

## APPLICATIONS OF LASER TECHNOLOGY AND NANOPARTICLES FOR SOIL REMEDIATION BY HEAVY METALS REMOVAL

A.E.El-Raie<sup>1</sup>, M.A. Aziz<sup>2</sup>, H.E. Hassan<sup>3</sup> and E.Abdelsalam<sup>4</sup>

### ABSTRACT

*Soil is the basic natural resource needed for more than 95 % of the global food and fiber production; thus it represents a basic requisite for life on earth. So, soil pollution attracts the attention of the researchers to reduce soil pollution. As a result of the irrigation by wastewaters and the use of chemical fertilizers and pesticides, the amount of heavy metals in the soil exceeds the maximum permissible limits. In the current investigation, the removal of heavy metals from soil layers (0-15, 15-30 and 30-45 cm) in soil columns, by iron nanoparticles (Fe NPs) and iron nanoparticles deposit on the surface of silica nanoparticles (SiO<sub>2</sub>/Fe NPs), has been studied. Fe NPs were prepared by borohydride reduction method and irradiated with 308 nm excimer laser pulses. The results indicated that the following points: 1) The maximum absorption of Fe NPs irradiated with 308 nm excimer laser pulses (50, 75 and 100 thousand pulses [tp]); found to be increased as the number of pulses increased, due to increasing of the number of particles and size reduction. The TEM photography gives good criteria about the size reduction process; 2) All sizes of Fe NPs and SiO<sub>2</sub>/Fe NPs proved to be a good technique for soil remediation in the case of Pb, Cd and Cu; 3) Removal efficiency of heavy metals was found to vary between soil layers (0-15 , 15-30 and 30-45 cm); by 84.62, 69.80 and 61.04%, for Pb, 98.05, 83.76 and 62.14% for Cd and 67.58, 63.76 and 59.33% for Cu, respectively, with treated 50 tp. This found to be decrease as increase of clay and organic matter content; and 4) The removal process was observed to much less efficient in the case of Ni found in the soil layers (0-15 , 15-30 and 30-45 cm) were 32.81, 39.83 and 8.53% respectively, with treated 50 tp.*

**Key words:** Soil remediation, Fe nanoparticles, Heavy metals, Excimer laser.

---

1- Prof. Dr., Agric. Eng. Dep., Fac. of Agric., Cairo Univ.

2 & 3- Assoc. Prof., Inst. of Laser Enhanced Sc. (NILES), Cairo Univ.

4- Assist. Lec., . Inst. of Laser Enhanced Sc. (NILES), Cairo Univ.

## INTRODUCTION

Inputs of trace elements through human activities have been increased since the last century. Both industrial and agricultural operations contribute to the elevation of trace metals in soil. The smelter-related industries often act as point sources of metals, which enter agroecosystems by dry and wet deposit or use of industrial byproducts. Use of metal-containing substances in agriculture has significantly increased to sustain crop production. Application of trace elements such as Cu, Zn, Fe, Mn, and B that are essential to plant growth is now common practice for correcting deficiencies in these elements (**Fageria et al., 2002**).

**Rabie and Abd El-Sabour (1999)** reported that the total Pb in the surface layer (0-15 cm) of soil irrigated with wastewater of Shebin El-Qanater collector, El-Shaboura canal and Mostorod collector drain was 233, 184 and 180 ppm, respectively. While, for the soil depth of (15-30 cm) was 169, 164 and 169.7 ppm, respectively.

**Rabie et al. (1999)** reported that the highest values of total Cd are observed in the surface layers (0-15 cm) of soil irrigated with polluted water of Shebin El-Qanater collector drain, E-Shaboura canal and Mostorod collector drains, reached 8.5, 13.0 and 7.9 mg/kg, respectively. While, the total Cd in deepest layers (15-30 cm) of these soils was 2.6, 4.0 and 7.1 mg/kg, respectively. Moreover, they reported that the total amounts of Cu in the surface layers (0-15 cm) of these soils were 197.3, 106.8, 112.4 and 135.5 mg/kg, respectively. While, in the soil layers (15-30 cm) were 142, 105, 104 and 103 mg/kg, respectively.

**Rashad et al. (1995)** found that the normal level of total Ni in alluvial soils of Nile delta ranged between 21.0- 44.0 ppm (average 32.0 ppm). Concerning contaminated alluvial soils of Egypt, **El-Sayed and Hegazy (1993)** reported that the total content of Ni in contaminated alluvial soils of El-Fayoum Governorate ranged between 33.5 and 77.0 with an average of 55.3 ppm.

**Makino et al. (2006)** reported that Calcium chloride and FeCl<sub>3</sub> were selected as soil-washing chemicals for use in Cd-contaminated paddy soils on the basis of their Cd-extraction efficiency, cost-effectiveness, and relatively low environmental impacts.

**Virkutyte et al. (2002)**, applied a low-level direct current (DC) across electrodes, inserted in the treated soil, to generate an electric field for removal of the contaminants. These electric fields induce the transport of heavy metals ions in soil pore water due to electromigration, as well as electroosmosis and electrophoresis (**Hamed et al., 1991**).

**Gardea-Torresdey et al. (2004)** reported that the remediation of heavy metal-contaminated sites using plants presents a promising alternative to current methodologies. The potential accumulation of *Convolvulus arvensis* L. for Cd(II), Cr(VI), and Cu(II) was determined using an agar-based medium. The shoots of *C. arvensis* plants exposed to 20 mg L<sup>-1</sup> of these heavy metals, demonstrated capability to accumulate more than 3800 mg of Cr, 1500 mg of Cd, and 560 mg of Cu per kg of dry tissue.

**Zhang (2003)** showed that the nanoscale iron particles represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. Nanoscale iron particles have large surface areas and high surface reactivity. Modified iron nanoparticles, such as catalyzed and supported nanoparticles have been synthesized to further enhance the speed and efficiency of remediation.

**Montas and Shirmohammadi (2004)** reported that a mathematical model of nanoparticle transport and pollutant interaction in soil is developed and evaluated. The model includes parameters that are commonly measured independently in non-flowing systems, or with tracers, and 3 “new” parameters emanating from size exclusion and dynamic filtration of nanoparticles. Accurate simulations of nanoparticle transport and pollutant removal were produced with values of the common parameters that compared well to independent experimental measurements.

**Badr and Mahmoud (2007)** showed that the Ag NPs exposed to 193 nm pulsed excimer laser undergo photofragmentation into small particles. The TEM photographs of the Ag NPs taken before and after the irradiation with 10 thousand pulses; 3.5 mJ/pulse, 6 ns duration Excimer laser showed that the particle size was decreased from (11±2 to 5±1 nm). The objectives of the present investigation are:

1) Preparation of Fe NPs via borohydride reduction method, then different sizes were obtained by irradiation with Excimer laser pulses (50, 75 and 100,000 pulse); 2) Preparation of Fe NPs deposits on the surface of Silica NPs ( $\text{SiO}_2/\text{Fe}$  NPs); 3) Removal of heavy metals from soil layers (0-15, 15-30 and 30-45 cm); and 4) Study the effects of particles size of Fe NPs on the removal process of heavy metals.

### **MATERIAL AND METHODS**

**Soil samples:** The samples were collected by using barrel auger from agricultural land; which irrigated by sewer and agricultural drain water in Khalf Allah village, Abu Keber district, El Sharkia governorate. The soil samples were taken from soil layers; surface layer (0-15 cm), middle layer (15-30 cm) and lower layer (30-45 cm), which containing adventitious roots of plants.

