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Review Article

Water Purification Using Nanotechnology an Emerging Opportunities

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ABSTRACT

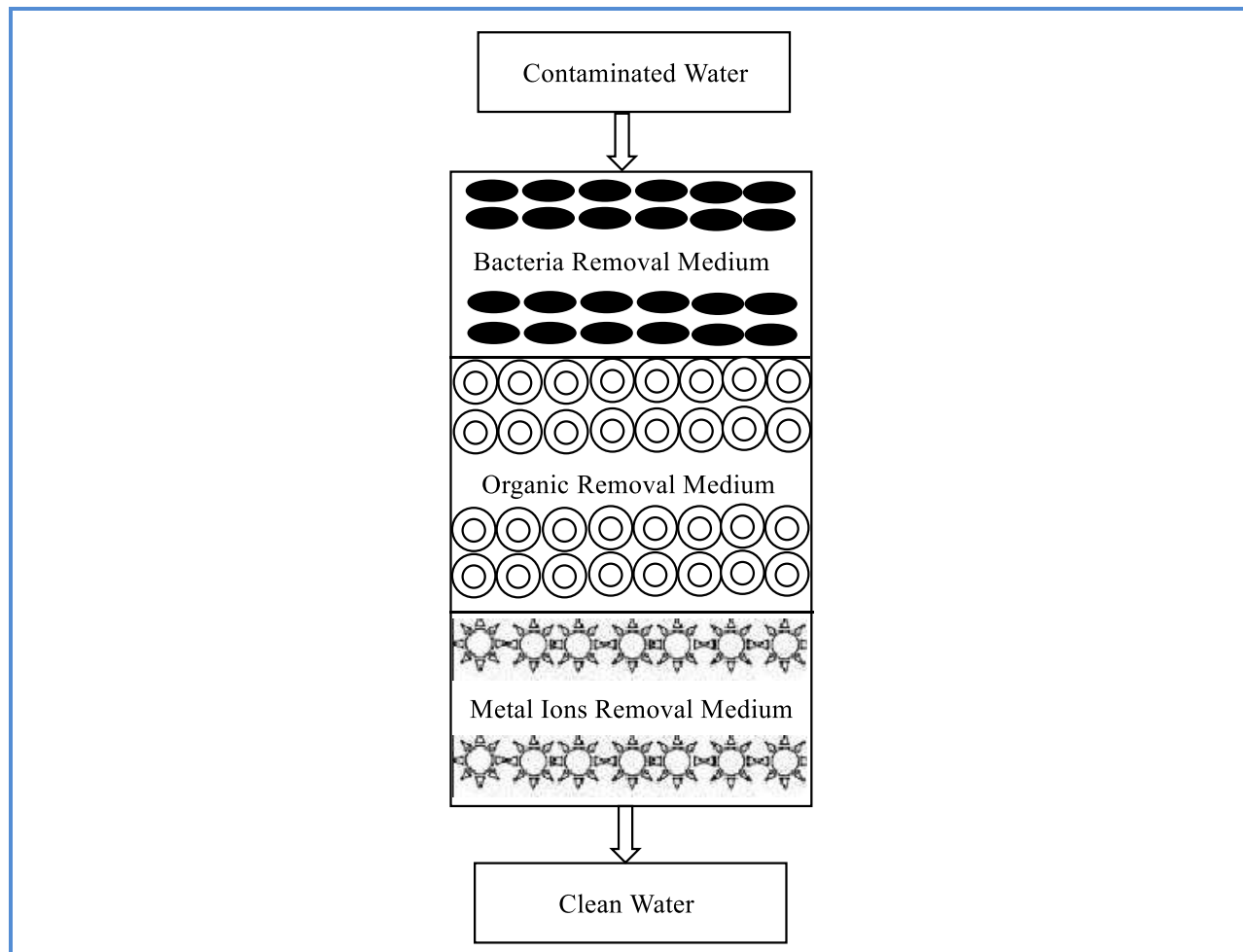
The most important component for living beings on the earth is access to clean and safe drinking water. Globally, water scarcity is pervasive even in water rich areas as immense pressure has been created by the burgeoning human population, industrialization, civilization, environmental changes and agricultural activities. The problem of access to safe water is inevitable and requires tremendous research. Nanotechnology has many successful applications in different fields but recently its application for water and wastewater treatment has emerged as a fast developing, promising area. This chapter highlights the recent advances on the development of nanoscale materials and processes for treatment of surface water, groundwater and industrial wastewater that are contaminated by toxic metals, organic and inorganic compounds, bacteria and viruses. In addition, the toxic potential of engineered nanomaterials for human health and the environment will also be discussed. This chapter also deals with the fate and transport of engineered nanomaterials in water and wastewater treatment systems along with the risks associated with nanomaterials.

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Graphical Abstract



Introduction

Most of the countries are nowadays facing pure drinking water problems and conditions are very bad especially in developing countries. The world is facing terrifying challenges in meeting rising demands of pure water, as the available supplies of fresh water are continuously reduce due to, (i) extended droughts, (ii) population growth, (iii) more stringent health based regulations and (iv) competing demands from a variety of users [1]. Clean water (i.e., water that is free of toxic chemicals and pathogens) is essential to human health. In developing countries such as India, 85% of the diseases are due to bacterial and microbial contamination of drinking water. The World Health Organization (WHO) suggest that any water intended for drinking should contain fecal and total coliform counts of 0, in any 100 mL sample. When either of these groups of bacteria is found in a sample, immediate investigative action should be taken. The removal or inactivation of pathogenic microorganisms is the last step in the process of treatment of wastewater. The

