.673B         |
| Si1       | 2.056H       | 3.866A         | 0.606J         | 2.177E | 0.271A       | 0.188G          | 0.077K | 0.178D         | 0.816G         |
| Si2       | 2.880E       | 3.266CD        | 2.513G         | 2.887B | 0.246B       | 0.203F          | 0.190G | 0.213A         | 0.850F         |
| Mg1       | 2.173H       | 3.386BC        | 2.900E         | 2.820B | 0.245B       | 0.163I          | 0.232CD | 0.213A         | 0.990E         |
| Mg2       | 3.993A       | 2.660FG        | 0.363K         | 2.338D | 0.142J       | 0.170HI         | 0.077K | 0.129E         | 0.936F         |
| Mean      | 2.658B       | 3.178A         | 2.053C         | 0.226A | 0.168C       | 0.176B          |       | 0.941B         | 1.105A         |
| 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       |

Table 6

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

It was clearly seen that the highest effect in the three trials that were studied in the present work including control, 5 mg kg$^{-1}$, and 10 mg kg$^{-1}$ was osculated among Zn2, Mg2, and Si1. The effects of Fe additives with two concentrations of 5 mg kg$^{-1}$ and 10 mg kg$^{-1}$ 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 osculating 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$^{-1}$, 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\(^{-1}\)) 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\(^{-1}\) 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\(^{-1}\), and 10 mg kg\(^{-1}\) on K availability were osculated among Zn2, Mg2, 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\(^{-1}\) and 10 mg kg\(^{-1}\) 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\(^{-1}\), 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\(^{-1}\)) 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 Cu to 10 mg kg\(^{-1}\) resulted in changing the order of effects of NPs on the increase the total concentrations of N in the plant to the following order Si2 > Si1 > Zn1 = Mg2 > C (control) > Zn2 = Mg1 > Zn1. 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\(^{-1}\), and 10 mg kg\(^{-1}\) were osculated among Mg2, Si2, and Si1, respectively. The effects of Cu additives with two concentrations of 5 mg kg\(^{-1}\) and 10 mg kg\(^{-1}\) 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 increase 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\(^{-1}\), 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\(^{-1}\)) 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\(^{-1}\) 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\(^{-1}\), and 10 mg kg\(^{-1}\) were osculated among Si1, Zn1, and Si1, respectively. The effects of Cu additives with two concentrations of 5 mg kg\(^{-1}\) and 10 mg kg\(^{-1}\) simultaneously 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\(^{-1}\), the effects of NPs application on the increment of total K were found to take the following order Zn1 > Zn2 > Mg2 > Si1 > Mg2 > C (control) > Si1 > Si2 > Mg1. The highest values of the effects of adding NPs on the artificially polluted soils with Cu (5 mg kg\(^{-1}\)) 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\(^{-1}\) 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 > Mg2 > 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\(^{-1}\), and 10 mg kg\(^{-1}\) 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\(^{-1}\) and 10 mg kg\(^{-1}\) 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 > Si1 > 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 treatments 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\(^{-1}\), the effects of NPs application on the increment of total N were found to take the following order Si1 > C (control) > Mg1 > Si1 > Zn1 > Mg2 = Zn2. The highest value of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg\(^{-1}\)) 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\(^{-1}\) 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$^{-1}$, and 10 mg kg$^{-1}$ were osculated among Mg2, Si1, and control, respectively. The effects of Fe additives with two concentrations of 5 mg kg$^{-1}$ and 10 mg kg$^{-1}$ 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$^{-1}$, 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$^{-1}$) 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$^{-1}$ 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$^{-1}$, and 10 mg kg$^{-1}$ were osculated among Si1, Si2, and Zn1, respectively. The effects of Fe additives with two concentrations of 5 mg kg$^{-1}$ and 10 mg kg$^{-1}$ 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 Cu was added to the soil as an external addition to increase the original exit values by 5 mg kg$^{-1}$, 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$^{-1}$) 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$^{-1}$ resulted in changing the order of effects of NPs on increase the total concentrations of K in the plant to the following order 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$^{-1}$, and 10 mg kg$^{-1}$ were osculated among Zn2, Zn1, and Si2, respectively. The trend of these results agreed with those reported by Ali, etal.,[51]and Hegab et 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$^{-1}$ and 10 mg kg$^{-1}$) 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$^{-1}$, 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$^{-1}$) 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 exit values of Cu by 10 mg kg$^{-1}$ 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$^{-1}$, and 10 mg kg$^{-1}$ 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 > Zn1 > Mg2 > 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 exit values by 5 mg kg$^{-1}$, 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$^{-1}$) 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 exit values of Cu addition by 10 mg kg$^{-1}$ 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 Zn2) and (Si2, Mg1, and Mg2). It was clearly seen that the highest effects in the three trials that were studied in the present work including control, 5 mg kg\(^{-1}\) and 10 mg kg\(^{-1}\) were relevant to the additives of control, Zn2, and Zn1, 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].

