

REMEDIATION OF SOIL POLLUTED WITH THIAMETHOXAM USING GREEN NANO – PHYTOTECHNOLOGY

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ABSTRACT

Nano zero-valent iron prepared from Marjoram (Mar-nZVI) and nano zero-valent iron prepared from Moringa (Mor-nZVI), with and without Helianthus annuus L. for the removal of thiamethoxam pesticide from soil has been investigated. Structure and morphology of Mar-nZVI and Mor-nZVI, were characterized by UV spectroscopy and High-resolution transmission electron microscopy (HRTEM).

The results showed that the Mar-nZVI played the most important role in the removal of thiamethoxam in the soil, compared with natural degradation in soil without nZVI. The percent removal of thiamethoxam in the soil by Mar-nZVI and Mor-nZVI reached 75.13 and 66.83% respectively, compared with 61.06% in soil without nZVI through 12 days. Thiamethoxam was removed more quickly in the presence of H. annuus plus nZVI than that by H. annuus alone. Thiamethoxam uptake into the H. annuus roots at high level and reached the maximum 17.35 µg/g after 6 days of exposure. While, in H. annuus roots treated with Mar- FeNps and Mor- FeNps reached 9.51 and 11.60 µg/g, respectively. The accumulation of thiamethoxam in H. annuus leaves were lower efficient under the treatments of H. annuus L. plus nZVI than that by H. annuus alone. This is attributed to the role of nZVI alone in degradation of thiamethoxam in soil.

Therefore, the concentration of thiamethoxam was more decreased in the roots and in the leaves of H. annuus

Conclusively, from these results it be concluded that helianthus annuus L. plus nZVI plays a major role for the remediation of thiamethoxam-contaminated soil.

Keywords: Thiamethoxam, green nanotechnology, phytoremediation, soil.

INTRODUCTION

Pesticides are the chemical intended to control the pests and weeds. They are widely used in agricultural fields to protect the crops from pest damages. Among the pesticides, find huge applications in the agricultural fields. However, more than 90% of the sprayed pesticides reach the destinations other than their targets because they are sprayed over the entire agricultural field. These chemicals reach the water bodies via agricultural run-offs, direct entry from the spray, industrial effluents, and dust (Khatri and Tyagi, 2015), causing decreases the quality of water (Khatri *et al.*, 2016). In addition, Residues of pesticides have significant environmental impacts on aquatic ecosystems and mammals (Joo and Cheng, 2006 and Maddah and Hasanzadeh, 2017). Thiamethoxam 1, (3-[(2-chloro-5-thiazolyl) methyl] tetrahydro-5- methyl-N-nitro-4H-1,3,5-oxadiazin-4-imine), thiamethoxam, one of the most commonly used pesticides from the neonicotinoid group. Thiamethoxam is the first representative of second-generation neonicotinoids and belongs to the thia-nicotinyl sub-class. It is marketed under the trademarks Actara® for foliar and/or soil treatment (of crops include fruiting vegetables, cucurbits, potatoes, pome, stone fruit, tobacco, pecans, strawberries, and cotton) and Cruiser® for seed treatments on a wide variety of crops including corn, cotton, sorghum, barley, wheat, potatoes, sunflowers, and legumes (Robinson, 2001; Simon-Delso *et al.*, 2015). The compound has a broad-spectrum insecticidal activity and offers excellent control of a wide variety of commercially important pests in many crops (Maienfisch *et al.*, 2001). Thiamethoxam has a relatively long half-life in soil and high water solubility (average $DT_{50} = 229$ days, 4,100 mg/L) which means it is persistent in the environment with high potential to be transported into surface water via run-off or groundwater discharge (Main *et al.*, 2014). A recent survey of water monitoring literature focusing on surface water contamination by neonicotinoids, found thiamethoxam levels to range from 0.001 to 225 ppb (Morrissey *et al.*, 2015). However, its characteristic properties, such as low soil sorption and high leaching capability, make it a potential contamination source of underground and surface waters (Muccio *et al.*, 2006). The detailed chemistry of thiamethoxam, its metabolism, bioavailability, human toxicology, ecotoxicology, approved uses, analytical procedures and potential risks are well documented in the literature (GOA, 2001 and HCPMRA, 2001). Few studies related to degradation of thiamethoxam include, hydrolysis and direct photolysis (De urzedo *et al.*, 2007 and Zheng *et al.*, 2006).

