
بسم الله الرحمن الرحيم

Immobilization of Cd and Pb in Polluted Soils Using Nano Particles

by

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Contents

Introduction

- Nano science and nanotechnology
- Nanotechnology tools
- Properties of Nano materials
- Nano materials: Carbon Sixty, Carbon Nanotube, nZVI

Remediation of Heavy Metals Polluted Soils

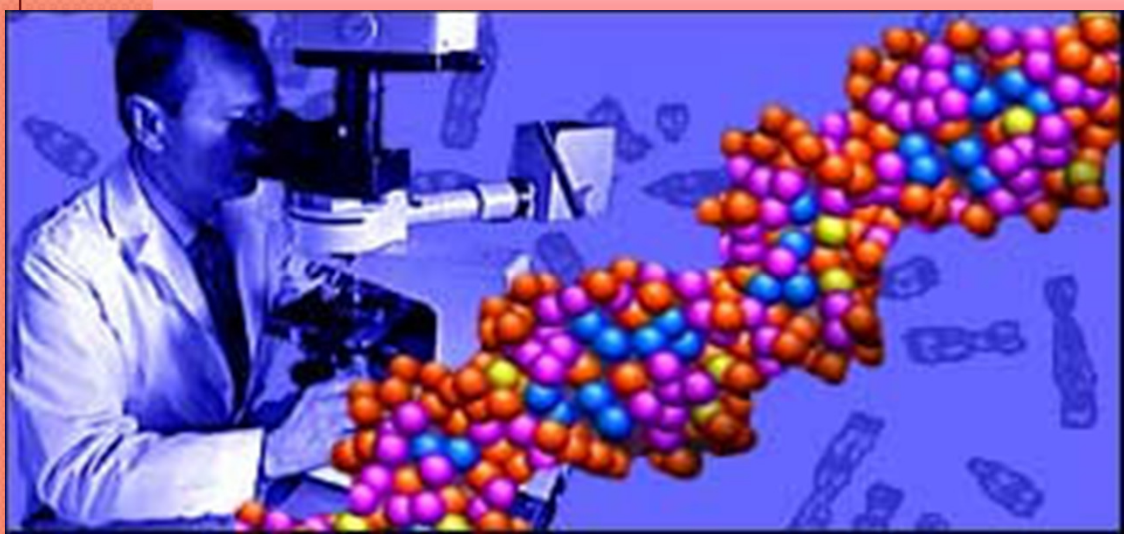
- Remediation Techniques:
- Immobilization of Cd and Pb in polluted soils
- Methods of production of nano particles
- Characteristics of the prepared nano particles
- Capacity of nano particles to adsorb and retain Cd &Pb.

INTRODUCTION

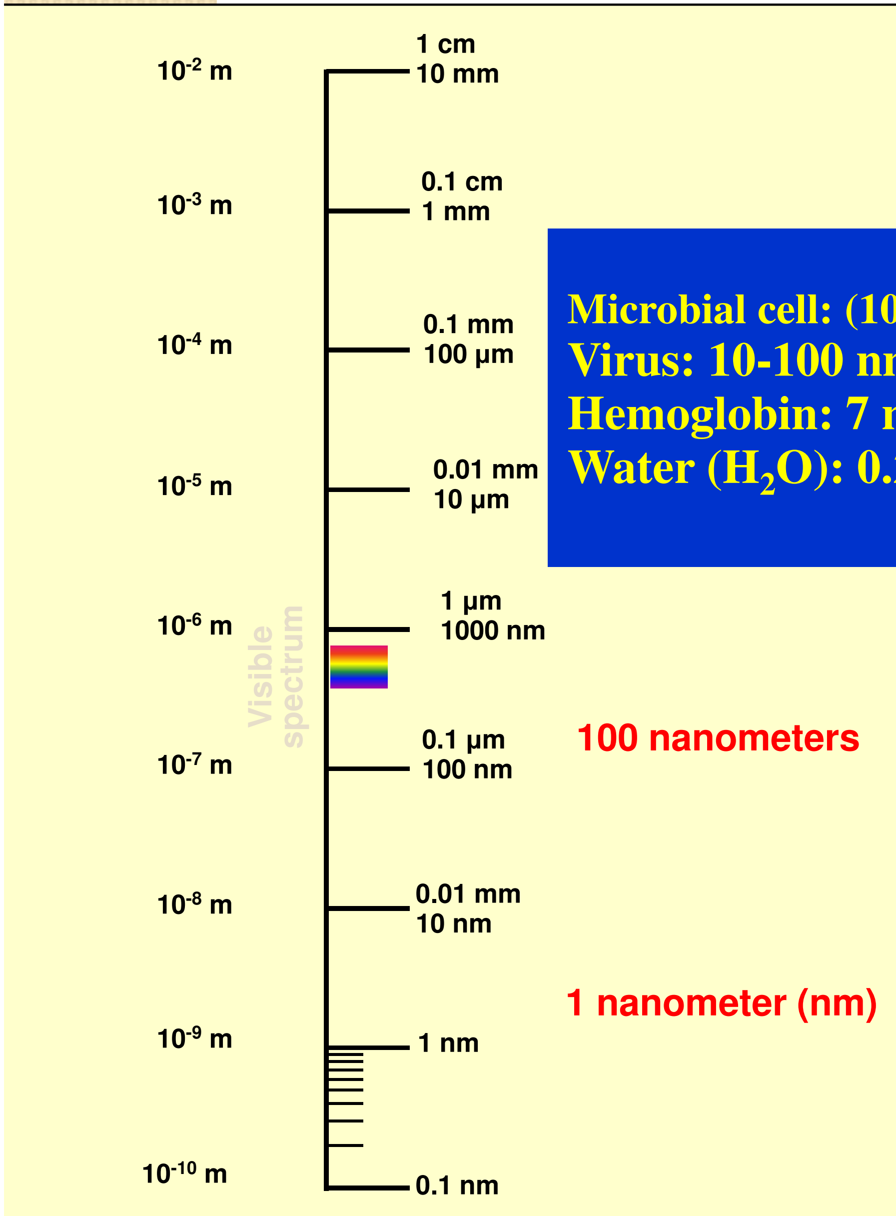
What is Nano?

The word *nano* comes from the Greek and Latin words, nanos or nanus which means *Dwarf*.

1 Nano = 10^{-9} m (one billionth).

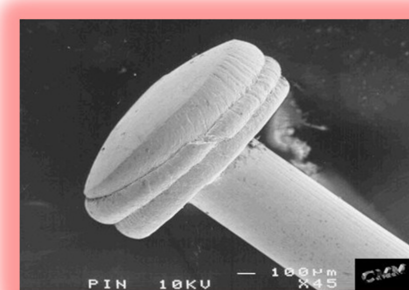


How small is Nano?



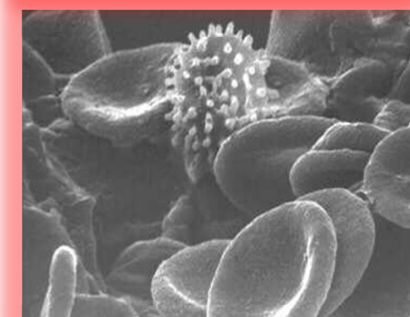
Microbial cell: (1000 nm)
Virus: 10-100 nm.
Hemoglobin: 7 nm.
Water (H_2O): 0.2 nm

Head of a pin
1mm=1,000,000nm

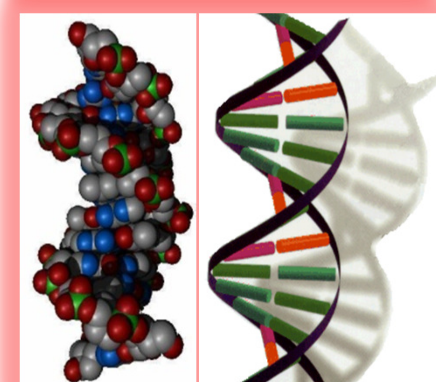


thickness of a human hair
10,000 nm

Length of the red blood cell
2,000 nm



DNA
~2.5 nm width



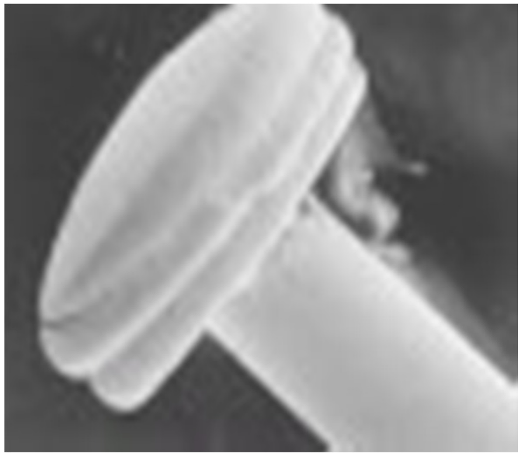
Origin of Nano Science and Nano Technology?

"Plenty of Rooms at the Bottom" (Feynman 1959).

- Arrange atoms the way we want, the very atoms, all the way down!.

Feynman 1959

- There is enough room on the head of a pin to store all pages of 25 volume of Encyclopedia Britannica.



Feynman 1959

- Feynman described a process for manipulating individual atoms and molecules using one set of precise tools to build and operate another proportionally smaller set, and so on down to the nth scale.

