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RESEARCH ARTICLE

Application of Nanotechnology in Remediation of Heavy Metals Polluted Soil: I- Preparation and Characterization of Nanoparticles

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Abstract

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Nanoparticles, remediation, adsorption, desorption, cadmium, lead, CEC, surface area, TEM. Heavy metals polluted soils are a significant worldwide environmental problem. The crops cultivated in polluted soils often contain significant levels of heavy metals (Cd, Pb,.. etc) that can impair human health. The technologies such as; removing of current up pollutants: stabilization/solidification of pollutants, vitrification, soil capping.., etc; used in remediation of polluted soils are not adequate. Smarter and cheaper techniques still to be addressed to decontaminate polluted soil. Nanotechnology offers a number of emerging techniques much more effective and less costly that could work to immobilize contaminants. In the present study, nanoparticles; nano scale zero valent iron "nZVI", nZVIbentonite, Nano alginite, nano carbon, bentonite, and dendrimers; are used as a potential sorbents to eliminate Cd and Pb from polluted soil. These nanoparticles are prepared in lab either using bottom-up or top-down, then characterized using transmission electron microscope (TEM). The prepared nanoparticles proved to have very small size (less than 70 nm), high surface area (155-257 m²/g) and cation exchange capacity (30.3-60.7Cmol_c/kg). Also, the prepared nanoparticles proved high adsorption capacity for Pb and Cd, and high retention for the adsorbed metal. The maximum adsorption capacity of nanoparticles ranged from 3954-25974 and 1598-93458 mg kg⁻¹ for Pb and Cd, respectively. That is besides, only small quantities (9.3-20% and 0.4-23%) were released from the previously adsorbed Pb and Cd, respectively.

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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 such as adsorption, filtration and microbial degradation have been use to decontaminate heavy metals polluted soils. However, these methods have many disadvantages, and certain limitations such as high cost, low efficiency and the possibility of future release of stabilized metals. Thus, in recent years, 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 broadly 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 [1]. The materials with particle size at the nano-scale exhibits superior activity due to their larger surface area and higher reactivity [2].

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[3]. 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)[4], the use of "nZVI" is an in situ remediation technique that 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 valent iron"nZVI" undergoes oxidation to Fe⁺² and then to the Fe⁺³ state with standard half cell reactions shown in the following [5,6].

The use of nZVI has been gaining increasing interest in the area of environmental remediation [7,8]. Transformation of a wide variety of environmental contaminants such as heavy metals, chlorinated hydrocarbons, pesticides, nitrate.. etc, have been extensively documented [9,10,11]. Nano scale zero valent iron"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 [12]. The nano-zero valent iron is capable to exchange the toxic substances to non toxic materials. 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)} [13].

Bentonite is a traditional low-cost efficient adsorbent, which has high potential for heavy metal removal form wastewater due to its abundance, chemical and mechanical stability, high adsorption capability and unique structural properties [14]. Removal of metal ions using bentonite is based on ion exchange and adsorption mechanisms due to its relative high cation exchange capacity (CEC) and specific surface area [14]. Bentonite was used for immobilize metals because it has surface functional groups, high specific surface area, chemical stability, layered structure, high cation-exchange capacity [15]. Bentonite clays is an excellent adsorbent materials [16], it decreased the soil available Pb, Cd and Ni extracted by DTPA [17].

Clay minerals have plasticity when wet, they are thermally chemically stable in geochemical media in a wide range of pH in addition to their low costs and wide availability. Clays of concern in this study, kaolinite and montmorillonite, are potential heavy metal adsorbents [18]. 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.

Poly amidoamine (PAMAM) Dendrimers are a new class of nanoscale materials that can function as water-soluble chelators. These highly branched macromolecular compounds consist of three key structural components: a core, interior repeating units and terminal functional groups [19,20].

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 sodium borohydride (NaBH₄) [21,22]. In this study, iron(II) chloride tetrahydrate (FeCl₂, $4H_2O$) was used as source of iron(II). The proposed reaction is:

 $Fe^{+2} + 2BH^{-} + 6H_2O \rightarrow Fe^{0} + 2B(OH)_3 + 7H_2 \uparrow$

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 FeCl₂.4H₂O 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. Poly(amidoamine)dendrimer

Poly(amidoamine)dendrimer was synthesized using a procedure firstly described by [23], in a two step synthesis methodology using 1.0 g (9.7 mmol) of diethy-lenetriamine in 20 ml of methanol. After subsequent addition of methyl acrylate (10 g, 116 mmol) at 25 °C an excess of ethylenediamine (33.5 mL, 0.5 mol) was added in a single portion. After 3 days of stirring all volatiles were evaporated in oil-pump vacuum, whereby was obtained as colorless oil.