Nanotechnology is the development and utilization of structures with a size range from 1 nm to about 100 nm where new physical, chemical and

biological properties occur such as extremely small size, high surface area to volume ratio, surface modifiability and excellent magnetic properties (Riu *et al.*, 2006). In recent years, zero-valent iron (ZVI) has been widely applied for treatment of contamination because of its easy accessibility, effective degradation of pollutants, generation of very little waste and secondary pollutants (Joo and Cheng, 2006 and Thompson *et al.*, 2010).

Many researchers have reported the green synthesis of iron nanoparticles using various plant extracts. Biosynthesis of iron nanoparticles (Fe NPs) has been mainly performed using extract of green tea, which is a cheap and local resource. (Hoag *et al.*, 2009). Fe⁰/Fe₃O₄ nanoparticles were successfully synthesised using pomegranate (*Punica granatum*) leaf extract by (Rao *et al.*, 2013). Makarov *et al.*, (2014) reported the synthesis of iron oxide nanoparticles using aqueous extract of *Hordeum vulgare* and *Rumex acetosa*.

Therefore, the objective of this study was to investigate the effects of green nanotechnology (iron nanoparticles from medicinal plant extracts, Fe⁰) and *Helianthus annuus* L. for remediation of thiamethoxam from soil.

MATERIALS AND METHODS

1. Pesticide and Plant Material

Thiamethoxam 25% W G was obtained from the Central Agriculture Pesticide Laboratory, Agriculture Research Center, 7 Nadi EL Said St., Dokki, Giza, Egypt. Sunflower, (*Helianthus annuus* L.) seeds were germinated in vermiculite growing medium and kept moist during the initial growth period (1 week), which may vary according to plant type. After the germination period, only healthy seedlings with uniform size were selected. Plants were then gently removed from growing medium, and the roots were rinsed off from any adhering material before transferring to the soil.

2. Synthesis of nano zero-valent iron (nZVI)

The nano zero-valent iron prepared from Marjoram (Mar-nZVI) and Moringa (Mor-nZVI) were prepared according to the method described by (Abbassi *et al.*, 2013).

For the synthesis of Mar-nZVI and Mor-nZVI, 20 g. of each dry Marjoram (*Origanum majorana* L) and Moringa (*Moringa oleifera* Lam) leaves powder were heated up to 80°C in 1L deionized water and filtered using a vacuum filter. A solution of 0.1M FeCl₃ was prepared by dissolving solid FeCl₃ in 1 L of deionized water. This solution was mixed for 1h using a stirrer. After mixing, the mixture was centrifuged at 5000 rpm for 30 min

and washed three times with ethylene to remove the residual ferric chloride. The wet paste was then dried in an oven at 60°C overnight, and the final product was grinded before use in the experiment.

3. Characterization and measurements of zero-valent iron (nZVI)

The formation and stability of iron nanoparticles (FeNps) was done by using UV-vis spectrophotometer (Version 530). The absorption spectrum of reaction solutions were recorded at wavelengths ranging from 200 to 500 nm (Narayan and Park 2014).

The morphology, size and shape of F-Fe⁰ were performed by High-resolution transmission electron microscopy (HRTEM), JOEL model JEM-2100 using an accelerating voltage of 200 kV. Sample preparation for TEM analysis involves depositing a drop of aqueous F-Fe⁰ suspension on a carbon-coated copper grid and allowed to dry at room temperature; the transmission electron micrographs is used for recording the particle size and morphology. HRTEM Samples were determined at Al-Azhar University.

4. Experimental design

The potential of Mar-nZVI and Mor-nZVI with and without *H. annuus* for removing thiamethoxam from aqueous solution (100 ml) at an initial concentration of 20 mg/L were evaluated.