In 1981, Feynman's radical vision became feasible after invention of Scanning Tunneling Microscope (STM). Then, the scientists are able to see individual atoms, and move the atoms using Electrical field and infinitesimal small probe.

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.
- Nanotechnology could be defined as "the understanding and control of matter at dimensions roughly ranged from 1 to 100 nanometer, where unique phenomena enable novel applications.

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

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
Surface Reactivity

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.

Surface Reactivity:

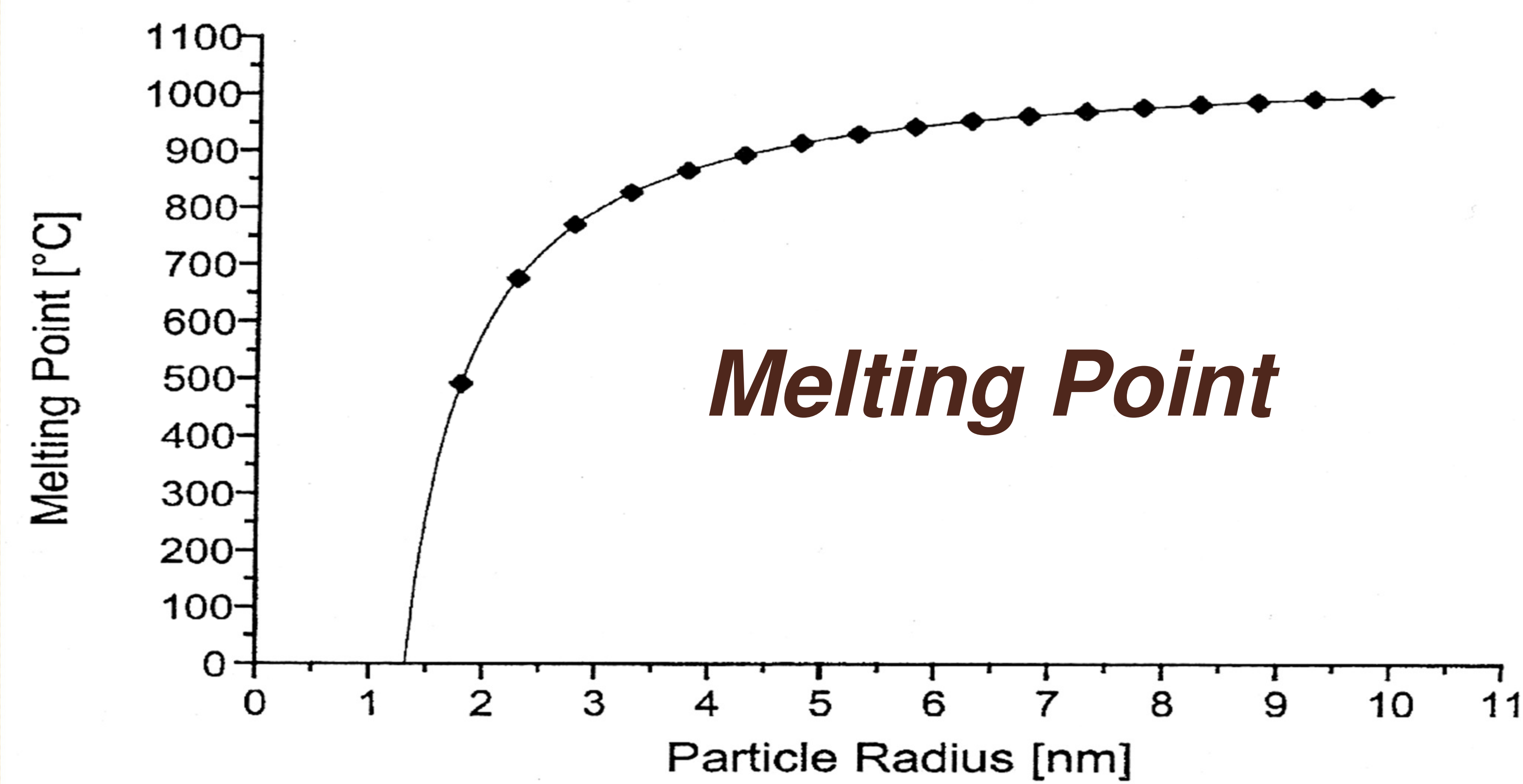
- The vastly increased ratio of surface area to volume opens new possibilities in surface-based science, such as catalysis.

  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.

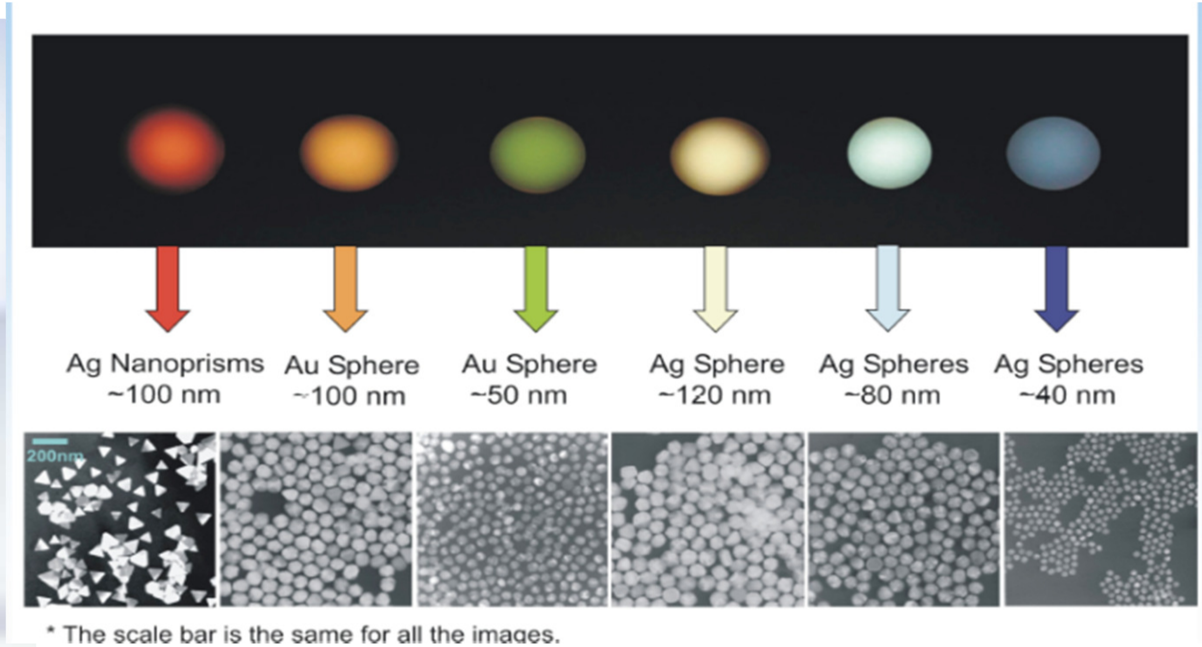
Properties of Nano materials

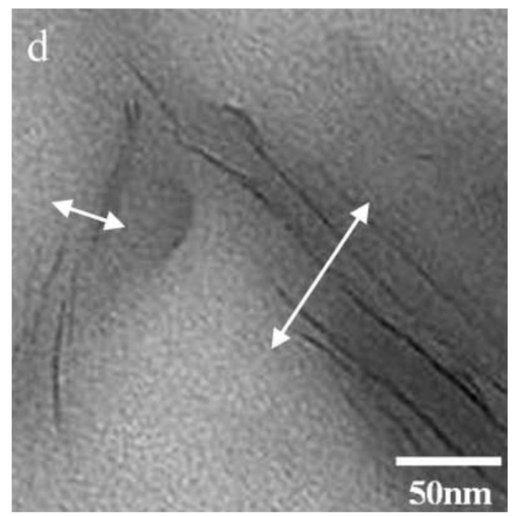
The melting point of gold particles decreases dramatically as the particle size gets below 5 nm



