بسم الله الرحمن الرحيم

Use of Nanotechnology in Remediation of Heavy Metals Polluted Soils

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INTRODUCTION

Nano-science :

is an emerging science which comprises the world of atoms, molecules, macromolecules, quantum dots, and macromolecular assemblies.

Nano-technology

- **Nanotechnology is the technology for design, fabrication and manipulation of nanometre scale systems, in the scale of 1-100 nm.**

- **Is any technology which exploits phenomena and structures that can only occur at nanometer scale.**

What is Nanotechnology?

Nanotechnology deals with the creation of USEFUL materials, devices and systems using the particles of nanometer length scale and exploitation of NOVEL properties (physical, chemical, biological) at that length scale

Nanomaterials

NMs are materials have at least one dimension of size ~ 70nm (1-100 nm).

Classification of Nanomaterials

1- Nanomaterials are categorized according to their Dimensions.

Example	Nanomaterial dimension
Nano films, layers and coatings	**One** dimension < 100 nm
Nanowires, Nanotubes, fibres	**Two** dimensions < 100 nm
Nanoparticles, quantum dots, nanoshells , nanorings , microcapsules	**Three** dimensions < 100 nm

Properties of Nano materials

Properties of Nano materials

- **Familiar materials can have completely different properties at nanoscale.**
- **The familiar classical physics guideposts of magnetism and electricity are no longer dominant.**
- **The applicable laws of physics shift as Newtonian mechanics give way to quantum mechanics.**

Properties of Nano materials

- Nanoscale sizes can lead to different physical and chemical properties:

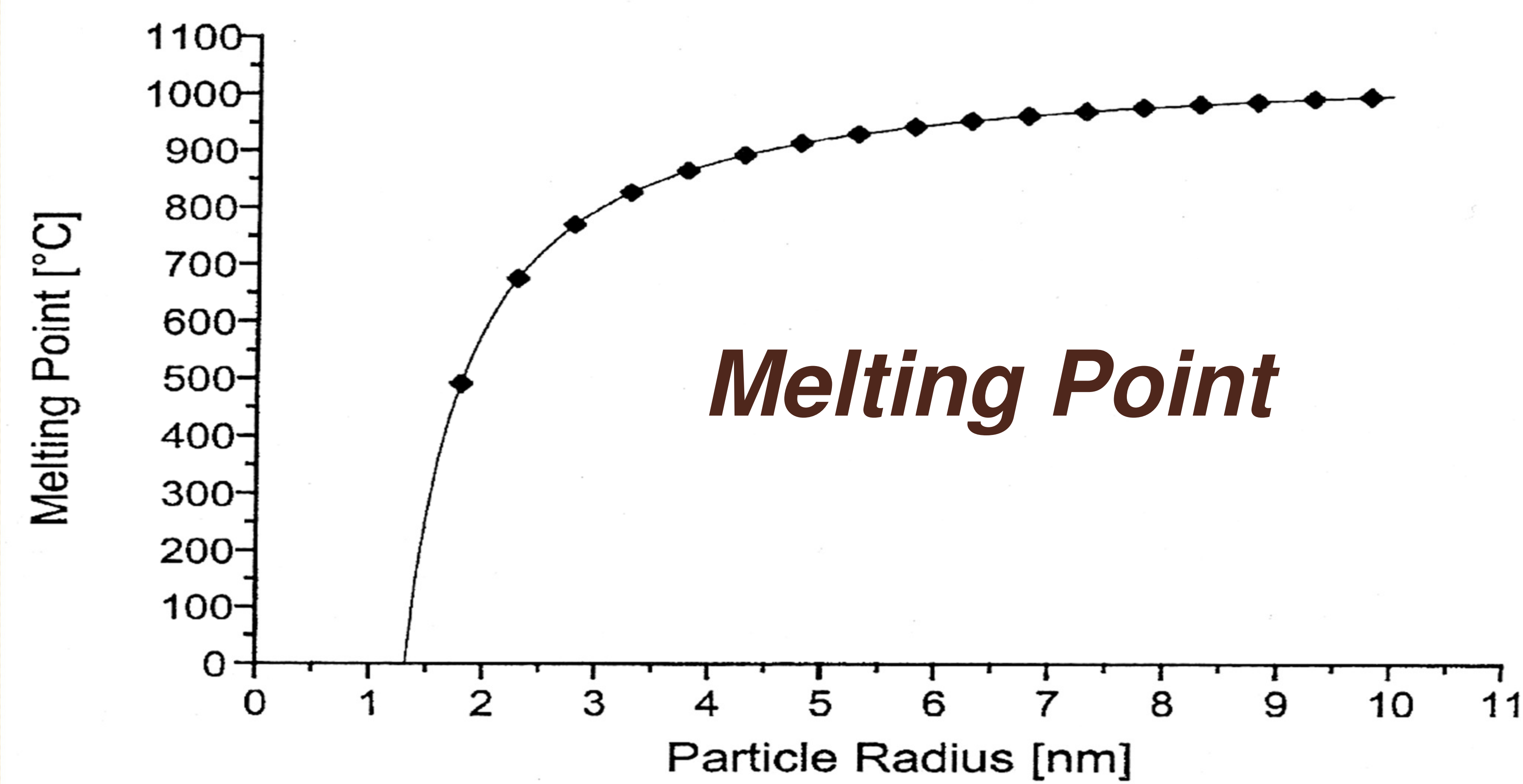
Melting point
Boiling point
Band gap
Optical properties
Electrical properties
Magnetic properties

For example, metals with a so-called grain size of around 10 nanometers are as much as seven times harder and tougher than their ordinary counterparts with grain sizes in the micro meter range.

- The vastly increased ratio of surface area to volume opens new possibilities in surface-based science, such as catalysis.
- Interactions of individual atoms and molecules take place
- Surface effects such as
  Van der Waals force attraction,
  hydrogen bonding,
  electric charge,
  ionic bonding,
  covalent bonding,
  hydrophobicity,
  hydrophilicity and quantum mechanical tunneling.