The experiment used a pot assay; the pot-culture experiment was arranged in a randomized design that contained six treatments and each treatment consisted of three replicates: (1) Thiamethoxam -contaminated soil with no plants, (2) Thiamethoxam -contaminated soil with *H. annuus* seedling, (3-6) Thiamethoxam -contaminated soil amended with Mar-nZVI and Mor-nZVI separately, with and without a *H. annuus*. A water solution of thiamethoxam was carefully added to the pots to avoid direct contact with the plant shoots. Two milliliters of each FeNps (2.0%) was diluted to 100 ml of water and amended to the soil (treatments, 3–6) until flooding (2 cm over the soil) to maintain an anaerobic condition, while treatments 1 and 2 were amended with water alone until flooding.

5. Sampling and analysis

After 1, 3, 6 and 12 days post treatment, Plant roots from the soil were rinsed in running tap water then blotted, 5 g of leaves, 5 g of roots and 10 g of soil were analyzed for the determination of thiamethoxam residues by high-performance liquid chromatography (HPLC). Thiamethoxam extracted from soil using the quick, easy, cheap, rugged and safe, QuEChERS. Soil samples were homogenized sieved (2 mm mesh) and air-dried at room temperature. A 10 g portion of soil was weighed into a 50 mL

polypropylene tube, then 5 mL of HPLC water was added and the mixture was energetically shaken for 1 min with a vortex device. After that, 10 mL of acetonitrile was added (acidified with acetic acid 1%, v/v for quinmerac analysis) and the mixture was shaken for 1 min by hand and for 1 min with a vortex device.

Four grams of anhydrous magnesium sulfate, and 1 g sodium chloride were added, and the mixture was immediately hand-shaken for 30 s, and centrifuged for 5 min at 4000 rpm in a Sigma 2–5 centrifuge (Sigma, Steinheim, Germany). Then, a clean-up dispersive solid phase extraction step was carried out by adding the supernatant (7.5 mL, i.e. 1.33 g of soil per mL), to a 15 mL polypropylene tube that contained 1.125 g of MgSO₄ (150 mg MgSO₄ per mL of extract) and 0.225 g of C₁₈ (30 mg C₁₈ per mL of extract), hand-shaken for 30 s and centrifuged for 5 min at 4000 rpm (Asensio-Ramos *et al.*, 2010 and Padilla-Sanchez *et al.*, 2010). For the determination of two pesticides, 1.0 mL of the final extract was analysed by HPLC. Fresh root and leaf samples were chopped, mixed well, and then homogenized with dry ice using a high-speed blender. Extraction and cleanup were conducted using QuEChERS method introduced by (Lehotay *et al.*, 2010) and modified as follows: Finely samples (5 g) were weighed into 50 mL Teflon centrifuge tubes; 8 mL of acetonitrile and 2 mL of methanol were added together and the samples were shaken vigorously for 1 min by shaker to ensure the solvent interacted well with the entire samples. The sample tubes were then stored in a refrigerator at –20°C for 20 min. After that, 4 g MgSO₄ and 1 g NaCl were added and the samples were vortexed immediately for 1 min. The extracts were then centrifuged for 5 min at 5000 rpm. From the upper layer of the prepared sample, 2 mL of the samples were transferred into a 10 mL tube containing 25 mg PSA sorbent, 125 mg MgSO₄ and the samples were again vortexed for 1 min and then centrifuged for 5 min at 5000 rpm. The obtained residue was finally filtered using a 0.22 µm Nylon syringe filter for HPLC analysis.

The operating parameters were as follows: a C₁₈ reversed-phase column was used (250 × 4.0 mm i.e.), mobile phase consisted of 100% acetonitrile with isocratic mode at a flow rate of 1.0 mL/min, and UV detection at 280 nm.

The injection volume was 10 µL for quantitative analysis. The retention time of Thiamethoxam was 2.83 min.