2.1. 4. Nano Alginite:

Alginite is a naturally occurred rock. It is greyish-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/cm² and its consistency is 2.1-2.4 g/cm³. Its water content is 17-35% which decreases to 4-5% under laboratory circumstances and its volume reduced to 1,122 kg/l. These data refer to a relatively large amount of clay minerals (montmorrilonite, 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 [24]. Nano alginit was prepared in lab using top-down method by ball-milling.

2.1.5.Nano Carbon :

Nano carbon was collected from ovens of bread in Iraq.

2.1.6. Bentonite:

Collected from Western desert in Al-Anbar province near Al-Qaim Phosphate Chemical Complex.

2.2. Characterization of nanoparticles

2.2.1.Particle size

All nano materials used in this study were examined using Transmission Electron Microscope "TEM" JEOL (JEM-1400 TEM). A drop of well dispersed nanoparticles 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 [25]. The tested nano materials were extracted either using H_2O and /or buffer solution before inspection using TEM. Many fields have been examined and the particle size was measured and printed on the image.

2.2.2. Cation exchange capacity (CEC)

Cation Exchange Capacity (CEC) is the quantity of cations reversibly adsorbed per unit mass of the material. The CEC was determined using batch tests with 1N ammonium acetate at pH 7 as described by [26].

2.2.3. Specific surface area(SSA)

The Specific Surface Area (SSA) of Nanomaterials were determined using O-phenanthroline method [27].

2.2.4. Adsorption /desorption of Cd and Pb

Portions of 0.1g of the studied nanomaterials (nano alginite, nZVI, bent.-nZVI, nano carbon., bentonite, and dendrimers) were shaken with 50 ml 0.01 M CaCl₂ containing Cd and Pb concentrations of 1.0, 5.0, 10, 20, 50, and 100 mg l⁻¹ for 24h at $25C^{\circ} \pm 1$. Solutions were adjusted to pH 7.0 before additions to the adsorbents using 0.1 N HCl or 0.1 N NaOH. The suspensions are then readjusted after addition. The final suspension is centrifuged at 5000 rpm for 10 minutes, then Cd and Pb concentrations were determined in the clear filtrate using Atomic Absorption Spectrophotometer (UNICAM 969) (APHA, 1998). The adsorbed quantities of Cd and Pb were calculated as the difference between the initial and final concentration of Cd and Pb in the equilibrium solution.

A solution of 1.0 M MgCl2, pH 7.0 is used for the desorption of the previously sorbed Cd and Pb at solid: solution ratio equals to that used for adsorption experiment. The suspension was shaked gently for reaction period of 2 h at $25\pm1C^{\circ}$. After centrifugation, Cd and Pb concentrations were determined in the clear solution, as the above mentioned.

2.2.5.Adsorption Models

The validity of Cd and Pb adsorption data to liner form of both Freundlich and Langmuir models were examined. Also, the quantities of both maximum adsorption capacity and affinity (binding energy) have been calculated.

-Freundlich Model

The modified Freundlich model used to describe the experimental data of the present work is as follows:

x/m = kC1/n

Where, x/m = Amount of metal adsorbed per unit mass of adsorbent (mg kg⁻¹)

C = Equilibrium concentration of metal in soil solution (mg l⁻¹)

k and n are constants which represent the affinity of metal to the adsorbent and maximum adsorption capacity, respectively

-Langmuir Model

Langmuir model used to describe adsorption is:

C/(x/m) = 1/kb+C/b

Where, x/m = Amount of metal adsorbed per unit mass of adsorbent (mg kg⁻¹)

C = Equilibrium concentration of metal in soil solution (mg l⁻¹)

k = is a constant related to bonding energy of metal to the adsorbent.

b = is the maximum adsorption capacity of the adsorbent.

3. Results and discussions

3.1.Characteristics of nanomaterials

3.1.1.Particle size

Nanomaterials used in this study were characterized using transmission electron microscope"TEM". Figures (1, 2) show the images of all tested nanomaterials in which the individual particles were detected and the particle size was measured in several fields. The images clearly show that all tested nanomaterials have particle size lower than 70 nm.

Nanoparticles was then used to investigate the size distribution of nanparticles using transmission electron microscope "nZVI having very thin distinguishable dark portions, The size distribution shows that all the nanoparticles are below 90 nm and that more than 10 nm [28].