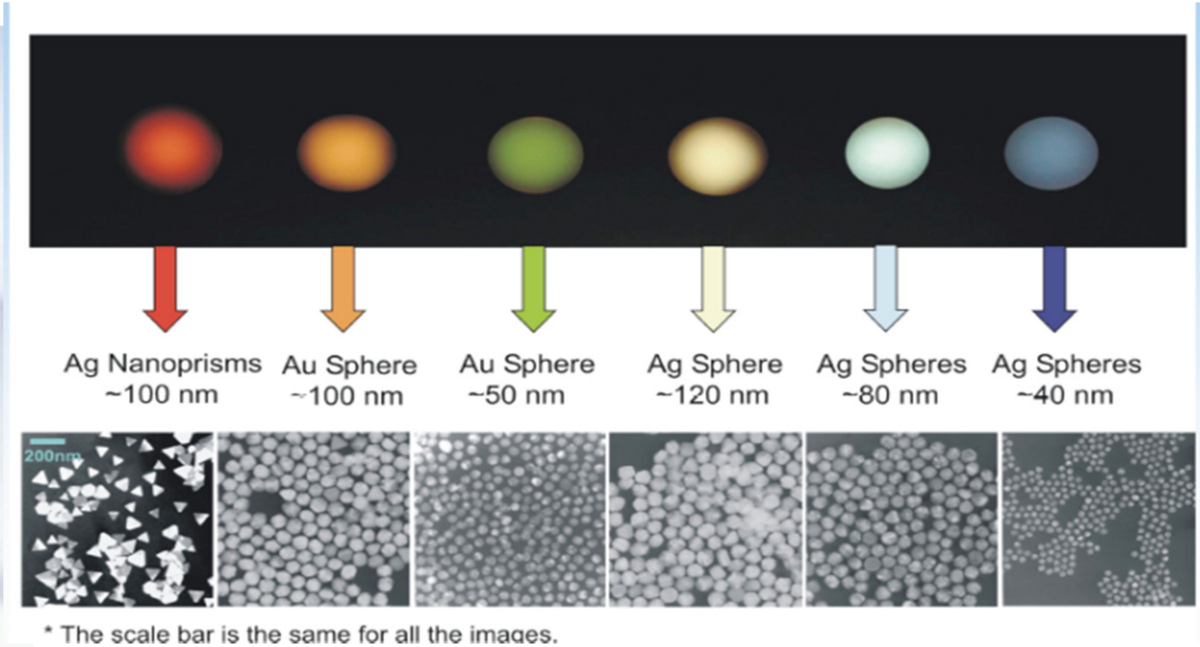
Properties of Nano materials

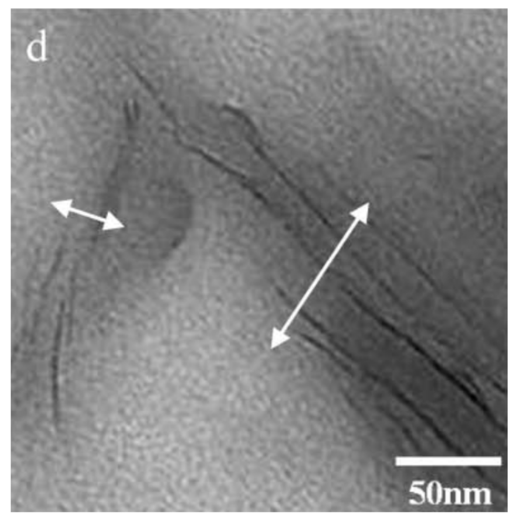
The melting point of gold particles decreases dramatically as the particle size gets below 5 nm



Source: Nanoscale Materials in Chemistry, Wiley, 2001

Properties of Nano materials

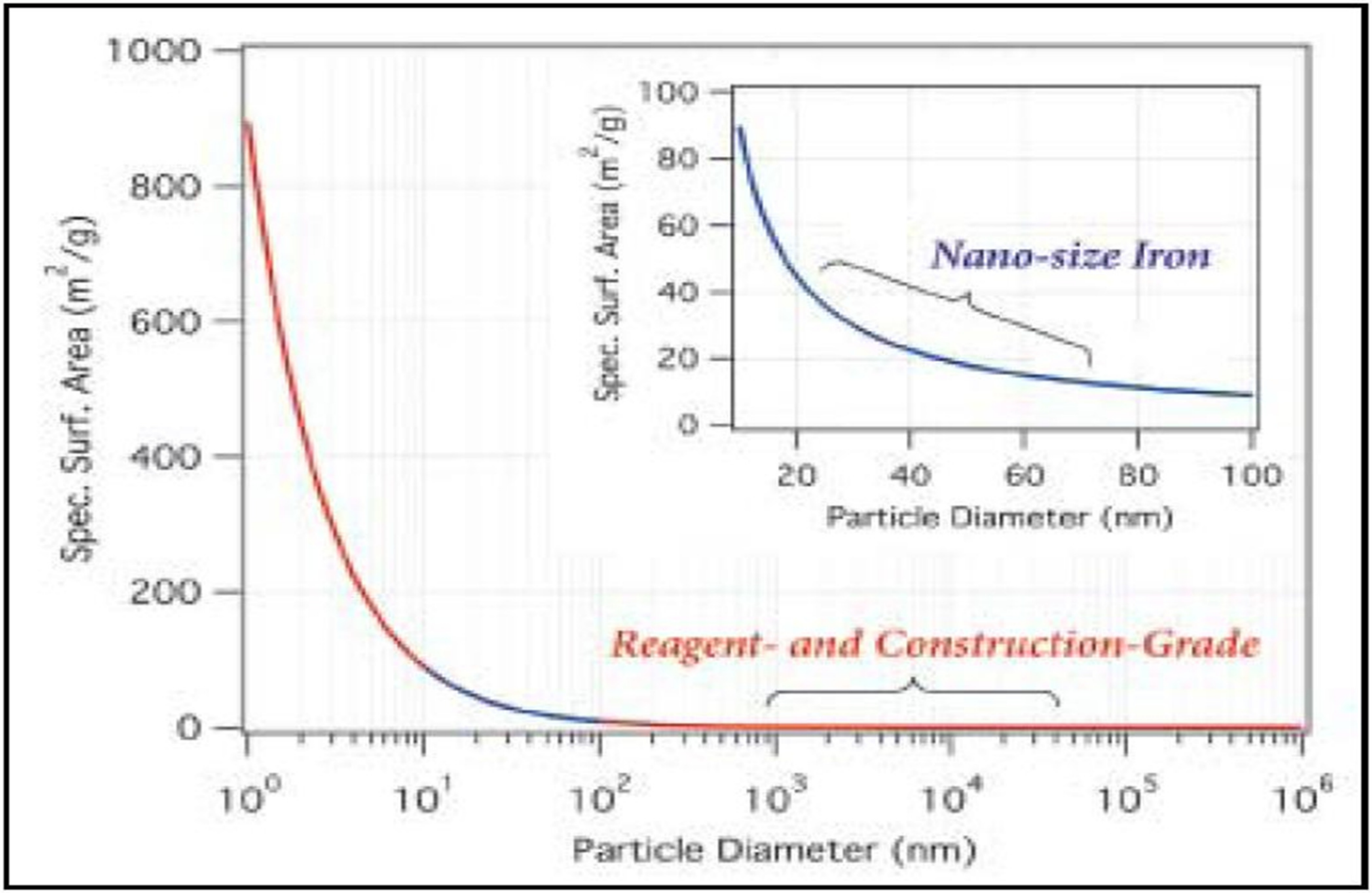




Optical properties – color changes with size

Properties of Nano materials

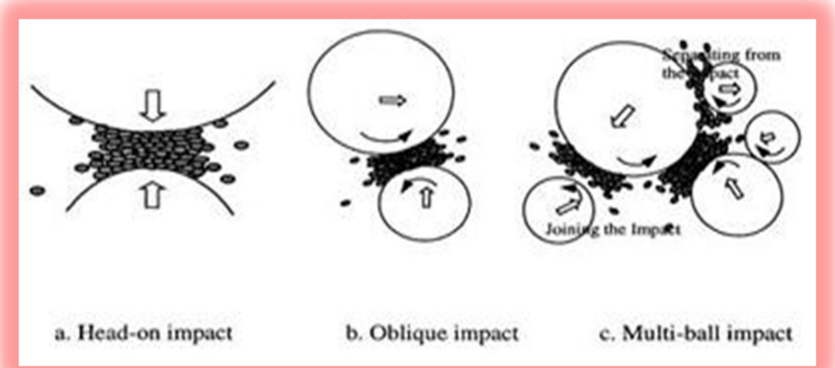
Surface area dependence on particle size



Importance of Nano Materials

- Nano particles are of interest because of the new properties (such as chemical reactivity and optical behavior) that they exhibit compared with larger particles of the same materials.