protection of water treatment systems against potential chemical and biological weapon for terrorist acts is also becoming a critical issue in water resources planning [1]. Today several techniques are used for treatment of water i.e., chemical and physical agent such as chlorine and its derivatives, ultraviolet light [2], boiling, low frequency ultrasonic irradiation [2], distillation, reverse osmosis, water sediment filters (fiber and ceramic) activated carbon, solid block, pitcher and faucet mount filters, bottled water, ion exchange water softener, ozonisation, activated alumina 'Altered' water. Halogens such as chlorine (Cl) and bromine (Br) are well known and widely used as antibacterial agents, but the direct use of halogens as bactericides has many disadvantages because of their high toxicity and vapour pressure in pure form NH_4^+ is a most common cation in water which affecting human and animal health. Removal of ammonia is very necessary in drinking water to prevent oxygen depletion and algae bloom and due to its extreme toxicity to most fish species It can be replaced with biologically acceptable cations, like Na^+ , K^+ or Ca^{2+} in the zeolite. During the past few decades, several investigations have been carried out concerning the use of synthetic and natural zeolites, polymer films and metal ions (Ag^+ , Cu^{++} , Zn^{++} , Hg^{++} , Ti^{+++} , Ni^{++} , Co^{++}) as bactericides for water disinfection [3]. Research is still continued on use of advance nanotechnology in water purification for safe drinking.

Nanotechnology is the controlled manipulation of matter at size scales of less than 100 nm, holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales, because of their high reactivity due to the large surface to volume ratio [4]. Nanoparticles are expected to play a crucial role in water purification [5]. The environmental fate and toxicity of a material are critical issues in materials selection and design for water purification. No doubt that nanotechnology is better than other technique used in water treatment but today the knowledge about the environmental fate, transport and toxicity of nanomaterials [6] is still in infancy. Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or totally diminished by using nonabsorbent, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, submicron, nanopowder, nanotubes, magnetic nanoparticles, granules, flake, high surface area metal particle supramolecular assemblies with characteristic length scales of 9-10 nm including clusters, micromolecules, nanoparticles and colloids have a significant impact on water quality in natural environment (Figure 1) [7]. Nanotechnology used for detection of chemical and biological substances including metals (e.g. Cadmium, copper, lead, mercury, nitrate, nitrite), cyanide organics, algae (e.g. cyanobacterial toxins) viruses, bacteria, parasites, antibiotics and biological agents are used as weapon for terrorism. Innovations and improvement in the development of

novel technologies to desalinate water are among the most exciting and seem to have promise [8]. Opportunities and challenges of using nanomaterials in the purification of surface water, groundwater and industrial wastewater streams is a matter of continuing concern. Misconceptions and one of the many impressions that people have about the future of nanotechnology is the expectation that nanoparticles can be used to kill harmful organisms, repair body tissue, in water quality improvement and to cure disease.

Recent research shows, applications of nanoparticulate silver have included open wound and burn treatment and preliminary studies have shown that a 20 ppm silver colloidal suspension (~30 nm diameter) in purified water has a 100% cure rate for malaria [8]. Titanium dioxide, especially as nanoparticulate anatase, is also an interesting antibacterial, with notable photocatalytic behavior. But ultrafine anatase has also been identified as cytotoxic and in vivo studies have shown that it can be severely toxic in the respiratory system [9, 10]. Nanocapsules and nanodevices may present new possibilities for drug delivery, gene therapy, medical diagnostics, antimicrobial activity etc. The effect of particle size on the adsorption of dissolved heavy metals to iron oxide and titanium dioxide nanoparticles is a matter laboratory scale experiments. Iron oxide and titanium dioxide are good sorbents for metal contaminants. Spherical aggregates of nanoparticles that have a similar size and shape to the resin beads already used in water purification. Ligands, fulvic acids, humic acids and their aggregates have a significant impact on contaminant mobility, reactivity and bioavailability. Nanoparticles can also be designed and synthesized in such manner to act as either separation or reaction media for pollutants. The high surface area to mass ratios of nanoparticles can enhance the adsorption capacities many times of sorbent materials. Nanotechnology is a deliberate manipulation of matter at size scales of less than 100 nm holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions. Their extremely small size is of the same scale as the critical size for physical phenomena for example, the radius of the tip of a crack in a material may be in the range 1-100 nm. The way a crack grows in a larger scale, bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable. Fundamental electronic, magnetic, optical, chemical and biological processes are also different at this level.

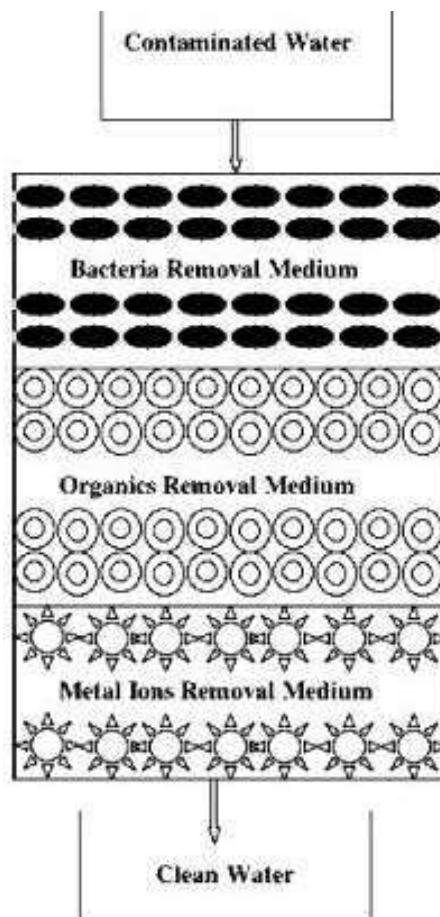


Figure 1. Schematic of a composite nanomaterial packed bed reactor for purification of water Contaminated by mixtures of (i) metal ions, (ii) Organic solutes and (iii) bacteria [112]

Status of groundwater contamination in India: man's activity at ground surface, unintentionally by agriculture, domestic and industrial effluents, unexpectedly by sub surface or surface disposal of sewage and industrial wastes has led to adverse effects on soil and groundwater quality. Since 1954 the dominant group of pesticides called organochlorine insecticides have been extensively used in India for agriculture as well as in public health sector. Almost every organochlorine which includes notorious pesticides like DDT, endosulfan, dioxin, HCH (hexachlorocyclohexane) and aldrin has been found to cause some environmental or human health hazard. The use of organochlorines which are banned or restricted in most developed countries are still being used in this country. As a result of the effects of intense agricultural activities, the studies conducted on the contamination of soil and groundwater quality Roorkee area, district Haridwar, India indicated the presence of 17 organochlorine and 9 organophosphorous pesticides which were found to be much above the permissible limits of Indian drinking water standards.

