Application of Nanotechnology in Remediation of Heavy Metals Polluted Soils

Mohamed I. D. HELAL*1), Hassan A. KHATER 1) and Ahmed MARZOOG 2)

Abstract: Nanotechnology offers a number of highly efficient and less costly techniques that could work to immobilize contaminants. Nano-particles; nano scale zero valent iron “nZVI”, nZVI-bentonite, nanoalginite, and nano carbon; are used as a potential sorbents to immobilize Cd and Pb in polluted soils. These nano-particles are prepared in lab either using top-down or bottom-up methods, then characterized using transmission electron microscope (TEM). The prepared nano-particles proved to have very small size (less than 70 nm), high surface area (194.2-259.7 m²/g) and cation exchange capacity (42.5-47.7 Cmol/kg). Also, the prepared nano-particles proved high adsorption capacity for Pb and Cd, and high retention for the adsorbate metal. The maximum adsorption capacity of nano-particles ranged from 37450-93450 and 17850-25970 mg kg⁻¹ for Pb and Cd, respectively. Moreover, except for nano carbon, only small quantities represent 10.8-33.4% and 13.7-35.6% of the previously adsorbed Cd and Pb, respectively, were desorbed. The tested nano particles proved very high efficiency in immobilizing Cd and Pb in polluted soils. The plant available Pb and Cd as extracted using DTPA extract in polluted soils treated with nano particles decreased to levels lower than those (0.06 and 2.88 mg/kg, for Cd and Pb, respectively) reported for non-polluted soils of Egypt.

Key Words: Adsorption, Cadmium, Lead, Nano-particles, Remediation.

1. Introduction

Heavy metals polluted soil is a significant worldwide environmental problem. Plants grown in polluted soils often contain significant levels of heavy metals (Pb, Cd,… etc ) that can impair human health. Various chemical, physical and biological processes have been proposed for decontamination of heavy metals polluted soils such as microbial degradation, filtration, adsorption, and others. However, these methods have many disadvantages, and certain limitations such as high cost, poor removal efficiency and possible future release of stabilized metals. Recently, reactions involving catalytic materials are becoming more ideal way which has been adopted to stabilize heavy metals in polluted soil.

In the last decade, nanotechnology has been increasingly used in soil remediation. Using materials and structures within nanoscale dimensions ranging from 1 to 100 nanometers (nm) is defined as nanotechnology. It includes nanoparticles, nanolayers, and nanotubes. Nanoparticles are defined as a collection of tens to thousands of atoms measuring only about 1 to 100 nm in diameter (Masciangioli and Zhang, 2003). The materials with particle size at the nano-scale exhibits superior activity due to their larger surface area and higher reactivity (Uzum, 2008). Nanoparticles could provide very high flexibility for both in situ and ex situ remediation. For example, nanoparticles are easily deployed in ex situ slurry reactors for the treatment of contaminated soils, sediments, and solid wastes. Alternatively, they can be anchored onto a solid matrix such as carbon, zeolite, or membrane for enhanced treatment of water, wastewater, and soil or gaseous process streams (Mansoori et al., 2008).

In recent years nano scale zero valent iron “nZVI” have received much attention for their potential application for the treatment of contaminated soils and water. According to Zhu et al. (2009), the use of “nZVI” as an in situ remediation technique is currently undergoing evaluation. The basic mechanism for removal initially proposed involves the reduction of contaminant metals followed by the subsequent precipitation of their insoluble forms. Nano scale zero valentiron “nZVI” undergoes oxidation to Fe²⁺ and then to the Fe³⁺ state with standard half cell reactions shown in the following equations (EP A, 1997 and 2004).

\[ \text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}^{0} E_0 = -0.037 \text{ V} \] (1)

\[ \text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}^{0} E_0 = -0.447 \text{ V} \] (2)

\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} E_0 = +0.771 \text{ V} \] (3)

The use of nZVI has been gaining increasing interest in the area of environmental remediation (Zhang, 2003; Li et al., 2006). Transformation of a wide variety of environmental contaminants such as heavy metals, chlorinated hydrocarbons, pesticides, nitrate etc, have been extensively documented (Ponder et al., 2000; Varanasi et al., 2007; Elliott et al., 2009). Nano scale zero valentiron “nZVI” is an excellent electron donor and has high capacity to reduce an array of toxicants, however its tendency for rapid oxidation and aggregation, reduces its reactivity. The “nZVI” is reported as an ideal candidate for in-situ remediation because of its large active surface area and high heavy metal adsorption capacity (Yaacob et al., 2012). The nano-zero valent iron is capable to exchange the toxic substances to non toxic materials.