	CEC (Cmol _(c) /kg)	Surface area (m²/g)	Cd (µ / g)		Pb (µ / g)	
Reagents			DTPA- extractable	Aqua regia	DTPA- extractable	Aqua regia
nano alginite	47.66	194.17	0.019	0.114	0.01	0.07
nZVI	42.46	235.74	0.000	0.000	0.00	0.00
bentnZVI	47.66	225.35	0.000	0.000	0.00	0.00
nano carbon	-	259.69	0.192	1.157	0.11	0.67
bentonite	43.3	150.96	0.031	0.187	0.08	0.48

Table 1. General characteristics of the studied nanomaterials

3.1.2.Cation Exchange Capacity

Cation exchange capacity "CEC" of the tested nanomaterials are shown in table (1). The results show that all tested nanomaterials have relatively high CEC table (1) ranged from $42.46-47.66 \text{ Cmol}_{(c)}/\text{kg}$.

3.1.3.Specific Surface Area

Surface area of the tested nanomaterials are listed in table (1). The results show that the nanomaterials have relatively high specific surface area ranged from 180-288 m^2/g .





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Figure 1. Transmission Electron Microscopy"TEM" images of nZVI (a), bent.-nZVI (b) and nano alginite (c).



Figure 2. Transmission Electron Microscopy"TEM" images of bentonite (a) and nano carbon (b).

3.2. Adsorption Isotherms of Cd and Pb on Nanomaterials

Figure (3) represents the adsorption isotherms of Cd in which the quantities adsorbed on tested nanomaterials are depicted against the equilibrium concentrations. The obtained isotherms show that high quantities of Cd (approximately 30-40 g kg⁻¹) are adsorbed on both nZVI and bent.-nZVI. The obtained curves are similar to H-Curve which means that the specific adsorption is the mechanism responsible for Cd removal. The results showed that, all added Cd was completely removed from solutions particularly from solutions contain relative low concentration. Relatively low quantities of Cd (approximately 20 g kg⁻¹) are adsorbed on nano alginite and nano carbon. The curve obtained for alginite was similar to L-Curve whereas that of nano carbon was similar to C-Curve which means that the adsorbent has endless surface sites ready to adsorb Cd. However, the lowest adsorbed quantities of Cd were obtained for bentonite and dendrimers.

The results show the high efficiency of nZVI to adsorb Pb comparing with other nano materials. The tested nanoparticles could be arranged descendingly according to their capacity to adsorb Pb as the following:

nZVI > nano alginite > bent.-nZVI > nano-carbon > bentonite > dendrimers

The adsorption isotherms of Pb on nano materials are shown in fig. (4). Generally the quantities of Pb adsorbed on nano particles are lower than their corresponding of Cd which indicate the higher capacity of these materials to adsorb Cd comparing with Pb.



Fig. 3: Adsorption isotherms of Cd on nano alginate, nZVI, bentonite, bent-nZVI, nano carbon and dendrimers.



The quantities of Pb sorbed on nZVI were much higher than those of bentonite-nZVI, nano alginite, ...)

Fig. 4: Adsorption isotherms of Pb on nanomaterials; nano alginate, nZVI, bentonite, bent-nZVI, nano carbon, and dendrimers.

3.3. Adsorption models

Cadmium and lead adsorption data were found to obey both Freundlich and Langmuir equations. High correlation coefficients (R^2) ranging from 0.891- 0.984 and 0.892-0.983 were calculated for Langmuir isotherm of Cd and Pb, respectively. Figures (5 and 6) show the linear forms of Cd and Pb adsorption on nanoparticles, respectively. Both maximum adsorption capacity and bonding energy (affinity) were calculated using linear Langmuir form for both Cd and Pb and listed in Table (2). The results indicate the high capacity of the tested nanoparticles to adsorb Cd. The maximum adsorption capacity ranged from 9.71-93.45 g Cd kg⁻¹. These values are much higher than the maximum adsorption capacity reported for other adsorbents in the literature; hematite (4.94mg g⁻¹), [29], chitin (14.7 mg g⁻¹) [30]. The highest value (93.45 g kg⁻¹) was recorded for nZVI, whereas the lower one was reported for dendrimers. However, the maximum adsorption obtained for nZVI (93.45 g kg⁻¹) was much lower than that reported (769.2 mg g⁻¹) by Boparai, et al., (2010) [31]. The bonding energy between Cd and adsorbent (affinity) ranged from 0.006 to 0.234. The highest affinity between Cd and adsorbent was recorded for bent.-nZVI, whereas the lowest one was reported for nano carbon. Comparing with the results of Bopari, et al. (2010), the value of bonding energy obtained for nZVI in our study (0.048) was lower that reported in his study.