Nanoparticle in waste water treatment

Four classes of nanoscale materials that are used as functional materials for water purification process: (1) dendrimers (2) metal-containing nanoparticles, (3) zeolites and (4) carbonaceous nanomaterials. These have a wide range of physicochemical properties that make them more attractive as separation and reactive media for water purification. Characterization of the interactions of the nanoparticles with the bacterial contaminant done by atomic force microscopy (AFM), transmission electron microscopy (TEM) and laser confocal microscopy, these show considerable changes in the integrity of the cell membranes, resulting in the death of the bacteria in most cases.

Dendrimer in water treatment

Reverse osmosis (RO) membranes have pore sizes in range of 0.1-1.0 nm and thus are very effective at retaining dissolved inorganic and organic solutes with molar mass below 1000 Da [11]. Nanofilter (NF) membranes removing hardness (e.g., multivalent cations) and organic solutes with molar mass between 1000-3000 Da (e.g., natural organic material) [11]. However, high pressures are required to operate both RO and NF membranes. Conversely, ultrafine (UF) membranes require lower pressure (200-700 kPa). Unfortunately, they are not very effective at removing dissolved organic and inorganic solute with molar mass below 3000 Da. Advances in macromolecular chemistry such as the invention of dendritic polymers are providing some opportunities to develop effective UF processes for purification of water which are contaminated by toxic metal ions, radionuclide, organic and inorganic solutes, bacteria and viruses.

Dendrite polymers, which 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 [12] and tissue silver levels with 10% silver. Dendrimers are symmetrical and spherical macromolecules, comprising a relatively dense shell composed of a core, branching sites and terminal groups that usually form a well defined surface. Their interior may be similar or may be different from the surface of the molecule. Chemical and/or physical properties, such as reactivity, complex or salt formation, hydrophilicity and so forth can be varied and optimized. As a proof of concept study, Diallo et al., (2005) [8] tested the feasibility of using dendron enhanced ultrafiltration (DEUF) and poly (amidoamine) (PAMAM) dendrimers with ethylene diamine (EDA) core and terminal NH₂ groups to recover Cu (II) ions from aqueous

solutions. On a mass basis, the Cu (II) binding capacities of the PAMAM dendrimers are much larger and more sensitive to solution pH than those of linear polymers with amine groups.

To obtain a dendrimer structure, several dendrons are reacted with a multifunctional core to form a dendrimers. Using two key synthetic strategies, over one hundred compositionally different dendrimer families have been synthesized and over 1000 differentiated chemical surface modifications have been reported already [13]. The first strategy to utilize highly functionalized cores and branched monomers to create phosphorus dendrimers. Several variations of the general synthetic scheme, which are interchangeable, have been developed, allowing multiplication of the number of terminal surface groups from 48 to 250 in one step. These dendrimers require just one step per generation performed in a minimum volume of solvent, allow facile purification (i.e., simple washings) and produce environmentally benign byproducts such as water and nitrogen [14, 15]. The second approach is based on click chemistry, i.e., the near perfect reliability of the Cu (I)-catalyzed synthesis of 1, 2, 3 triazoles from azides and alkynes to produce dendrimers with various surface groups in high purity and excellent yield. As early as 1984, PAMAM dendrimers were the first complete dendrimer family to be synthesized and characterized followed by commercialization in 1990 [16, 17]. They are synthesized by the divergent method which involve two step iterative reaction sequence that produces concentric shells of branch cells (generations) around a central initiator core. This PAMAM core shell architecture grows linearly in diameter as a function of added generations, while the surface groups amplify exponentially at each generation. Poly (amidoamine) PAMAM dendrimers are obtained by the iterative branching of L-alanine repeat units. Due to their bio friendly nature [18] and unique carrier properties, they show great performance than other polymeric materials for medical applications. Diffusion of dendrimers through membranes is the function of generation (due to their spherical and monomodal character) and appropriately selected membranes may retain dendrimer hosts with 100% selectivity. PAMAMs are also stable and soluble in water. PAMAM dendrimers have a very low tendency to foul commercially available regenerated cellulose (RC) membranes [8]. Because of the globular shape PAMAM dendrimers have much smaller intrinsic viscosities than linear polymers with the same molar mass. Dendritic polymers exhibit many features that make them particularly more attractive as functional materials for water purification. These 'soft' nanoparticles, with sizes in the range of 1-20 nm, can be used as high capacity and recyclable water soluble ligands for toxic metal ions, radionuclide and inorganic anions [19].

Dendritic polymers have some more application like (i) recyclable unimolecular micelles for recovering organic solutes from water [20] and (ii) scaffolds and templates for the preparation of

redox and catalytically active nanoparticles. Dendritic polymers have also been successfully used as delivery vehicles or scaffolds for antimicrobial agents such as Ag (I) and quaternary ammonium chlorides [21]. Poly (amidoamine) dendrimer (PAMAM) based silver complexes and nanocomposites proved to be effective antimicrobial agents in vitro. Due to the atomic/molecular level dispersion of the guest in a dendrimer host, the activity is retained if the microorganism is able to contact with the organized silver domains of the nanocontainers. Macroscopically, the silver remained conjugated to the dendrimer in the form of ions, stable metallic silver clusters or silver compounds. Because the dendrimer host is soluble, it is able to deliver the immobilized silver in the agar medium *via* its own diffusion. Due to higher surface area the silver clusters remain active. Reaction with chloride and sulfate ions neither blocks the diffusion of the silver nor the activity against *S. aureus*, *Ps. aeruginosa* and *E. coli*. The protected silver and silver compounds displayed high antimicrobial activity in several cases without the loss of solubility. However, the diffusion of dendrimers can be totally prevented if common cellulose membranes are used.