* Corresponding Author: midhilal@hotmail.com

Giza, Egypt

1) Department of Soil Sciences, Faculty of Agriculture, Cairo University
2) Department of Soil and water Sciences, College of Agriculture, University of Anbar, Iraq
Nano-zero valent iron can also be used to promote the reduction and precipitation of toxic metals such as chromium {Cr (VI)} to more stable form of chromium {Cr (III)} (Blowes et al., 2000).

Bentonite is a traditional low-cost efficient adsorbent, which has high potential for heavy metal removal from wastewater due to its abundance, chemical and mechanical stability, high adsorption capability and unique structural properties (Bhattacharyya and Gupta, 2008). Clay minerals have plasticity when wet, they are chemically thermal stable in geochemical media in a wide range of pH in addition to their low costs and wide availability. Clays (e.g., kaolinite, montmorillonite, bentonite, etc) are potential heavy metal adsorbents (Shahwan et al., 2000). These properties make clay minerals suitable filling and/or support materials for zero valent iron nanoparticles for in situ remediation methods. The most important of all is the potential of kaolinite and Bentonite for the dispersion of zero valent iron nanoparticles. If the dispersion of nanoparticles is achieved, specific surface area and probably specific surface reactivity of nanoparticles will increase, resulting in a great enhancement in remediation capacity.

2. Materials and Methods

2.1. Preparation of nanoparticles

2.1.1. Nanoscale zero valent iron (nZVI)

Synthesis of nZVI is based on reduction of Fe (II) using borohydride (Wang and Zhang, 1997; Wang et al., 2006). Iron (II) chloride tetrahydrate (FeCl$_2$·4H$_2$O) and sodium borohydride (NaBH$_4$) were used for iron (II) and borohydride sources, respectively. The proposed reaction is:

\[ \text{Fe}^{2+} + 2\text{BH}^- + 6\text{H}_2\text{O} \rightarrow \text{Fe}^0 + 2\text{B(OH)}_3 + 4\text{H}_2 \]

2.1.2. Bentonite Supported nZVI (bent.-nZVI)

Bentonite-supported nZVI was synthesized such that final bentonite: zero valent iron ratio was 1:1 (m/m). For 1:1 ratio sample; 5.34 g FeCl$_2$·4H$_2$O was dissolved in a 4:1 (v/v) ethanol/water mixture (24 ml ethanol + 6 ml deionized water). Then 1.5 g bentonite was added to this solution and the mixture was held on a magnetic stirrer to be mixed.

2.1.3. Nanoalginate

Alginite is a naturally occurred rock. It is grayish-green, greenish-grey, sometimes pitted, similar to Aleurite and it has high-specific surface area, number of functional groups and cation exchange capacity. Its solidity is 0.5-1.5 kg/cm$^2$ and its consistency is 2.1-2.4 g/cm$^3$. Its water content ranged from 17-35%. It contains relatively large amount of clay minerals (Montmorillonite, Illite, Cornish stone). Particle content studies state that Alginite contains 20-60% clay fraction. Aleurite is the other important component. Its calcite and dolomite contents varied between 15-26%, and 3-18%, respectively (Solli, 2007). Nanoalginit was prepared in lab using top-down method by ball-milling.

- Nano Carbon: Nano Carbon was collected from ovens of bread in Iraq.

2.2. Nano particle characterization

2.2.1. Particle size

The average particle size distribution and morphology of nanoparticles, nZVI, bent.-nZVI, nanoalginate, and nano carbon, were studied using JEOL transmission electron microscope (JEM-1400 TEM, Japan). A drop of well dispersed nanoparticle dispersion was placed onto the amorphous carbon-coated 200 mesh carbon grid, followed by drying the sample at ambient temperature, before it was loaded into the microscope (Wang et al., 2014).

2.2.2. Cation exchange capacity (CEC)

Cation exchange capacity of nanoparticle were determined using ammonium acetate method as described by Page et al. (1982).

2.2.3. Specific surface area (SSA)

Specific surface area of nanoparticles were determined using O-phenanthroline method (Sparks, 1998).