Methods of Production of Nanoparticles



General Methods:

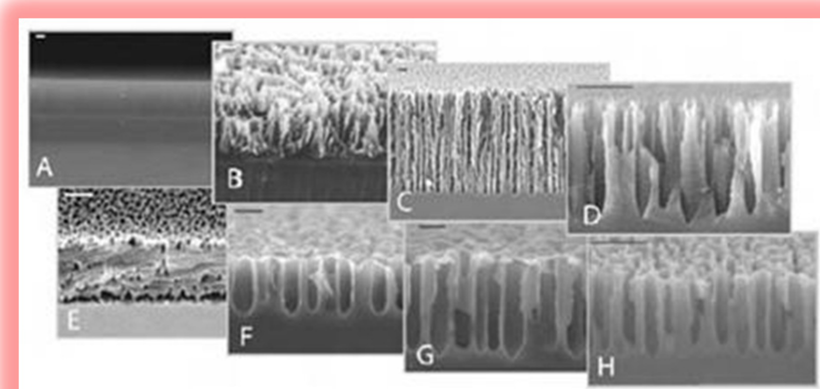
First : (top-down) method

Start from bulk until you reach the nano-cutting through the following:

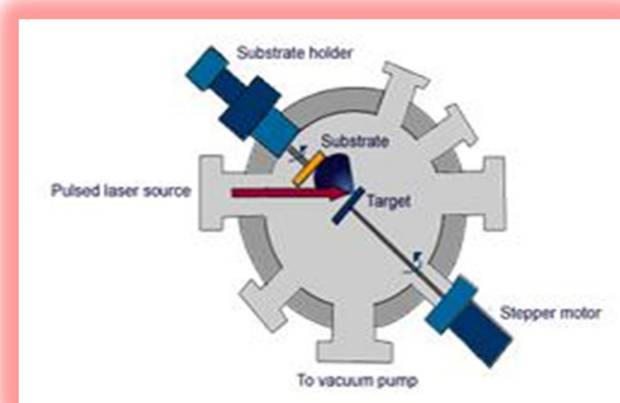
1 – Milling method

2 - Scratching or etching method :

This method is used to produce particles of silicon nano particles

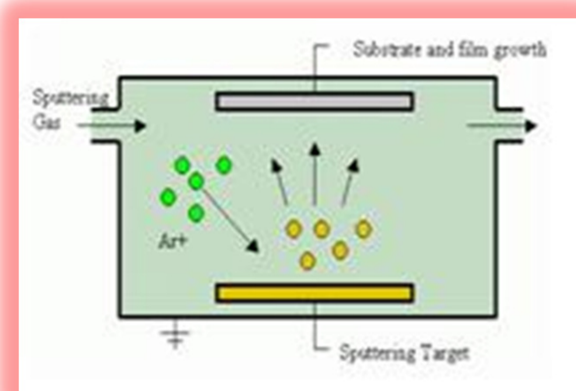


3- Laser ablation method : use of a laser pulse with a high-energy focused on the goal of the heart



4- (Sputtering) method :

Used to make thin film



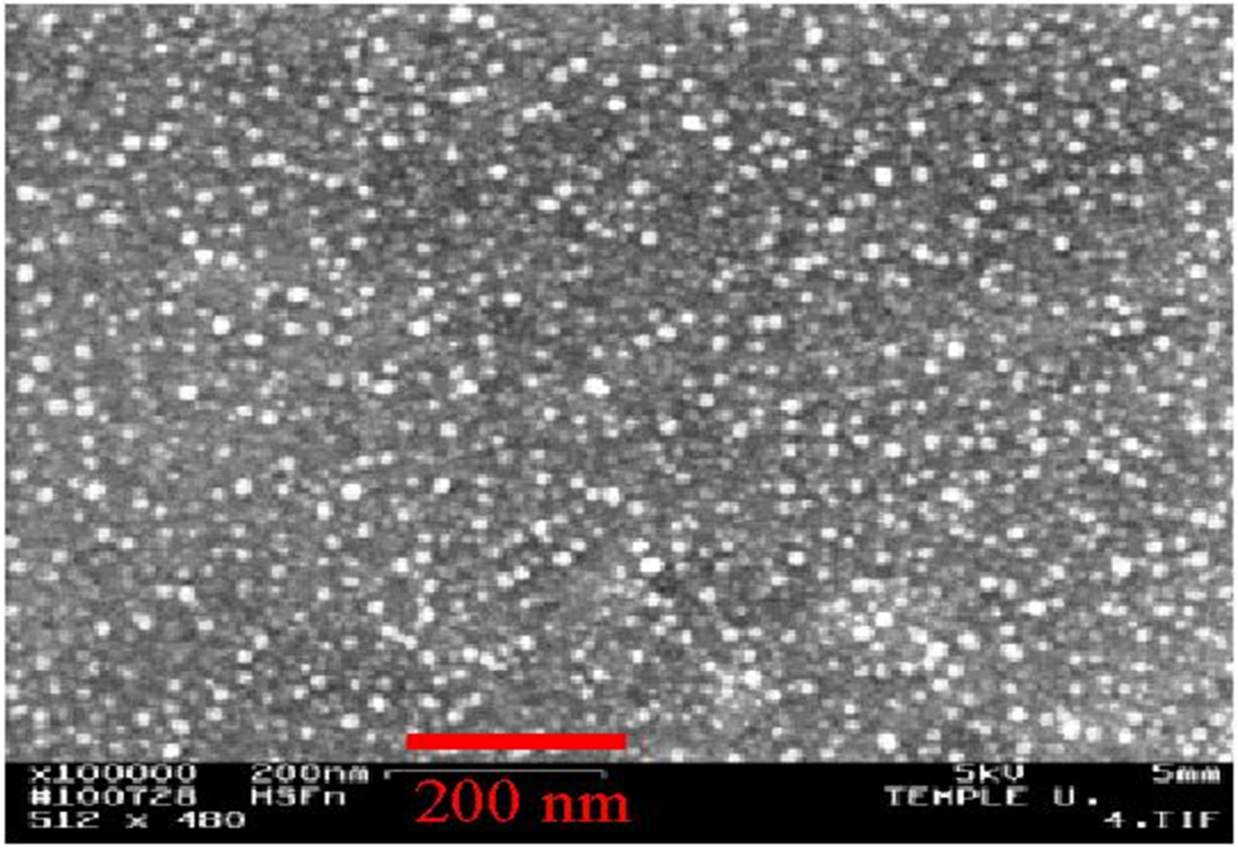
Second : (Bottom-up) method

This method starts from the bottom of any of the atoms begin to separate them and then aggregated up to the level of nano scale methods used :

1 - (sol-gel) method

2- Aerosol method

3- Chemical vapor deposition method (CVD)



Iron Nano Particle

Remediation of Heavy Metals Polluted Soil

Remediation of Heavy Metals Polluted Soil

Definition:

-Heavy metals are widely defined as metallic elements that have a specific gravity of 5.0 g/cm^3 or more.

