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Environmental Nanotechnology: Nanoparticles for Bioremediation of Toxic Pollutants

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13.1 Introduction

The size dependent behaviour of any particle relates to some of its unique properties. This gave rise to rapidly growing field of Nanosciences. Nanotechnology has attracted considerable interest of both scientific and industrial community in the past few years. Nanotechnology inter-relates various research areas and applied sciences like physics, chemistry, biology, electronics and material sciences. It is often described as an emerging technology which is truly capable of revolutionizing our approaches to common problems. Nanotechnology involves the design, characterization, production and application of structures/particles by controlling their size and shape at nanoscale. An important challenge in nanotechnology is to engineer particles with desired optical and electronic properties by controlling their size and shape. This can be achieved by chemical processes and also by biological agents. Utilization of microorganisms for intracellular/extracellular synthesis of nanoparticles with different chemical composition, size, shapes and controlled monodispersity (of similar size and shape) can be a novel biological, economically viable and eco-friendly means for biosynthesis of nanoparticles. Nanotechnology holds promise in improving various aspects of life ranging from medicine to industrial materials. Also, Nanotechnology has much more to offer to environmental protection, reduction and clean-up of pollution, energy production and conservation. This chapter is an attempt to introduce the readers to the nanoworld and its use for bioremediation of toxic pollutants in

the environment. This discussion also raises some of the important questions like what will be the fate of nanomaterials released in the environment and their consequent impact on the ecosystem.

13.2 What are Nanoparticles?

The word 'Nano' derived from the Greek word "nanos", which means dwarf or extremely small. The nanoscale (1 nm=10^{-9} m) is a billionth of a metre. Generally dimensions of nano particles ranges from 0.1-100 nm. A nanometre (nm) is one billionth of a metre, or roughly the length of three atoms kept side by side. A DNA molecule is 2.5 nm wide, a flu virus about 100 nm and human hair is approximately 10,000 nm thick (Fig. 13.1). A nanoparticle is a microscopic particle with at least one dimension less than 100 nm. Nano-sized particles have large surface areas relative to their volumes and thus have enhanced chemical and biological reactivity. Owing to their small dimensions nanoparticles can be tailored possessing novel properties for specific applications not exhibited by the particles of the same material at micro or macroscale. Nanostructures exist in various shapes and sizes commonly being the spheres, rods, wires and tubes.
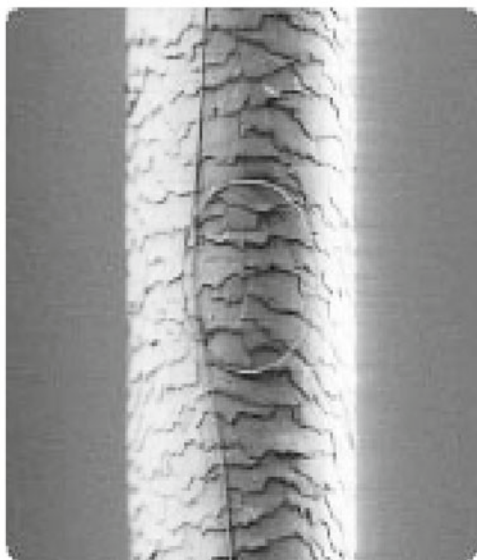

Fig. 13.1: Micrograph of looped nanowire against the backdrop of a human hair (Mazur Group, Harvard University, 2008).

13.3 Nanoparticles in Nature

Nanoparticles can be grouped into three major categories: natural, incidental and engineered. Naturally occurring nanomaterials such as volcanic ash, ocean spray, magnetosomes present in magnetotactic bacteria, mineral composites etc.

exist ubiquitously in our environment. Incidental nanoparticles, also known as anthropogenic nanoparticles, arise from industrial processes like diesel exhaust, coal combustion, welding fumes etc. The third category of nanoparticles is engineered nanoparticles, the real contribution of nanotechnology. Engineered nanoparticles are subclassified by the type of basic material and/or their use: metals, semiconductors, metal oxides, nanoclays, nanotubules, and quantum dots. Both natural and incidental nanoparticles may have irregular or regular shapes. Engineered nanoparticles most often have regular shapes, such as tubes, spheres, rings, etc. Table 13.1 summarizes the various categories of nanoparticles.

Table 13.1: Major groups of nanoparticles

Natural nanoparticles	*Incidental nanoparticles*	*Engineered nanoparticles*
Volcanic ash	Combustion products	Carbon nanotubes
Ocean spray	Frying, cooking	Quantum dots
Biogenic magnetite Magnetosomes in magnetotactic bacteria, meteorite dust	Sand blasting Mining Metal working Biomaterial degradation	Sunscreen pigments (Titanium dioxide nanoparticles for white coloration)
Forest fire smoke		Fullerenes
Mineral composites		Semiconductor wires
Ferritin (12.5 nm) lipoprotein particles (1-75 nm, plasma)		
Clouds		

Quantum dots are unique class of semiconductors having very small size, ranging from 2-10 nanometres (10-50 atoms) in diameter discovered by Louis E. Brus, a professor of chemistry at Columbia University. The term "Quantum dots" was coined by Mark A. Reed. These are a special class of materials known as semiconductors, which are generally composed of elements belonging to periodic groups II-VI, III-V or IV-VI. At these small sizes materials behave differently, giving quantum dots unprecedented tunability and enabling never before seen applications in science and technology. Within each category the shapes, sizes, and surface coatings further determine structure and function of these molecules.

The best example of use of natural and incidental nanoparticles is the *Kaajal* which the Indian women have been using as eye-liner without knowing that it is a product of advanced technology. Scientists at the Indian Institute of Technology (IIT), Kanpur have shown that *kaajal* actually contains Carbon Nanotubes (CNTs). These objects, much thinner than human hair, have strange properties and are considered the building block of ultra-small (nano) electronic and other devices. While researchers worldwide are trying to develop newer and

better methods for producing CNTs, the age-old practice of making *kaajal* by burning mustard oil is the simplest, fastest and the cheapest one. Synthesis of *kaajal* is well known and its use is even mentioned in epics like the *Ramayana* and the *Mahabharata*.

13.4 Nanoparticles and their Role in Bioremediation

Detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides, poly-chlorinated hydrocarbons (PCH), toxic metal compounds using microorganisms and/or their products is known as bioremediation. Recently, the emerging field of nanotechnology has also contributed significantly in remediating these common soil and water pollutants in environment friendly manner. Some of noteworthy applications of nanomaterials in remediation of toxic environmental pollutants are highlighted below.

13.4.1 Degradation of PCHs

Polychlorinated hydrocarbons, class of organic compounds having several chlorine atoms attached to benzene rings are major recalcitrant environmental pollutants. PCHs/PCBs are widely used for many applications, especially as dielectric fluids in transformers, capacitors and coolants. Due to their inherent PCB's toxicity and classification as persistent organic pollutants, PCB production was banned by the United States Congress in 1976 and by the Stockholm Convention on Persistent Organic Pollutants in 2001.