Metal nanoparticle

Nanoparticles have two main key properties that make them more attractive as sorbents. On a mass basis, they have much larger surface areas than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds. It has been found that the unique properties of nanoparticles to develop high capacity and selective sorbents for metal ions and anions. Characterization of the interactions of the nanoparticles with the bacteria by atomic force microscopy (AFM), transmission electron microscopy (TEM) and laser confocal microscopy showed considerable changes in the integrity of the cell membranes, resulting in the death of the bacteria in most cases. Photocatalytic nanomaterials allow ultraviolet light also used to destroy pesticides, industrial solvents and germs.

Stoimenov et al., 2002 [22]; showed that MgO nanoparticles and magnesium (Mg) nanoparticles are very effective biocides against Gram-positive and Gram-negative bacteria (*Escherichia coli* and *Bacillus megaterium*) and bacterial spores (*Bacillus subtilis*). Magnesium oxide nanoparticles or magnesia nanoparticles (MgO), nanodots or nanopowder are spinel, high surface area particles. Nanoscale magnesium oxide nanoparticles or magnesia particles are typically 5-100 nanometers (nm) with specific surface area (SSA) in the 25-50 m² g⁻¹ range and magnesium (Mg) nanoparticles, nanodots or nanopowder are spherical black high surface area particles. Nanoscale magnesium particles are typically 20-60 nanometers (nm) with specific surface area (SSA) in the 30-70 m² g⁻¹ range. Preparation of magnesium oxide (MgO) nanoparticles to absorb large amounts of halogen

molecules up to 20% by weight, making them safer to handle and measured their bactericidal activity on three representative strains of bacteria and bacterial spores [22]. These MgO nanoparticle particles are allowed to contact certain bacteria and spore cells. Bacteriological test data show that these materials are more effective against Gram-positive and Gram-negative bacteria.

Ag (I) and silver compounds have been used as antimicrobial compounds for coliform found in waste water [23]. Silver (Ag) nanoparticles, nanodots or nanopowder are spherical or flake high surface area metal particles having high antibacterial activity [24, 25] are used in wound. Nanoscale silver particles are typically 1-40 nanometers (nm) with an average particle size of 2-10 micron range with a specific surface area of approximately $1 \text{ m}^2 \text{ g}^{-1}$. Applications for silver nanocrystals include as an anti microbial, anti biotic and anti fungal agent when incorporated in coatings, nanofiber, first aid bandages, plastics, soap and textiles, in treatment of certain viruses, in self cleaning fabrics, as conductive filler and in nanowire and certain catalyst applications. It has been reported that Ag nanoparticles were active biocides against Gram-positive Gram-negative bacteria including *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Pseudomonas aeruginosa* [26]. Stable Ag nanoparticles of narrow size [27], various monometallic nanoparticles e.g. Au, Ag, Pt, Pd [28] and Sugar assisted stable monometallic nanoparticles can be synthesized in the laboratory. Gold (Au) nanoparticles, nanodots and nanopowder are brown spherical high surface area metal particles. Nanoscale gold particles are typically 20-100 nanometers (nm) with specific surface area (SSA) in the $1\text{-}3 \text{ m}^2 \text{ g}^{-1}$ range. Nanoparticles of gold coated with palladium are very zinc oxide nanoparticles have been used to removal agent for arsenic from water, even though bulk zinc oxide cannot absorb arsenic. Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron containing minerals, such as akaganeite, ferroxhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite. Adsorption of organics to the nanoparticle media was extremely rapid. More than 90% of the organics is adsorbed within 30 minutes. The isotherm studies indicated that, on a surface area basis, the adsorption capacities of the nanoparticle media were significantly (>2 folds) higher than the ferric oxide media which are mainly used in water treatment. The smaller size of magnetic nanoparticles, which are 2-3 orders of magnitude smaller than a bacterium, provides extra benefits compared to magnetic beads. When their surface is appropriately elaborated, magnetic nanoparticles can also provide efficient binding to the bacteria because their high surface/volume ratio increases more magnetic iron oxide compounds. Ferrites have property of spontaneous magnetization, they are crystalline in nature and soluble only in strong acid. Iron atoms in iron ferrite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) can be replaced by many

other metal ions without making any serious spinel structure change. It is already reported that various ferrites and natural magnetite were used in batch modes for actinide and heavy metal removal from wastewater. Iron (Fe) nanoparticles, nanodots or nanopowder are spherical or faceted high surface area metal nanostructure particles. Nanoscale iron particles are typically 20-40 nanometers (nm) with specific surface area (SSA) in the 30-50 m² g⁻¹ range. Other recent studies have demonstrated the magnetic enhanced removal of cobalt and iron from simulated groundwater. The magnetic field enhanced filtration/sorption process differs significantly from magnetic separation processes used in the processing of minerals and more recently, for water treatment and environmental applications. Conventional processes use for example, fine stainless steel wool to form a magnetic matrix within a flow field of a solution containing mineral particles to be separated. For this reason, in order for such processes to remove metal ions and nanoparticles from solution, precipitating or flocculating agents must first be added to effect formation of large particles. In contrast, the magnetic filtration/sorption process is unique because metals are removed in most conventional wastewater treatment processes in the form of metal hydroxides since they have low solubility. As noted above, ferric hydroxide is often added to scavenge a wide variety of heavy metal contaminants. The use of iron ferrite and magnetite in wastewater treatment has a number of advantages over conventional flocculent precipitation techniques for metal ion removal. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions. The effect of particle size on the adsorption of dissolved heavy metals to iron oxide and titanium dioxide nanoparticles will be studied in laboratory scale experiments. Iron oxide and titanium dioxide are good sorbents for metal contaminants.