**Soil columns:** The columns were designed and fabricated in Laboratory of Laser Applications in Agricultural Engineering at National Institute of Laser Enhanced Sciences (NILES), Cairo University. It fabricated from poly vinyl chloride (PVC) cuboids with dimensions of (4 x 4 x 50 cm). The elevation of the column made from transparent plastic to insure the height of each layer equal to 15 cm inside the column, as shown in Fig. (1). After treatment, the transparent side was removed to collect samples for analysis. The base of the column was closed using square rubber end. The treatment solution was drained from the column by small plastic hose sealed in the center of the rubber end to conical flask to maintain vertical movement of iron nanoparticles.

**Digestion chemicals:** Metals extractions were performed by digestion of soil samples with Hydrochloric Acid (HCl 37%, Sigma) and Nitric Acid ( $\text{HNO}_3$  70%, Sigma).

**Chemicals used for nanoparticles preparation:** Iron and silica coated with iron nanoparticles were prepared using the following chemicals: Sodium borohydride ( $\text{NaBH}_4$ , powder 98%, ALDRICH), Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , granulated 99%, Riedel-de Haën), Tetraethyl orthosilicate (TEOS,  $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ ,  $\geq 98\%$ , Fluka),  $\text{HNO}_3$  70% and Ethyl Alcohol (Ethanol,  $\text{C}_2\text{H}_6\text{O}$ , 96%, Sigma).

**Chemicals required for calibration curves:** Standards solutions of (1000 µg/mL, Merck-Aldrich Grade) were used to generate a calibration curve for each Cd, Cu and Pb.

**Digestion system:** Metals extraction was performed using digestion system which consists of Hotplate (BIBBY, 0-450°C), Boiling flask (250 mL) and Glass condenser (50 cm).

**Atomic Absorption Spectrophotometer (AAS):** It's an analytical equipment (Varian, SpectrAA 55), used to measure the concentration of the metal ions in the sample solution, (Fig 2). The basic components of AAS are Atomization system (spray chamber), Thermal environment (flame), Light Source (hollow cathode lamp), Monochromometer, Detector (photomultiplier) and Acquisition and recording unit.

**Laser photofragmentation system:** it is a system used for controlling the size of iron nanoparticles and consists of 1) Excimer laser XeCl (LAMBDA PHYSIK, LASERTECHNIK, 3 mj/pulse, 6 ns pulse width) operating at 308 nm, 2) Quartz lens for focusing the laser beam on the nanoparticles solution, 3) Quartz cell (4x4x4 cm) filled with the iron nanoparticles solution, 4) Magnetic stirrer (200 rpm) for rotation the solution of the nanoparticles and 5) Small magnet, as shown in Fig. (3).

**Uv-Vis. spectrophotometer:** The absorption spectra of Fe NPs after exposed to the Excimer laser pulses were measured by using Uv-Vis. Spectrophotometer (Varian, Biocary 50). The exciting source is xenon lamp; in the range of 190-1100 nm; while the quartz cell was used for solutions measurement.

**Transmission electron microscopy (TEM):** The TEM images of Fe NPs before and after irradiated by Excimer laser pulses were taken by electron microscopy (Zeiss, 120 kV).

**Samples treatment and preparation:** 1) Soil samples of each layer were air dried and mixed thoroughly, 2) Transfer samples into the soil columns according to its depth, Fig (1), 3) Saturate the soil columns by nanoparticles (50 mL NPs mixed with 450 mL distilled water), 4) Collect several treated soil samples along each layer from the columns after removing the transparent side, 5) Dry the samples in oven (BINDER, 5 °C above ambient up to 300°C) at ...110 °C for 12 h, then ground to

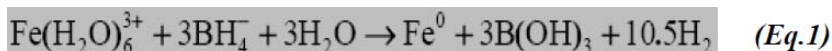
pass through a 2 mm sieve and 6) Store in sealed plastic bags at >20 °C prior to analysis.

**Aqua regia extraction procedure:** Total metals content in the soil sample were estimated using aqua regia extraction method, following the procedure recommended by the International Organization for Standardization (**ISO 11466, 1995.**). Aqua regia extraction leads to the maximum soluble acid amount of metals (**Kalbitz and Wennrich, 1998**), with recoveries from 89 to 110% for some metals in soils and sediments (**Bettinelli et al., 2000.**)

**Metals analysis:** The extracted solution of soil samples were analyzed by flame atomic absorption spectrophotometer (AAS), where the sample solution converts into a fine mist or aerosol to be feed to the flame (air-acetylene gas an oxidant/fuel combination). In the flame, a complicated process involving desolvation of the solution droplets and dissociation of the chemical compounds results in the production of gaseous atoms of the constituent elements, which could be determine by standard or calibration curve.

**Construction of calibration curve:** Three dilutions of standard solution were used to generate a calibration curve for each analysis, from stock standard solutions (1000 µg/mL Merck-Aldrich Grade) of the analytes elements. The calibration curve was obtained by measuring the absorbance of each stander solution, and then plotting the curve of absorbance versus the corresponding concentration.

**Preparation of iron nanoparticles (Fe NPs):** Fe NPs were prepared chemically by reduction method of ferric ions *via* sodium borohydride;



(0.2 M) NaBH<sub>4</sub> was added drop-wise under vigorously stirring into (0.05 M) ferric chloride solution (FeCl<sub>3</sub>.6H<sub>2</sub>O), till the mixture be colorless just before the aggregation of the iron particles. The high concentration difference between the two solutions leads to the formation of iron nanoparticles (**Wang and Zhang, 1997**), according to the following reaction:

**Preparation of silica nanoparticles (SiO<sub>2</sub> NPs):** Silica nanoparticles (SiO<sub>2</sub> NPs) were prepared, using tetraethyl orthosilicate (TEOS) and HNO<sub>3</sub> as an acid catalyst (**Jiang et al., 2004**). TEOS and ethanol with volumes of 10 mL were mixed together; the resulting mixture was dropped in 60 mL 0.1 N HNO<sub>3</sub> solution, the final mixture was stirred for 8 h at 60 °C for complete hydrolysis of TEOS to SiO<sub>2</sub> NPs. The concentration of SiO<sub>2</sub> NPs solution was found to be (30 g/L) after it was completed to 100 mL by distilled water.

**Preparation of Fe NPs adsorbed on the surface of SiO<sub>2</sub> NPs:** Fe NPs deposited on the surface of SiO<sub>2</sub> NPs was prepared by mixing 0.676g of FeCl<sub>3</sub> with 50 mL SiO<sub>2</sub> NPs under vigorously stirring for 5 min. Then, 0.2 M NaBH<sub>4</sub> was added drop-wise to the solution (**Kamat et al., 2002**).

**Photofragmentation of Fe NPs:** Although, the chemical methods are the simplest methods used for preparation of nanoparticles (e.g. metallic), the optimum method used here for preparation of controllable size is the simple chemical method, where particle size is reduced and particle size distribution is decreased (**Badr et al., 2006**). Fe NPs solution exposed to 308 nm excimer laser pulses; the particles undergo photofragmentation into small nanofragments. The quartz cell filled with the solution of Fe NPs and the small magnet is placed inside, then the magnetic stirrer is operated at (200 rpm). Finally, the cell is exposed to the Excimer laser, and the cell is bombarded by certain number of pulses (50, 75 and 100 thousand pulse [tp]) at repetition rate (200 Hz).