### 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\(^{-1}\) and 10 mg kg\(^{-1}\) 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) > Si2 = Mg1 > Si1 > Zn1 > Mg2 > Zn2. The highest values of means for dry weight were 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 on Marjoram dry weight to the following

| Cu additives | NPs Treatments | 5 mg kg\(^{-1}\) | 10 mg kg\(^{-1}\) | Mean | 5 mg kg\(^{-1}\) | 10 mg kg\(^{-1}\) | Mean |
|--------------|----------------|----------------|----------------|------|----------------|----------------|------|
|              | Dry weight     | Wet weight     |                 |      |                 |                 |      |
| C            | 36.96A         | 15.30DEF       | 14.96DEF       | 22.41A | 51.66A         | 25.33DEF       | 25.66DEF | 34.22A |
| Zn1          | 17.96CDE       | 14.30DEF       | 18.96CD        | 17.07BC | 22.66EF       | 25.66DEF       | 36.66B  | 28.33B |
| Zn2          | 11.96F         | 17.96CDE       | 16.96CDE       | 15.63C  | 20.33F         | 32.66BC        | 26.66DEF | 26.55B |
| Si1          | 20.96BC        | 13.63EF        | 14.30DEF       | 16.41BC | 30.66BCD       | 26.00DEF       | 20.66F  | 25.77B |
| Si2          | 23.96B         | 15.96DEF       | 15.63DEF       | 18.52B  | 32.66BC        | 22.00EF        | 26.66DEF | 25.77B |
| Mg1          | 23.96B         | 13.63EF        | 14.30DEF       | 17.30BC | 32.66BC        | 25.66DEF       | 23.33EF | 27.22B |
| Mg2          | 17.96CDE       | 17.30CDE       | 16.96CDE       | 17.41BC | 27.66CD        | 26.00DEF       | 22.66DEF | 25.44B |
| Mean         | 21.96A         | 15.49B         | 16.01B         | 31.19A  | 26.19B         | 25.47B         |        |

| LSD at 5%   | P=1.82         | N=2.78         | P*N=4.83       |      |

| Fe additives | NPs Treatments | 5 mg kg\(^{-1}\) | 10 mg kg\(^{-1}\) | Mean | 5 mg kg\(^{-1}\) | 10 mg kg\(^{-1}\) | Mean |
|--------------|----------------|----------------|----------------|------|----------------|----------------|------|
|              | Dry weight     | Wet weight     |                 |      |                 |                 |      |
| C            | 36.96B         | 19.96EF        | 19.96EF        | 25.63B | 51.66B         | 32.66EF        | 38.66D | 41.00B |
| Zn1          | 17.96FG        | 16.96G         | 16.96G         | 17.30D  | 22.66J         | 22.66J         | 26.00HI | 23.77E |
| Zn2          | 11.96H         | 19.96EF        | 19.96EF        | 17.30D  | 20.33J         | 32.66EF        | 32.66EF | 28.55D |
| Si1          | 20.96DE        | 22.96CD        | 15.30G         | 19.74C  | 30.66FG        | 35.66DE        | 22.00IJ | 29.44D |
| Si2          | 23.96C         | 15.63G         | 34.96B         | 24.85B  | 32.66EF        | 28.00GH        | 52.66B  | 37.77C |
| Mg1          | 23.96C         | 23.96C         | 65.96A         | 37.96A  | 32.66EF        | 43.66C         | 94.66A  | 57.00A |
| Mg2          | 17.96G         | 15.96G         | 19.96EF        | 17.96D  | 27.66GH        | 21.66J         | 32.66EF | 27.33D |
| Mean         | 21.96B         | 19.34C         | 27.58A         | 31.19B  | 31.00B         | 42.76A         |        |

| LSD at 5%   | P=1.09         | N=1.67         | P*N=2.90       |      |

| P=2.41      | N=3.68         | P*N=6.38       |     |

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\(^{-1}\) and 10 mg kg\(^{-1}\) 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) > 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 Mg1. When Fe was added to the soil as an external addition to increase the original exit values by 5 mg kg\(^{-1}\), the effects of NPs application on Marjoram dry weight took the following order Mg1 > Si1 > C (control) = Zn2 > Zn1 > Mg2 > Si2. The highest value of the effects of adding NPs on the artificially polluted soils with Fe (5 mg kg\(^{-1}\)) was found when Mg1 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 Zn2) and (Zn1, Si2, and Mg2)[49, 53]. Increasing the values of original exit values of Fe by 10 mg kg\(^{-1}\) resulted in changing the order of effects of NPs on Marjoram dry weight to the following...
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 mg kg\(^{-1}\), and 10 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 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 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 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 mg kg\(^{-1}\), and 10 mg kg\(^{-1}\) was relevant to the additives of control, Mg1, and Si2, respectively. These results are in close conformity with Tripathi et al.,[59] who reported that Supply of SiO2 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\(_2\) 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\(_2\) 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

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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$_2$, and ZnO nanoparticles synthesized by lemon peel extract.
Figure 3

The FTIR spectra of the MgO, SiO$_2$, 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$^{-1}$ adsorbent, 10 ml of 50 mg L$^{-1}$ of ions, duration of oscillation time of 24h at temperature 25°C).
|       | Cu$^{2+}$ | Fe$^{3+}$ |
|-------|-----------|-----------|
| ZnO   | ![Graph](image1) | ![Graph](image2) |
| SiO$_2$| ![Graph](image3) | ![Graph](image4) |
| MgO   | ![Graph](image5) | ![Graph](image6) |

**Figure 5**
Linearized Freundlich isotherms for Cu$^{2+}$ and Fe$^{3+}$ ions adsorption on ZnO, MgO, and SiO$_2$ NPs at different temperatures.

**Figure 6**
Linearized Langmuir isotherms for Cu and Fe ions adsorption on ZnO, MgO, and SiO$_2$ NPs at different temperatures.