The removal efficiency of thiamethoxam was calculated as follows:

$$\text{Removal (\%)} = (C_0 - C_e) / C_0 \times 100$$

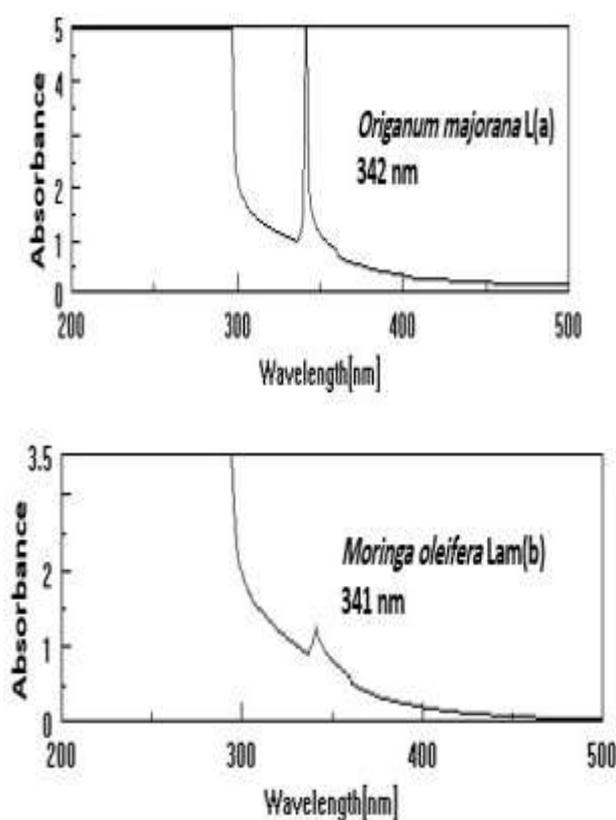
Where: C₀ and C_e are the concentration of Thiamethoxam at initial post treatment of each period µg/ml, or µg/g.

RESULTS AND DISCUSSION

1. Characterization

The surface plasmon resonance (SPR) peaks were found to be 342 and 341, respectively, for FeNps from *Origanum majorana* L and *Moringa oleifera* Lam (Figure 1 a & b), causing the synthesis of FeNps in the size from 2 to 100 nm (Bar *et al.*, 2009; Philip *et al.*, 2011 and Mittal *et al.*, 2013).

The analysis of electron microscopy shows that the formed nanoparticles of nano zero-valent iron prepared from Marjoram (Mar-nZVI), and B, zero-valent iron prepared from Moringa (Mor-nZVI) were circular shapes and sizes. The Mar-nZVI and Mor-nZVI were well separated and there was no agglomeration. The shapes of nanoparticles were circular, with sizes lower than 100nm (Figure 2. A& b).



Figure(1). UV-visible spectroscopy of iron nanoparticles (FeNps) synthesized with two medicinal plant leaf extracts in 0.1M FeCl₃ solution. (a) Marjoram - FeNps. (b) Moringa - FeNps.