Bimetallic nanoparticles have been used in place of granular zero-valent metal nanoparticles in environmental clean up of chlorinated hydrocarbon contaminants because of the following advantages:

(i) Small size enables the nanoparticles to penetrate or diffuse in contaminated area where micro sized particles fail to reach.

(ii) Nanosized particles have higher reactivity to redox-amenable contaminants.

Studies have shown that oxide-coated Fe^0 can form weak and outer sphere complexes with organic contaminants such as carbon tetrachloride (CTC). By electron transfer it can be broken down into methane, carbon monoxide or formate. Organic contaminants like benzoquinone, trichloroethene and several other chlorinated aliphatic hydrocarbons can be converted to compounds having less toxicity (Nurmi et al., 2005).

TiO_2 nanotubes have been used in labscale degradation of pentachlorophenol (PCP) through a photoelectrocatalytic reaction (Quan et al., 2005).

The use of nanoparticles as biocatalyst for reductive dechlorination of organic contaminants has also been demonstrated by De Windt et al., 2005. In one of the study palladium Pd(0) are deposited on the cell wall and inside the cytoplasm of *Shewanella oneidensis* and charged with H* radicals by using

various substrates such as hydrogen, acetate and formate as electron donors in a bioreductive assay containing Pd(II). When these charged Pd(0) bearing cells are brought in contact with chlorinated compounds, the H* radical on Pd(0) catalyse the dechlorination of the chlorinated compounds (De Windt et al., 2005).

13.4.2 Degradation of Hydrophobic Compounds

Nanoparticles are also being used to increase the bioavailability of hydrophobic organic compounds for their enhanced bioremediation. Polymeric nanoparticles prepared from a Poly(ethylene) glycol- Modified Urethane Acrylite (PMUA) precursor was applied to enhance the availability of polynuclear aromatic hydrocarbons (PAHs) in soil and aqueous solutions. Due to the hydrophobicity of interior regions of PMUA there is increased affinity between PAHs and outer hydrophilic surfaces of PMUA. This promotes particle mobility; increases amount of PAHs released into the aqueous phase and enhances the rate of mineralization (Tungittiplakorn et al., 2004, 2005). Subsequently the released PAHs can be treated by natural attenuation or pump-and-treat process in which polymeric nanoparticles can be recovered and recycled after microbial degradation of PAHs.

Further nanoparticles can also be used to immobilize bacterial cells which are capable of degrading specific toxic compound or to biorecover certain compounds. In one of the study, magnetic nanoparticles (Fe_3O_4) were functionalized with ammonium oleate and coated on the surface of *Pseudomonas delafieldii*. On application of external magnetic field to the microbial cells, the nanoparticle coated cells concentrate on particular site of the reactor wall separating them from the whole solution and enabling recycling of the cells for the treatment of the same compound. These coated cells were applied for the desulfurization of organic sulfur from the fossil fuel (i.e., dibenzothiophene) in a bioreactor and were observed to be as efficient as the non-nanoparticle coated microbial cells (Shan et al., 2005).

13.5 Nanoparticles for Water Purification

Progress in nanoscale sciences may provide solution to many of the current problems involving water quality. The use of nanosorbents, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes and nanoparticle enhanced filtration products and processes resulting from the development of nanotechnology would greatly help to get potable drinking water. Innovations in the development of novel technologies to desalinate water are among the most exciting and promising. The development of novel nanoscale materials and processes for treatment of surface water, ground water and industrial wastewater contaminated by toxic metal ions, radionuclides, organic and inorganic solutes like pesticides, bacteria and viruses would be the major environmental contribution of nanotechnology.

Recent studies prove that many of the issues involving potable water quality could be resolved using nanoparticles, nanofiltration or other nanomaterials. Innovative use of nanoparticles for treatment of industrial wastewater is another potentially useful application of nanomaterials as many industries generate large amounts of wastewater contaminated with toxic and non-biodegradable effluents. Removal of contaminants and recycling of the contaminated water would provide significant reductions in cost, time, and labour for the industries and increase their eco-friendliness.

Aquifer and groundwater remediation are also critical issues, becoming more important as potable water supply is steadily decreasing. Most of the remediation technologies available at present, while being effective, very often are costly and time consuming, particularly pump-and-treat methods. The ability to remove toxic compounds from subsurface and other environments are very difficult to access in situ, and doing so rapidly, efficiently and within reasonable costs is the ultimate goal of nanotechnology. Some of the nanomaterials used for water purification are discussed in the following paragraphs.

Nanosorbents

Nanomaterials have two important key properties that make them effective sorbents:

 (i) Due to their small size nanoparticles have larger surface areas.
 (ii) These can also be functionalized with various chemical groups to increase their affinity towards the target compound/compounds.

Efforts are being made by several research groups to exploit the unique properties of nanoparticles to develop high capacity and selective sorbents for metal ions and anions which are common water contaminants. Li et al. (2003) have reported the sorption of Pb(II), Cu(II) and Cd(II) onto multiwalled carbon nanotubes (MWCNTs). The maximum sorption capacities of 97.08 mg/g for Pb(II), 24.49 mg/g for Cu(II) and 10.86 mg/g for Cd(II) at room temperature, pH 5.0 and metal ion equilibrium concentration of 10 mg/l. It was also found that the metal-ion sorption capacities of the MWCNTs was 3–4 times higher than that of powder activated carbon and granular activated carbon which are two commonly used sorbents in water purification. Qi & Xu (2004) have evaluated the sorption of Pb(II) onto chitosan nanoparticles (40–100 nm) prepared by ionic gelation of chitosan and tripolyphosphate. The phosphate-functionalized chitosan nanoparticles have a maximum Pb(II) sorption capacity of 398 mg/g. Peng et al. (2005) have recently developed a novel sorbent with high surface area (189 m^2/g) consisting of cerium oxide supported on carbon nanotubes (CeO_2-CNTs). It was observed that the CeO_2-CNT particles are effective sorbents for As(V). As(V) is very toxic metalloid and proven carcinogen found in the ground waters of some districts (Midnapur, 24-Parganas etc.) of West Bengal, India and also in Bangladesh. Interestingly, Peng et al. (2005) found that the addition (from 0 to 10 mg/l) of two divalent cations [Ca(II) and Mg(II)]

resulted in a substantial increase of the amount of sorbed As(V) from 10 to 82 mg/g. Deliyanni et al. (2003) have also synthesized and characterized a novel As(V) sorbent consisting of akaganeite [β-FeO(OH)] nanocrystals. In addition, Lazaridis et al. (2005) have shown that nanocrystalline akaganeite is also an effective sorbent for Cr(VI).