-Heavy metals are the most toxic inorganic pollutants exist in soils.

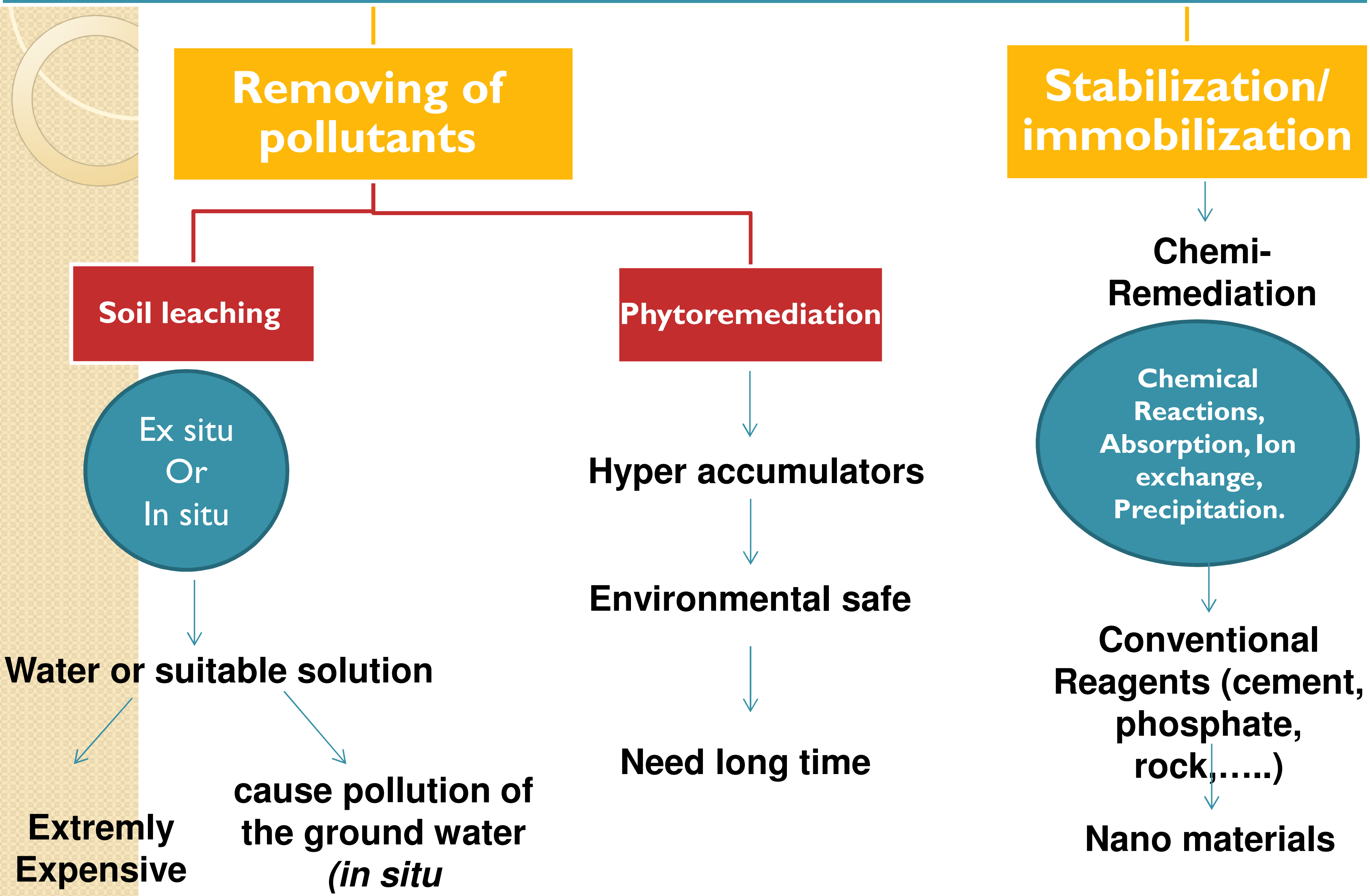
- They can be of natural or anthropogenic origin *(Bradl, 2004 and Sedgwick, 2005)*.

- There are about 50 elements can be classified as heavy metals, but only 17 are considered to be very toxic, e.g., Hg,, Pb, Cd, Ni and Cr.

Remediation of Heavy Metals Polluted Soil

Remediation technologies are scientific techniques used to remove pollutants and/or rehabilitate polluted natural materials.

Remediation techniques



EXPERIMENTAL

&

RESULTS

Nano Immobilizing Materials

- Several nano particles are prepared and used for immobilization of Cd and Pb in polluted soils;

1- nZVI

2 - Bentonite supported nZVI (Bent-nZVI),

3 - Nano carbon

4 - Nano alginit

Methods of production of Nano Particles

Methods of production of Nano Particles

Nano particles used in our research are prepared using either:

I - Chemical Methods

(nZVI and bent-nZVI)

II - Physical Methods

(nano alginit)

Methods of production of Nano Particles

I - Chemical Methods:

A - Nano-scale Zero Valent Iron (nZVI):

Synthesis of nZVI is based on reduction of Fe (II) using borohydride ***(Wang and Zhang, 1997 and Wang et al., 2006).***

$FeCl_2$. $4H_2O$ and $NaBH_4$ are used. The proposed reaction is:

$$Fe^{+2} + 2BH^{-} + 6H_2O \rightarrow Fe^{0} + 2B(OH)_3 + 4H_2 \uparrow$$

- Sample of the product was inspected using TEM, and the particle size ranged from 13- 103 nm.