**Uv-Vis. spectra of Fe NPs:** The absorption spectra of Fe NPs samples un-irradiated and after exposed to the Excimer laser (50, 100 thousand pulses), were obtained to study the effect of Excimer laser on the particle size of iron nanoparticles.

**Determine the size of Fe NPs:** The average diameters and size distributions of Fe NPs samples after irradiated by Excimer laser were calculated by counting over 150 particles from the enlarged TEM (Zeiss, 120 kV) photography. The samples were prepared by putting a drop of solution on a copper carbon grid and setting the drop dry completely in a desiccator (**Badr and Mahmoud, 2005**).

## RESULTS AND DISCUSSION

### **1. Photofragmentation of iron nanoparticles (Fe NPs)**

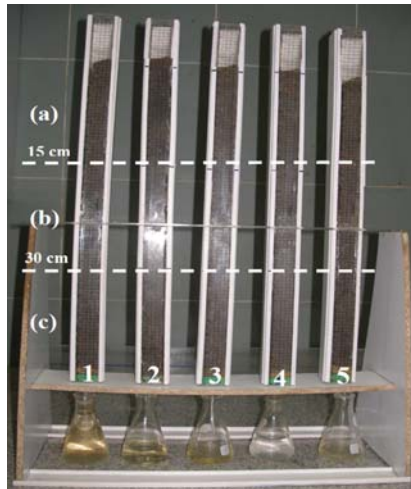
Accordingly in the present work, the iron nanoparticles (Fe NPs) were similarly subjected to 50, 75 and 100 thousand pulses of (XeCl) Excimer laser (3 mJ/pulse, 6 ns pulse width, 200 Hz) operating at 308 nm. The same results were obtained, Fe NPs has an absorption peak corresponding to the surface Plasmon oscillation; the position of this peak was found to depend on their particle size (**Badr et al., 2006**). Fig. (4) shows the absorption spectra of Fe NPs before and after irradiation with 50, 100 thousand pulses of 3mj/pulse excimer laser. A blue shift was observed by increasing the number of pulses which are in the order (350, 345 and 341 nm). Moreover, the peaks intensities were found to be increased; due to increasing of the number of particles, resulting from the photofragmentation. The FeCl<sub>3</sub> has no characteristic peak in the measurement area.

### **2. Effect of the number of laser pulses on the size of Fe NPs:**

The samples of Fe NPs were exposed to laser pulses; 3 mJ/pulse, 308 nm and 6 ns duration excimer laser. Absorption spectra after irradiation were compared with the corresponding untreated samples. In addition, the TEM photography supports the optical measurements. The blue shift and the increasing of the peek intensities were observed due to the increasing of the laser pulses. The TEM images were found to support the size reduction idea as shown in Figs. (5). The particle size distribution as well as the particle size of un-irradiated Fe NPs was 50±5 nm. While, the particles size was decreased due to irradiation by 50, 75 and 100,000 pulses to 40±2, 35±2 and 30±1 nm, respectively. To summarize, the particles size of Fe NPs were decreased as the number of the laser pulses increased.

On the other hand, the SiO<sub>2</sub> NPs showed a spherical shape with large distribution (15±8 nm) **Badr et al., 2008**. While in case of Fe NPs deposited on the surface of SiO<sub>2</sub> NPs the particles size was approximately (25±5 nm) due to the appearance of Fe NPs on the surface of SiO<sub>2</sub> NPs (Fig. 5(E)).

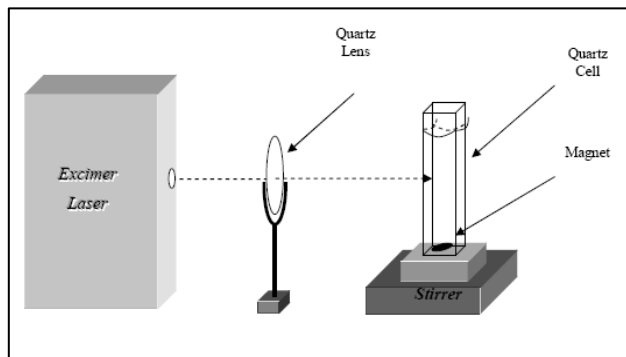




**Fig. (1):** Soil columns containing samples treated with nanoparticles (a) surface layer(0-15 cm), (b) middle layer (15-30 cm) and (c) lower layer (30-45 cm).



**Fig. (2):** Atomic Absorption Spectrophotometer (Varian, SpectrAA 55)



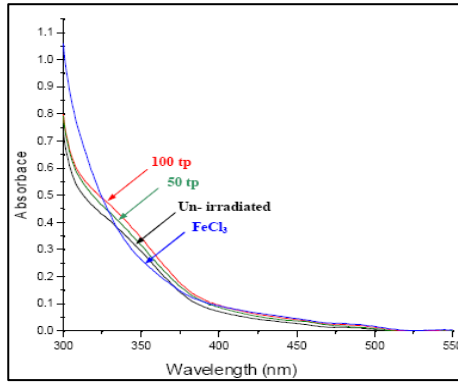
**Fig. (3):** The setup used in photo fragmentation of Fe NPs

### 3. Characterization of soil sample:

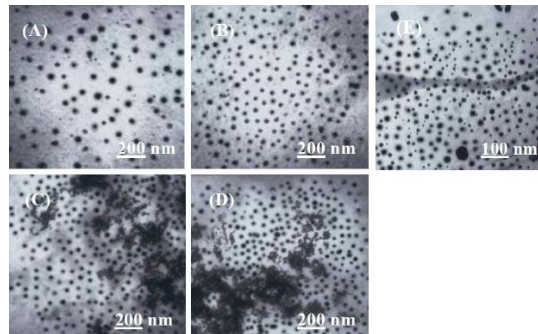
The surface layer (0-15 cm) is the most important layer; because most of the top plant roots (70%) supply 57-65% of plant water requirements from it; such as wheat, barley and maize. Furthermore, it receives all precipitates from the atmosphere, fertilizers and pesticide. In comparison of the controlled values and the maximum permissible limits (MPL) for each metal, the concentrations of the metals ions present in this layer are exceeded than that MPL except for Fe and Mn ions as shown in Fig. (7). Therefore, Fe nanoparticles can be used for soil remediation if the concentration of Fe ions is not exceeds MPL. To characterize soil sample, physical and chemical properties were obtained to different soil layers of the control, as well as heavy metals content. The soil texture of the surface layer (0-15) was sandy, while the other two layers were sandy clay. The percentage of organic matter (O.M.) in the surface layer was lower than middle and lower layers, as shown in Table (1).