2.3. Adsorption/desorption of Cd and Pb on nanoparticles

2.3.1. Adsorption

A wide solid: solution ratio of (1:500), relatively low Cd and Pb concentration, and equilibrium period of 24 h, were adopted for the adsorption experiment. Portions of 0.1g of studied nanoparticles (nZVI, bent.-nZVI, nano alginate and nano carbon) were gently shaken with 50 ml 0.01 M CaCl$_2$ containing Cd or Pb concentrations of 1.0, 5.0, 10, 20, 50, and 100 mg l$^{-1}$ for 24 h at 25°C $\pm$1. The solutions were adjusted to pH 7.0 before additions to the adsorbents using 0.1 NHCl or NaOH. The suspensions were then readjusted after addition. The final suspension is centrifuged at 5000 rpm for 10 minutes, and then Cd and Pb concentrations were determined in the clear filtrate using Atomic Absorption Spectrophotometer (UNICAM 969). The adsorbed amounts of Cd and Pb were calculated as the difference between their initial and final concentrations in the equilibrium solution.

2.3.2. Desorption

A solution of 1.0 M MgCl$_2$, pH 7.0 is used for desorption of the previously sorbed Cd and Pb at solid: solution ratio equals to that used for adsorption experiment. The suspension was shaken gently for reaction period of 2 h at 25$^\circ$C. After centrifugation, Cd and Pb concentrations were determined in the clear solution, as the above mentioned.
2.4. Adsorption Models
The validity of Cd and Pb adsorption data to linear form of both Freundlich and Langmuir models were examined. Also, the quantities of both maximum adsorption capacity and affinity (binding energy) have been calculated.

2.4.1. Freundlich Model
The modified Freundlich model used to describe the soils of the present work is as follows:
\[ x/m = kC^{1/n} \]
Where, \( x/m \) is the amount of metal adsorbed per unit mass of adsorbent (mg kg\(^{-1}\)), \( C \) is equilibrium concentration of metal in the reacted solution (mg l\(^{-1}\)), and \( k \) and \( n \) are constants which represent the affinity of metal to the adsorbent and maximum adsorption capacity, respectively.

2.4.2. Langmuir Model
Langmuir model used to describe adsorption is:
\[ C/(x/m) = 1/kb+C/b \]
Where, \( x/m \) and \( C \) have been mentioned above, \( k \) is a constant related to bonding energy of metal to the adsorbent, and \( b \) is the maximum adsorption capacity of metal ions on the adsorbent.

2.5. Immobilization of Cd and Pb in polluted soils

2.5.1. Soil samples
Surface (0-30 cm) soil samples were collected from different polluted sites received heavy metals from different sources; Domestic sewage sludge polluted sites (Abo-Rawash and El-Gabal El-Asfer), Industrial residues discharge polluted sites (Mostorod), Vehicle exhausts polluted site (Shubra). The collected soil samples were air-dried, crushed, sieved to remove gravels, then the fine earth (< 2 mm) were stored for lab experiments.

2.5.2. Immobilization technique
The studied soil samples were treated with nano particles (nZVI, bentonite-nZVI, nano alginit and nano carbon). The nano particles were added to heavy metals polluted soils at three rates of 0.1, 0.5, and 1.0 %. Portions of 100 g of each soil were transferred to 250 ml glass bottle. Each bottle received 100 ml of deionized water containing the appropriate amount of nano particles. The treated soils were left to air dry for one week, then alternatively wetted with 50 ml of deionized water and left for sir dray. The treated soils submit to 8 wetting and air drying cycles conducted for 8 weeks, each week form one cycle, then the soils submitted to chemical analysis in which plant available Cd and Pb were determined in the soils as extracted using DTPA.

2.6. Analytical procedures

2.6.1. Total contents of Cd and Pb
Aqua-Regia method was used to determine Cd and Pb as described by Cottenie et al. (1982). In this procedure the soil sample intake was 1 g, which were placed in 100 ml Pyrex digestion tubes, then 3 ml distilled water was added to obtain slurry. Thereafter, 5 ml of 3:1 mixture (7.5 ml of 37% HCl and 2.5 ml of 70% HNO\(_3\)) was added to the digestion tube which was covered and left overnight. Then, the suspension was digested at 130°C for 2 h, in a reflux condenser. The obtained suspension was then filtered through an Whatman filter, then diluted to 25 ml with 0.5 mol l\(^{-1}\) HNO\(_3\), and stored in polyethylene bottle at 4°C for analyses.Cadmium and lead concentrations were measured in the extract using Atomic Absorption Spectrophotometer (UNICAM 969, APHA, 1998).