Zeolites are effective sorbents and ion-exchange media for metal ions. NaP1 zeolites ($Na_6Al_6 Si_{10}O_{32}$, 12H_2O) have a high density of Na ion exchange sites. These can be inexpensively synthesized by hydrothermal activation of fly ash with low Si/Al ratio at 150°C in 1.0–2.0 M NaOH solutions (Moreno et al., 2001). NaP1 zeolites have been used as ion exchange media for the removal of heavy metals from acid mine wastewaters (Moreno et al., 2001). Alvarez-Ayuso et al. (2003) reported the successful use of synthetic NaP1 zeolites to remove Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from metal electroplating wastewaters. Self-assembled monolayers on mesoporous supports (SAMMS) made via surfactant templated synthesis of mesoporous ceramics are more effective sorbents for toxic metal ions (Yantasee et al., 2003), anions (Kelly et al., 2001) and radionuclides (Fryxell et al., 2005). This produces nanoporous ceramic oxides with very large surface areas (1000 m^2/g) and high density of sorption sites that can be functionalized to increase their selectivity toward target pollutants.

Carbonaceous nanomaterials have been proved as high capacity and selective sorbents for organic solutes in aqueous solutions. Mangun and coworkers (2001) have synthesized nanoporous activated carbon fibres (ACFs) with an average pore-size of 1.16 nm and surface areas ranging from 171 to 483 m^2/g. The sorption of benzene, toluene, p-xylene and ethylbenzene onto the ACFs at 20°C was quite effective. Peng et al. (2003) have evaluated the sorption of 1, 2-dichlorobenzene (DCB) onto CNTs. They reported that it takes only 40 min for DCB sorption onto the CNTs to reach equilibrium with a maximum sorption capacity of 30.8 mg/g. Li et al. (2004) observed that MWCNTs were better sorbents of volatile organic compounds than carbon black in aqueous solutions. Fugetsu et al. (2004) have successfully encapsulated MWCNTs inside cross-linked alginate vesicles. The caged MWCNTs showed high sorption capacity and selectivity for four water-soluble dyes (acridine orange, ethidium bromide, eosin bluish and orange G). Zhao and Nagy (2004) have synthesized hybrid inorganic-organic nanosorbents by incorporation of sodium dodecyl sulfate (SDS) into magnesium-aluminum layered double hydroxides (LDHs). They reported that the SDS functionalized Mg/Al LDHs had higher sorption capacity for chlorinated alkenes [tetrachloroethylene (PCE) and trichloroethylene (TCE)] in aqueous solutions than organoclays. Fullerenes can also serve as sorbents for polycyclic aromatic compounds (PAHs) such as naphthalene (Cheng et al., 2004). The amphiphilic polyurethane nanoparticles can also sorb PAHs (e.g., naphthalene) and increase their bioavailability in aqueous solutions (Tungittiplakorn et al., 2004, 2005).

13.6 Nanocatalysts and Redox Active Nanoparticles

Nanoparticles have great potential as water-purification catalysts and redox active media. This feature is due to their large surface areas and their size and shape dependent optical, electronic and catalytic properties. During the past few years, titanium dioxide (TiO_2) nanoparticles have emerged as promising photocatalysts for water purification (Adesina, 2004). They can serve both as oxidative and reductive catalysts for organic and inorganic pollutants. Chitose et al. (2003) reported enhanced removal of total organic carbon from waters contaminated with organic wastes by the addition of TiO_2 nanoparticles in the presence of ultraviolet light. Kabra et al. (2004) documented the successful use of TiO_2 nanoparticles to (i) degrade organic compounds (e.g. chlorinated alkanes and benzenes, dioxins, furans, PCBs, etc.) and (ii) to reduce toxic metal ions [e.g., Cr(VI), Ag(I) and Pt(II)] in aqueous solutions under UV light. One of the most cited studies by Asahi et al. (2001) in which they reported the synthesis of N-doped TiO_2 nanoparticles capable of photodegrading methylene blue under visible light. Bae and Choi (2003) have synthesized visible light-activated TiO_2 nanoparticles based on TiO_2 modified by ruthenium-complex sensitizers and Pt deposits. The $Pt/TiO_2/RuIIL_3$ nanoparticles drastically enhanced the rate of reductive dehalogenation of trichloroacetate and carbon tetrachloride in aqueous solutions under visible light.

Nanoscale zero valent iron (Fe^0) and bimetallic Fe^0 particles are also effective redox media for the detoxification of organic and inorganic pollutants in aqueous solutions. These nanomaterials have larger surface areas and reactivity than bulk Fe^0 particles (Schrick et al., 2002; Zhang, 2003; Nurmi et al., 2005). Zhang (2003) has reported the synthesis, characterization and use of nanoscale Fe^0 particle and Fe^0/Pd^0, Fe^0/Pt^0, Fe^0/Ag^0, Fe^0/Ni^0 and Fe^0/Co^0 in environmental remediation. These nanoparticles can reduce various organic pollutants (e.g., chlorinated alkanes and alkenes, chlorinated benzenes, pesticides, organic dyes, nitro aromatics, PCBs) and inorganic anions (e.g., nitrates) in aqueous solutions to less toxic by-products. Fe^0 and bimetallic Fe^0 nanoparticles have been efficiently used to reduce redox active metal ions such as Cr(VI) to less toxic and mobile Cr(III) (Zhang, 2003). Immobilized metalloporphyrinogens in soil-gel matrices have also been effectively used to prepare redox and catalytically active nanoparticles for the reductive dehalogenation of chlorinated organic compounds (PCE, TCE and carbon tetrachloride) in aqueous solutions (Dror et al., 2005).

13.7 Nanostructured and Reactive Membranes

Ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are emerging as key components of advanced water purification and desalination technologies (US Bureau of Reclamation, 2003). Van der Bruggen and Vandercasteele (2003) have discussed the use of nanofiltration to remove cations, natural organic

matter, biological contaminants, organic pollutants, nitrates and arsenic from ground water and surface water. Favre-Reguillon et al. (2003) demonstrated that nanofiltration can be used to remove minute quantities of U(VI) from seawater. Mohsen et al. (2003) have used nanofiltration to desalinate water and found that nanofiltration in combination with reverse osmosis could effectively render brackish water potable. Srivastava et al. (2004) reported the successful use of carbon nanotube filters which were effective in removing bacteria (*Escherichia coli* and *Staphylococus aureus*) and *Poliovirus sabin 1* from contaminated water. The carbon nanotube filters can be easily cleaned by ultrasonication and autoclaving. DeFriend et al. (2003) reported the successful fabrication of alumina UF membranes using alumina (A-alumoxanes) nanoparticles (7–25 nm). The new UF membranes, which have molecular weight cut-off (MWCO) between 1000 and 10,000 Da and average pore diameter of 4 nm, showed selectivity toward a number of synthetic dyes (e.g., Direct Red 81, Direct Blue 71 and Direct Yellow 71). The selectivity and permeate flux through the UF membranes can be increased by doping the alumina nanoparticles with Fe, Mn and La. Stanton et al. (2003) have fabricated novel NF membranes by deposition of 4.5–5.0 layer pairs of poly(styrene sulfonate)/poly(allylamine hydrochloride) onto porous alumina. The new NF membranes exhibit high water flux, high retention of divalent cations [Ca(II) and Mg(II)] and (Cl/SO_4^{-2}) selectivity ratios up to 80. Meyer et al. (2004) successfully prepared reactive membranes by incorporation of bimetallic Fe^0/Pt^0 nanoparticles into cellulose acetate films. The embedded metal domains of the membranes have an average diameter of 24 nm and were very effective in reducing TCE with ethane as the only observed by-product.