**Table (1):** Some physical and chemical properties and heavy metals content of different soil layers.

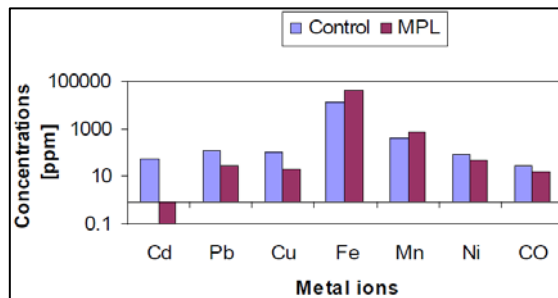
<b>Soil layers</b>	<b>0-15 cm</b>	<b>15-30 cm</b>	<b>30-45 cm</b>
<b>Soil properties</b>			
<b>C. Sand (2-0.2 mm)</b>	<b>7.9</b>	<b>43.9</b>	<b>42.3</b>
<b>F. Sand (0.2-0.02 mm)</b>	<b>51.6</b>	<b>16.7</b>	<b>20.9</b>
<b>Silt (0.02-0.002 mm)</b>	<b>21.2</b>	<b>14.3</b>	<b>15.7</b>
<b>Clay (&lt; 0.002 mm)</b>	<b>19.3</b>	<b>25.1</b>	<b>21.1</b>
<b>Texture Class</b>	<b>Sandy</b>	<b>Sandy Clay</b>	<b>Sandy Clay</b>
<b>pH</b>	<b>7.20</b>	<b>7.32</b>	<b>7.41</b>
<b>EC (dS/m)</b>	<b>0.80</b>	<b>0.48</b>	<b>0.45</b>
<b>Organic Matter (%)</b>	<b>1.44</b>	<b>1.85</b>	<b>1.50</b>
<b>CaCO<sub>3</sub> (%)</b>	<b>5.0</b>	<b>-</b>	<b>-</b>
<b>Cd (ppm)</b>	<b>52.74</b>	<b>97.9</b>	<b>86.1</b>
<b>Pb (ppm)</b>	<b>129.1</b>	<b>261.9</b>	<b>217.9</b>
<b>Cu (ppm)</b>	<b>90.44</b>	<b>170</b>	<b>149</b>
<b>Co (ppm)</b>	<b>24.89</b>	<b>35.7</b>	<b>43.9</b>
<b>Ni (ppm)</b>	<b>101.8</b>	<b>236</b>	<b>211</b>
<b>Mn (ppm)</b>	<b>384.1</b>	<b>1542</b>	<b>1278</b>



**Fig. (4):** The absorption spectra of Fe NPs samples after exposed to 50 and 100 thousand pluses of Excimer laser, un-irradiated and ferric chloride solution ( $\text{FeCl}_3$ ).



**Figs.(5):** The TEM images of Fe NPs; (A) Un-irradiated, (B) irradiated by 50,000 pulses, (C) irradiated by 75,000 pulses, (D) irradiated by 100,000 pulses of excimer laser and (E) Fe NPs deposit on the surface of  $\text{SiO}_2$  NPs.



**Fig. (7):** The concentration of metal ions in the surface layer (0-15 cm) compared with maximum permissible limits (MPL).

#### **4. The concentration of heavy metals in different soil layers after treatments:**

The total metals content in soil layers (0-15, 15-30 and 30-45 cm) was determined before and after treatment by iron nanoparticles (Fe NPs) prepared by the chemical method, Fe NPs after irradiation with (50, 75, 100 thousands pulses [tp]); 308 nm 2.5 mj/pulse excimer laser. Also, another treatment was carried out by Fe NPs deposit on the surface of silica nanoparticles  $\text{SiO}_2$  /Fe NPs.

##### **4.1. Lead:**

###### **The surface layer:**

Because of the toxic effects of lead and to indicate the efficiency of the proposed technique in the present work for soil remediation; a pilot study was carried out by enriching the surface layer of the soil with Pb and by measuring the concentration before and after treatment with Fe NPs, an astonishing result was obtained. The concentration of Pb drop from 2975 ppm to 28.45 ppm after treatment by Fe NPs. i.e, the proposed technique for soil remediation reduced the amount of Pb to less 1% of its value before remediation. This might give an idea about the efficiency of this mechanism. The total content of lead (Pb) in the surface layer (0-15cm) before the treatment by nanoparticles (control) was found to be 129.1 ppm. While the total content of lead was decreased to 16.78, 19.86, 51.80 and 15.53 ppm, after treatment by Fe NPs un-irradiated and irradiated with (50, 75 and 100 thousands pulses [tp]), respectively. Also, the treatment by silicon oxide nanoparticles ( $\text{SiO}_2$  NPs) coated with Fe NPs ( $\text{SiO}_2$ /Fe NPs) decreased the untreated value to 21.36 ppm as shown in the Fig. (8).

###### **The middle layer:**

Fig. (8) Showed that the total Pb content present in soil depth (15-30 cm). It was noticed that, the highest concentration of Pb was found to be 261.9 ppm before treatment (control). After the treatment by Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp) this amount was decreased to 91.8, 79.1, 86.5 and 86.6 ppm, respectively. Also, the treatment by silicon oxide nanoparticles ( $\text{SiO}_2$  NPs) coated with Fe NPs ( $\text{SiO}_2$ /Fe NPs) decreased the untreated value to 70.1ppm.

**The lower layer:**

Fig. (8) Represents the total Pb content found in soil depth (30-45 cm). It was noticed that, the highest concentration of Pb was found to be 217.9 ppm before treatment (control). After the treatment by Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp) this amount decreased to 71.6, 84.9, 82.3 and 93.4 ppm, respectively. Also, the treatment by (SiO<sub>2</sub>/Fe NPs) decreased the untreated value to 102.3 ppm.

**The effect of treatment on lead concentration:**

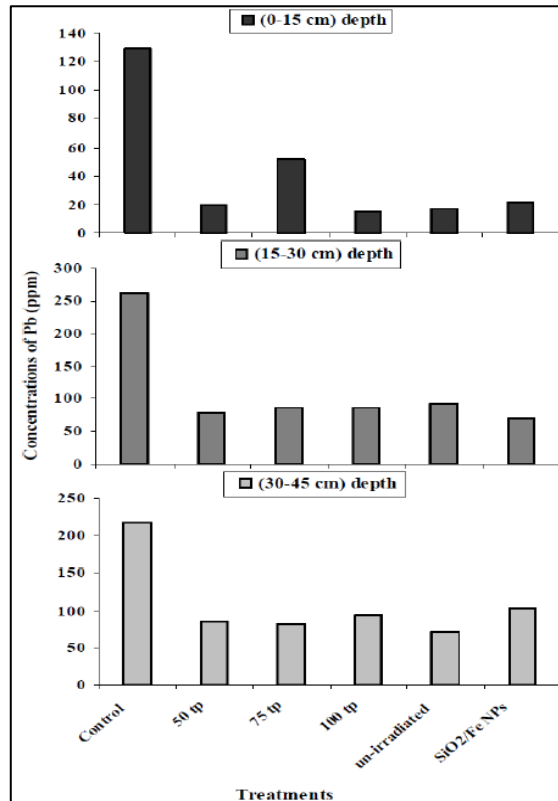
According to the obtained results, it is clearly seen that all sizes of nanoparticles used succeeded in removing high percentage of Pb from soil layers to meet the maximum permissible limit of Pb. Moreover, as indicated in Fig. (9), the effect of treatments on Pb concentration in the surface layer is more than other layers except with the treatment by Fe NPs irradiated with 75 tp, however, the removal percentage in middle and lower layers was increased with this treatment. By comparing the treatments effect in the surface layer, the highest removal % was 87.97 with the treatment by Fe NPs irradiated with 100 tp. While, among all treatments the best effect of the Pb removal with the treatment by the small size of Fe NPs (100 tp) and SiO<sub>2</sub>/Fe NPs.