Source: Nanoscale Materials in Chemistry, Wiley, 2001

Properties of Nano materials

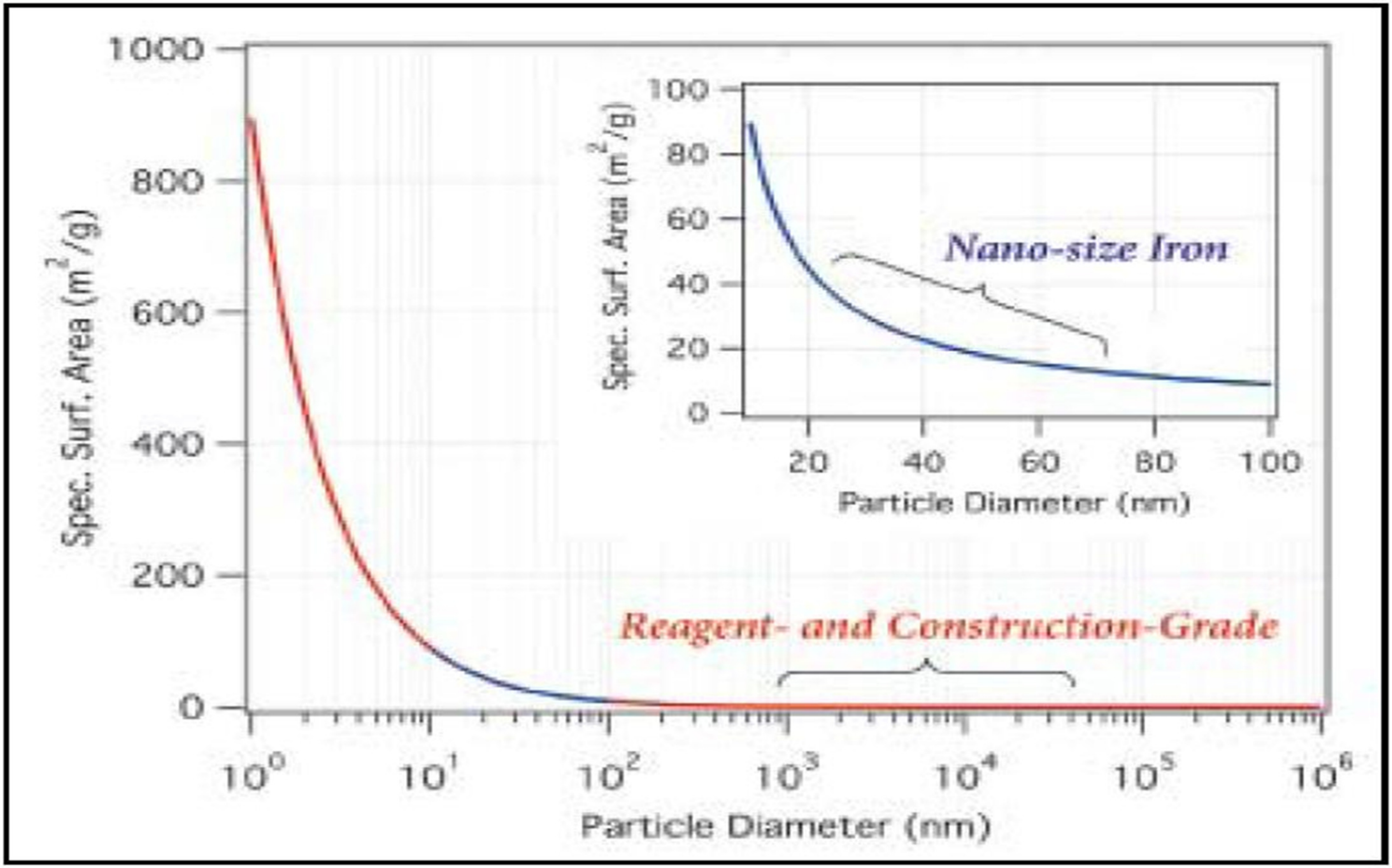




Optical properties – color changes with size

Properties of Nano materials

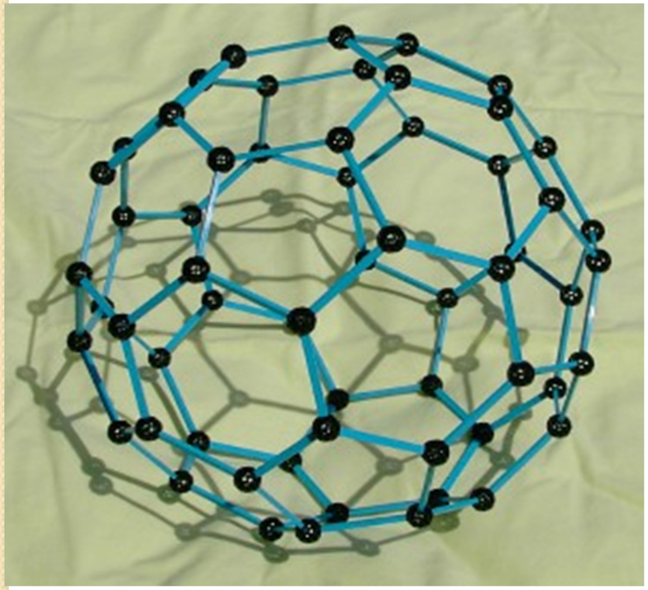
Surface area dependence on particle size



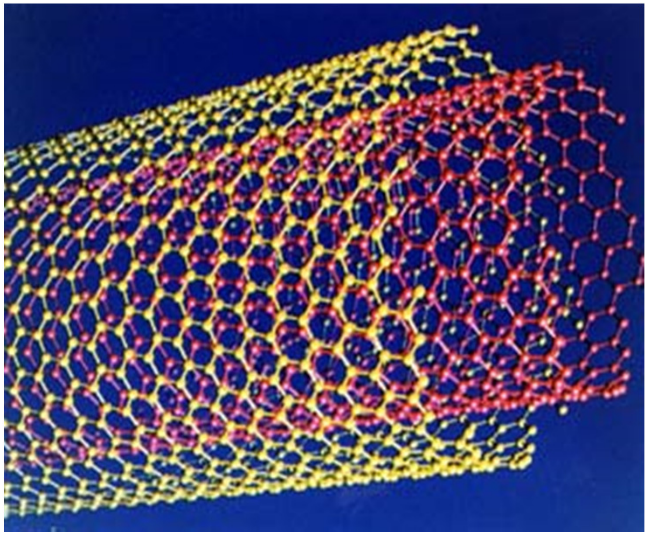
Nano Materials

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

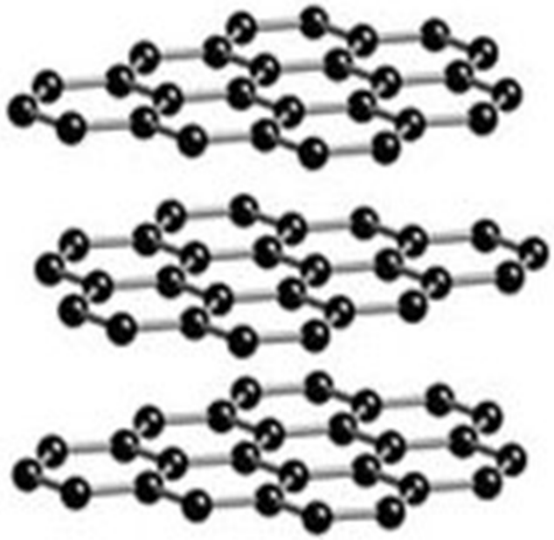
Carbon Nano Tube and Carbon Sixty



C60 : The Fluorine
(discovered 1985)



Carbon Nano Tube
(discovred,1991)



Graphite

Diamond

Carbon Nanotubes (CNT)

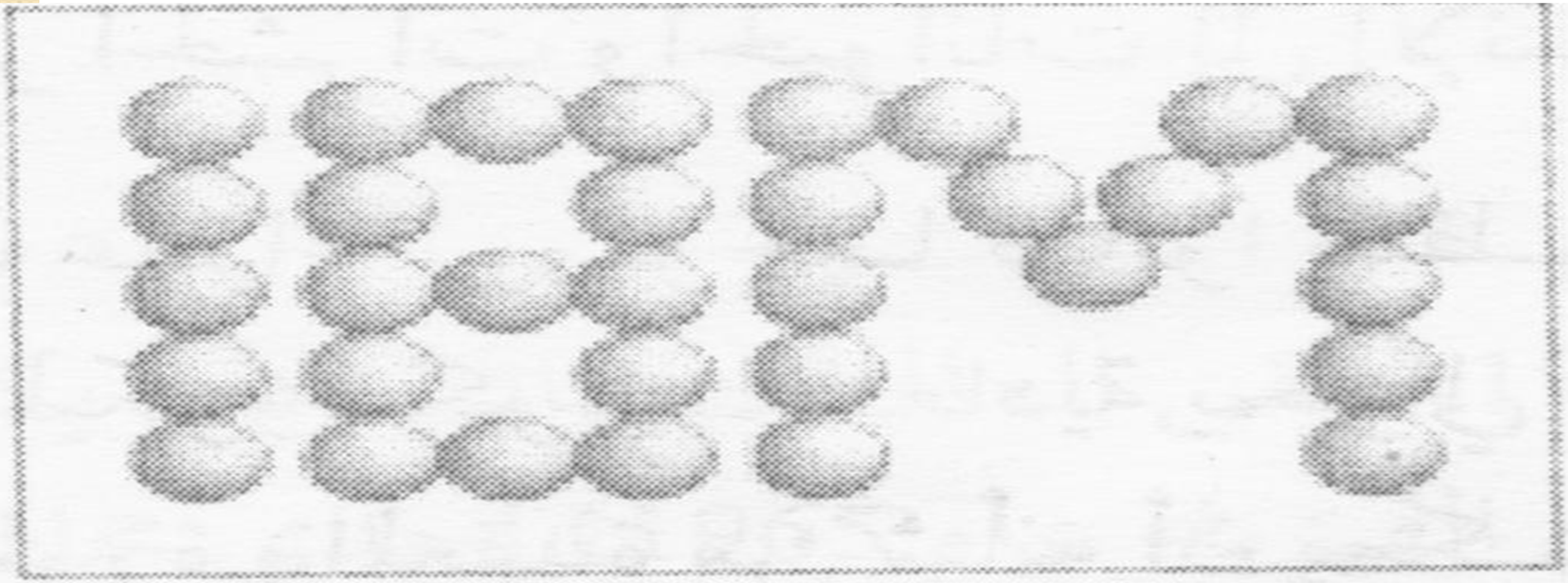
- It is now known that carbon molecules at nanoscale can form cylindrical tubes, called carbon nanotubes (CNT), which are much stronger (100 times) than steel, and conduct electricity (even at higher degrees, 100 ˚C) neither of which is possible with the carbon found in coal or diamonds.