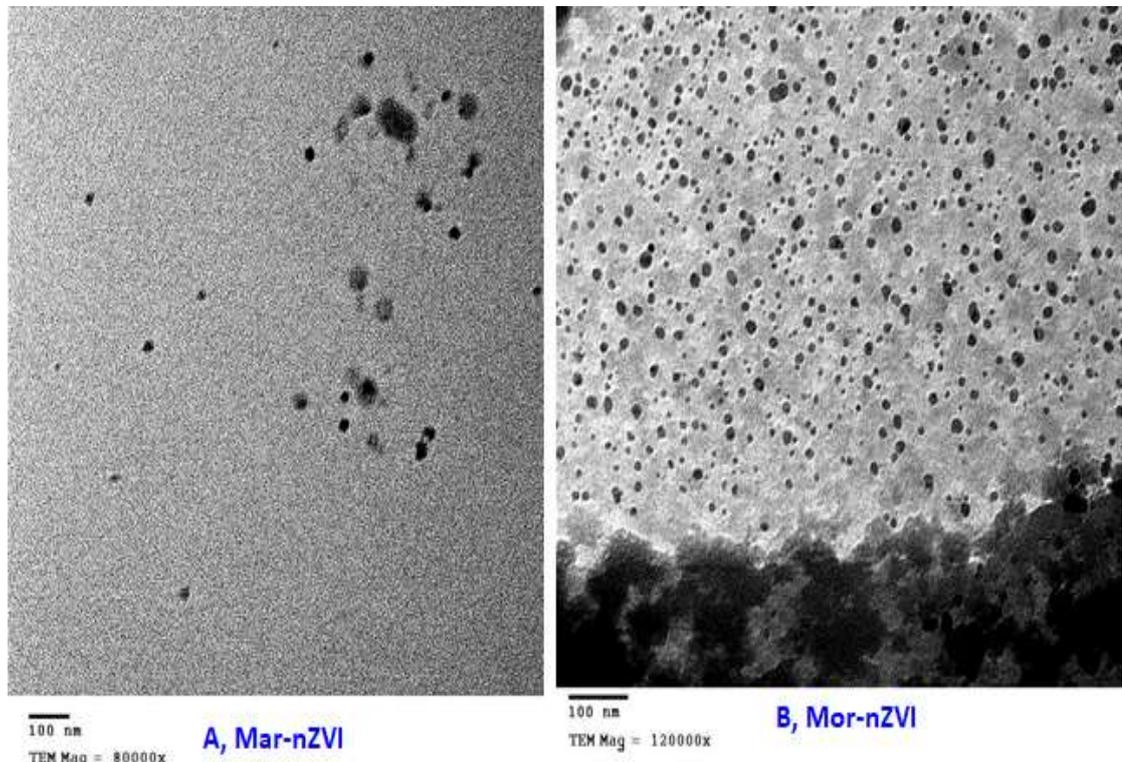


Figure 2. High-resolution transmission electron microscopy (HRTEM). A, nano zero-valent iron prepared from Marjoram (Mar-nZVI), and B, zero-valent iron prepared from Moringa (Mor-nZVI).

2. Remediation of soil polluted by thiamethoxam by nZVI

The preparation of nano zero-valent iron prepared from Marjoram (Mar-nZVI) and nano zero-valent iron prepared from Moringa (Mor-nZVI) with and without *H. annuus* for the removal of thiamethoxam pesticide from flooded soil has been investigated in Figures (3 and 4).

The percent removal of thiamethoxam in the soil by Mar-nZVI and Mor-nZVI reached 75.13 and 66.83% respectively, compared with 61.06% in soil without nZVI through 12 days (Figure 4). The results showed that the Mar-nZVI played the most important role in the removal of thiamethoxam in the soil, compared with natural degradation in soil without nZVI. Studies have shown that many pesticides can be destroyed using ZVI. It also has been successfully used in dechlorination of highly recalcitrant pesticides and herbicides (Doong and Lai, 2006 and Sayles *et al.*, 1997). When halogenated organic pollutants are treated with ZVI, oxidation of ZVI and Fe(II) provides electrons for dechlorination (Satapanajaru *et al.*, 2008). Young-Soo

and Li (2003) studied the reduction of eleven nitroaromatic pesticides with zero-valent iron powder.

The removal of other pollutants such as chlorinated organic compounds, pesticides, phenols, amines, and organic acids through such nanoparticles has been studied (Wang *et al.*, 2013). Nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides, and polychloro biphenyls (Elliott and Zhang, 2001; Glazier *et al.*, 2003; Ivanov *et al.*, 2004; Quinn *et al.*, 2005 and Mauter and Elimelech, 2008). The iron-based soil treatment has shown promising results over relatively long treatment periods (e.g., up to six years) in a variety of contaminated soils (Mench *et al.*, 2006).