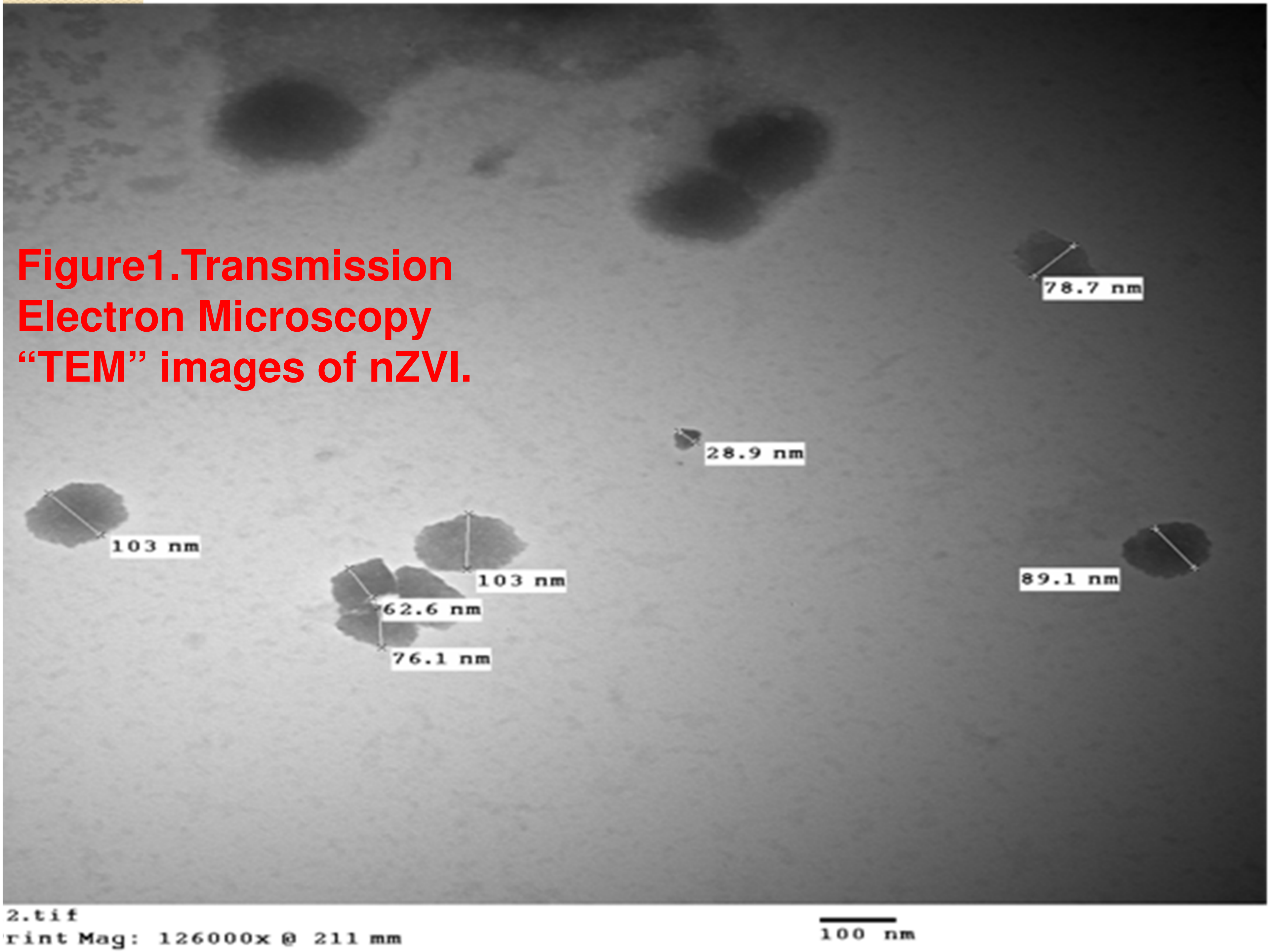


Figure1.Transmission Electron Microscopy "TEM" images of nZVI.

B - Bentonite Supported nZVI (bent-nZVI):

- 5.34 g $FeCl_2.4H_2O$ was dissolved in a 4:1 (v/v) ethanol/water mixture (24 ml ethanol + 6 ml deion. H2O), then 1.5 g bentonite was added.
-The mixture was held on a magnetic stirrer to be mixed.
- Solid particles were washed three times with 25 ml portions of absolute ethanol to remove all water.
- Drying the synthesized nanoparticles overnight at 45 C°.

- TEM showed that particle size ranged from 28-110 nm

Methods of production of Nano Particles

- **II- Physical methods:**
- **Nano alginite:**
  Alginite is a naturally occurring rock. It is greyish-green, it has high specific surface area, high number of functional groups and high CEC.

- Nano alginit was prepared in lab by ball-milling (Photon company, Egypt). Portions of alginit were placed in a stainless steel canister with metal balls of different three sizes, and stirred for 27 hours at speed of 1000 rpm.

- A sample of milled alginite was inspected using TEM, and the size of the alginite particle ranged from 13 – 23nm.

Nano Carbon : Thermal Preparation

- Nano carbon was collected from ovens of bread in Iraq.
- TEM showed that particle size ranged from 12.9-23.9 nm

Table 1. Important characteristics of nanoparticles

Reagents	Particle Size Range (nm)	Surface area (m^2/g)	CEC ($Cmol_{(c)}/kg$)
Nanoalginite	53.5 – 63.1	194.2	47.7
nZVI	12.7 – 103	235.7	42.5
Bent-nZVI	27.8 – 110	225.4	47.7
nano carbon	12.9 – 23.9	259.7	-

Reaction Mechanisms of Nanoscale Zero Valent Iron (nZVI)

Reduction Power of nZVI

- nZVI has been used extensively to reduce (dehalogenate) chlorinated solvents and sequester metals.
- The small particle size and high surface area make iron nano particles highly reactive and extremely versatile.
- Nano-particles can remediate more material at a higher rate and with a lower generation of hazardous byproducts (Zhang, 2003).

Oxidation of Organic Contaminants using Nanoparticles Zero Valent Iron (ZVI)

- In an experiment with the pesticide molinate and ZVI, no change was observed in the concentrations of either one when bubbling nitrogen gas through the solution.
- Air showed a marked reduction in molinate.