**4.2. Cadmium:****The surface layer:**

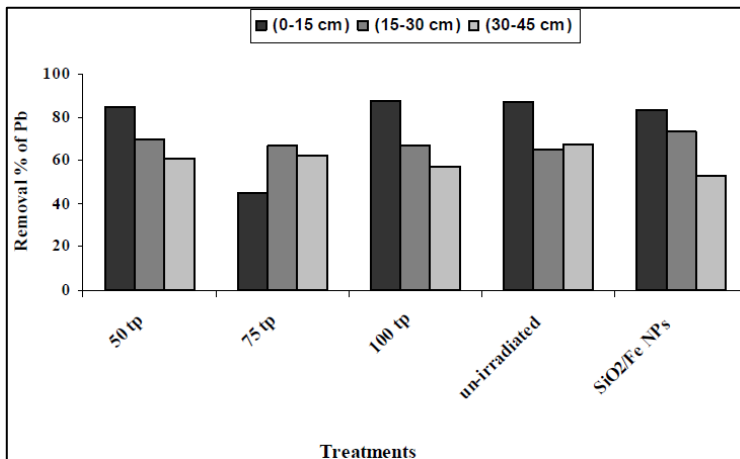
Fig.(10) showed that total Cadmium (Cd) content present in the surface layer (0-15 cm) was 52.74 ppm as a control value. Moreover the treatment by Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp) decreased this amount to 0.25, 1.03, 0.15 and 2.39 ppm, respectively. While, the treatment by (SiO<sub>2</sub>/Fe NPs) decreased the control value by large amount to 0.09 ppm.

**The middle layer:**

The concentration of total Cd present in the middle layer (15-30 cm) was 97.9 ppm as a control value. Moreover, this amount decreased to 32.8, 15.9,



**Fig. (8):** The total content of Pb in soil layers (0-15, 15-30 and 30-45 cm) before and after treatment by nanoparticles.



**Fig. (9):** The removal percent of Pb from different soil layers after treatment by Fe NPs and SiO2/Fe NPs.

20.6 and 28.1 ppm, after the treatment by Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp), respectively. While, the treatment by (SiO<sub>2</sub>/Fe NPs) decreased the control value to 39.5 ppm as shown in Fig. (10).

#### **The lower layer:**

As shown in Fig. (10) the concentration of total Cd present in the lower layer (30-45 cm) was 86.1ppm as a control value. While, this amount decreased to 36.1, 32.6, 37.5 and 39.4 ppm, after the treatment by Fe NPs un-irradiated and irradiated with (50, 75, 100 tp), respectively. Also, the treatment by (SiO<sub>2</sub>/Fe NPs) decreased the control value to 33.7 ppm.

#### **The effect of treatment on cadmium concentration:**

The obtained results showed that, all size of iron nanoparticles succeeded in removing high percentage of Cd from different soil layers. Fig. (11) indicated that the removal % of Cd form surface layer was over 95 % for all treatments; however the highest removal % with SiO<sub>2</sub>/Fe NPs was 99.83 %. By comparing the treatment effects in the middle layer; the highest removal % was 83.76 with Fe NPs irradiated by 50 tp. also, in the lower layer the highest percent of Cd removal was 62.14%. The treatment by Fe NPs irradiated by 50 tp have greater effect on Cd removal from soil layers although the high concentration of the control.

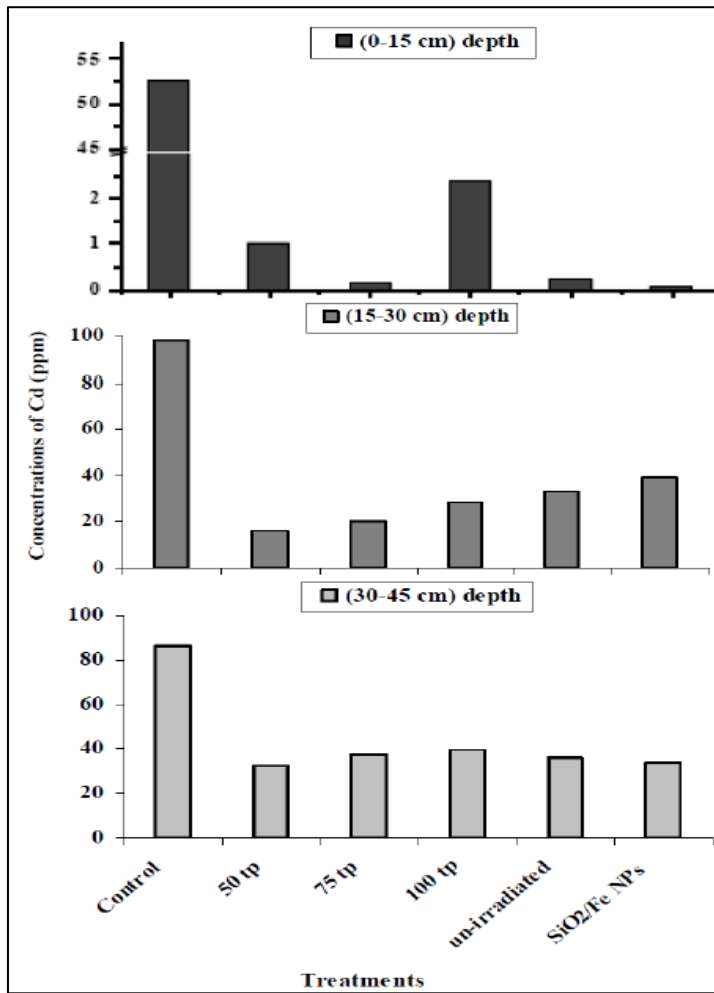
### **4.3. Copper:**

#### **The surface layer:**

As shown in Fig. (12) the total content of copper (Cu) at the soil depth (0-15 cm) was 90.44 ppm as control value. This value was decreased to 36.02, 29.32, 29.99 and 33.28 ppm, by the treatment of Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp), respectively. Also, the treatment by (SiO<sub>2</sub>/Fe NPs) was decreased the control value to be 33.73 ppm.

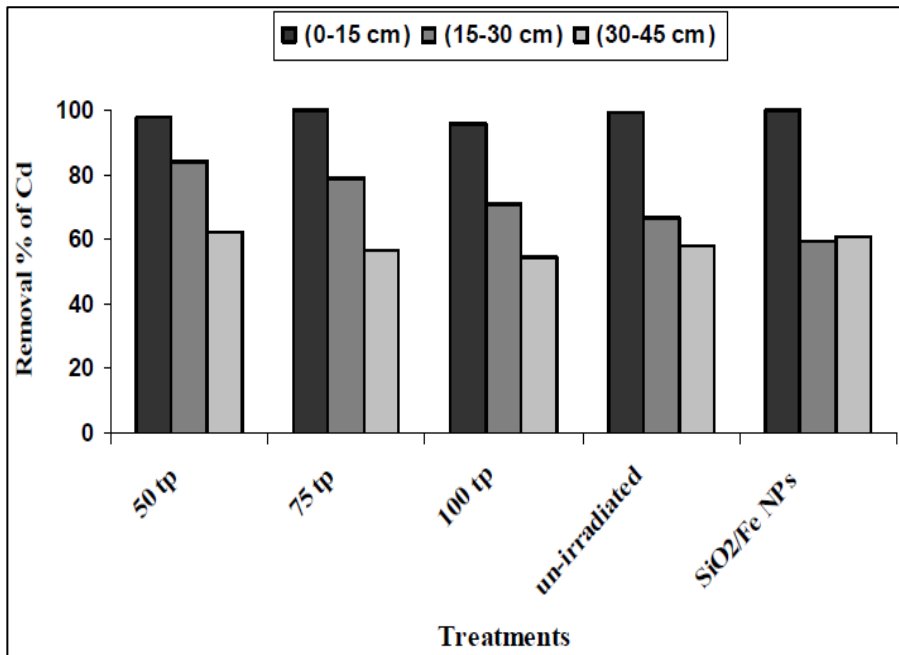
#### **The middle layer:**

The total Cu content at the soil depth (15-30 cm) was 170 ppm as control value. This value was decreased by the treatment of Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp) to 70.5, 61.6, 71.4 and 72.4 ppm,



**Fig. (10):** The total content of Cd in soil layers ( 0 - 15, 15 - 30 and 30 - 45cm) before and after treatment by nanoparticles.