13.8 Bioactive Nanoparticles

Strong oxidants (e.g., chlorine) are usually applied as disinfectants for pathogens (e.g., bacteria and viruses) in water treatment. These compounds generate toxic disinfection byproducts such as trihalomethanes, haloacetic acids and aldehydes. Thus, alternative disinfectants are needed to comply with the Stage 1 Disinfection Byproduct Rule of the 1996 Safe Drinking Water Act Amendments (USEPA, 1998b). Disinfectants such as chlorine inactivate water-borne pathogens by (1) impairment of pathogen cellular function by destruction of major constituents (e.g., cell wall), (2) interference with the pathogen cellular metabolic processes, and (3) inhibition of pathogen growth by blockage of the synthesis of key cellular constituents (e.g., DNA, coenzymes and cell wall proteins). Nanomaterials are also providing unparalleled opportunities to develop chlorine-free biocides. Stoimenov et al. (2002) demonstrated that MgO nanoparticles are very effective biocides against Gram-positive and Gram-negative bacteria (*Escherichia coli* and *Bacillus megaterium*), as well as against spores of *Bacillus subtillus*. Studies by atomic force microscopy (AFM), transmission electron microscopy (TEM), and laser confocal microscopy

showed considerable changes in the integrity of the cell membranes when the nanoparticles interact with the bacteria, resulting in their death in most cases. Ag(I) and silver compounds have been used as antimicrobial compounds in various biomedical products and applications. Sondi and Salopek-Sondi (2004) have prepared stable Ag nanoparticles of narrow size distribution by reducing silver nitrate solutions with ascorbic acid in the presence of Daxad 19 (sodium salt of a high molecular weight naphthalene sulfonate formaldehyde condensate) as stabilizing agent. They found that Ag nanoparticles were effective biocides against *Escherichia coli*. Son et al. (2004) reported that cellulose acetate (CA) fibres with embedded Ag nanoparticles were effective against Gram-positive and Gram-negative bacteria including *Staphylococcus aureus, Escherichia coli, Klebsiella pneumonia* and *Pseudomonas aeruginosa.*

13.9 Dendrimer Enhanced Ultrafiltration

Advances in macromolecular chemistry such as the invention of dendritic polymers are providing effective UF processes for purification of water contaminated by toxic metal ions, radionuclides, organic and inorganic solutes, bacteria and viruses. The name dendrimer is derived from Greek words *dendron* meaning "tree" and *meros* meaning "part". Major difference between linear polymers and dendrimers is that a linear polymer consists of long chains of molecules, like coils, crisscrossing each other (Fig. 13.2). A dendrimer consists of molecular chains that branched out from a common centre, and there is no entanglement between each dendrimer molecules. Dendritic polymers, which
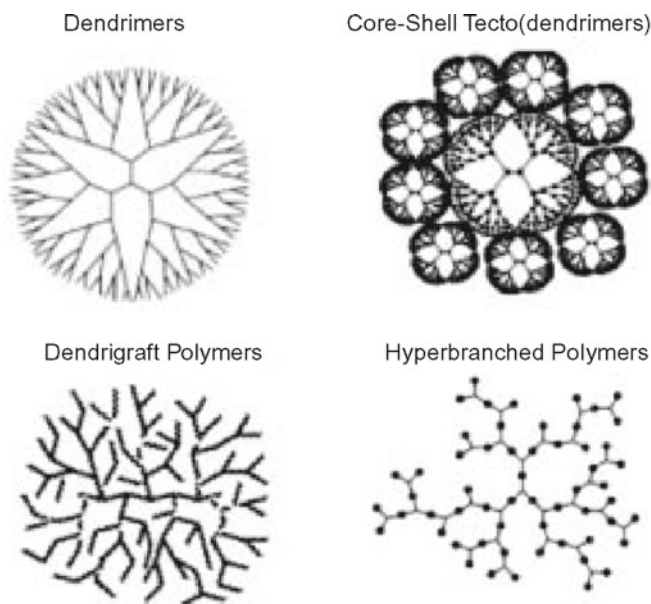

Fig. 13.2: Stucture of Dendrimers (Diallo et al., 2005).

include random hyperbranched polymers, dendrigraft polymers, dendrons and dendrimers, are relatively monodispersed and highly branched macromolecules with controlled composition and architecture consisting of three components: a core, interior branch cells and terminal branch cell (Fre´chet and Tomalia, 2001). Dendritic polymers have many features that make them attractive as functional materials for water purification. These 'soft' nanoparticles (1–20 nm) can be used as high capacity and recyclable watersoluble ligands for toxic metal ions, radionuclides and inorganic anions (Ottaviani et al., 2000; Birnbaum et al., 2003). Dendritic polymers are also reported to be used in (i) recyclable unimolecular micelles for recovering organic solutes from water (Arkas et al., 2003) and (ii) scaffolds and templates for the preparation of redox and catalytically active nanoparticles (Niu et al., 2005).

Dendrimer-enhanced ultrafiltration (DEUF) process for recovering metal ions from aqueous solutions was successfully developed by Diallo (2004). Diallo et al. (2005) tested the feasibility of using DEUF and poly (amidoamine) (PAMAM) dendrimers with ethylene diamine (EDA) core and terminal NH_2 groups to recover Cu(II) ions from aqueous solutions. On a mass basis, the Cu(II) binding capacities of the PAMAM dendrimers are much better and more sensitive to solution pH than those of linear polymers with amine groups. Separation of the dendrimer-Cu(II) complexes from solutions can be achieved simply by UF membranes with the appropriate MWCO. Used dendrimers can be regenerated by decreasing the solution pH to 4.0 (Diallo et al. 2005); thus enabling the recovery of the bound Cu(II) ions and recycling of the dendritic polymer. Advantage of PAMAM dendrimers is that they have low tendency to foul as compared to commercially available regenerated cellulose (RC) membranes (Diallo et al., 2005). Lesser operating pressure and energy consumption could be achieved with dendritic polymers in tangential/cross-flow UF systems typically used in water purification because of their smaller intrinsic viscosities than linear polymers with the same molar mass. For further details readers may refer to interesting reviews by Theron et al. (2008) and T. Pradeep and Anshup (2009).

13.10 Limitation of Nanomaterials for Water Purification

A key bottleneck to the applications of nanotechnology to water purification will be the availability of suppliers that can provide large quantities of nanomaterials at economical cost. A recently completed study on the nanomaterials industry was done by Freedonia in 2005. These forecasts anticipate that most nanomaterials will be nanoscale versions of established products such as silica, titanium dioxide, clays, metal powders, polymers and chemicals (Freedonia, 2005). Larger quantities of carbon nanotubes, fullerenes and dendrimers will also be available as these nanomaterials become key components of electronic products, drug delivery systems, batteries, fuel cells, water purifiers etc.