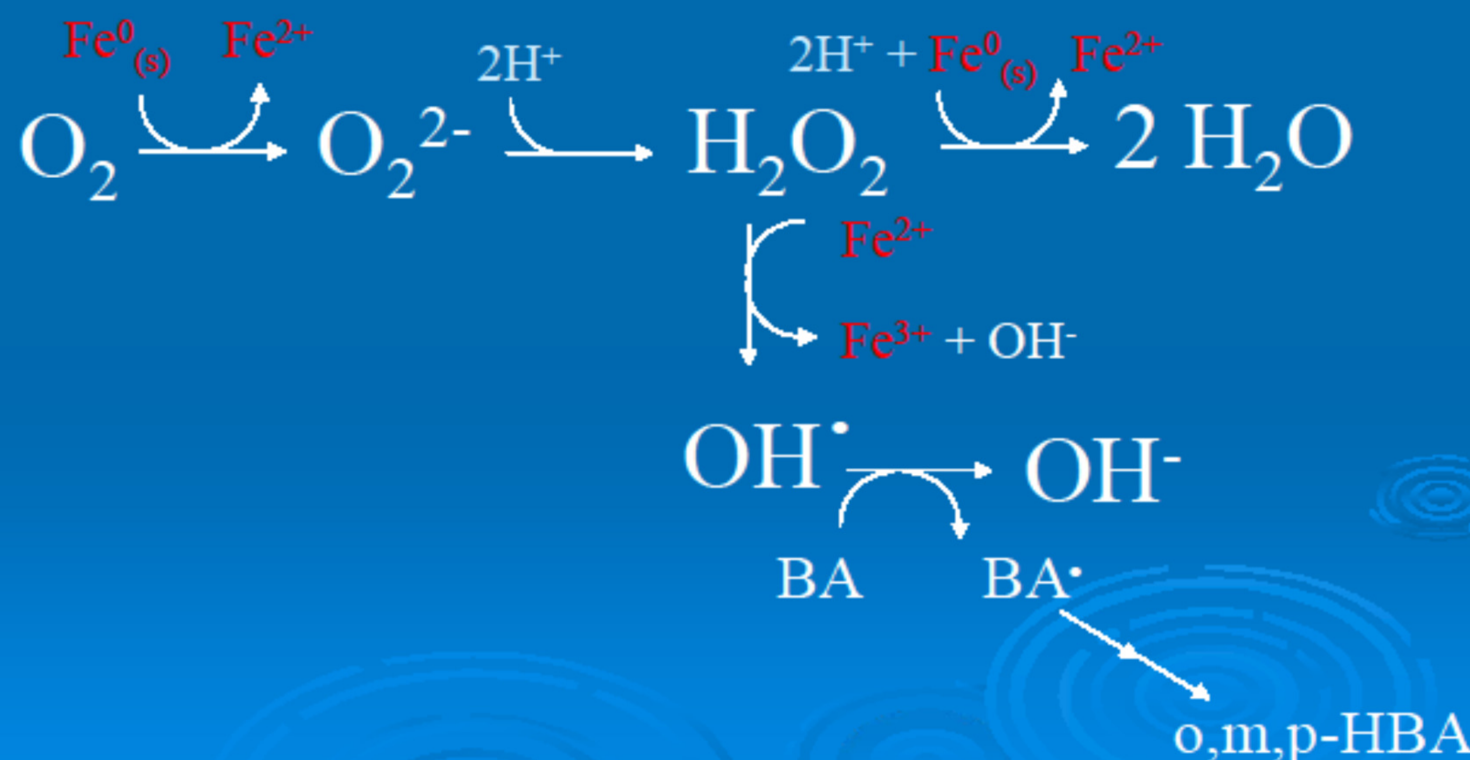
Oxidative Power of nZVI

- Oxygen reacts with ZVI in two fashions.
- In the useful pathway : Fe0 reacts with O2 to form Fe+2 and O2-2. The O2-2 reacts with hydrogen to form hydrogen peroxide which reacts with Fe+2 to form Fe+3 and hydroxyl radicals (Fenton's reaction) that are highly reactive oxidants.

- The usefulness of the reaction depends on the efficiency of the branching process to favor hydroxyl radical formation.

Oxygen Activation by ZVI

- Efficiency determined by branching ratio



IMMOBILIZATION OF

Cd and Pb

IN

POLLUTED SOIL

REMEDIATION OF HEAVY METALS POLLUTED SOIL

The concept of immobilization technique based on:

-The soluble/mobile form of an element in soil is considered to be a better indicator of the risk associated with heavy metals (e.g. leaching, bio-uptake) than the total metal concentration.

- Heavy metals are immobilized in soil through different processes, e.g., specific adsorption, cation-exchange and precipitation (carbonates, phosphates, sulfides, ….).

Immobilization of Cd and Pb in polluted soil

- Heavy metals polluted soils are treated with nano materials at different ratios, 0, 0.1, 0.5 and 1%, and incubated for one month. During this period the samples were submitted to four cycling of wetting and drying.

- *The samples were extracted using DTPA* before and after treating with nano materials.

- *DTPA 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.

- DTPA solution is *recommended to extract amount of metal represent the so called " plant available Cd and Pb" in polluted soil*

Table 2 : Initial contents of plant available (DTPA), and total Cd and Pb (mg/kg), and their ratios in polluted soils

Soil	DTPA-Cd	Total - Cd	*Ratio (DTPA/ Total)%*	DTPA-Pb	Total - Pb	*Ratio (DTPA/ Total)%*
1	3.2	8.9	*36.6*	52.7	180.0	29.3
2	19.9	47.5	*42.0*	47.3	275.0	17.2
3	3.7	8.7	*43.0*	41.5	150.0	27.7
4	7.6	21.0	*36.3*	33.6	135.0	24.9

Table 3 : Plant available Cd (mg/kg) in polluted soils before and after treating with Nano particles

DTPA- extractable Cd (mg/kg)					
Treatment	Rate of addition %	Soil 1	Soil 2	Soil 3	Soil 4
nZVI	0.0	3.24	19.9	3.74	7.61
	0.1	1.71	9.36	1.66	3.21
	0.5	0.91	4.73	1.04	2.65
	1.0	0.23	2.01	0.11	2.17
Level of non polluted soil (Aboulroos et al,1988)		0.06	0.06	0.06	0.06

Table 4 : Plant available Cd (mg/kg) in polluted soils before and after treating with Nano particles

DTPA- extractable Cd (mg/kg)					
Treatment	**Rate of addition %**	**Soil 1**	**Soil 2**	**Soil 3**	**Soil 4**
Bent-nZVI	**0.0**	**3.24**	**19.9**	**3.74**	**7.61**
	0.1	**1.56**	**10.05**	**1.48**	**3.14**
	0.5	**0.78**	**5.83**	**0.62**	**2.39**
	1.0	**0.15**	**3.79**	**0.15**	**1.51**
Level of non polluted soil (Aboulroos et al,1988)		**0.06**	**0.06**	**0.06**	**0.06**

Table 5: Plant available Pb (mg/kg) of polluted soils before and after treating with nano particles

DTPA- extractable Pb (mg/kg)					
Treatment	**Rate of addition %**	**Soil 1**	**Soil 2**	**Soil 3**	**Soil 4**
nZVI	**0.0**	**52.7**	**47.3**	**41.5**	**33.6**
	0.1	**24.6**	**25.1**	**21.5**	**11.5**
	0.5	**8.7**	**9.8**	**8.44**	**3.4**
	1.0	**3.2**	**3.5**	**2.9**	**1.62**
Level of non polluted soil (Aboulroos et al. 1988)		**2.2**	**2.2**	**2.2**	**2.2**

Table 6: Plant available Pb (mg/kg) of polluted soils before and after treating with nano particles

DTPA- extractable Pb (mg/kg)					
Treatment	**Rate of addition %**	**Soil 1**	**Soil 2**	**Soil 3**	**Soil 4**
Bent-nZVI	**0.0**	**52.7**	**47.3**	**41.5**	**33.6**
	0.1	**21.8**	**22.2**	**21.5**	**11.6**
	0.5	**7.3**	**8.2**	**8.4**	**2.9**
	1.0	**3.2**	**3.5**	**2.9**	**0.9**
Level of non polluted soil (Aboulroos et al, 1988)		**2.2**	**2.2**	**2.2**	**2.2**