**Fig. (11):** The removal percent of Cd from different soil layers after treatment by Fe NPs and SiO<sub>2</sub>/Fe NPs.

respectively, while the treatment by (SiO<sub>2</sub>/Fe NPs) was decreased to be 63.5 ppm as shown in Fig. (12).

#### **The lower layer:**

Fig. (12) represents the total Cu content found in soil layer (30-45 cm). The control value of Cu was 149 ppm. This value was decreased by the treatment of Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp) to 62.4, 60.6, 60.5 and 69.5 ppm, respectively. Also, the treatment by (SiO<sub>2</sub>/Fe NPs) was decreased the control value to be 69.8 ppm.

#### **The effect of treatment on copper concentration:**

According to the results of treatment by nanoparticles, all size of iron nanoparticles succeeded in removing over 53 % of Cu concentration from soil layers. As shown in Fig. (13) the removal percentage of Cu from the soil layers was almost the same for all treatments. The highest ones was 67.58, 63.76 and 59.33 % for surface, middle and lower layers, respectively, by the treatment of Fe NPs irradiated by 50 tp .

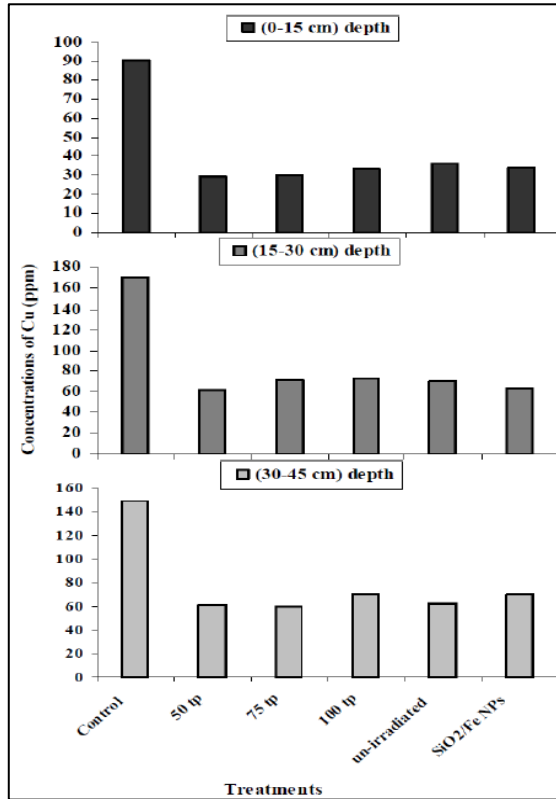
### **4.4. Nickel:**

#### **The surface layer:**

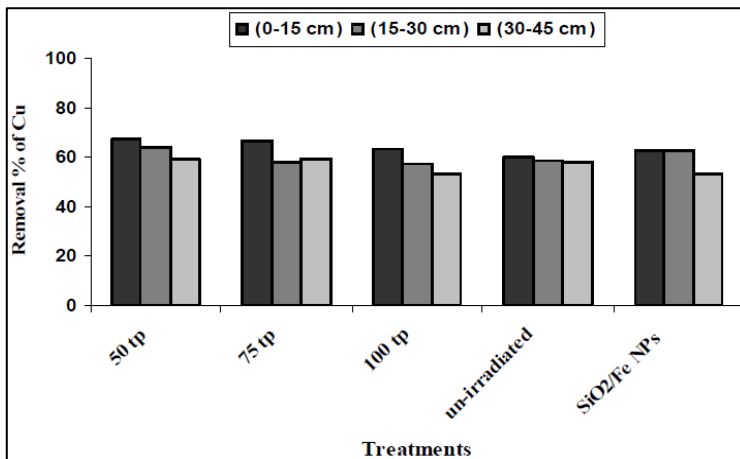
The total nickel (Ni) content present in the surface layer (0-15 cm) was found to be 101.8 ppm before treatment by nanoparticles. Moreover the treatment by Fe NPs un-irradiated and irradiated with (50, 75, 100 tp) decreased this amount to 59.5, 68.4, 76.2 and 88.7 ppm, respectively. Also, the treatment by (SiO<sub>2</sub> / Fe NPs) decreased the untreated value to 71.2 ppm as shown in Fig. (14).

#### **The middle layer:**

The total Ni content present in the middle layer (15-30 cm) was found to be 236 ppm before the treatment by nanoparticles. Moreover, the treatment by Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp) decreased this amount to 220, 142, 122 and 141 ppm, respectively. Also, the treatment by (SiO<sub>2</sub> / Fe NPs) decreased the untreated value to 128 ppm as shown in Fig. (14).



**Fig. (12):** The total content of Cu in soil layers (0-15, 15-30 and 30-45 cm) before and after treatment by nanoparticles.



**Fig. (13):** The removal percent of Cu from different soil layers after treatment by Fe NPs and SiO<sub>2</sub>/Fe NPs.

**The lower layer:**

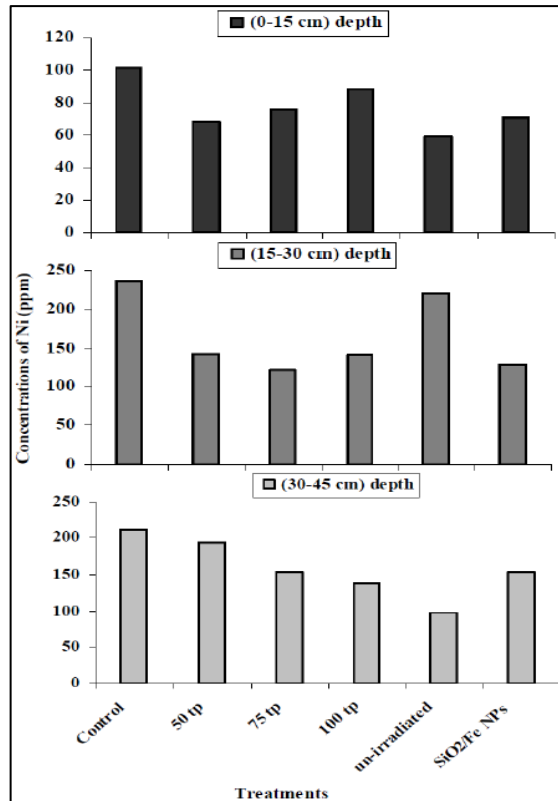
The total Ni content present in the lower layer (30-45 cm) was found to be 211 ppm before treatment. After the treatment by Fe NPs un-irradiated and irradiated with (50, 75 and 100 tp), this amount decreased to 97, 193, 155 and 138 ppm, respectively. Also, the treatment by (SiO<sub>2</sub> / Fe NPs) decreased the untreated value to 155 ppm, as shown in Fig. (14).