The integration of nanomaterials into existing water purification systems is another key challenge for their efficient use in water purification. Membrane processes such as RO, NF and UF are becoming the 'standard' water purification technologies for public utilities and industry because they are flexible, scalable, modular and relatively easy to operate and maintain. The environmental fate and toxicity of a material are critical issues in materials selection and design for water purification. Not much is known about the environmental fate, transport and toxicity of nanomaterials. Clean water is essential to human health and is a critical feedstock in a variety of key industries including electronics, pharmaceuticals and food. There is rising demand of clean water due to the decrease in available supplies of freshwater as a result of (i) extended droughts, (ii) population growth, (iii) more stringent health-based regulations, and (iv) competing demands from users. Nanomaterials have a number of key physicochemical properties that make them particularly attractive as separation media for water purification and holds promise for their extensive use for water purification in future.

13.11 Biogenic Synthesis of Nanoparticles and Metal Detoxification

Microbes are emerging as highly efficient nanofactories for nanoparticle synthesis. Microorganisms can survive and grow even at high metal ion concentrations. Microorganisms play an important role in remediation of metals through reduction of metal ions. They are often exposed to extreme environmental conditions, forcing them to resort to specific defense mechanisms to combat the toxicity of foreign metal ions or metals present in the microenvironment. The toxicity of metal ions is reduced or eliminated by changing the redox state of the metal ions and/or precipitation of the metals intracellularly/extracellularly thus, forming the basis of the synthesis of nanoparticles.

13.12 Magnetotactic Bacteria—Nature's Marvel

The first peer-reviewed article on magnetotactic bacteria appeared in the year 1975 in *Science* by Richard Blakemore, a microbiologist at the Woods Hole Oceanographic Institution. Blakemore observed that these microorganisms were following the direction of Earth's magnetic field, thus coined the term "magnetotactic" bacteria. Interestingly, Alivisatos in 2001 reported the presence of inorganic crystals in magnetotactic bacteria of the size between 35 and 120 nm. These crystals were of iron compounds (magnetite or greigite) which help to align bacteria with the external magnetic field. In natural environments, this magnetotactic behaviour enables the bacteria to navigate with respect to the earth's magnetic field towards their ideal environment in the upper microaerobic sediments of ponds, streams, oceans.

Toxic metal compounds can be transformed by microorganisms very efficiently to nanoparticles in the process of their detoxification. In the following paragraphs biosynthesis of nanoparticles of As, Se, Te and CdS are discussed which are major soil and water pollutants.

13.13 Biogenesis of Arsenic Nanoparticles

Arsenic is very toxic metalloid as it targets ubiquitous enzyme reactions and affects nearly all organ systems. Arsenic is strongly associated with lung and skin cancers. Pigment changes and palmoplantar hyperkeratosis are characteristic effects of chronic arsenic exposure. Arsine gas causes a hemolytic syndrome.

Several microorganisms have been isolated from the arsenic rich environments which can detoxify toxic arsenic compounds but very few have been reported to produce arsenic nanostructures during this reduction process. In one study Ji-Hoon Lee et al. (2007) studied the production of an extensive extracellular network of filamentous, arsenic-sulfide (As-S) nanotubes (20–100 nm in diameter by ~30 μm in length) by the dissimilatory metal-reducing bacterium *Shewanella* sp. HN-41. The As-S nanotubes, formed by the reduction of As(V) and $S_2O_3^{2-}$, were initially amorphous As_2S_3 but evolved with increasing incubation time toward polycrystalline phases of the chalcogenide minerals realgar (AsS) and duranusite (As_4S). The As-S nanotubes behaved as metals and semiconductors in terms of their electrical and photoconductive properties. In another study it was found that under anaerobic conditions Fe(III)-reducing microorganisms can couple the reduction of solid phase Fe(III) hydroxides with the oxidation of organic carbon. Nutrients and trace metals, such as arsenic, associated with Fe(III) hydroxides may be mobilized through microbially-mediated surface reduction. Arsenic mobilization mechanisms was studied using a series of controlled microcosm experiments containing aggregated arsenic-bearing ferrihydrite nanoparticles and an Fe(III)-reducing microorganism, *Geobacter metallireducens*. The phase distribution of iron and arsenic was determined through filtration and ultracentrifugation techniques. Biotic activity resulted in changes in nanoparticle surface potential and caused deflocculation of nanoparticle aggregates. Arsenic mobilized over time in the biotic trials was found to be exclusively associated with the nanoparticles. As arsenic contamination of natural waters due to mobilization from mineral surfaces is a significant route of human arsenic exposure, improved understanding of the biologically-mediated mechanisms that partition arsenic between solid and solution phases is required for development of effective treatment and remediation strategies.

13.14 Biogenesis of Selenium and Tellurium Nanoparticles

Selenium is an essential trace element, used particularly in the glutathione peroxidase enzyme system which protects intracellular structures against

oxidative damage. Substantial toxicity can occur with excessive selenium consumption or exposure. Selenium, like arsenic, inactivates the sulphydral groups of amino acids. Chronic oral exposure of selenium results in disease called selenosis. Toxicity has been associated with a garlicky odour in the breath (caused by methylated selenium), fatigue, gastrointestinal disturbances, and transverse lines on the nails, hairloss, alopecia and peripheral neuropathy.

The potential use of microorganisms to biotransform metals has led to another new dimension of exploring the biological mechanisms towards generation of zero-valent elements, bi/multi elemental quantum dots, and metal-containing nanoparticles. The biogenesis of selenium nanomaterials was demonstrated by Oremland et al. (2004) and Baesman et al. (2007) who reported effectively reduction of two chalcogenide oxyanion species viz., selenite/nate and tellurite/rate, to elemental selenium and tellurium by two anaerobic bacteria, *Bacillus selenireducens* and *Sulfurospirillum barnesii*. In the case of selenium, extracellular granules formed consisting of stable, uniform nanospheres (diameter ~300 nm) of Se^0 and having monoclinic crystalline structures. In the case of tellurium, *B. selenireducens* formed initially as nanorods (~10 nm) that cluster together forming larger rosettes (~1000 nm) composing of numerous individual shards. In contrast, *S. barnesii* forms extremely irregular shaped nanospheres (diameter <50 nm) that coalesce into large composite aggregates. The microbial synthesis of Se^0 nanospheres results in unique, complex, compacted nanostructural arrangements of Se atoms. These arrangements probably reflect a diversity of enzymes involved in the dissimilatory reduction that are ingeniously different in different microbes. Remarkably, these conditions cannot be achieved by current methods of chemical synthesis reported in the literature.

13.15 Biogenesis of CdS Nanoparticles

Chronic cadmium exposure primarily affects the kidneys and secondarily the bones. Acute inhalation of fumes containing cadmium affects the lungs. The well known "Itai-itai" or ouch-ouch disease due to cadmium was first described in post-menopausal Japanese women exposed to excessive levels of cadmium over their lifetimes. These women were exposed through their diet because the region of Japan in which they resided was contaminated with cadmium (Watanabe et al., 2000). Symptoms and signs of "itai-itai" disease are severe osteoporosis and osteomalacia with simultaneous severe renal dysfunction, normochromic anemia and low blood pressure sometimes also occur (Alfven et al., 2002), and average urinary cadmium level in these patients is 20-30 μg/g-creatinine of cadmium in urine (Ezaki et al., 2003).