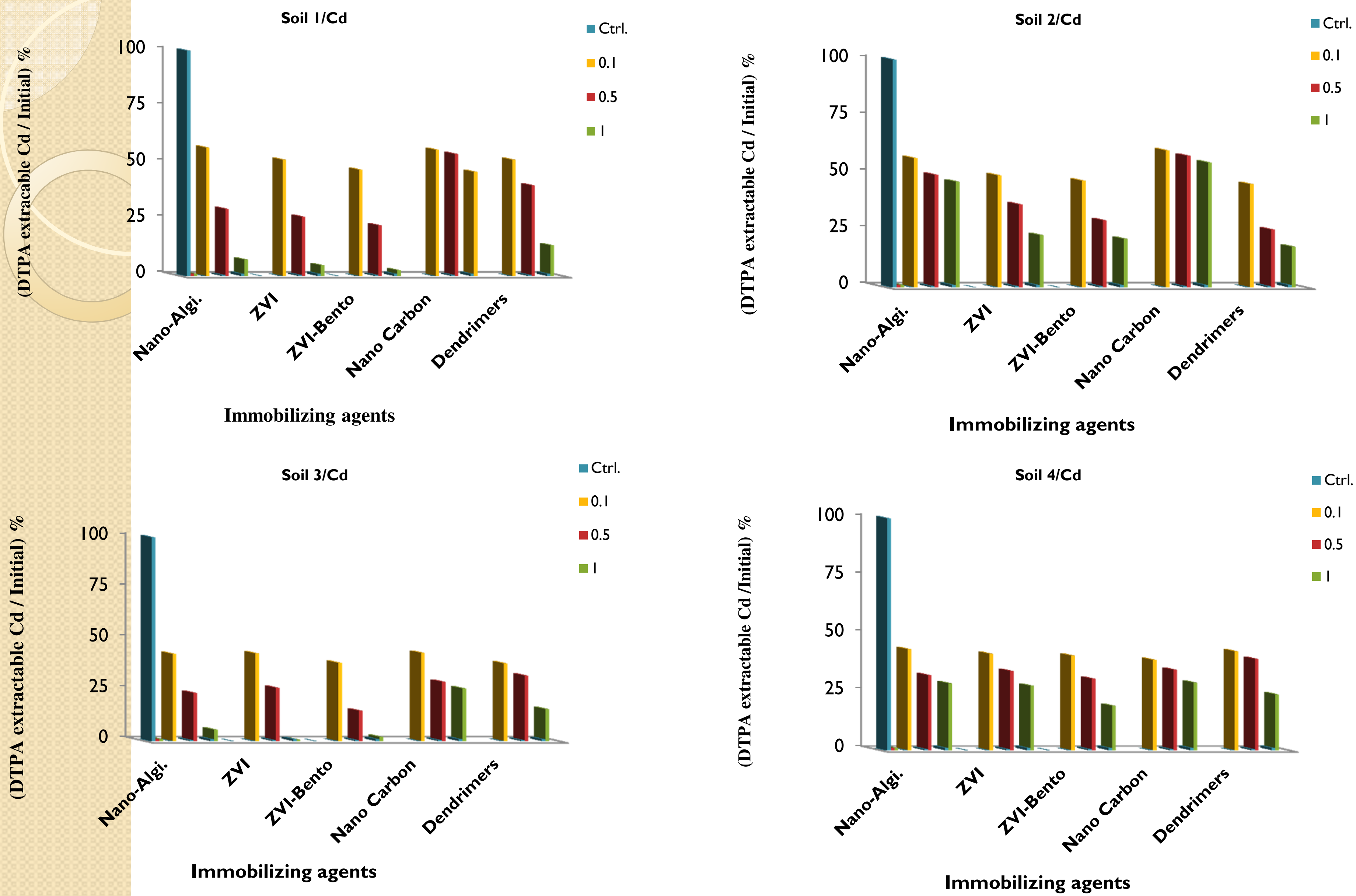


Fig. 2. DTPA extractable-Cd expressed as percentages of the initial values of the studied samples after treating with three rates of nano immobilizing materials.

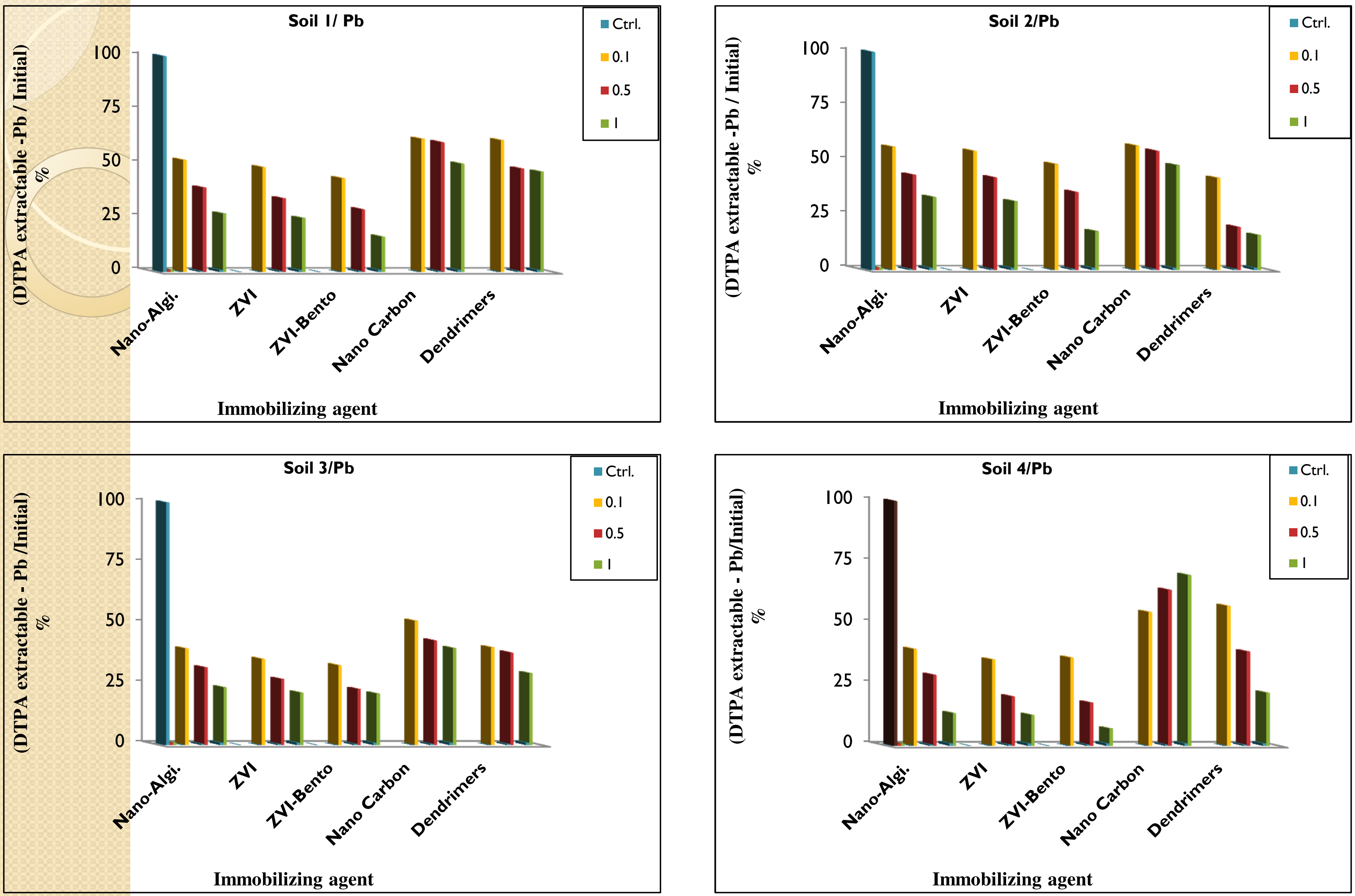


Fig. 3. DTPA extractable-Pb expressed as percentages of the initial values of the studied samples after treating with three rates of nano immobilizing materials.

PARTIONING
OF
Cd AND Pb

AMONG

DIFFERENT
SOIL FRACTIONS

Partitioning of Cd and Pb among different soil fractions:

- A sequential extraction procedure was employed to study the effect of nano immobilizing materials on the distribution of Cd and Pb among various soil chemical forms;
- 1- exchangeable (EXCH),
- 2- bound with carbonate (CARB),
- 3- organic matter (OM),
- 4- oxides (OX) and
- 5- residual (RES).