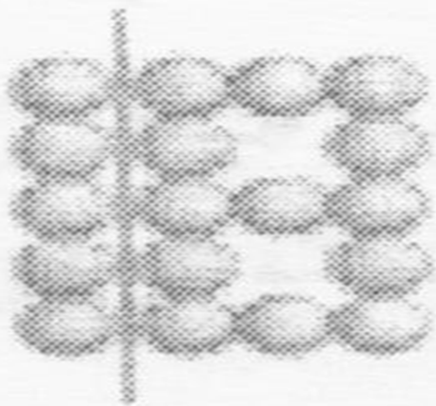
- Since their discovery (1991), carbon nanotubes have fascinated scientists because of their extraordinary properties.

- CNT may one day provide the key breakthroughs in medicine and electronics.

Nanotechnology Tools

- The Scanning Tunneling Microscope (STM),
- Atomic Force Microscope (AFM)
- Scanning Probe Microscope (SPM)
- Transmission Electron Microscope (TEM)


IBM



- ***Applications of Nanotechnology***

- **Nanoscience and nanotechnology encompass a range of rather than a single discipline, touching,**

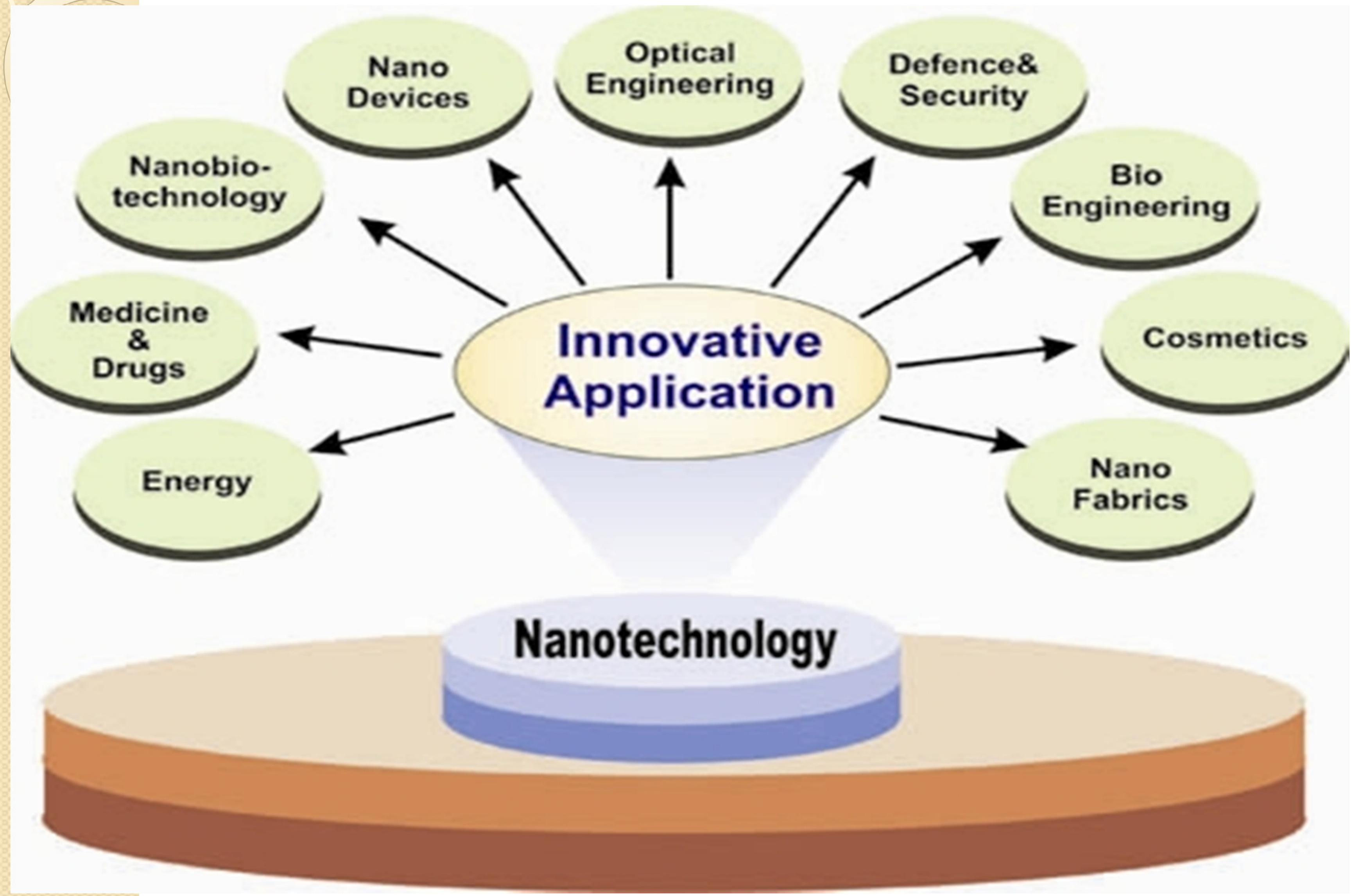
medicine,

physics,

engineering, and

chemistry.

Applications of Nanotechnology



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.

Risks of Cd and Pb on human health:

- Cd and Pb are non-essential and toxic elements for human, and have no use for plant or animals either.

- Cd can damage the kidneys, causing excess production of proteins in the urine

- Cd is associated with skeletal damage, evidenced by low bone mineralization, a high rate of fractures, increased osteoporosis and intense bone pain.

- Exposure to Pb during the early stages of children's development is linked to a drop in intelligence

REMEDIATION OF HEAVY METALS POLLUTED SOIL

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

Tow different techniques are employed.

I - Removing of pollutants:

A – Leaching the soil which can be done *in situ* (on-site), or *ex situ* (removed and treated off-site). Water and suitable solution are used to extract pollutants from the soil matrix (FRTR, 2001).

Both are extremely expensive and/or cause pollution of the ground water *(in situ)* .

:

REMEDIATION OF HEAVY METALS POLLUTED SOIL

B- Phyto-remediation:

in which hyper accumulator plants that tolerate and accumulate high contents of heavy metals by translocating the metals from soil to shoot tissues, allowing the metals to be removed from the soil through harvesting (Brown *et al.* 1994).

II - Immobilization/Stabilization of pollutants in soil:

In which chemical amendment are used to reduce the leachability and/or bioavailability of metals in polluted soils (Ramply and Ogden 1998). Immobilize the metal pollutants within the soil matrix through a combination of chemical reaction.

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 pollutants:

- Several nano particles are used ;

1- nZVI,

2 - bentonite supported nZVI (bent-nZVI),

3 - nano carbon,

4 - nano alginit, and

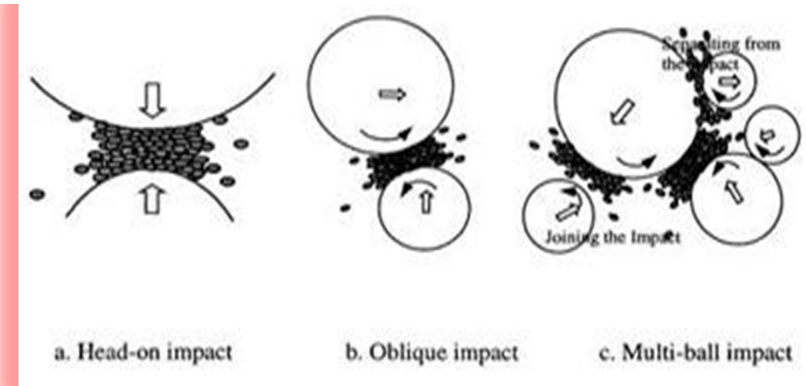
5 – Poly amidoamine (dendrimer) ,

are prepared and used in immobilization of heavy metals in polluted soils.

Methods of Production of Nanoparticles

General Methods:

First : (top-down) method

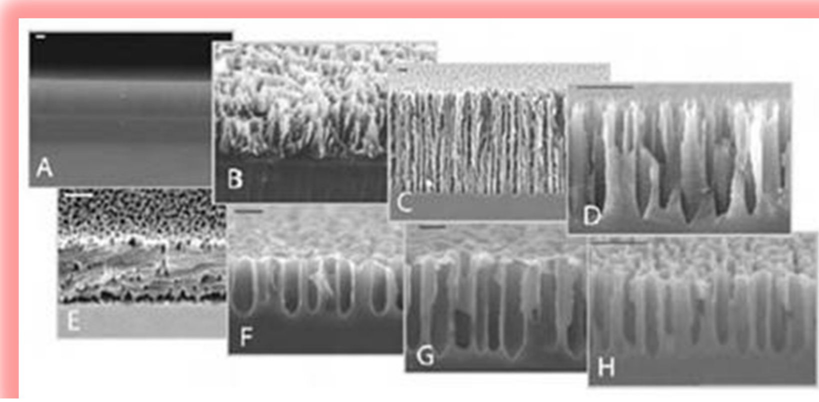


Start from bulk until you reach the nano-cutting through the following:

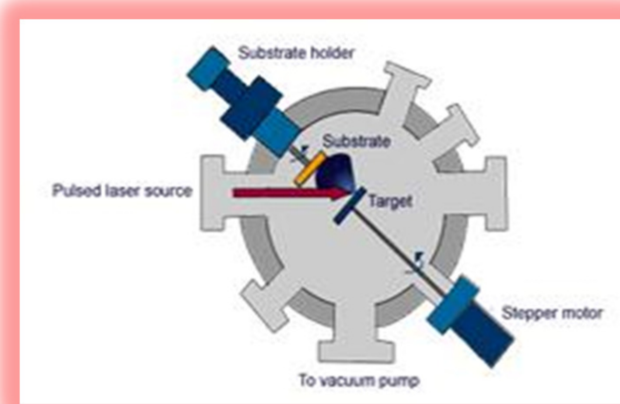
1 – Milling method

2 - Scratching or etching method :

This method is used to produce particles of silicon nano particles

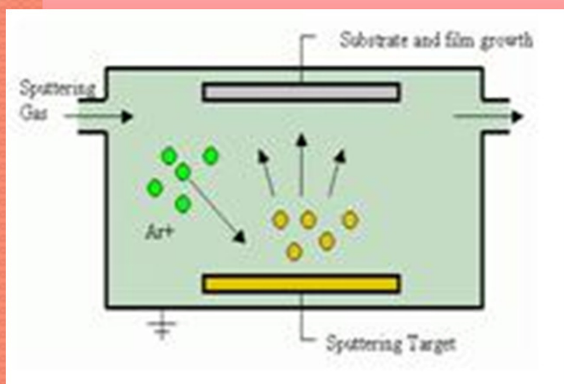


3- Laser ablation method : use of a laser pulse with a high-energy focused on the goal of the heart



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 vapour deposition method (CVD)

Methods of production of Nano Particles

Nano particles used in our research are prepared using chemical (e.g., nZVI, bent-nZVI, Dendrimers) and/or physical methods (e.g., nano alginit) as the following:

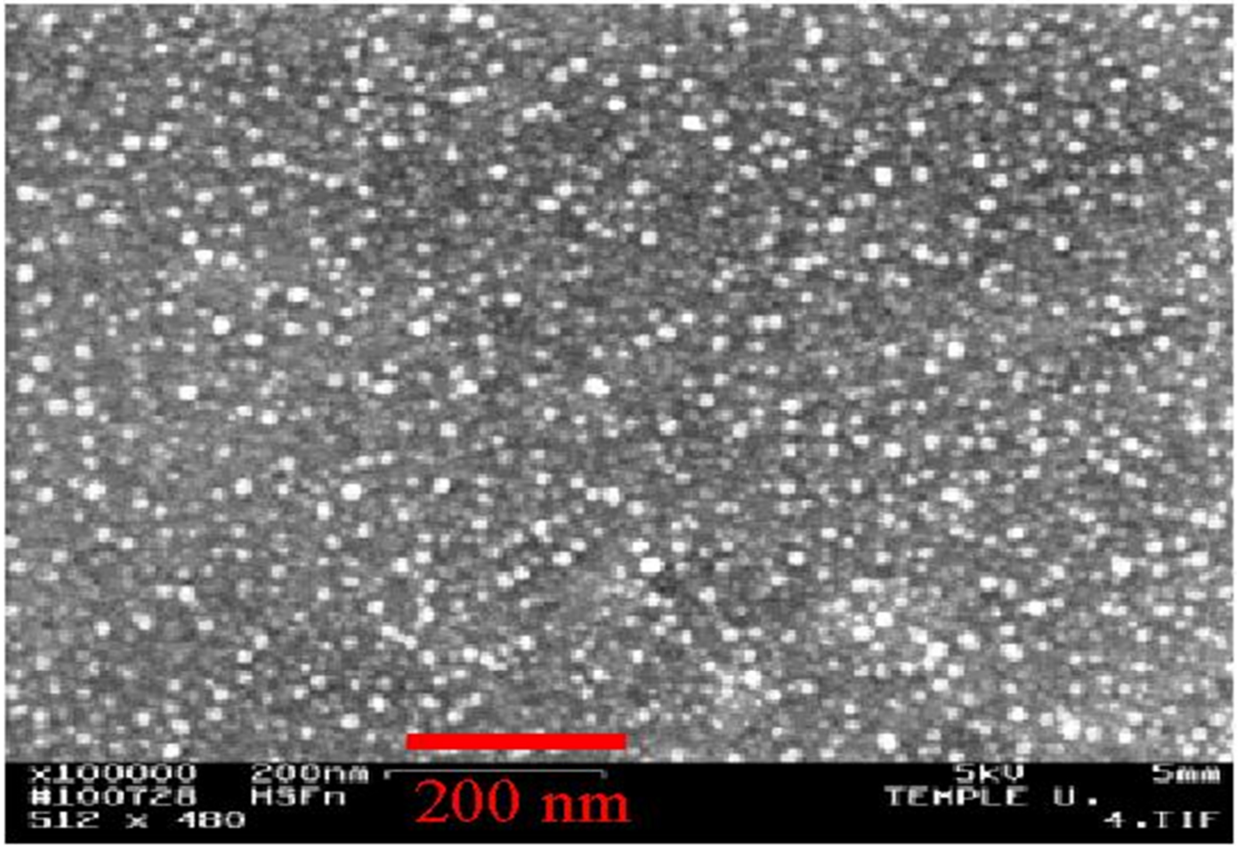
A - Nano-scale Zero Valent Iron (nZVI): I- Chemical methods:

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 $NaBH_4$ were 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.



Iron Nano Particle

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 cation exchange capacity value.
- 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 size, and stirred for 27 hour at speed of 1000 rpm/minute.
- A sample of milled alginite was inspected using TEM, and the size of the alginite particle ranged from 13 – 23nm.

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.