Only a few microorganisms have been reported to synthesize cadmium nanoparticles. Among the first reports of intracellular semiconductor nanoparticle synthesis, Sweeney et al. demonstrated that *Escherichia coli*, when incubated with cadmium chloride ($CdCl_2$) and sodium sulfide (Na_2S), spontaneously formed cadmium sulfide (CdS) semiconductor nanocrystals. They showed

that the formation of nanocrystals was markedly affected by physiologic parameters. Indeed, the entry into stationary phase increased the yield by 20-fold. Cunningham and Lundie found that *Clostridium thermoaceticum* precipitates CdS at the cell surface as well as in the medium when exposed to $CdCl_2$ in the presence of cysteine hydrochloride as a source of sulfide in the growth medium. *Rhodopseudomonas palustris*, a photosynthetic bacteria, forms cadmium sulfide nanoparticles of an average size of 8.01 ± 0.25 nm. The cadmium sulfate solution incubated with *R. palustris* biomass changed to a yellow colour from 48 h onward, indicating the formation of cadmium sulfide nanoparticles.

Electron diffraction pattern confirmed the face-centered cubic (fcc) crystalline structure of cadmium sulfide. Furthermore, it was observed that the cysteine desulfhydrase producing S^{2-} in the *R. palustris* was located in cytoplasm, and the content of cysteine desulfhydrase depending on the growth phase of cells was responsible for the formation of CdS nanocrystal, while protein secreted by the *R. palustris* stabilized the cadmium sulfide nanoparticles. In addition, *R. palustris* was able to efficiently transport CdS nanoparticles out of the cell (Bai et al., 2009). The yeasts *Schizosaccharomyces pombe* and *Candida glabrata* were successfully cultured in a fed-batch process at cadmium levels up to 100 mg l^{-1}. *S. pombe* incorporated 20 mg Cd g^{-1} dry biomass within 24 h. *Candida glabrata* accumulated 8 mg Cd g^{-1} dry biomass in 24 h. The higher Cd uptake from *S. pombe* cells correlate with the elevated glucose concentrations during and at the end of the cultivation. Analysis of the cells with energy-filtering transmission electron microscopy-element specific imaging (EFTEM-ESI) revealed that cadmium is not precipitated outside the cells or at the cell wall but evenly distributed inside the cell plasma. Cd is immobilized by an intracellular detoxification mechanism. Size exclusion chromatography showed that Cd is associated to a protein fraction between 25 and 67 kDa which corresponds to the theoretical molecular weight of CdS nanoparticles of 35 kDa coated with phytochelatins.

13.15.1 Pt Nanoparticles

Platinum as a metal is not very dangerous, but platinum salts can cause several health effects, such as DNA alterations, cancer, allergic reactions of the skin and the mucous membrane, damage to organs such as intestines, kidneys and bone marrow and hearing damage. A danger of platinum is that it can cause potentiation of the toxicity of other toxic chemicals in the human body, such as selenium.

Using green chemistry approach metal ion-reducing bacterium *Shewanella algae* was used to form platinum nanoparticles. Resting cells of *S. algae* in presence of lactate as electron donor were able to reduce aqueous $PtCl_6^{2-}$ ions into elemental platinum at room temperature and neutral pH within 60 minutes. Biogenic platinum nanoparticles of about 5 nm were formed and found to be located in the periplasm—a preferable, cell surface location for easy recovery of biogenic nanoparticles (Konishi et al., 2007).

A consortium of sulphate-reducing bacteria was used to study the enzymatic mechanism for the total bioreduction of platinum(IV) into platinum(0) nanoparticles. It was established that two different hydrogenase enzymes were involved. First the platinum(IV) was reduced to platinum(II) by a two-electron bioreduction using an oxygen-sensitive novel cytoplasmic hydrogenase. Second the platinum(II) ion was reduced to platinum(0) nanoparticle by another two-electron bioreduction involving an oxygen-tolerant/protected periplasmic hydrogenase. No exogenous electron donors were necessary as endogenous production of hydrogen/electrons, via the oxidation of metabolites, was generated in situ by the cytoplasmic hydrogenase (Riddin et al., 2009).

13.15.2 Other Metallic Nanoparticles e.g. Gold, Silver

Pure metallic (elemental) gold and silver are non-toxic and non-irritating when ingested. Soluble compounds (gold salts) such as gold chloride are toxic to the liver and kidneys. Common cyanide salts of gold such as potassium gold cyanide, used in gold electroplating, are toxic both by virtue of their cyanide and gold content. In recent years the syntheses of gold nanoparticles have been the focus of intense interest because of their emerging applications in a number of areas such as bioimaging, biosensors, biolabels, and biomedicines. Numerous microorganisms summarized in Table 13.2 are reported to biosynthesize gold and silver nanoparticles by NADPH-dependent reductase enzymes that reduce metal salts to nanoparticles through electron shuttle enzymatic metal reduction process (Kaushik et al., 2010).

Table 13.2: Biogenic synthesis of gold and silver nanoparticles by various microorganisms

Microbe	Location	Size range (nm)
Silver (Ag) nanoparticles		
Bacteria		
Pseudomonas stutzeri	Intracellular	~ 200
Morganella sp.	Extracellular	20-30
Lactobacillus strains	Intracellular	-
Plectonema boryanum (Cyanobacteria)	Intracellular	1-10, 1-100
Klebsiella pneumonia	Extracellular	5-32
Stenotrophomonas maltophila		
Yeast		
MKY3	Extracellular	2-5
Fungi		
Phoma sp. 3.2883	Extracellular	71.06-74.46
Verticillium	Intracellular	25±12
		(Contd.)

Aspergillus fumigates	Extracellular	5-25
Trichoderma asperellum	Extracellular	13-18
Phaenerochaete chrysosoporium	Extracellular	50-200

Gold (Au) Nanoparticles

Bacteria		
Lactobacillus strains	Intracellular	-
Shewanella alga	Intracellular, pH 7	10-20
	Extracellular, pH 1	1-50
Escherichia coli DH5α	Intracellular	25-33
Thermomonospora sp.	Extracellular	8
Rhodococcus sp.	Intracellular	5-15
Pseudomonas aeruginosa	Extracellular	15-30
Fungi		
Fusarium oxysporum	Extracellular	20-40
Algae		
Sargassum wightii	Extracellular	8-12
Chlorella vulgaris	-	9-20

Adapted with some modification from Thakkar et al., 2009.