2.6.2. Plant available Cd and Pb
The plant available Cd and Pb was extracted as described by ISO 11466 (1995). The extracting solution consists of 0.005 M DTPA (Diethylene-triamine-penta acetic acid), 0.01 M CaCl\(_2\), and 0.1 M TEA (Tri ethanolamine), at pH 7.3. Cadmium and lead concentrations were measured in the extract using Atomic Absorption Spectrophotometer (UNICAM 969).

2.7. Statistical analysis
A randomized complete block design with three factor was used for analysis all data with three replications. The treatment means were compared by least significant difference (L.S.D.) test as given by Snedecor and Cochran (1994). Statistical analysis was carried out by special statistical program “Assistat” (Silva and Azevedo, 2009).

3. Results and Discussions

3.1. Characteristics of nanoparticles
3.1.1. Particle size
The size of the nanoparticle greatly influences the reactivity of the material, hence, control the level of pollutants in the soil. Fine particles (<100 nm) are more reactive and have higher surface area than coarser ones (UNEP, 2007). Immobilizing agents used in this study were characterized using transmission electron microscopy (TEM). Figures 1 and 2 show the images of all tested nanoparticles “nZVI, bent-nZVI, nanoalginateand nano carbon” in which the individual particles were detected and the particle size was measured in several fields in the TEM. The magnification (focal length) of the objective remains fixed while the focal length of the projector lens is changed to vary magnification. As the same sample look to be different sizes under different magnifications (Image Size = Actual Size × Magnification).

The images show that nanoparticles have very thin distinguishable dark portions, the size distribution are below 90 nm and greater than 10 nm. These results agree with UNEP (2007) who reported that, nanotechnology is a field of applied
science concerned with the control of matter at dimensions of roughly 1 to 100 nanometers. Kanel et al. (2005) reported that, the size distribution of nZVI particles are in the range of 1-120 nm, in which more than 60% are less than 50 nm.

3.1.2. Cation exchange capacity

Cation Exchange Capacity “CEC” of nanoparticles determined using 1M ammonium acetate at pH 7 are listed in Table 1. The results show that all tested nanoparticles have relatively high CEC ranged from 42.5 to 47.7 Cmol(c)/kg. The tested nanoparticles had approximately the same CEC values.

3.1.3. Specific surface area

Surface area of immobilizing agent is one of the important parameters affecting the remediation efficiency. As the surface area of the immobilizing agents increase, the surface reactivity and adsorption capacity increase, hence immobilization of pollutants in soils increase. Ponder et al. (2000) reported that increasing the surface area of the particles should also increase the rate of remediation. The surface area of the nanoparticles used as immobilizing agents in the present study were measured using O-phenanthroline method and listed in Table 1. The results show that the nano-materials have high specific surface area ranged from 194.2 to 259.7 m²/g. The highest values was recorded for nanocarbon (259.7 m²/g), whereas the lowest one was recorded for nanoalginite (194.2 m²/g). The value of surface area obtained for nZVI (235.7 m²/g) in the present study is greater than that of Wang et al. (2014). They reported that, the values of surface area of the reduced graphite oxide (RGO) and nZVI-RGO as measured by a BET analyzer are 147.6 and 100.6 m²/g. The surface area of the nonporous resin “Ferragels” (polymeric resin, silica gel, or sand), after treatment with borohydride (but in the absence of nZVI) was 3-3.5 m²/g, depending on the average diameter of the particles. The surface area of the Ferragels supported with nZVI, was 21.7±1.5 m²/g (Ponder et al., 2000). Thereby, a support prevents agglomeration of the iron and therefore presents a higher specific surface area of iron. All tested immobilizing agents could be arranged descendingly according to their surface area values as the following: Nano carbon > nZVI > bent-nZVI > nanoalginite.

3.1.4. Contents of Cd and Pb

The results presented in Table 1 show that, except for nanocarbon, all immobilizing agents are almost free of Cd and Pb. The total contents of Cd (0-1.16) and Pb (0-0.67 ug/g) in immobilizing agents as well as their quantities extracted using
DTPA (0.019 and 0.011 µg/g, respectively) were too low. The highest total contents of Cd (1.16) and Pb (0.67 µg/g) as well as DTPA-extractable ones (0.18 and 0.11 µg/g, respectively) were recorded for nano carbon. However, nano scale zero valent iron “nZVI” was free of Cd and Pb, and the other two nanoparticles (nanoalginate and bent-nZVI) contain traces of Cd and Pb.