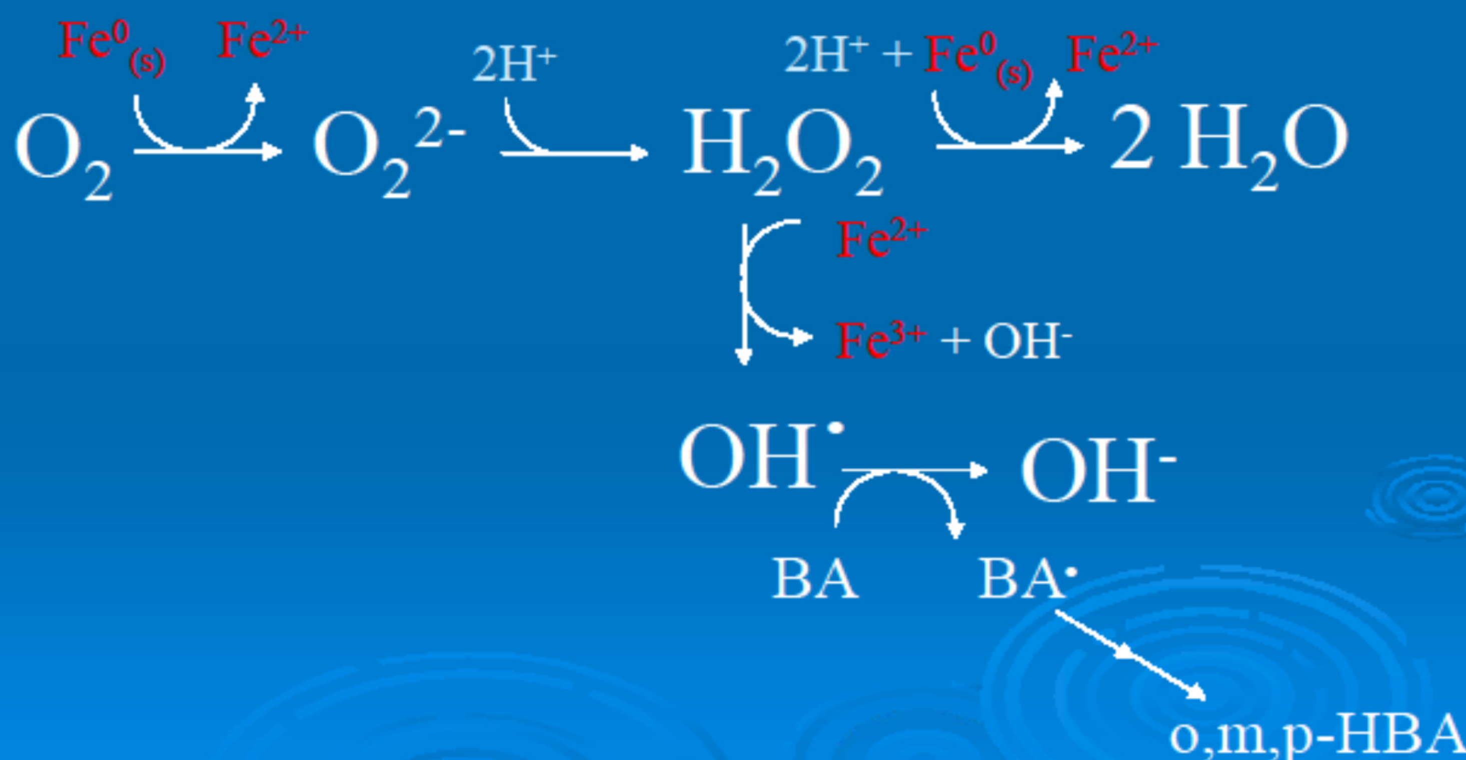
Oxidative Power of nZVI

- 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

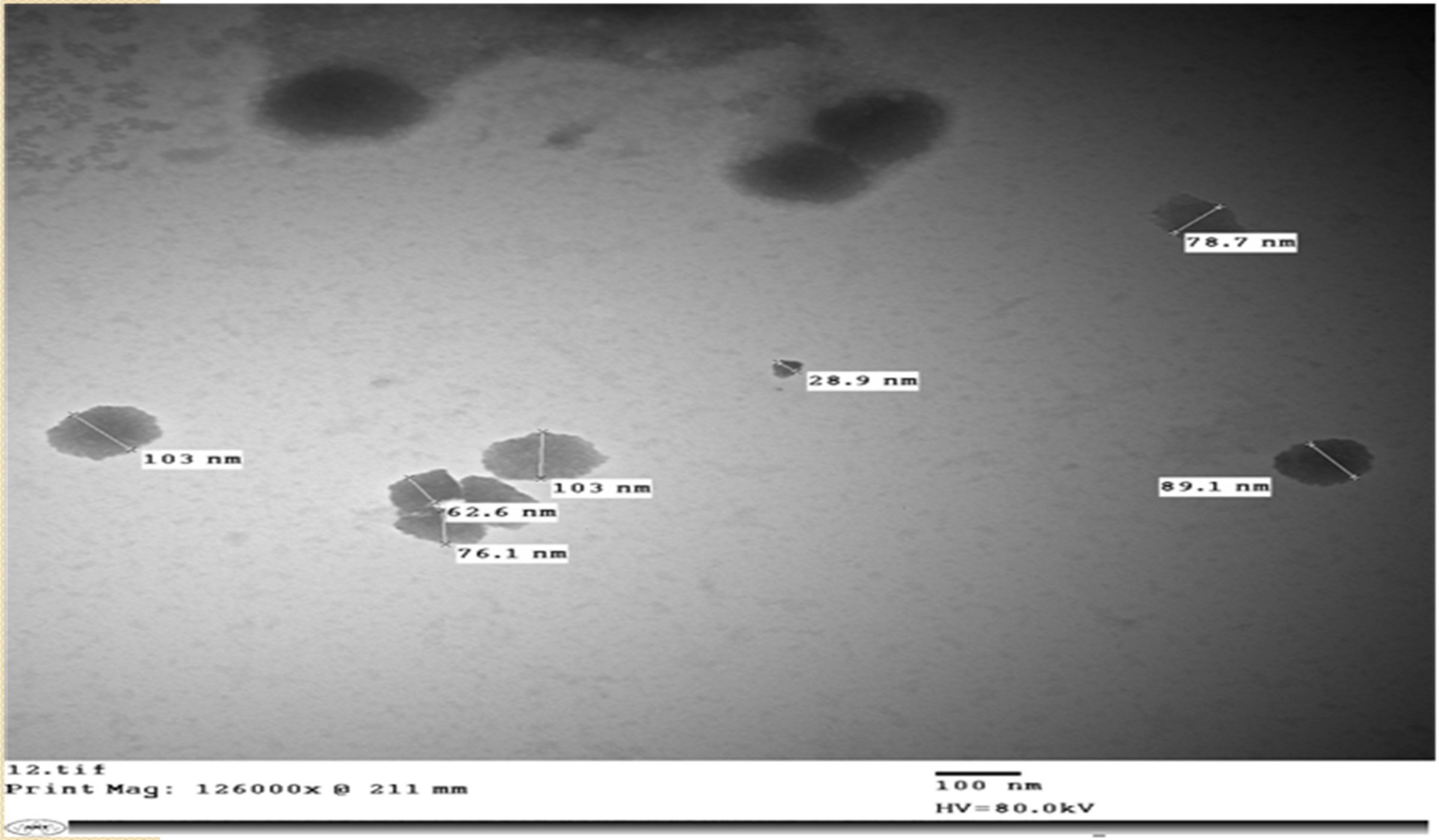


Nano particles characterization

Particle size: The average particle size distribution and morphology of nano particales, were studied using JEOL Transmission Electron Microscope (JEM-1400 TEM, Japan).

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

Figure1.Transmission Electron Microscopy "TEM" images of nZVI



Nano particle characterization

- **- Specific surface area(SSA):** Specific surface area of nano particles were determined using O-phenanthroline method (Sparks, 1998).

Nano particles characterization

Table 1. Important characteristics of nano particles

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

Adsorption Capacity of Nano particle

Adsorption of Cd and Pb on nano particles

-**Adsorption:**

-Portions of 0.1g of studied nano particles were gently shaked 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 24h at 25C° ±1.

-The adsorbed quantity was calculated as the difference between the initial concentration and equilibrium one and presented as mg metal /kg adorbent

Fig 2 : *Adsorption Isotherms of Cd on Nano particles (Langmuir Isotherm, x/m = kbc/1+kb)*

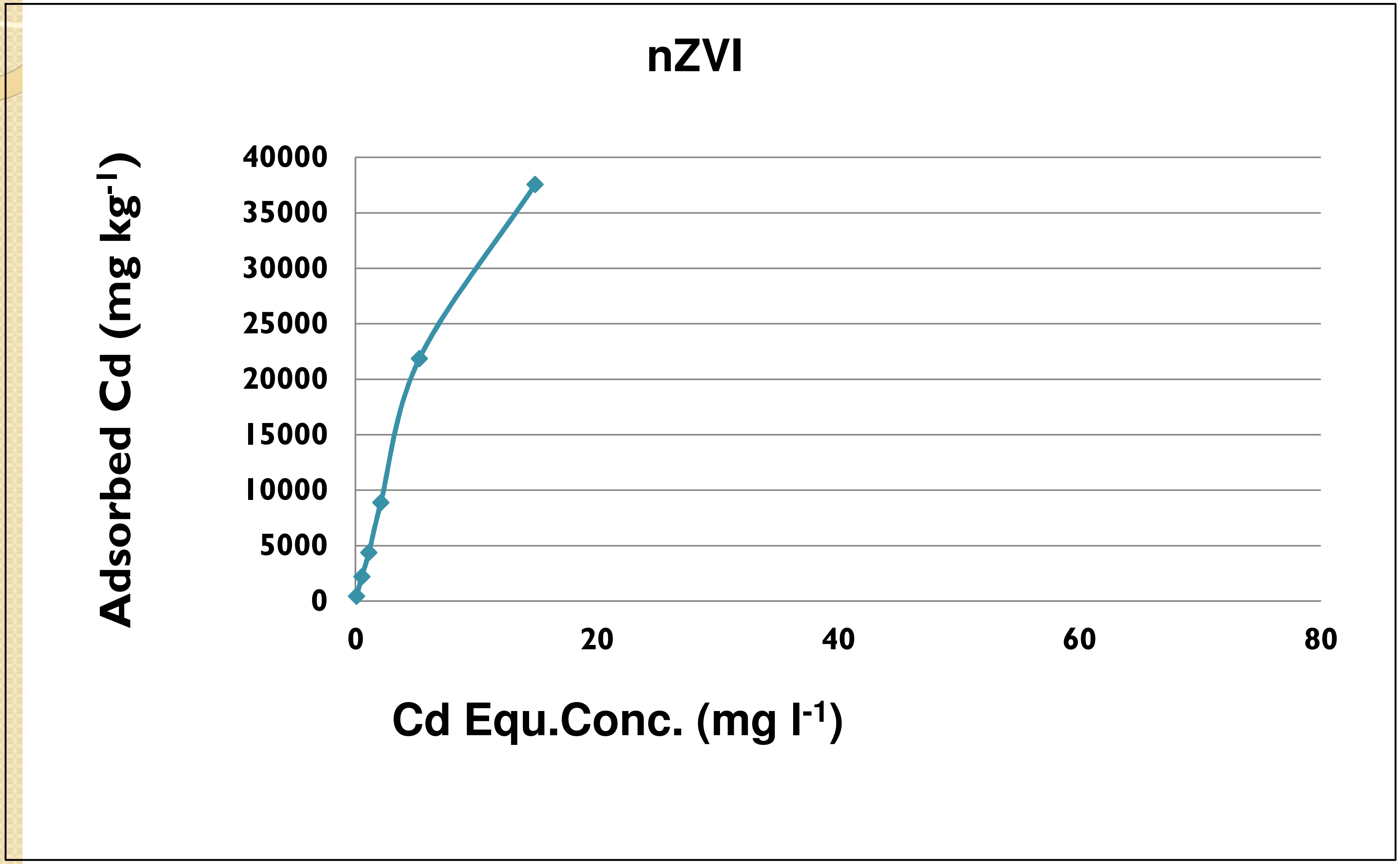


Fig 3 : Adsorption Isotherms of Pb on Nano particles (Langmuir Isotherm, x/m = kbc/1+kb)