13.16 Case Studies

Nanomaterials have been applied to a number of contaminated sites with some preliminary success. These sites discussed below are contaminated with hazardous chlorinated hydrocarbons, hydrophobic recalcitrant compounds which are among the major environmental pollutants. Nanomaterials have also been used to remediate contaminated groundwater. The use of metallic nanomaterials as remediating agent is based on the redox (oxidation-reduction) reaction concept in which a neutral electron donor (usually a metal) reduces an electron acceptor (contaminant). This property of metals leads to their potential use as reducing agents for site remediation.

13.16.1 Nease Chemical Site, Ohio

The Nease Chemical Superfund site is 44 acres land, two and a half miles northwest of Salem on the Columbiana-Mahoning county line. From 1961 to 1973, Nease Chemical produced various household cleaning compounds, fire retardants and pesticides—some of which included an uncommon chemical called mirex which is used to control fire ants and as flame retardant in plastic, rubber, paints, paper and electric goods. It was banned in US in 1978. Mirex

degrades very slowly and remains in the environment for years. The company used unlined ponds to treat waste from its manufacturing process. Hazardous substances seeped into the soil and ground water from these ponds. Here the soil is contaminated with mirex and ground water is contaminated by a group of chemicals called volatile organic compounds (VOCs). Surface water runoff from the waste treatment ponds flowed into nearby Feeder Creek tributaries that run through the site causing pollution in the Middle Fork of Little Beaver Creek. The remediation plan and site description specifies the use of NZVI (Nano-ZeroValent Iron) technology employing palladium-coated colloidal iron. The reactive medium was administered through injection wells reaching deep ground water containing a plume of volatile organic compounds (VOCs).

13.16.2 RCRA Site, Alaska

NZVI was also used for remediation purposes in an Alaskan facility regulated under EPA's Resource Conservation and Recovery Act (RCRA) programme. The site contaminants include VOCs constituents of diesel fuel, which was released during an earlier tanker spill, in addition to perchloroethylene (PCE) and trichloroethylene (TCE). Studies indicate that ZVI (Fig. 13.3) may effectively reduce the chlorinated compounds in groundwater plumes as well as soil. Field-scale tests were conducted in both shallow and deep treatment zones. If field-scale tests yield the anticipated positive results, the project will be expanded to full-scale as was reported in 2006.
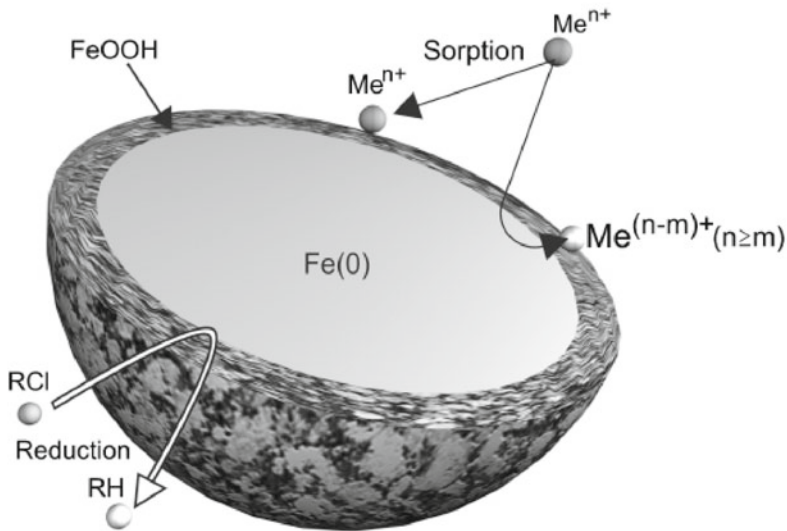

Fig. 13.3: The core shell model of Zero-Valent Iron (nZVI) nanoparticle. The core consists of mainly metallic iron and the shell consists of iron oxides and hydroxides.

13.16.3 Manufacturing Plant, Trenton, New Jersey

The site of a manufacturing plant in Trenton, New Jersey, was selected for testing of emulsified zero-valent iron (EZVI) technology to decontaminate plume that had migrated downgradient from the facility. The soil and ground water at this site was contaminated with PCE (Perchloroethylene), TCE (Trichloroethylene), c-DCE (cis-1,2-dichloroethene), vinyl chloride, chloroform, carbon tetrachloride, and 1,1-DCE. The test employed ZVI in the form of nanoscale particles suspended in a hydrophobic fluid, thus providing micelles to act as a means of transporting NZVI to non-aqueous phase liquid (NAPL). The micelle membranes are bound by a surfactant that allows cell transport through the groundwater plume (Fig. 13.4a). EZVI was injected in a water-based slurry through an injection well ("DGC-15") which also served as a monitoring well. Three multi-depth monitoring wells, or piezometers (PZ-1, PZ-2, and PZ-3) also were installed (Fig. 13.4b). After the injection process, researchers noted significant trichloroethylene TCE reductions in ground water of the second monitoring well but little concentration change in the third. According to *Environmental Science & Technology* journal article, the primary purpose of this field study was to obtain NZVI "proof of concept," i.e., evidence that ZVI administered in the slurry was nanoscale in dimension. The following redox reaction was provided by the authors to show how BNP are manufactured on the nanoscale through the process of reductive deposition:
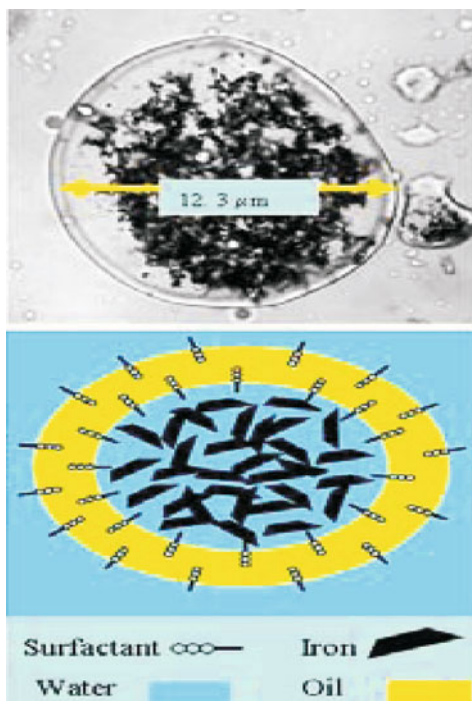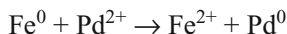
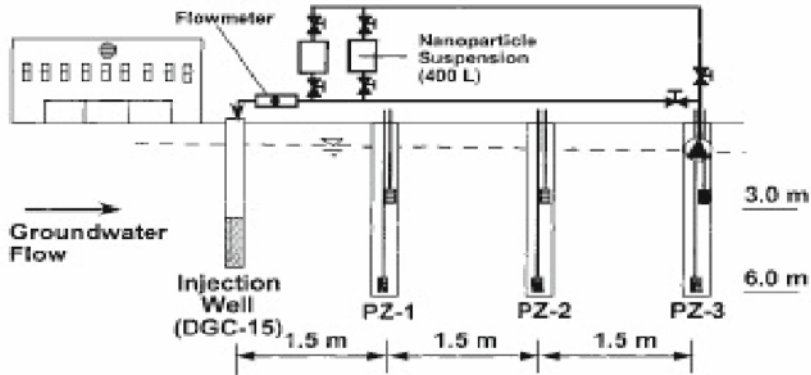$$Fe^0 + Pd^{2+} \rightarrow Fe^{2+} + Pd^0$$

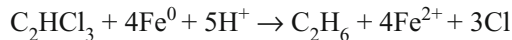
Fig. 13.4a: EZVI agglomerated particle.