### 3.2. Adsorption isotherms of Cd and Pb on nanoparticles

Figure 3 represents the adsorption isotherms of Cd in which the quantities adsorbed on tested nanoparticles are depicted against the equilibrium concentrations. The obtained isotherms showed that, high quantities of Cd (approximately 30-40 g kg\(^{-1}\)) are adsorbed on both nZVI and bent-nZVI, and the obtained curves are similar to H-Curve, particularly for nZVI, which means that the specific adsorption is the mechanism responsible for Cd removal. Whereas that of bent-nZVI is similar to L-curve. The results showed that, all added Cd was completely removed particularly from solution of low concentrations of Cd. However, relatively lower quantities of Cd (approximately 20 g kg\(^{-1}\)) are adsorbed on nanoalginate and nanocarbon. The curve obtained for alginate was similar to L-Curve, whereas that of nanocarbon was similar to C-Curve which means that the adsorbent has endless surface sites ready to adsorb Cd. The results show the high capacity of nZVI to adsorb Cd comparing with other nano materials. The tested nano-materials could be arranged descendingly according to their capacity to adsorb Cd as the following: nZVI > nanocarbon > nanoalginate > bent-nZVI.

Figure 4 represents the adsorption isotherms of Pb on nano-materials. The results showed that, the quantities of Pb adsorbed on nano-materials (approximately ranging from 3-22 g/kg) are much lower than their correspondings of Cd which indicate the high capacity of these materials to adsorb Cd rather than Pb. The highest adsorbed quantities were recorded for nZVI, whereas the lowest ones belonged to nanocarbon. The obtained isotherms are more similar to L-Curve rather than other known isotherms. The tested nanoparticles could be arranged descendingly according to their capacity to adsorb Pb as the following: nZVI > nanoalginate > bent-nZVI > nanocarbon.

### 3.3. Adsorption models

The validity of Cd and Pb adsorption data to linear forms of both Freundlich and Langmuir models were examined. Also, the quantities of both maximum adsorption capacity and affinity (binding energy) have been calculated using Langmuir models. Cadmium and lead adsorption data were found to obey both Freundlich and Langmuir models. High correlation coefficients (R\(^2\)) ranging from 0.891-0.984 and 0.892-0.983 (were obtained for Langmuir isotherm of Cd and Pb, respectively. Both maximum adsorption capacity and binding energy (affinity) were calculated using linear form of both Freundlich and Langmuir models. The validity of Cd and Pb adsorption data to linear forms of both Freundlich and Langmuir models was examined. Also, the quantities of both maximum adsorption capacity and affinity (binding energy) have been calculated using Langmuir models. Cadmium and lead adsorption data were found to obey both Freundlich and Langmuir models. High correlation coefficients (R\(^2\)) ranging from 0.916-0.986 and 0.892-0.983 (were obtained for Langmuir isotherm of Cd and Pb, respectively. Both maximum adsorption capacity and binding energy (affinity) were calculated using linear form of both Freundlich and Langmuir models. The results indicated the high capacity of the tested nano-materials to adsorb Cd. The calculated maximum adsorption capacities ranged from 9.71-93.45 g Cd kg\(^{-1}\). The highest value was recorded for nZVI, whereas the lowest one belonged to dendrimers. The maximum adsorption capacities of the tested nano materials are roughly lie in the range of values reported for several adsorbents in the literature; activated carbon (3.37 mg g\(^{-1}\)) (An et al., 2001), hematite (4.94 mg g\(^{-1}\)) (Singh et al., 1998), orange waste (48.3 mg g\(^{-1}\)) (Perez-Marin et al., 2007), bone char (64.1 mg g\(^{-1}\)) (Cheung et al., 2001), and biogenic Mn oxides (229.3 mg g\(^{-1}\)) (Meng et al., 2009). The tested immobilizing agents could be arranged descendingly according to their maximum adsorption capacity as the following: ZVI > nanocarbon > nanoalginate > bent-NZVI > dendrimers.

On the other hand, the maximum adsorption capacity of Pb on nanoparticles ranged from 3.95-25.97 g kg\(^{-1}\). Similar to Cd, the highest max adsorption capacity was recorded for nZVI, whereas the lowest one was reported for dendrimers. However, these values are lower than their corresponding of Cd. So, the tested nanoparticles have highest capacities to adsorb Cd than Pb. The tested immobilizing agents could be arranged descendingly according to their Pb maximum adsorption capacity as the following: nZVI > nanoalginate > bent-nZVI > nanocarbon.