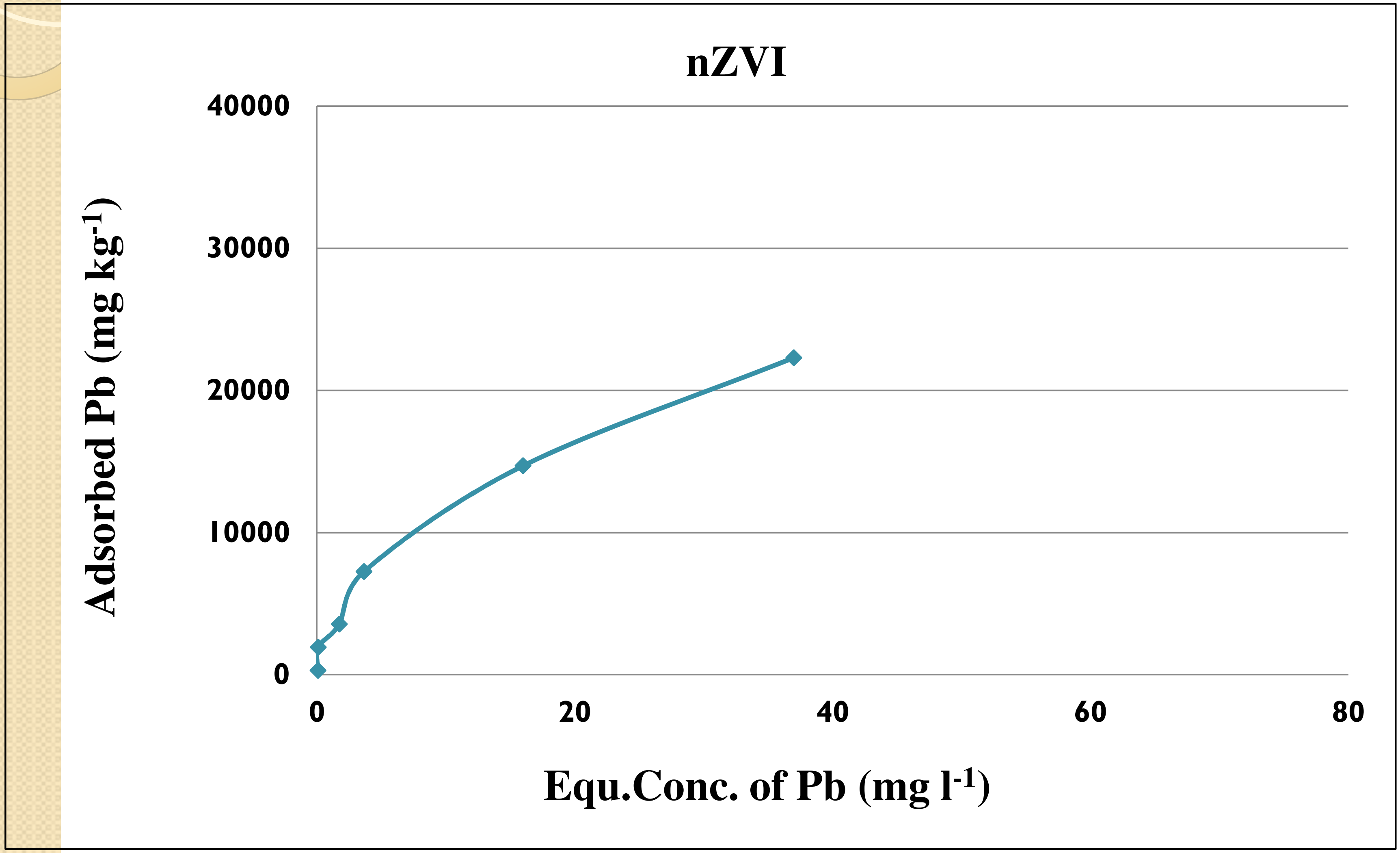


Fig 4 : **Linear form** of ***Adsorption Isotherms of Pb on Nano particles (Langmuir Isotherm, C/x/m= 1/kb + C/b)***

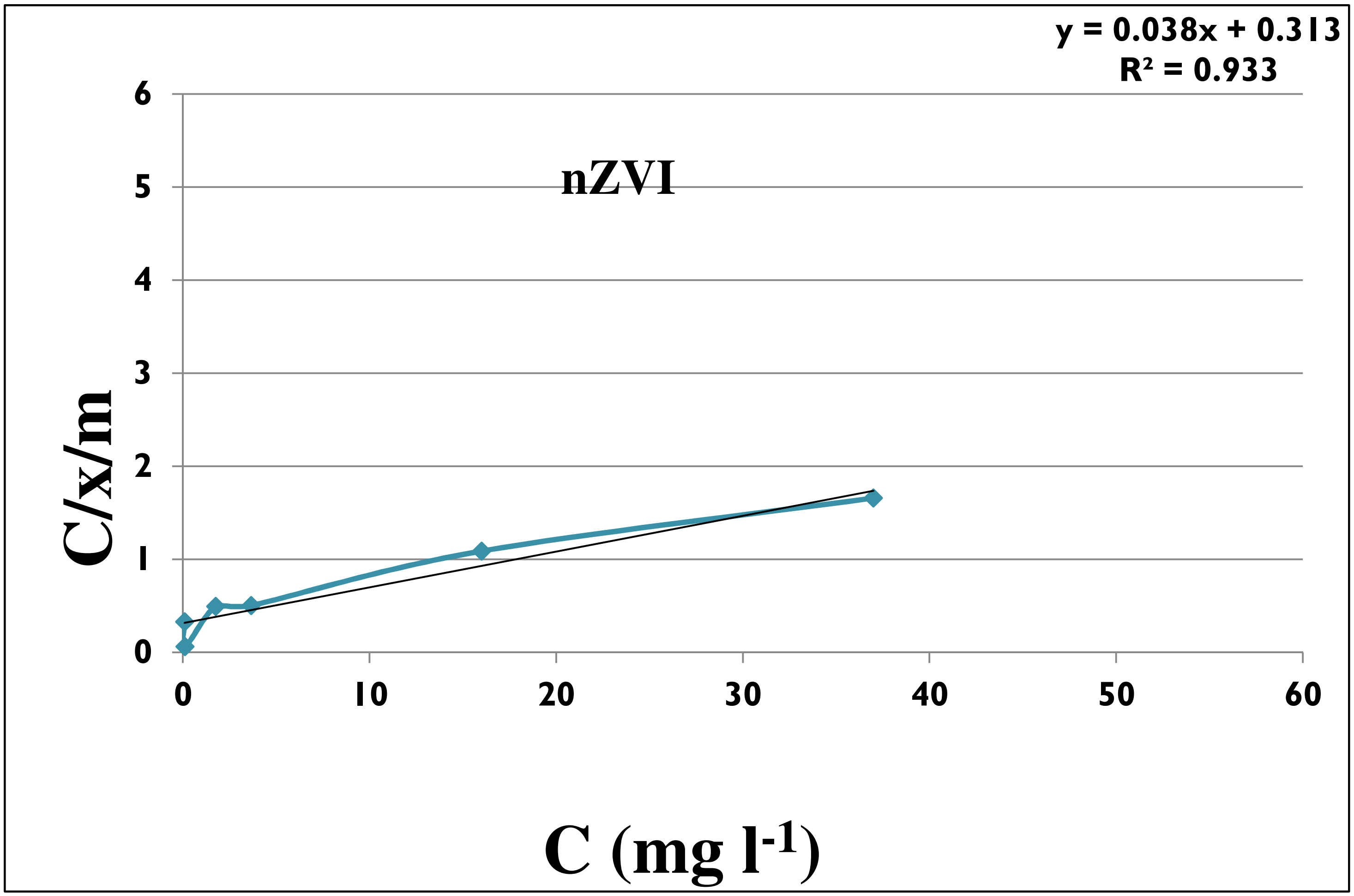


Table 2 : Maximum Adsorption capacity (b) and affinity (k) calculated from Linear form $(C/(x/m) = 1/kb + C/b)$ of Langmuir

No.	Nano Particles	Maximum Adsorption Capacity ($gCd\ kg^{-1}$)(b)	Affinity (k) $l\ g^{1-}$	Maximum Adsorption Capacity ($gPb\ kg^{-1}$)(b)	Affinity (K) $l\ g^{1-}$
1	nZVI	93.45	0.048	25.97	0.123
2	Bent–nZVI	37.45	0.234	24.74	0.024
3	NanoAlginite	41.15	0.006	24.87	0.037
4	Nano Carbon	76.92	0.006	17.85	0.050

Efficiency of Nano Particles to Retain Adsorbed Heavy Metals

- **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 shaked gently for reaction period of 2 h at 25±1C°. After centrifugation, Cd and Pb concentrations were determined in the clear solution, as the above mentioned.