Fig. 13.4b: Injection setup at Trenton manufacturing plant.

Reduction of a chlorinated compound can then proceed via the following reaction:
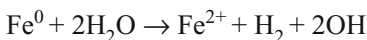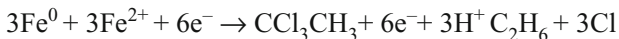
$$C_2HCl_3 + 4Fe^0 + 5H^+ \rightarrow C_2H_6 + 4Fe^{2+} + 3Cl$$

The success of the operation was revealed when up to 96% reductions in TCE concentrations were observed.

13.16.4 Klockner Road Site, Hamilton Township, New Jersey

The area of contamination covers approximately four acres of uncultivated and vacant property historically used as a disposal area for various industrial wastes. Geologically, the site exhibits a perched water aquifer 2-8 feet below ground surface and a bedrock formation 130-160 feet. The major contaminants in ground water of this site were TCE, DCE, TCA and DCA with concentration as high as 400-1600 ppb. Administration of ZVI reactive agent Nanoiron slurry (NanoFe Plus) was performed through a 20-point injection system on a square grid. Reduction in dissolved chlorinated contaminants up to 90% was observed. The operation was carried out in two phases: Phase I of 20 days and Phase II of 10 days. Chemical reduction of contaminants occurred through the following reactions:

$$3Fe^0 + 3Fe^{2+} + 6e^- \rightarrow CCl_3CH_3 + 6e^- + 3H^+ C_2H_6 + 3Cl$$
$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH$$
$$CCl_3CH_3 + 3H_2 \rightarrow C_2H_6 + 3HCl$$
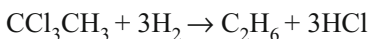
13.16.5 NASA Launch Complex 34, Cape Canaveral, Florida

This site was famous for its use as a launch pad for shuttle craft and other space-bound vehicles using rocket propulsion in the 1960s. The use of rocket fuel resulted in contamination of site's ground water, soil, and sediment with chlorinated compounds such as TCE. Three methods were employed for administering NZVI as alternatives to the direct-injection method to remediate

the site: pressure pulsing, pneumatic fracturing, and hydraulic fracturing. First, pressure pulsing involved forced administration of NZVI particles to various and relatively predictable subsurface depths. Second, pneumatic fracturing employs compressed air to create subsurface crevices and small pathways that facilitate distribution of the reactive medium. Similar to pneumatic fracturing, third method of hydraulic fracturing uses high-pressure liquids to enhance reagent distribution in the subsurface. These methods were expected to show reductions in groundwater contaminants.

13.17 Fate of Nanoparticles in the Environment and their Toxicity

Although nanoparticles have wide applications in various fields but what will be effect of these nanoparticles released in the environment is an important issue to be addressed. It is likely that the waste generated during nanaoparticle synthesis and their substantial use and subsequent release in the environment will also be of concern in the coming years. Exposure of humans to nanoparticles can be through inhalation, dermal adsorption and ingestion. Various studies have shown potential adverse effects of nanoparticles on human health and the environment (Auffan et al., 2009; Mortimer et al., 2010). In some studies the cytotoxicity of QDs (Quantum dots) of CdSe on different cell lines has been highlighted. It was found that cadmium hepatotoxicity (binding of thiol groups in mitochondria) correlates well with the release of free Cd^{2+} ions inside the cells due to the degradation of CdSe core. The degradation of the CdSe core is also affected by the chemistry of the surface modification of water soluble QDs. The studies further revealed that the extent of cell viability is influenced by oxidation, UV exposure time and dose of QDs (Derfus et al., 2004; Kirchner et al., 2005). It is minimized if QDs are properly coated with shell materials such as ZnS. Also nanoparticles can be easily absorbed on to the cell membrane and degraded leading to their cytotoxic effects. Nanowires and nanotubes are comparable to microneedles which can damage cell walls and thus impair cell growth and antimicrobial activity of silver nanoparticles against *E. coli*. These particles were shown to be an effective bactericide. Scanning and transmission electron microscopy (SEM and TEM) confirmed that the treated *E. coli* cells were damaged, showing formation of "pits" in the cell wall of the bacteria, while the silver nanoparticles were found to accumulate in the bacterial membrane. A membrane with such morphology exhibits a significant increase in permeability, resulting in death of the cell. These nanomaterials, which can be prepared in a simple and cost-effective manner, may be suitable for the formulation of new types of bactericidals (Sondi and Salopek-Sondi, 2004). Several types of nanoparticles have proven to induce oxidative stress, suggesting that particles of different types could initiate and aggravate inflammation and tissue damage leading to neurodegenerative and cardiovascular disease, carcinoma, and other disorders (Biswas et al., 2005; Wu et al., 2005; Scalbert et al., 2005).

The potential toxic effects of the nanoparticles in the natural environment and organisms which are still unknown will be revealed in the coming years. Thus, there is urgent need to understand the potential toxic effects of nanoparticles on human health and the other organisms before there is massive contamination of the environment by these nanoparticles. Extensive research is now needed to understand the fate and transport of free nanoparticles in the environment, the degree of the persistence and their toxicological effects on various biological system including human beings.

13.18 Conclusion and Future Trends

Nanoparticles exhibit unique properties in terms of photoemission, electrical conductivity, heat conductivity and catalytic activity. Owing to their unique properties these particles are being applied in different biological studies including medicine like biomolecule detection, separation, purification, concentration of sample, substrate coding, signal transduction, amplification, drug delivery in medicine to mention a few. Nanoparticles are also being widely applied in environmental research in degradation/transformation and recovery of toxic/nontoxic chemical compounds. Understanding potential environmental hazards of nanomaterials will require the ability to determine not only the chemical nature of the nanoparticles but also their size, shape, and number released in the environment. It is well known that chemicals can have different effects in plants and animals than in humans. The additive effect, or potential synergism, of exposure to different nanoparticles to human beings is also matter of investigation. As discussed earlier the immediate question of concern in the scientific world is whether we have understood the physicochemical properties of nanomaterials with the existing sophisticated instruments and techniques well enough to effectively use the materials for remediation purposes resulting in their subsequent release in the environment. This is an important question which will definitely find some answers in the coming years as we progress with nanotechnology. In conclusion, the field of nanotechnology is at an exciting stage of development. Timely understanding of the impacts with ongoing studies is essential before widespread adoption of nanotechnology in different fields particularly in bioremediation. The benefits of environmental nanotechnology are immense and with effective scientific studies, it can be ensured that the technology has minimal deleterious impacts on the environment and human beings.

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