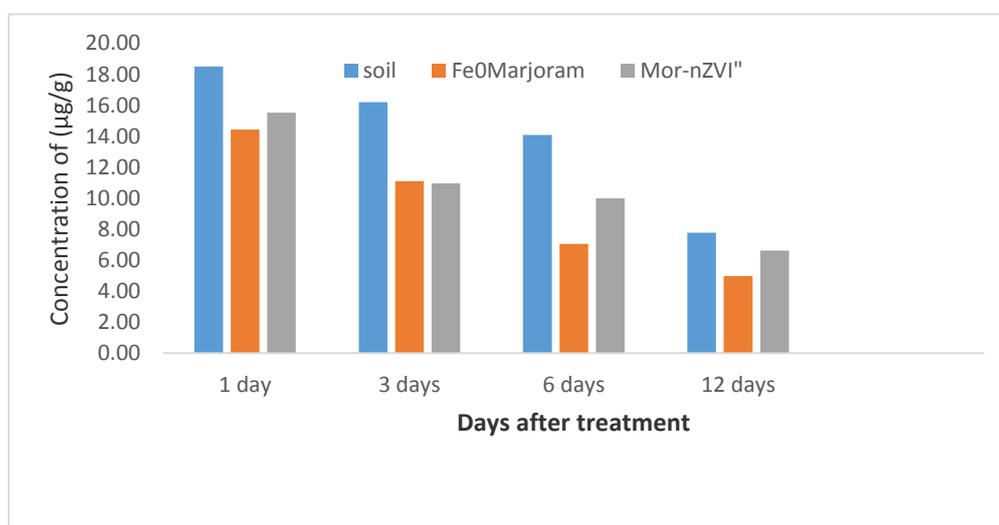


Figure (3) Degradation of thiamethoxam in soil by zero-valent iron nanoparticles.

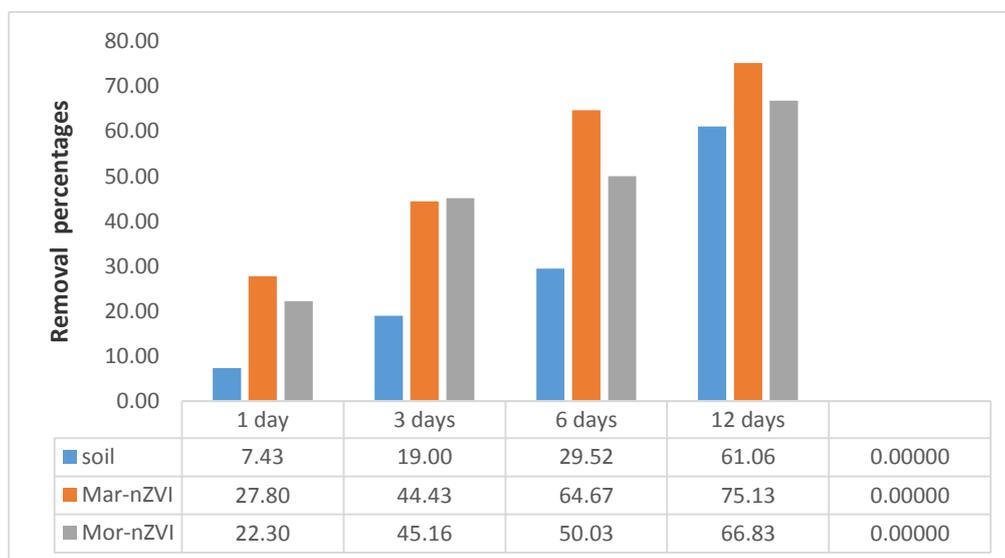


Figure (4) Percent removal of thiamethoxam in soil by zero-valent iron nanoparticles.

3. Nano-Phytotechnological removal of thiamethoxam polluted soil

The degradation of thiamethoxam by FeNps amended with *H. annuus* in flooded soil is shown in Fig. 5. The percent removal of thiamethoxam by Mar-nZVI amended with *H. annuus*, Mor-nZVI amended with *H. annuus* and *H. annuus* alone in flooding soil within 12 days was 89.46, 80.98, and 77.32%, respectively (Fig. 5). The degradation percentage of thiamethoxam in the controls without FeNps and without *H. annuus* within 12 days was 61.06 % (Fig. 4). Thiamethoxam was removed more quickly in the presence of *H. annuus* plus nZVI than that by *H. annuus* alone (Table 1). Soil moisture played an important role to increase ionization and activation of nZVI (Kim *et al.*, 2010). This may be because soil saturation with water decreases the oxygen levels and thus prevent the oxidation of nZVI (El-Temsah and Joner, 2013).