Reduction of transition metal salts is the oldest, easiest and still a widely used method for the preparation of metal nanoparticles. As far as magnetic metals are concerned, the most common reducing agents are borohydride derivatives, extensively studied [28]. This method provides an easy route to nanoparticles of Fe, Co and Ni as well as to alloys such as Fe/Pd. The disadvantage of the method is the incorporation of boron into the particles which leads to a modification of the magnetic properties of the particles. Cobalt particles were for example prepared with the microemulsion method in the binary system of DDAB (di-dodecyldimethylammonium bromide)/toluene by reduction of CoCl₂ with NaBH₄. The average particle size of the samples could be varied from 1.8 to 4.4 nm by controlling the concentration of CoCl₂ in the solution of DDAB in toluene. ratio at 150 °C in 1.0-2.0 M NaOH solutions [29].

Zeolite

Zeolites are more effective sorbents and ion exchange media for metal ions. NaP1 zeolites have been evaluated as ion exchange media for the removal of heavy metals from acid mine wastewaters [30, 31] reported the successful use of synthetic NaP1 zeolites to remove Cr (III), Ni (II), Zn (II), Cu (II) and Cd (II) from metal electroplating wastewater. Nonporous ceramic oxides with very large surface areas ($1000 \text{ m}^2 \text{ g}^{-1}$) and high density of sorption sites that can be functionalized to increase their selectivity toward target pollutants.

Zeolite nanoparticles are prepared by laser induced fragmentation of zeolite LTA microparticles using a pulsed laser. Zeolite nanoparticle formation is attributed to absorption of the laser at impurities or defects within the zeolite microcrystal generating thermoelastic stress that mechanically fractures the microparticle into smaller nanoparticle fragments. Experimentally, it is found that nanoparticles have a wide size and morphology distribution. Large nanoparticles ($>200 \text{ nm}$) are typically irregularly shaped crystals of zeolite LTA, whereas small nanoparticles ($<50 \text{ nm}$) tend to be spherical, dense and amorphous, indicative of destruction of the original LTA crystal structure. Increasing the laser energy density irradiating the sample was found to be a trade off between increasing the amount of fragmentation and increasing the amount of structural damage to the zeolite crystal. It is suggested that in the presence of strongly absorbing defects, plasma formation is induced resulting in dramatically higher temperatures. On the basis of these results it is concluded that the optimal laser processing conditions are 355 nm and 10 mJ/pulse laser energy for our LTA samples [32].

Carbonaceous nanoparticle

Carbonaceous nanomaterials can serve as high capacity and selective sorbents for organic solutes in aqueous solutions. A number of polymers that exhibit antibacterial properties were developed for this purpose including soluble and insoluble pyridinium type polymers which are involved in surface coating [33] azidated poly (vinyl chloride) [34] which can be used to prevent bacterial adhesion of medical devices, PEG polymers that can be modified on polyurethane surfaces and also prevent initial adhesion bacteria to the biomaterial surfaces [35] and polyethylene mine (PEI) [36] that exhibit high antibacterial and antifungal activity. High activity of polycationic agents is related to absorption of positive charged nanostructures onto negative by charged cell surfaces of the bacteria. This process is thought to be responsible for the increase of cell permeability and may disrupt the cell membranes.

Cross linked poly cations are prepared as nanoparticles. These are formed from PEI by cross linking and alkylation followed by methylation in order to increase degree of amino group substitution [37]. Because of its positive charge and hydrophobicity, PEI nanoparticles have got more attention as possible antimicrobial agents. Studies on PEI nanostructured compounds are made to evaluate its antibacterial properties as a function of hydrophobicity, molecular weight, particle size and charge that can play a important role in antibacterial effect of the tested compound. The antibacterial activity is evaluated against *Streptococcus mutants* cariogenic bacteria. Various PEI nanoparticles from 100 nm to 1 micron in diameter are prepared having different degree of cross linking, particle size and zeta potential that are achieved by alkylation with a bromoalkane followed by methylation. Their antibacterial effects are examined against *Streptococcus mutants* in direct contact with bacteria. Most significant feature of the antibacterial agent is to maintain antibacterial activity over a long time. However, only the PEI nanoparticle samples including long chain alkyls demonstrated high antibacterial effect against *Streptococcus mutants* for more than four weeks [36].

Techniques used for water purification

Several techniques are already reported for water purification. Nanotechnology has boost the water purification using techniques such as the electronic, chemical, biotechnology and biomedical industries [38]. Whereas various industries produce different varieties of nanomaterials there are increasing efforts to use nanotechnology in environmental engineering to protect the environment by pollution control, treatment and as a remedial measure to long term problems such as contaminated waste sites [39]. This technique has proved to be an effective alternative to the conventional practices for site remediation. Further research has also been still carried out and its application is found useful in the treatment of in drinking water. Despite their potential benefits, there is one major concern is that nanoparticles may exert deleterious effects. Toxicological risk assessment requires more information about both exposure and uptake of nanoparticles and their immediate effects once they enter the human system. But, the reported data on these topics are very limited to form conclusions and recommendations [40]. In response to these concerns, various scientific communities are trying to gain more knowledge in exposing their toxicological effects on human [41] and ecological health [42].