### Table 1. Important characteristics of nanoparticles.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Particle Size Range (nm)</th>
<th>Surface area (m(^2)/g)</th>
<th>CEC (Cmol(_e)/kg)</th>
<th>Cd (µg/g) Aqua Regia</th>
<th>DTPA-extractable</th>
<th>Pb (µg/g) Aqua Regia</th>
<th>DTPA-extractable</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoalginate</td>
<td>12.9 – 23.9</td>
<td>194.2</td>
<td>47.7</td>
<td>0.11</td>
<td>0.02</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>nZVI</td>
<td>12.7 – 103</td>
<td>235.7</td>
<td>42.5</td>
<td>nd</td>
<td>nd</td>
<td>0.24</td>
<td>0.04</td>
</tr>
<tr>
<td>bent-nZVI</td>
<td>27.8 - 110</td>
<td>225.4</td>
<td>47.7</td>
<td>0.09</td>
<td>0.01</td>
<td>0.24</td>
<td>0.04</td>
</tr>
<tr>
<td>nano carbon</td>
<td>53.5 – 63.1</td>
<td>259.7</td>
<td>-</td>
<td>1.16</td>
<td>0.19</td>
<td>0.67</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*CEC of nano carbon was not determined.
Fig. 3. Adsorption isotherms of Cd on nanoparticles; nano alginate, nZVI, bent-nZVI, and nano carbon.

Fig. 4. Adsorption isotherms of Pb on nanoparticles; nano alginate, nZVI, bent-nZVI and nano carbon.

Table 2. Maximum adsorption capacity and binding energy (affinity) for Cd and Pb on nano-materials.

<table>
<thead>
<tr>
<th>No.</th>
<th>agents</th>
<th>Maximum Adsorption Capacity</th>
<th>Affinity</th>
<th>Maximum Adsorption Capacity</th>
<th>Affinity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(gCd kg(^{-1})) (b)</td>
<td>(k) 1 g(^{-1})</td>
<td>(gPb kg(^{-1})) (b)</td>
<td>(k) 1 g(^{-1})</td>
</tr>
<tr>
<td>1</td>
<td>nZVI</td>
<td>93.45</td>
<td>0.048</td>
<td>25.97</td>
<td>0.123</td>
</tr>
<tr>
<td>2</td>
<td>Nano Carbon</td>
<td>76.92</td>
<td>0.006</td>
<td>17.85</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>Nano Alginite</td>
<td>41.15</td>
<td>0.006</td>
<td>24.87</td>
<td>0.037</td>
</tr>
<tr>
<td>4</td>
<td>Bent-nZVI</td>
<td>37.45</td>
<td>0.234</td>
<td>24.74</td>
<td>0.024</td>
</tr>
</tbody>
</table>

The affinity between Cd and the tested adsorbents ranged from 0.006-0.234 \(1 \text{g}^{-1}\). The highest affinity value was reported for bent-nZVI, whereas the lowest one belonged to nano alginate. The affinity between Pb and the tested adsorbents ranged from 0.024-0.123. The highest affinity value was reported for nZVI, whereas the lowest one belonged to bent-nZVI.
3.4. Desorption of Cd and Pb

The quantities of Cd desorbed from the previously adsorbed ones are listed in Table 3. The results show that, generally small quantities of Cd were desorbed from the previously adsorbed ones. Except for nano carbon, the desorbed quantities were found to represent small percentages of the previously adsorbed ones. These percentages varied from 10.8 to 33.4% (Table 3).

In generally, the lowest percentage was recorded for nZVI (10.8-22.1), whereas the highest ones belonged nano carbon (21.6-93.3). As the desorbed percentages decreased, the future release of the adsorbed Cd decreased, hence the validity of the material to immobilize Cd increased. The tested nano-materials could be arranged descendingly according to their validity to immobilize Cd as the following: nZVI > bent-nZVI > nanoalginite > nanocarbon.

Table 3. Adsorption/Desorption of Cd and Pb on nanoalginite, nZVI, bent-nZVI and nano carbon.