**The effect of treatment on nickel concentration:**

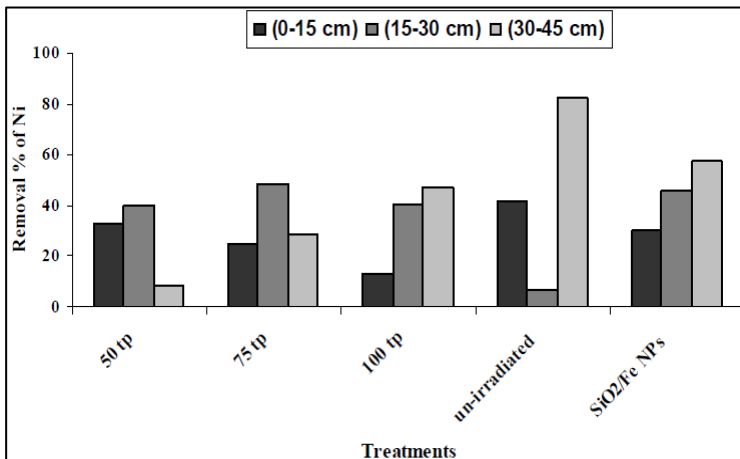
According to the given here data, it is clearly seen that all size of Fe NPs and SiO<sub>2</sub>/Fe NPs could produce slight removal of Ni from soil first layers, then the removal efficiency increased in the lower layer by 82.61 % in the case of un-irradiated Fe NPs. While, the highest removal percentage in the middle layer was 48.31 % in the case of Fe NPs irradiated by 100 tp. It is also indicated that the smallest size of Fe NPs (irradiated with 100tp) removed Ni from the middle and lower layers more than the surface layer, because the small size will move faster through the surface layer, where the % of Ni removal was 12.87, 40.25 and 47.10 %, respectively. The removal % of Ni with the treatment by SiO<sub>2</sub>/Fe NPs was increased with soil depth by 30.06, 45.76 and 57.73 %, respectively, as shown in Fig. (15).

**5. The Reduction Adsorption Mechanism of Nanoparticles:**

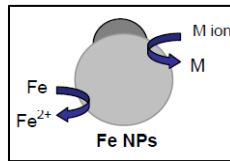
The suggested mechanism for the soil remediation by Fe NPs involves concerted adsorption of metal ions on the surface of nanoparticles and oxidation-reduction reaction between the iron atoms and the adsorbed ions, as shown in Fig. (16). Each iron atom supplies the metal ion by two electrons and reduced it to the corresponding metal and the ferrous ion will produced, the formed metal adsorbed on the surface of Fe NPs as given in equations (2) and (3). Moreover, the adsorbed ions could have a stander reduction potential higher than the stander reduction potential of iron (-0.44 V, 298 k) **Li and Zhang, 2006**. Table (2) represents the stander reduction potentials of the target metal ions.



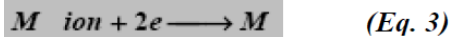
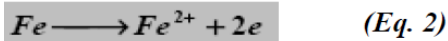
**Fig. (14):** The total content of Ni in soil layers (0-15, 15-30 and 30-45 cm) before and after treatment by nanoparticles.



**Fig. (15):** The removal percent of Ni from different soil layers after treatment by Fe NPs and SiO<sub>2</sub>/Fe NPs.



**Fig. (16):** Mechanism of remediation of metal ions by Fe NPs.



**Table (2):** The stander reduction potentials of the target metal ions.

Metal ions	Stander Reduction Potential (V, 298 k)
Cd <sup>2+</sup>	-0.4
Ni <sup>2+</sup>	-0.25
Pb <sup>2+</sup>	-0.13
Cu <sup>2+</sup>	0.34

### 6. The Effect of Particle Size on Heavy Metals Removal:

It was noticed that from the obtained results, iron nanoparticles (i.e. 20-50 nm), have the ability to remove some heavy metals from soil layers, as well as iron deposit on the surface of silica nanoparticles. But on the other hand, the effect of particles size of iron nanoparticles showed a different removal effects. This observation might refer to the percent of organic matter, calcium carbonate and pH of the soil.

### CONCLUSION

The main conclusion of the present work can be summarized as follows:

1. The maximum absorption of Fe NPs irradiated with 308 nm excimer laser pulses (50, 75 and 100 thousand pulses [tp]); found to be increased as the number of pulses increased, due to increasing of the number of particles and size reduction. The TEM photography gives good criteria about the size reduction process.
2. All sizes of Fe NPs and SiO<sub>2</sub>/Fe NPs proved to be a good technique for soil remediation in the case of Pb, Cd and Cu.

3. Removal efficiency of heavy metals was found to vary between soil layers (0-15 , 15-30 and 30-45 cm); by 84.62, 69.80 and 61.04%, for Pb, 98.05, 83.76 and 62.14% for Cd and 67.58, 63.76 and 59.33% for Cu, respectively, with treated 50 tp. This found to be decrease as increase of clay and organic matter content.
4. The removal process was observed to much less efficient in the case of Ni found in the soil layers (0-15 , 15-30 and 30-45 cm) were 32.81, 39.83 and 8.53% respectively, with treated 50 tp.

**Acknowledgement:** We would like to express our deepest gratitude and thanks to **Prof. Dr. Yehia Badr**, Professor of Laser Physics, Former Dean of National Institute of Laser Enhanced Sciences, and Head of Laser Interaction with Matter and Laser Systems Departments, Cairo University, for providing all the facilities during carrying out this study and for his valuable advice.

### REFERANCES

- Abdel-Sabour, M. F.; F.M. Abdou; I.M. Elwan and Y.J. Al-Salama. 2002.** Chromium fractions changes compared with total-Cr as determined by neutron activation analysis technique. Sixth Radiation Physics Conference, October 27-30, 2002, Assiut, Egypt.
- Alwan, I.; M.A. Rizk and M. F. Abdel-Sabour. 2002.** Effect of irrigation with wastewater on Zn fractions in some contaminated soils in Egypt. *Egypt. J. Appl. Sci.* 17(10): 850-864.
- Badr, Y.; M.G. Abd El-Wahed and M.A. Mahmoud. 2006.** On 308 nm photofragmentation of the silver nanoparticles. *Applied Surface Science.* 253: 2502–2507.
- Badr Y. and M.A. Mahmoud. 2007.** Excimer laser photofragmentation of metallic nanoparticles. *Physics Letters A.* 370: 158–161.
- Badr, Y. M.G. Abd El-Wahed and M.A. Mahmoud. 2008.** Photocatalytic degradation of methyl red dye by silica nanoparticles. *Journal of Hazardous Materials* 154: 245–253.
- Bettinelli, M.; G.M. Beone; S. Spezia and C. Baffi. 2000.** Determination of heavy metals in soils and sediments by microwave-

assisted digestion and inductively coupled plasma optical emission spectrometry analysis. *Analytica Chimica Acta*. 424 (2)289-296.