Site remediation

In response to a growing need to cure environmental contamination, many remediation technologies have been developed to treat soil, leachate, wastewater and groundwater

contaminated by various pollutants, using in situ and ex situ methods [43]. In particular, a contaminated site may require a combination of procedures to allow the maximum remediation for the prevailing conditions. Chemical, physical and biological technologies may be used in accordance with one another to reduce the contamination to a safe level. Hence, for a successful treatment, proper selection, design, and adjustment of the remediation technology's operations should be carried out based on the properties of the contaminants and soils and on the performance of the system [44]. Previously, conventional methods include primarily pump and treat operations. This method involves process like extraction of groundwater through wells and trenches and treating groundwater by above ground (ex situ) processes such as air stripping, carbon adsorption, biological reactors or chemical precipitation. But unfortunately, most of these methods produce highly contaminated waste which then has to be disposed off, resulting in high operation time.

A commonly used in situ or below ground remediation method for cleaning up contaminated groundwater is the permeable reactive barrier (PRB). PRBs have a treatment zones composed of materials that can degrade or immobilize contaminants as the groundwater passes through the barrier. They can be installed as permanent, semi permanent or replaceable barriers within the flow path of a contaminant plume. The material chosen for the barrier is based on the contaminant(s) of concern. One disadvantage of PRBs is that they can only remediate contaminant plumes that pass through them; they do not treat dense non aqueous phase liquids NAPLs (DNAPLs) or contaminated groundwater that is beyond the barrier.

Nanoremediation

In these days, nanoremediation has become the main focus of research and development. There is great potential to utilize this technology to clean up the contaminated sites and protect the environment from pollution. This ecofriendly technology is considered to be an effective alternative to the current practices of site remediation. Nanoremediation methods involve application of reactive materials for the detoxification and transformation of pollutants. These materials initiate both chemical reduction and catalysis of the pollutants of concern [39]. The unique properties of nanomaterials make them best suited for in situ applications. Their small size and novel surface coatings enable them to achieve farther and wider distribution when compared to large sized particles [41].

The use of nanotechnology for site remediation could potentially provide a solution for faster and more cost effective site remediation. Many different nanomaterials have been evaluated for use in nanoremediation. They include nanoscale zeolites, metal oxides, carbon nanotubes, noble metals

and titanium dioxide. Of these, nanoscale zerovalent iron (nZVI) is currently widely used in groundwater remediation [39]. In addition to groundwater remediation, nanotechnology has also contributed towards reducing the presence of non aqueous phase liquids (NAPL). For this purpose, a material utilizing nano sized oxide is used *in situ* to clean up heating oil spills from underground oil tanks. Compared to previous remediation methods, this approach provided an overall reduction in the contaminant levels.

Nanoscale iron nanoparticle (nZVI)

Iron nanoparticles are an attractive component for nano remediation. Iron at the nanoscale was synthesized from Fe (II) and Fe (III), using borohydride as the reductant. Nanoscale zero valent iron particles range from 10 to 100 nm in diameter. They exhibit a typical core shell structure. The core consists primarily of zero valent or metallic iron whereas the mixed valent [i.e., Fe (II) and Fe (III)] oxide shell is formed as a result of oxidation of the metallic iron. Iron typically exists in the environment as iron (II) and iron (III) oxides [45]. nZVI are generally preferred for nano remediation because of large surface area of nanoparticles and more number of reactive sites than micro sized particles [40] and it possess dual properties of adsorption and reduction, as shown in figure 1. This enables it to be used for the remediation of wide range of contaminants present *in situ*. Moreover, when zero valent iron was allowed greater access to the contaminant site, it was found to give out less amount of hazardous waste during the treatment process [46]. Zero valent iron can also be modified based on the contaminants present. It could be modified to include catalysts like palladium, coatings such as polyelectrolyte or triblock polymers [47] or can be encased in emulsified vegetable oil micelles [48].

In 2003, nanoscale iron particles were investigated for their effect on a number of common pollutants in groundwater and contaminated soil. The results showed that the nanoscale iron particles were highly effective for the transformation and detoxification of a number of pollutants especially chlorinated organic solvents, organochlorine pesticides and polychlorinated biphenyls (PCBs) [40]. The large specific surface area nanoparticles are significantly more active than larger particles of the same material to remove arsenic from ground water [50]. This was evident as the nanoparticles were able to bind arsenic five to ten times more than micro sized particles.

To remove the contaminants, the super paramagnetic property of iron nanoparticle was manipulated and retrieved using a magnetic field without the negligence of being released into the environment. Laboratory tests have indicated that in excess of 99% of arsenic in water samples can be removed using 12 nm diameter iron oxide nanoparticles [51].

For the treatment of trichloroethane (TCE), a hazardous organic contaminant present in water, the surface of the zero valent iron nanoparticle is modified to contain an oil liquid membrane. This oil liquid membrane which is generally composed of food grade surfactant, biodegradable oil and water is hydrophobic and forms an emulsion with ZVI. This is termed as emulsified zero valent iron (EZVI) [52]. Since all DNAPLs (dense non aqueous phase liquids), such as the trichloroethane are hydrophobic, the emulsion is miscible with the contaminant, allowing an increased contact between TCE DNAPL and the ZVI present within the oil emulsion droplet [53]. Whereas the ZVI in the emulsion remains reactive, the chlorinated compounds are continuously de chlorinated within the aqueous emulsion droplet which produces a concentration gradient within the oil membrane, which in turn acts as a driving force to allow additional TCE migration into the membrane and additional degradation is carried out. A potential benefit of EZVI over NZVI for environmental applications is that the hydrophobic membrane surrounding the NZVI protects it from other groundwater constituents, such as some inorganic compounds, that might otherwise react with the NZVI, reducing its capacity or passivating the iron [54].

Another type of nanoparticle used for environmental application is the Bi metallic nanoparticle (BNP). Bimetallic nanoparticle consists of elemental iron or other metals in conjunction with a metal catalyst, such as platinum (Pt), gold (Au), nickel (Ni), and palladium [53]. The combination of metals to form a nanoparticle increases the kinetics of oxidation reduction (redox) reaction, therefore catalyzing the reaction.