Pesticides, which are persistent in aerobic environments, are more readily degraded under reducing conditions (Comfort *et al.*, 2001). Data in Table 1 and Fig. 5 showed that thiamethoxam uptake into the *H. annuus* roots at high level and reached the maximum 17.35 µg/g after 6 days of exposure. While, in *H. annuus* roots treated with Mar- FeNps and Mor-FeNps reached 9.51 and 11.60 µg/g, respectively, may be due to increasing degradation processes in soil by FeNps. The accumulation of thiamethoxam in *H. annuus* leaves were lower efficient under the treatments of *H. annuus* L. plus nZVI than that by *H. annuus* alone. This is attributed to the role

nZVI alone in degradation of thiamethoxam in soil; therefore, the concentration of thiamethoxam was more decreased in the roots and in the leaves of *H. annuus* (Table 1). Pillai and Kottekottil (2016) show that the removal of endosulfan reached 82% within 7 days when nano phytoremediation experiments were conducted with *A. calcarata* then gradually decreased, probably due to the activity of nZVI decreased over time. In addition, removal efficiency was found to be highest when nano-phytoremediation experiments were conducted in soil with the TNT/nZVI ratio of 1/10 with the complete TNT remediation (initial TNT concentration: 100 mg/kg) within 60 days (Jiamjitpanich *et al.*, 2013). Earlier researches have proven the combination of nanoparticles and plant species performed significant contaminants removal from contaminated soil. (Ma and wang, 2010; Pillai and Jesitha, 2016 and Souri *et al.*, 2017).

Table 1. Degradation of Thiamethoxam in soil by zero-valent iron nanoparticles plus *H. annuus*.

Treatments	Days after treatments			
	1 day ($\mu\text{g/g}$)	3 days ($\mu\text{g/g}$)	6 days ($\mu\text{g/g}$)	12 days ($\mu\text{g/g}$)
SOIL				
<i>H. annuus</i>	15.32	14.75	10.73	4.54
Mar-nZVI + <i>H. annuus</i>	12.35	9.62	7.02	2.11
Mor-nZVI+ <i>H. annuus</i>	13.02	9.75	6.17	3.80
Roots				
<i>H. annuus</i>	3.69	12.49	17.35	10.44
Mar-nZVI + <i>H. annuus</i>	0.17	4.47	9.51	3.71
Mor-nZVI+ <i>H. annuus</i>	1.79	7.92	11.60	5.72
Leaves				
<i>H. annuus</i>	2.23	5.86	11.83	16.18
Mar-nZVI + <i>H. annuus</i>	0.16	2.27	4.18	10.76
Mor-nZVI+ <i>H. annuus</i>	1.22	3.13	9.44	12.63