- El-Sayed, E.A. and M.N. Hegazy. 1993.** Total contents and extractable amounts of Cd, Co, Cr and Ni in some soils of El-Fayoum Governorate. *J. of Agric. Resh. and Develop.* 7:46-56.
- Fageria, N.K.; V.C. Baligar and R.B. Clark. 2002.** Micronutrients in crop production. *Adv. Agron.* 77:185–268.
- Gardea-Torresdey, J.L.; J.R. Peralta-Videa; M. Montes; G. de la Rosa and B. Corral-Diaz. 2004.** Bioaccumulation of cadmium, chromium and copper by *Convolvulus arvensis* L.: impact on plant growth and uptake of nutritional elements. *Bioresource Technol.* 92: 229–235.
- Hamed, J.; Y.B. Acar and R.J. Gale. 1991.** Pb(II) removal from kaolinite using electrokinetics. *J. Geotech. Eng.* 117: 241–271.
- ISO 11466, 1995.** Soil quality, Extraction of Trace Elements Soluble in Aqua Regia.
- Jiang, Z.; C. Liu and Y. Liu. 2004.** Formation of silver nanoparticles in an acid-catalyzed silica colloidal solution. *Appl. Surf. Sci.* 233: 135-140.
- Kalbitz, K. and R. Wennrich. 1998.** Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Sci. Total Environ.* 209(1):27-39.
- Kamat, P.V.; M. Flumiani and A. Dawson. 2002.** Metal–metal and metal–semiconductor composite nanoclusters. *Colloids Surf. A* 202: 269-279.
- Li, X. and W. Zhang. 2006.** Iron nanoparticles: the core-shell structure and unique properties for Ni(ii) sequestration. *Langmuir.* 22: 4638-4642
- Makino, T.; K. Sugahara; Y. Sakurai; H. Takano; T. Kamiya; K. Sasaki; T. Itou and N. Sekiya. 2006.** Remediation of cadmium contamination in paddy soils by washing with chemicals: Selection of washing chemicals. *Environ. Pollution.* 144: 2-10.



- Montas, H. J. and A. Shirmohammadi. 2004.** Modeling of soil remediation by nanoscale particles. ASAE/CSAE Annual International Meeting. 2004, No. 043053
- Rabie, F.H.; M.F. Abdel-Sabour; A.T. Mostafa and S.A. Hassan. 1999.** Enrichment factor of heavy metals in different soil grain size fractions as indicator for soil pollution. Assiut Univ. Bull. Environ. Res. 2 (1) 55-68.
- Rabie, F.H. and M.F. Abdel-Sabour. 1999.** Studies on Fe, Mn, Ni and Pb load on soil and its enrichment factor ratios in different soil grain size fractions as an indicator for soil pollution. Assiut Univ. Bull. Environ. Res. 2 (2) 11-23.
- Rashad, I.F.; A.O. Abdel Nabi; M.E. El-Hemely and M.A. Khalaf. 1995.** Background levels of heavy metals in the Nile Delta soils, Egypt. J. Soil Sci. 35:239-252.
- Virkutyte, J.; M. Sillanpaa and P. Latostenmaa. 2002.** Electrokinetic soil remediation-critical overview. Sci. Total Environ. 289: 97–121.
- Wang, C. and W. Zhang. 1997.** Nanoscale metal particles for dechlorination of PCE and PCBs. Environ. Sci. Technol. 31(7): 2154–2156.
- Zhang, W. 2003.** Nanoscale iron particles for environmental remediation: An overview. J. of Nanoparticle Res. 5: 323–332.

### الملخص العربي

## تطبيقات تكنولوجيا الليزر وجسيمات النانو في علاج التربة الزراعية بإزالة المعادن الثقيلة

أ.د. أحمد الراعي إمام سليمان<sup>1</sup> د. مني عبد العزيز<sup>2</sup> د. حلمي السيد حسن<sup>3</sup> عصام عبد السلام<sup>4</sup>

تعتبر التربة المورد الطبيعي الأساسي اللازم لإنتاج أكثر من 95% من الغذاء العالمي وكذا إنتاج الألياف. ولهذا فهي تعد مطلب أساسي للحياة علي الأرض. وقد أدى الري بالمياه الملوثة والحاوية للمخلفات واستخدام المخصبات الكيميائية و المبيدات الحشرية إلي زيادة كمية المعادن الثقيلة ليتجاوز الحدود القصوى المسموح بها. مما أدى إلي انتقالها للإنسان بواسطة النباتات المزروعة في تربه ملوثة.

1- أستاذ الهندسة الزراعية - كلية الزراعة - جامعة القاهرة.

2- أستاذ مساعد تطبيقات الليزر في التكنولوجيا الحيوية الزراعية- المعهد القومي لعلوم الليزر- القاهرة

3- أستاذ مساعد تطبيقات الليزر في الهندسة الزراعية - المعهد القومي لعلوم الليزر- جامعة القاهرة

4- مدرس مساعد- تطبيقات الليزر في الهندسة الزراعية- المعهد القومي لعلوم الليزر- جامعة القاهرة.

ولذلك أجريت تقنيات عده لإزالة المعادن الثقيلة من التربة مثل الغسيل والتنقية النباتية للتربة والحركة الكهربائية. لذا فقد كان الهدف من هذا البحث تحضير جسيمات الحديد النانوية وكذا جسيمات الحديد النانوية المترسبة على سطح جسيمات السليكا النانوية بطريقة كيميائية وتشجيعها بليزر الأكسجين النبضي وذلك لإزالة المعادن الثقيلة من التربة.

تم إجراء هذه الدراسة في المعهد القومي لعلوم الليزر (NILES) بجامعة القاهرة. تم جمع عينات من تربة زراعية (قرية خلف الله- أبو كبير- محافظة الشرقية) ذات محتوى تلوث عالي حيث تروي بمياه صرف صحي وزراعي. تم أخذ العينات من طبقات مختلفه: الطبقة السطحية (0-15 سم)، الطبقة الوسطى (15-30 سم)، والطبقة السفلى (30-45 سم). وقد تم إعداد عينات التربة قبل المعالجة بتجفيفها هوائياً وخطها جيداً ثم وضعها في أعمدة التربة طبقاً لعمقها. وقد تم تقدير تركيز العناصر الثقيلة (الرصاص، الكاديوم، النحاس والنيكل) في العينات الغير معالجة وكذلك بعد تشبع أعمدة التربة بالجسيمات النانوية ( 50مل جسيمات نانوية مخلوطة مع 450 مل مياه مقطرة). تم استخدام تقنية الامتصاص الذري (AAS) لتقدير سريع ودقيق للعناصر كميًا. كما تم تأكيد النتائج المتحصل عليها في المعمل المركزي لتحليل العناصر والنظائر بهيئة الطاقة الذرية.

ويمكن تلخيص النتائج المتحصل عليها في هذه الدراسة كمايلي:

1. عند تشبع جسيمات الحديد النانوية بواسطة أكسيمر الليزر النبضي 308 نانومتر لوحظ أن هناك زيادة في الامتصاص تبعاً للزيادة في عدد النبضات (50- 75- 100 ألف نبضه) وذلك بسبب زيادة عدد الجسيمات و صغر حجمها، وبالنظر إلي الصور التي تم الحصول عليها من الميكروسكوب الالكتروني تبين أنها تصف عملية تصغير الحجم.
2. كل أحجام جسيمات الحديد النانويه و كذلك جسيمات الحديد النانويه المترسبة على سطح جسيمات السليكا النانويه تعتبر تقنيه جيده فى تنقيه التربه من الرصاص و الكاديوم و النحاس.
3. وجد أن كفاءة إزالة المعادن الثقيلة تختلف بين طبقات التربة الثلاثة وكانت للرصاص 84,62 ، 69,80 ، 61,04 % وللكاديوم 98,05 ، 83,76 ، 62,14 % وللنحاس 67,58 ، 63,76 ، 59,33 % علي الترتيب وذلك بالمعالجة باستخدام جسيمات الحديد النانويه المشع بـ 50 ألف نبضة ليزر.
4. لوحظ أن الإزالة ذات كفاءة أقل في حالة النيكل وكانت 32,81 ، 39,83 ، 8,53 % لطبقات التربة الثلاثة.