<table>
<thead>
<tr>
<th>Agents</th>
<th>Adsorbed Quantities (mg kg(^{-1}))</th>
<th>Desorbed Amounts (mg kg(^{-1}))</th>
<th>Des. /Ads. (%)</th>
<th>Adsorbed Quantities (mg kg(^{-1}))</th>
<th>Desorbed Amounts (mg kg(^{-1}))</th>
<th>Des. /Ads. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoalginite</td>
<td>285 - 20000</td>
<td>90 - 2708</td>
<td>13.5 - 33.4</td>
<td>220 - 16800</td>
<td>64 - 4400</td>
<td>18.9 - 35.6</td>
</tr>
<tr>
<td>nZVI</td>
<td>435 - 37550</td>
<td>96 - 4038</td>
<td>10.8 - 22.1</td>
<td>305 - 22300</td>
<td>68 - 4020</td>
<td>13.7 - 23.4</td>
</tr>
<tr>
<td>bent-nZVI</td>
<td>435 - 32000</td>
<td>92 - 4475</td>
<td>14.0 - 21.2</td>
<td>200 - 14300</td>
<td>61 - 4200</td>
<td>22.9 - 33.4</td>
</tr>
<tr>
<td>nano carbon</td>
<td>235 - 18500</td>
<td>88 - 4000</td>
<td>21.6 - 93.9</td>
<td>255 - 13300</td>
<td>70 - 4826</td>
<td>21.9 - 36.3</td>
</tr>
</tbody>
</table>

3.5. Immobilization of cadmium and lead in polluted soils

Soil samples, Mostord (S1, S2); Abo-Rawash (S3, S4); Shubra (S5) and El-Gabal El-Asfer (S6) are used in this experiment. These samples varied widely in their initial contents of plant available Cd and Pb as extracted using DTPA (Tables 4 and 5). DTPA extractable Cd and Pb in these soils varied from 3.24-12.85 and 4.01-15.4 mg/kg, respectively. Also the source of Cd and Pb pollutants varied between the tested soil samples (domestic sewage, industrial waste and vehicle exhausts). All soils were treated with nanoparticles; nZVI, bent-nZVI, nano alginate and nano carbon; at three rates, 0.1, 0.5 and 1.0% and incubated for 60 days at 30°C. These nanoparticles are used as immobilizing agents to immobilize Cd and Pb in polluted soils. Tables 4 and 5 show the level of DTPA extractable Cd and Pb in the soils before and after the incubation. The data show that all immobilizing agents were able to reduce the level of DTPA extractable Cd and Pb in all soil. However, the magnitude of decrease varied between samples depending on the type of immobilizing agent and the rate of its application. For all agents, the level of DTPA extractable Cd and Pb in the soil decreased with increasing the rate of application from 0.1 to 1.0%. Bentonite supported nano scale zero valent iron (bent-nZVI) was the most effective immobilizing agent, particularly for soil 1 and 3 (moderately polluted soils containing 3.24 to 3.74 mg/kg DTPA extractable Cd). Application rate of 1% of nZVI, bent-nZVI and nano alginate...
Table 5. DTPA extractable–Pb (mg/kg) of the studied soils before and after treating with three rates of five immobilizing agents.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Rate of addition %</th>
<th>Soil 1</th>
<th>Soil 2</th>
<th>Soil 3</th>
<th>Soil 4</th>
<th>Soil 5</th>
<th>Soil 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>nZVI</td>
<td>Initial</td>
<td>6.28</td>
<td>6.49</td>
<td>6.31</td>
<td>5.72</td>
<td>15.4</td>
<td>4.01</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3.07</td>
<td>2.84</td>
<td>2.85</td>
<td>3.14</td>
<td>5.49</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2.17</td>
<td>2.42</td>
<td>2.14</td>
<td>2.45</td>
<td>4.22</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.6</td>
<td>1.75</td>
<td>1.56</td>
<td>1.83</td>
<td>3.36</td>
<td>0.54</td>
</tr>
<tr>
<td>nZVI-bentonite</td>
<td>0.1</td>
<td>2.73</td>
<td>2.63</td>
<td>2.81</td>
<td>2.78</td>
<td>5.07</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.83</td>
<td>1.48</td>
<td>1.7</td>
<td>2.05</td>
<td>3.57</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.04</td>
<td>0.64</td>
<td>0.8</td>
<td>1.03</td>
<td>3.28</td>
<td>0.3</td>
</tr>
<tr>
<td>nano alginite</td>
<td>0.1</td>
<td>3.27</td>
<td>2.93</td>
<td>3.21</td>
<td>3.24</td>
<td>6.15</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2.47</td>
<td>2.45</td>
<td>2.61</td>
<td>2.51</td>
<td>4.95</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.72</td>
<td>1.58</td>
<td>1.19</td>
<td>1.93</td>
<td>3.68</td>
<td>0.56</td>
</tr>
<tr>
<td>nano carbon</td>
<td>0.1</td>
<td>3.88</td>
<td>3.09</td>
<td>3.16</td>
<td>3.27</td>
<td>7.9</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3.78</td>
<td>2.97</td>
<td>2.91</td>
<td>3.13</td>
<td>6.65</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.16</td>
<td>2.53</td>
<td>2.81</td>
<td>2.76</td>
<td>6.17</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The results listed in Table 5 show the DTPA extractable Pb of the studied soils before and after treating with nanoparticles. The obtained data show that all nanoparticles were able to reduce the plant available Pb as extracted by DTPA. The results show that, except for nanocarbon, application rates of 0.5 and 1% of all nanoparticles were able to reduce plant available Pb in all soils (except for heavily polluted one, No. 5) to levels (ranging from 0.3-2.61) lower than that (2.88 mg/kg) reported by Aboulroos et al. (1996) for non-polluted soils of Egypt. These results prove the efficiency of nanoparticles in immobilizing Pb in polluted soils. Bentonite supported nZVI and nZVI were by far the most effective immobilizing agents used in the present study to immobilize Pb.