Switch on to Pb, the maximum adsorption capacity 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 nanomaterials have higher capacities to adsorb Cd than Pb. The affinity between Pb and adsorbed ranged from 0.024-0.123. The highest value was reported for nZVI, where the lowest one was reported for bent-nZVI.

No.	agents	Maximum Adsorption gCd kg- ¹ (b)	Affinity (k)	Maximum Adsorption gPb kg- ¹ (b)	Affinity (k)
1	nZVI	93.45	0.048	25.97	0.123
2	nano carbon	76.92	0.006	17.85	0.050
3	nano alginite	41.15	0.006	24.87	0.037
4	bent. – nZVI	37.45	0.234	24.74	0.024
5	bentonite	19.61	0.0145	16.47	0.061
6	dendrimers	9.71	0.022	3.95	0.059

Table 2. Maximum adsorption capacity and affinity for Cd and Pb on nanomaterials.





Fig. 5 Linear form of Langmuir model for Cd adsorption on nanoparticles



Fig. 6. Linear form of Langmuir model for Pb adsorption on nanoparticles

3.4. Desorption of Cd and Pb

The quantities of Cd desorbed from the previously adsorbed ones are depicted in figure (7). The results show that, generally small quantities of Cd are desorbed from the previously adsorbed ones. Except for bentonite and dendrimers desorbed quantities were found to represent small ratios of the previously adsorbed ones varied from 10.75 to 39.93 (Table 3). The lowest ratios were recorded for nZVI, whereas the highest ones for bentonite and dendrimers. As the ratio decreased, the future release of adsorbed Cd decreased, hence the validity of the material in pollution abatement increased. The tested nanomaterials could be arranged descendingly according to their validity to control pollution as the following:

nZVI > bent.-nZVI > nano alginite > nano carbon > bentonite > dendrimers

Figure (8) shows the quantities of Pb desorbed from the previously adsorbed ones. The ratio of Pb desorbed from the previously adsorbed ones varied widely between the tested nanomaterials and ranged from 13.74 to 39.82 (Table 4). The lowest ratios were recorded for nZVI 13.74 to 23.39, whereas the highest ones for dendrimers 46.21 to 97.04 (Table 4). The validity of the tested nanomaterials to control pollution could be arranged descindingly as the following;

nZVI > nano alginite > bento.- nZVI > nano carbon > bentonite > dendrimers





Fig. 7. Desorption of the previously adsorbed Cd on (nZVI, bentonite, bent.-nZVI, nano alginite, nano carbon and dendrimers).





Fig. 8. Desorption of the previously adsorbed Pb on (nZVI, bentonite, b-nZVI, nano alginite, nano carbon and dendrimers)

Table 3. Adsorption/Desorption of Cd on (nano alginite, nZVI, bentonite, bent.-nZVI, nano carbon, dendrimers)

Agents	Adsorbed quantity (mg kg ⁻¹)	Desorbed quantity (mg kg ⁻¹)	Des. / Ads. (%)
nano alginite	285 - 20000	90 - 2708	13.54 - 33.39
nZVI	435 - 37550	96 - 4038	10.75 - 22.07
bent nZVI	435 - 32000	92 - 4475	13.98 - 21.15
nano-carbon	235 - 18500	88 - 4000	21.62 - 93.93
bentonite	185 - 10000	92 - 4847	48.47 - 61.01
dendrimers	135 - 5795	90 - 5036	61.87 - 86.90

 Table 4. Adsorption/Desorption of Pb on nanomaterials (nano alginite, nZVI, bentonite, bent.-nZVI, nano carbon, dendrimers)

Agents	Adsorbed quantity (mg kg ⁻¹)	desorbed quantity (mg kg ⁻¹)	Des. / Ads. (%)
nano alginite	220 - 16800	64 - 4400	18.90 - 35.62
nZVI	305 - 22300	68 - 4020	13.74 - 23.39
bent nZVI	200 - 14300	61 - 4200	22.93 - 33.37
nano-carbon	255 - 13300	70 - 4826	21.90 - 36.29
bentonite	260 - 12800	71 - 5000	27.31 - 39.06
dendrimers	145 - 3300	67 - 3156	46.21 - 97.04

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