The most commonly used and commercially available BNPs are the Palladium and Iron BNPs (Pd/Fe). The surface area normalized rate constant of BNPs of iron combined with palladium (NZVI/Pd) was two orders of magnitude higher than that of NZVI [55]. Palladium and Iron BNPs are generally used in the removal of TCE (trichloroethane). In one of the studies, palladium converts TCE into ethane with minimal formation of vinyl chloride and other chlorinated intermediates that often occur with anaerobic bioremediation and with iron metal [56].

Risks

Apart from using nZVI for various classes of contaminants, there is little information or research being conducted based on the potential toxicological effect they might pose. There are insufficient data on the potential for accumulation of nanoparticles in environmentally relevant species [57] and there have been few studies on the effects of many nanoparticles on environmental microbial communities [57]. Under standard environmental conditions i.e., using aerated water and pH

ranging from 5 to 9, Fe^{2+} will readily and spontaneously oxidizes to form Fe^{3+} and precipitate out of the groundwater as insoluble iron oxides and oxyhydroxides.

Ongoing studies are evaluating surface coatings and other modifications that would maximize subsurface mobility of nZVI [58]. Whereas increased mobility would allow more efficient remediation, it could also result in the possibility of the nanomaterials migrating beyond the contaminated plume area, seeping into drinking water aquifers or wells or discharging to surface water during the remediation process. Nanoparticles may have a negative impact on human health when nanoscale particles are inhaled, absorbed through skin or ingested [57]. Because of their small size, the particles have the potential to migrate or accumulate in places that larger particles cannot. One such area is the alveoli of lungs, hence potentially increasing toxicity.

Problems of toxicity and safety have limited the use of nanotechnology for remediation by some private sector companies. A work done by duPont, for example, has ruled out the use of nZVI for site remediation at any of its sites until problems concerning fate and transport have been more thoroughly researched. Their research has cited questions of post remediation persistence and potential human exposure to the particles as areas of particular concern during nanoremediation.

Carbon nanotubes (CNT)

In recent years, nanotechnology has introduced different types of nanomaterials to the water industry and has produced some promising outcomes. Since its discovery, carbon nanotubes have attracted great attention due to its unique properties. CNTs are nanomaterials that are rolled into a tube and are classified as single walled carbon nanotubes (SWNT) and multi walled carbon nanotubes (MWNTs) (Figure 2).

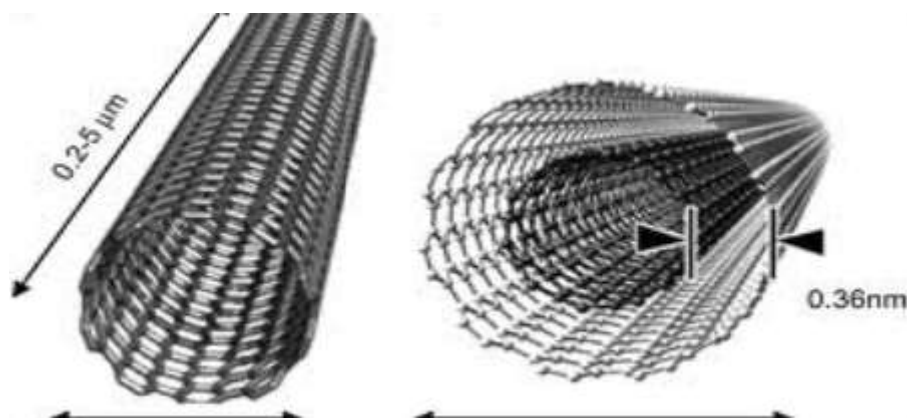


Figure 2. A schematic Representation of Carbon Nanotube and Multi walled Carbon Nanotube

According to the carbon atom layers in the walls of the nanotubes [59]. Removal of contaminants and recycling of the purified water would provide significant reductions in cost, time and labor to the industry and result in improved environmental stewardship. One such nanomaterial is the carbon nanotube (CNT). These nanosorbents are increasingly attractive since their discovery, due to their exceptional adsorption properties, their ability to be attached to a functional group to increase the affinity towards the target molecule.

The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface have a strong interaction with other molecules or atoms, which make CNTs a promising adsorbent material substituted for activated carbon in many ways [60]. They are utilized for the removal of heavy metals like Cr^{3+} , Pb^{2+} , and Zn^{2+} , metalloids such as arsenic compounds, organics, biological impurities, and removing many kinds of organic and inorganic pollutants such as dioxin and volatile organic compounds [61]. On comparing CNTs with other adsorbents, the researchers assert that nCNTs are effective adsorbents for environmental applications. The carbon nanotubes (CNTs) are unique and one dimensional macromolecules that possess high chemical and thermal stability. This property of the nanoparticles have been manipulated for the treatment of natural organic matter (NOM) which could produce carcinogenic agents and even enhance the bacterial regrowth and bio film formation [62]. Hence, thermally treated CNTs were employed for the treatment of natural organic matter to realize effective absorption. Thus, CNTs possess all the essential properties to maintain water of the high quality. Here we look at various methods in which CNTs can be used effectively to retrieve the various types of contaminants present in water for drinking and for reuse.

For groundwater remediation, there are stringent regulation methods. Any increase in the discharge of heavy metals into the aquatic environment is toxic as they can accumulate in the living tissues. Hence, they have to be removed from water. This is done using multi walled carbon nanotubes (MWCNTs). To increase the absorption capacity of MWCNTs, it is oxidized with nitric acid resulting to which a higher level of adsorption was achieved. According to Li and coworkers (2003), the sorption of Pb (II), Cu (II) and Cd (II) on to MWCNTs were 3-4 times larger than those of powdered activated carbon and granular activated carbon which are the two conventionally used sorbents in water purification.