In case of heavily polluted soils, the rate of application of 1% of nZVI, bent-nZVI and nano alginite were able to reduce the DTPA extractable Cd from 12.85 to 3.01, 2.79 and 5.98 mg/kg respectively in soil (2), and from 7.61 to 2.17, 1.51 and 2.22 mg/kg respectively in soil (4). Nano carbon had relatively low efficient in reducing Cd particularly in case of highly polluted soil.

The level of DTPA extractable Cd decreased by 47.0, 71.0 and 93.0%, and 55.6, 72.2 and 97.0% in soil 1 and 3 (moderately polluted soil) as the soil treated with nZVI at rates of 0.1, 0.5 and 1.0% respectively. Their corresponding values for soil 2 and 4 (heavily polluted soils) were 50.5, 63.0 and 76.5%, and 57.8, 65.1 and 71.5% respectively. Statistical analysis show that increasing the rate of application of immobilizing agent (nZVI) significantly (p=0.05) decrease DTPA extractable Cd.

The results show that the source of Cd pollutants had no effect on the effectiveness of the various agents in reducing plant available Cd in soil as extracted using DTPA. According to the obtained results, the tests agents could be arranged in a descending order with respect to their efficiency in immobilizing Cd in the studied polluted soils as follows: bent-nZVI > nZVI > nano alginite > nano carbon.

The results listed in Table 5 show the DTPA extractable Pb of the studied soils before and after treating with nanoparticles. The obtained data show that all nanoparticles were able to reduce the plant available Pb as extracted by DTPA. The results show that, except for nanocarbon, application rates of 0.5 and 1% of all nanoparticles were able to reduce plant available Pb in all soils (except for heavily polluted one, No. 5) to levels (ranging from 0.3-2.61) lower than that (2.88 mg/kg) reported by Aboulroos et al. (1996) for non-polluted soils of Egypt. These results prove the efficiency of nanoparticles in immobilizing Pb in polluted soils. Bentonite supported nZVI and nZVI were by far the most effective immobilizing agents used in the present study to immobilize Pb.

Generally, the results (Table 5) show that the efficiency of various agents in immobilizing Pb increased as the rate of application of immobilizing agents increased. The trend of the effect of immobilizing agents on reducing the content of DTPA extractable Pb was almost similar to that of Cd. The level of DTPA extractable-Pb in soil 1 decreased by 51, 65 and 75% as treated with nZVI at rates of 0.1, 0.5, and 1.0%, respectively. Their corresponding values of soil 6 which has the lowest DTPA-Pb were 64, 79 and 87%, respectively. Whereas those of soil 5 (heavily polluted one) were 64.5, 75 and 78%, respectively. Increasing the rate of application of the immobilizing agents significantly decreased (p=0.05) DTPA extractable-Pb of all tested soils.

4. Conclusion

The obtained results indicate the high capacity of all tested nano-materials, except for nanodendrimers, to adsorb Cd. Among these tested nano-materials, nZVI, bent-nZVI and nanoalginit had the highest affinity to retain the adsorbate element. Regarding Pb, all tested nano-materials had high capacity to adsorb Pb, but their adsorption capacities are lower than those reported for Cd. The best nano-materials recommended to be used for remediation of Cd and Pb polluted soils are nZVI, bent-nZVI and nanoalginit, with special preference for nZVI which has the highest capacity to adsorb and retain Cd and Pb. That is besides, nZVI is easily prepared and non-expensive. Also, these three nano-materials could be recommended to be used for treatment of Cd and Pb polluted wastewater.
References