Table 7 : Sum of all all fractions of Cd and Pb, total contents (mg/kg), and their ratios in soils

Soil	Cd			Pb		
	Sum of fractions	Total	*Ratio (SUM/Total)%*	Sum of fractions	Total	*Ratio (SUM/Total)%*
1	8.2	8.9	93.0	179.2	180.0	99.6
2	44.7	47.5	94.1	267	275.0	97.1
3	8.4	8.7	96.6	149.7	150.0	99.8
4	19.6	21.0	93.3	132	135.0	97.8

Table 8. Different fractions of Cd sequentially extracted from soil (1) before and after treating with nano particles

Treatment	Cd fractions (mg/kg)					
	EXCH	CARB	OX	OM	RES	SUM
Initial	2.8	0.8	1.3	0.6	2.7	8.2
nZVI	0.4	1.9	2.5	0.6	3.0	8.4
Bent-nZVI	0.6	2.7	1.4	0.7	3.2	8.6

Table 9. Different fractions of Cd sequentially extracted from soil (2) before and after treating with nano particles

Treatment	Cd fractions (mg/kg)					
	EXCH	CARB	OX	OM	RES	SUM
Initial	23.3	5.2	7.3	2.4	6.5	44.7
nZVI	3.2	11.9	8.6	4.0	15.1	42.7
Bent-nZVI	3.1	10.3	8.1	3.8	22.2	47.5

Table 10: Different fractions of Pb sequentially extracted from soil (1) before and after treating with nano particles

Treatment	Pb fractions (mg/kg)					
	EXCH	CARB	OX	OM	RES	SUM
Initial	22.3	29.6	36.0	17.5	73.8	179.2
nZVI	9.8	22.4	70.5	20.3	54.6	177.6
Bent-nZVI	9.1	36.2	67.5	20.3	47.7	180.8

Table 11: Different fractions of Pb sequentially extracted from soil (2) before and after treating with nano particles

Treatment	Pb fractions (mg/kg)					
	EXCH	CARB	OX	OM	RES	SUM
Initial	20.3	26.7	44.9	103.6	71.6	267.0
nZVI	10.1	66.4	82.1	60.3	55.8	274.7
Bent-Nzvi	10.1	68.4	78.3	65.8	51.2	27.0

Conclusion

- All immobilizing nano materials efficiently reduced the contents of plant available Cd and Pb in polluted soils as extracted in DTPA solution.

- The magnitude of the reduction of plant available Cd and Pb varied as the immobilizing nano materials and its rate of application varied.

- Increasing application rate of immobilizing nano materials significantly decreased DTPA extractable-Pb of all tested soils.

- The immobilizing nano materials could be arranged in descending order according to their efficiency in immobilizing Cd and Pb as follows:

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

Conclusion

Regarding partitioning of soil-Cd and -Pb among different factions;

- **the exchangeable Cd was the dominant one in all soils, followed by carbonate one, which indicates the high mobility of soil Cd.**

- **Whereas a great potion of soil Pb exists in immobile fractions, e.g., residual and oxide ones.**

- **All immobilizing nano materials significantly reduced the contents of exchangeable Cd and Pb in polluted soils, whereas those of other fractions; carbonate, oxide, organic and residual; significantly increased, indicating high efficiency of nano immobilizing materials to alter Cd and Pb form mobile to immobile fraction.**

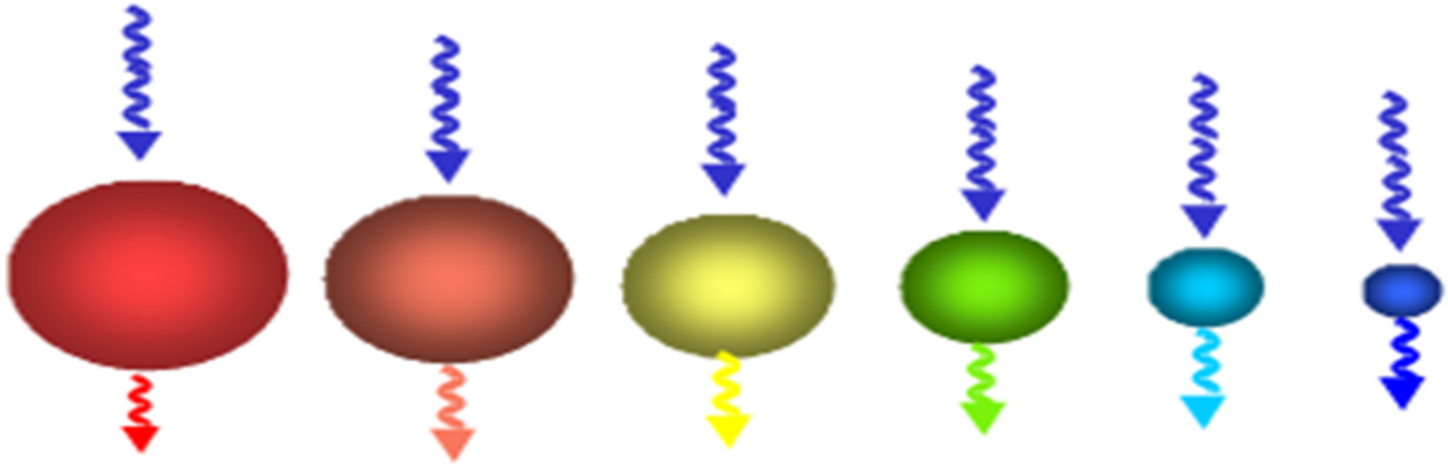
- **All immobilizing nano materials, particularly nZVI and bent-nZVI, are recommended to be used for remediation of Cd and Pb polluted soils due to their high efficiency, low cost, and safety to environment and human hygiene.**

THANK YOU

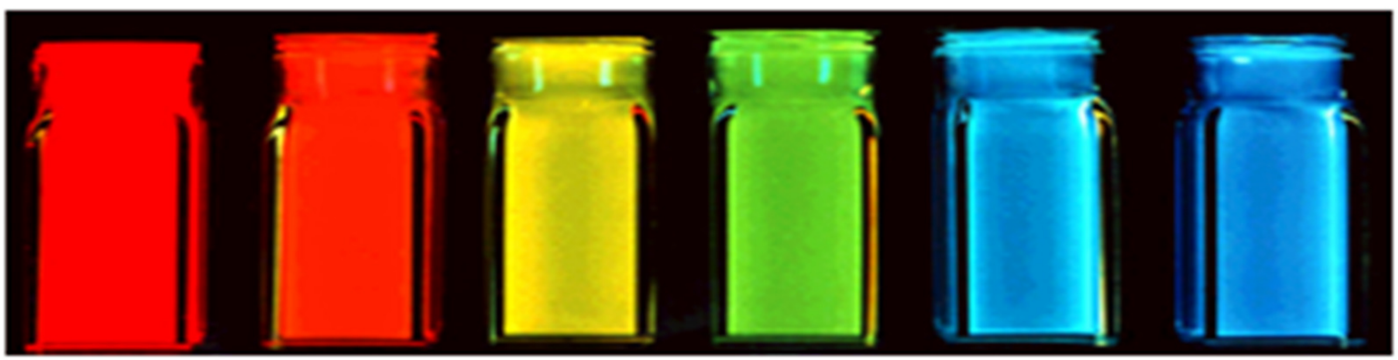
THANK YOU

Optical Properties

Ordinary light excites all color quantum dots.
(*Any* light source "bluer" than the dot of interest works.)



Quantum dots change color with size because additional energy is required to "confine" the semiconductor excitation to a smaller volume.



Source: Bala Manian, Quantum Dot Corp.