Fig 5: Adsorption/desorption of Cd on nano particles

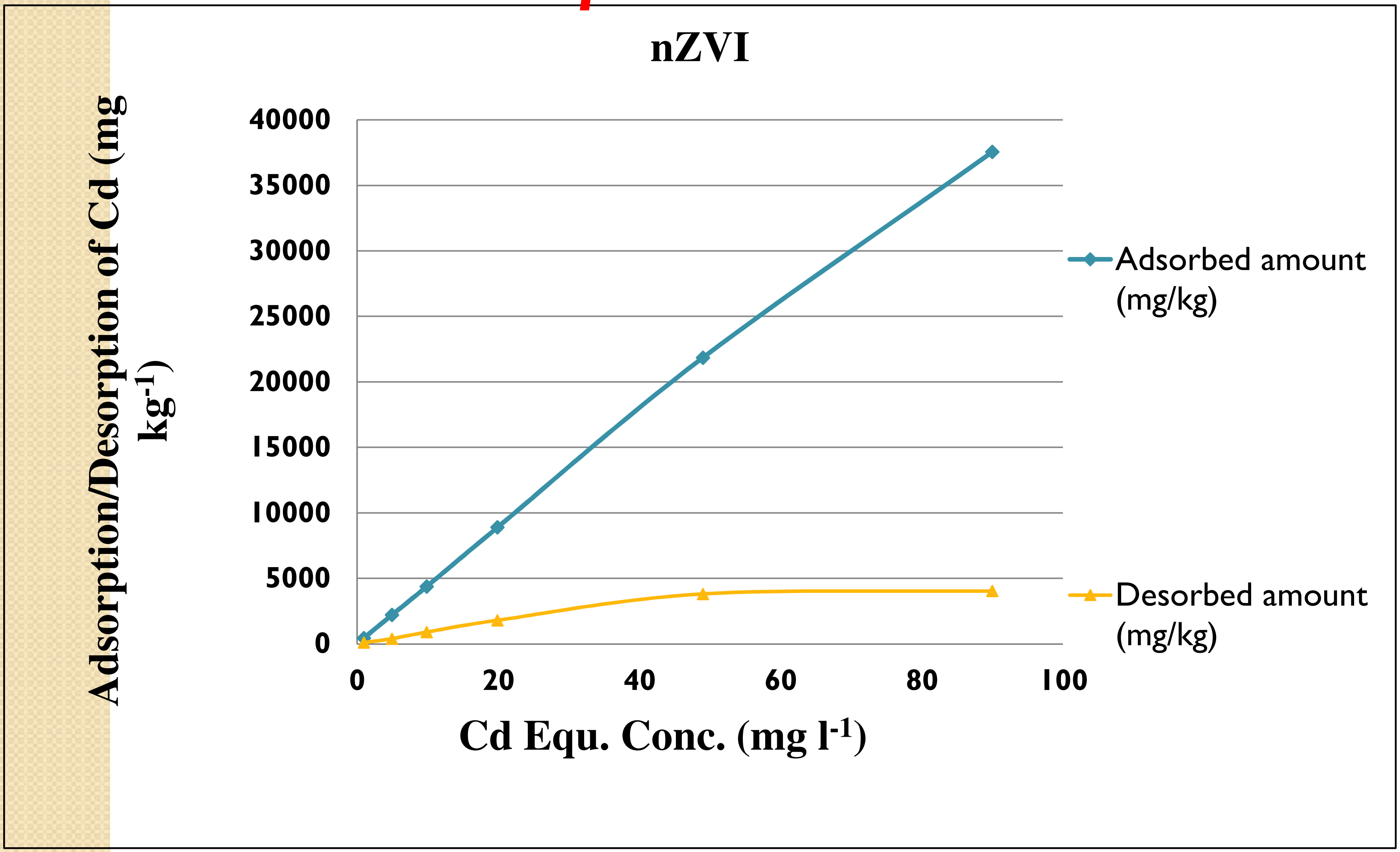


Table 3: Adsorption/Desorption of Cd on nano-particles.

Nano particles	Cd		
	Adsorbed Quantities (mg kg^{-1})	Desorbed Amounts (mg kg^{-1})	Des. /Ads. (%)
nZVI	435 - 37550	96 - 4038	10.8 - 22.1
bent- nZVI	435 - 32000	92 - 4475	14.0 - 21.2
nanoalginite	285 - 20000	90 - 2708	13.5 - 33.4
nano carbon	235 - 18500	88 - 4000	21.6 - 93.9

Fig 6 : Adsorption/desorption of Pb on nano particles

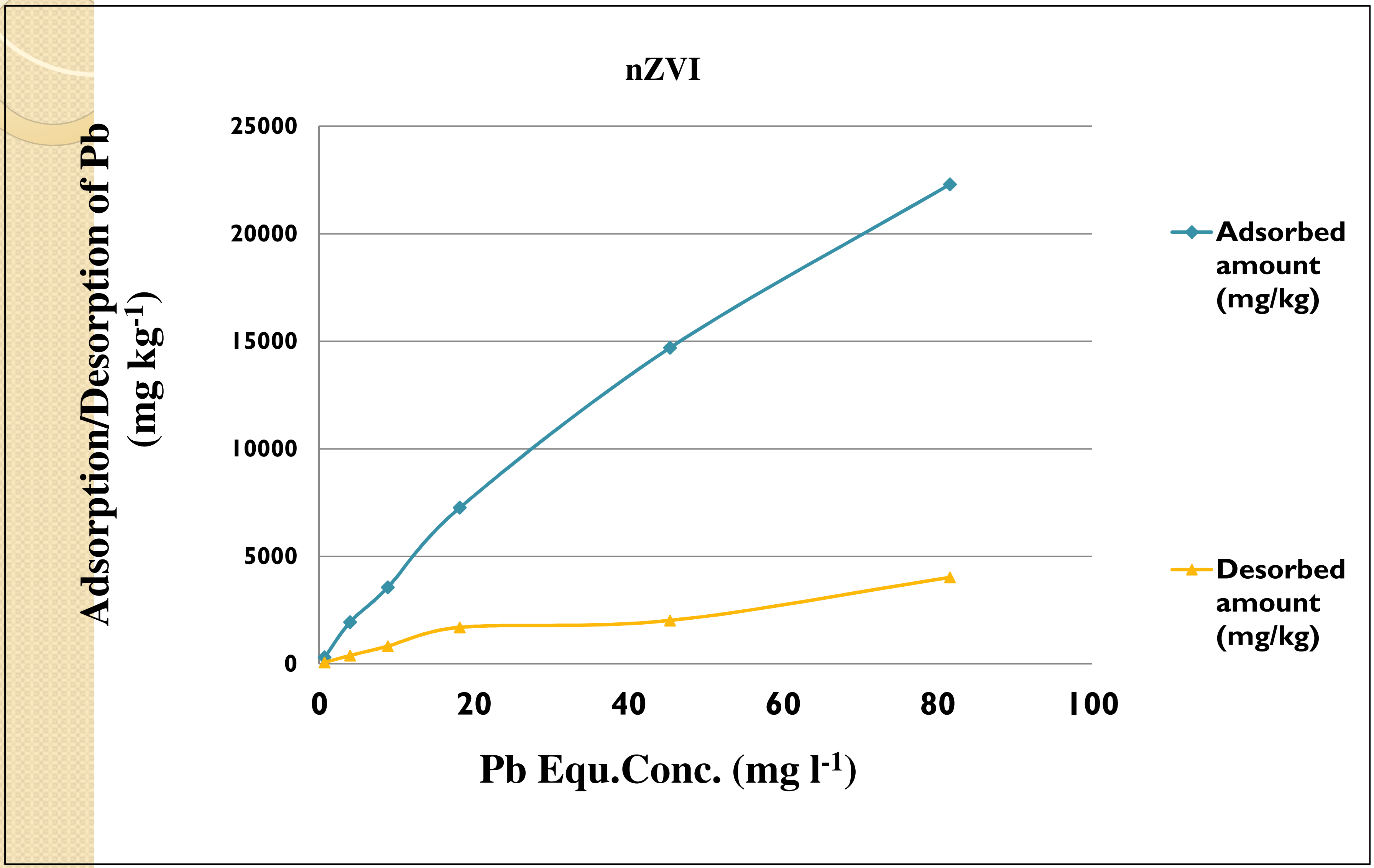


Table 4 : Adsorption/Desorption of Pb on nano-particles.

Nano particles	Pb		
	Adsorbed Quantities ($mg\ kg^{-1}$)	desorbed Amount ($mg\ kg^{-1}$)	Des. /Ads. (%)
nZVI	305 - 22300	68 - 4020	13.7 – 23.4
bent- nZVI	200 - 14300	61 - 4200	22.9 – 33.4
nanoalginite	220 - 16800	64 - 4400	18.9 - 35.6
nano carbon	255 - 13300	70 - 4826	21.9 – 36.3

Immobilization of Cd and Pb in polluted soil

Immobilization of Cd and Pb in polluted soil

- The heavy metals polluted soils were treated with nano particles 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 solution which is recommended to extract amount of metal represent the so called " plant available Cd and Pb" in polluted soil

Table 5 : 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	Initial	3.24	12.85	3.74	7.61
	0.1	1.56	6.05	1.48	3.14
	0.5	0.78	3.83	0.62	2.39
	1.0	0.15	2.79	0.15	1.51
Level of non polluted soil (Aboulroos et al.1988)		0.06	0.06	0.06	0.06

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**
nZVI-bentonite	**Initial**	**6.28**	**6.49**	**6.31**	**5.72**
	0.1	**2.73**	**2.63**	**2.81**	**2.78**
	0.5	**1.83**	**1.48**	**1.70**	**2.05**
	1.0	**1.04**	**0.64**	**0.80**	**1.03**
Level of non polluted soil (Aboulroos et al, 1988)		**2.2**	**2.2**	**2.2**	**2.2**

Distribution of Cd and Pb among different fractions:

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

Table 7. Different fractions of Cd sequentially extracted from the tested soils before and after treating with nano particles

Treatment	Cd fractions (mg/kg)					
	Exch.	Carb.	Oxide.	Orga.	Res.	Sum
Initial	2.80	0.80	1.30	0.63	2.70	8.23
nZVI	0.4	1.85	2.52	0.62	3.0	8.39
bent-nZVI	0.56	2.66	1.42	0.71	3.2	8.55

Table 8: Different fractions of Pb sequentially extracted from the tested soils before and after treating with nano particles

Treatment	Pb fractions (mg/kg)					
	Exch.	Carb.	Oxide.	Orga.	Res.	Sum
Initial	22.3	29.6	36	17.5	73.8	179.2
nZVI	9.77	22.43	70.5	20.31	54.6	177.61
bent-nZVI	9.1	36.22	67.5	20.31	47.7	180.83

THANK YOU

THANK YOU