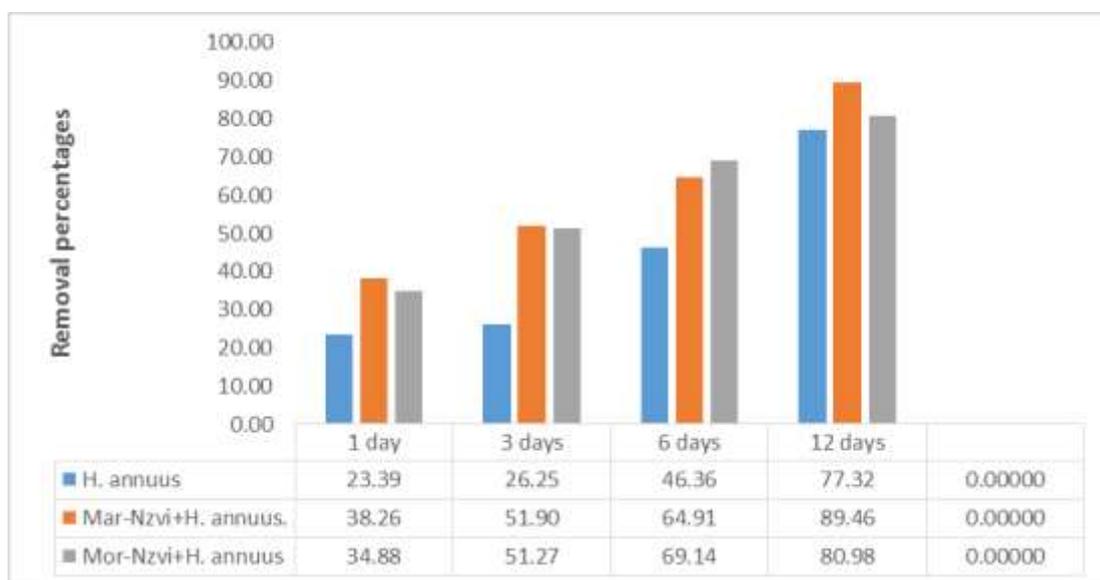


Figure (5) Percent removal of Thiamethoxam in soil by zero-valent iron nanoparticles plus *H. annuus*.

Conclusively, from these results it be concluded that helianthus annuus L. plus nZVI plays a major role for the remediation of thiamethoxam-contaminated soil.

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معالجة التربة الملوثة بالثياميزوكسام باستخدام تكنولوجيا النانو الخضراء والمعالجة النباتية

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فُحص إزالة مبيد الثياميزوكسام من التربة عن طريق استخدام الصورة النانوية للحديد الصفري الذي تم تحضيره من نباتي البردقوش والمورنجا في حالة وجود أو عدم وجود نبات دوار الشمس. تم تحديد الشكل والتركيب للصورة النانوية للحديد الصفري من نباتي البردقوش والمورنجا بواسطة مطيافية الأشعة فوق البنفسجية المرئية والميكروسكوب الإلكتروني النافذ عالي الدقة. أظهرت النتائج أن الصورة النانوية للحديد الصفري باستخدام نبات البردقوش كان له الدور الأكبر في إزالة مبيد الثياميزوكسام في التربة بالمقارنة مع التحطم الطبيعي في التربة بدون وجود معالجة النانو. كانت النسبة المئوية لإزالة الثياميزوكسام في التربة بواسطة النانو المحضر من البردقوش والمورنجا ٧٥.١٣% و ٦٦.٨٣% على التوالي بالمقارنة مع ٦١.٠٦% في التربة بدون معالجة النانو خلال ١٢ يوم. تم إزالة الثياميزوكسام من التربة بشكل أسرع في حالة وجود نبات دوار الشمس بالإضافة لمعاملة النانو بالمقارنة مع نبات دوار الشمس فقط. إنتقل مبيد الثياميزوكسام إلى جذور نبات دوار الشمس بنسبة كبيرة وكان الحد الأقصى له ١٧.٣٥ ميكروجرام/مليجرام بعد ٦ أيام من التعرض للمبيد.

وصل مبيد الثياميزوكسام في جذور نبات دوار الشمس إلى ٩.٥١ و ١١.٦٠ ميكروجرام/مليجرام على التوالي في كل من معاملة النانو من البردقوش والمورنجا. كان تراكم مبيد الثياميزوكسام في أوراق نبات دوار الشمس اقل كفاءة تحت تأثير معاملة النانو ونبات دوار الشمس بالمقارنة مع نبات دوار الشمس فقط. وهذا يُعزي إلى دور معاملة النانو فقط في تحطم الثياميزوكسام في التربة. لذلك كان تركيز الثياميزوكسام اقل في الجذور والأوراق لنبات دوار الشمس.

التوصية: من هذه النتائج يوصى بان نبات دوار الشمس بالإضافة إلى معاملة النانو دورا رئيسيا في معالجة التربة الملوثة بالثياميزوكسام.