Some studies showed that underivatized CNTs tend to be water insoluble and toxic. Carbon nanotubes, in order to be highly dispersed in water and to be easily separated from their dispersion for their reuse, are functionalized with various functional groups (e.g. hydroxyl, carboxyl, amines, etc.) to increase their water solubility and biocompatibility in some cases [63]. Jin and coworkers [64] functionalized MWCNTs with Fe nanoparticle for their effective disposal of aromatic

compounds which are considered as carcinogens. In addition to this, to make CNTs water soluble, it is made to decompose thermally with azodiisobutyro nitrile (AIBN) and refluxed with sodium hydroxide to form nanoparticle functionalized water soluble MWNTs (Fe-MWNT CH₂COONa). According to the analytical data the adsorbed percentages of benzene, toluene, dimethylbenzene and styrene were found to be 79%, 81%, 83% and 88% respectively, which showed that Fe-MWNT CH₂COONa can be used as a potential sorbent for the removal of benzene and its aromatic compounds. Fe-MWNT CH₂COONa could also be reused due to their exceptional magnetic separation capability [64].

Risks

The design and synthesis of biocompatible carbon nanotubes (CNTs), on the other hand, are very challenging. Only a few peer reviewed studies of the toxicity of CNTs have been published by various researchers [65]. However, it has to be pointed out that metal containing particles also exhibit a size dependent toxicity [66]. Thus, a key challenge will be to gain regulatory and public acceptance for using nanomaterials in water purification because of their unknown toxicity and environmental impact. Scientists have found that carbon nanotubes, if inhaled in large proportions, could be as dangerous as asbestos. Researchers found carbon nanotubes causing the same kind of damage as asbestos in mice. According to Lam and its coworkers, CNTs are light and could get air borne and when it enters the lungs, lesions were formed and toxicity greater than that of quartz was observed. Another set of experiments reveal that exposure to nanotubes on mice could cause mesothelioma, a cancer which affects the lung lining. All these factors have affected the use of these nanomaterials in nanoremediation by various organizations. Hence, extreme degree of safety and caution must be maintained when carrying out experiments using carbon nanotubes (CNTs).

Water treatment

Clean water is a requirement for all properly functioning societies worldwide, but is often limited. New approaches are continually being examined to supplement traditional water treatment methods. These need to be lower in cost and more effective than current techniques for the removal of contaminants from water. In this context, also nanotechnological approaches are considered. In this section, the following application areas will be covered: nanoparticles used as potent adsorbents, in some cases combined with magnetic particles to ease particle separation; nanoparticles used as catalysts for chemical or photochemical destruction of contaminants; nanosized zero valent iron used for the removal of metals and organic compounds from water; and nano filtration membranes.

Adsorption of pollutants

Sorbents are widely used in water treatment and purification to remove organic and inorganic contaminants. Examples are activated carbon and ion exchange resins. The use of nanoparticles may have advantages over conventional materials due to the much larger surface area of nanoparticles on a mass basis. In addition, the unique structure and electronic properties of some nanoparticles can make them especially powerful adsorbents. Many materials have properties that are dependent on size [67]. Hematite particles with a diameter of 7 nm, for example, adsorbed Cu ions at lower pH values than particles of 25 or 88 nm diameter, indicating the uniqueness of surface reactivity for iron oxides particles with decreasing diameter. However, another study found that normalized to the surface area the nanoparticles had a lower adsorption capacity than bulk TiO₂ [68]. Several types of nanoparticles have been investigated as adsorbents: metal containing particles, mainly oxides, carbon nanotubes and fullerenes, organic nanomaterials and zeolites. For the removal of metals and other inorganic ions, mainly nanosized metal oxides [69, 70] but also natural nanosized clay have been investigated. Also, oxidized and hydroxylated CNTs are good adsorbents for metals. This has been found for various metals such as Cu, Ni, Cd and Pb. Adsorption of organometallic compounds on pristine multi walled CNTs was found to be stronger than for carbon black [71].

Chemically modified nanomaterials have also attracted a lot of attention, especially nanoporous materials due to their exceptionally high surface area. The particle size of such materials is, however, not in the nano range but normally 10–100 nm. Another option is to modify chemically the nanoparticle itself [72]. TiO₂ functionalized with ethylenediamine was, for example, tested for its ability to remove anionic metals from groundwater. CNTs have attracted a lot of attention as very powerful adsorbents for a wide variety of organic compounds from water. Examples include dioxin, polynuclear aromatic hydrocarbons (PAHs), DDT and its metabolites, PBDEs, chlorobenzenes and chlorophenols, trihalomethanes, bisphenol a and nonylphenol, phthalate esters, dyes, pesticides (thiamethoxam, imidacloprid and acetamiprid) and herbicides such as sulfuron derivatives, atrazine and dicamba [73-75]. Cross linked nanoporous polymers that have been copolymerized with functionalized CNTs have been demonstrated to have a very high sorption capacity for a variety of organic compounds such as p-nitrophenol and trichloroethylene. It was found that purification (removal of amorphous carbon) of the CNTs improved the adsorption [73, 74]. The available adsorption space was found to be the cylindrical external surface; neither the inner cavity nor the inter wall space of multi walled CNT contributed to adsorption [76]. Unlike the case with fullerenes, no adsorption–desorption hysteresis was observed, indicating reversible

adsorption [76]. Fullerenes have also been tested for adsorption of organic compounds. Adsorption depends to a great extent on the dispersion state of the C_{60} , which is virtually insoluble in water. Because C_{60} forms clusters in water, there are closed interstitial spaces within the aggregates into which the compounds can diffuse, which leads to significant adsorption–desorption hysteresis [76]. Fullerenes are only weak sorbents for a wide variety of organic compounds (e.g. phenols, PAHs, amines), whereas they are very efficient for the removal of organometallic compounds (e.g. organolead). An interesting application is oxide CNTcomposites, which have been explored for the removal of metals and also of anions such as arsenate and fluoride [77, 78] . Specially designed polymers and dendrimers are exploited for their potential removal of metals and organics.

Magnetic nanoparticles

Magnetic nanoparticles offer advantages over non magnetic nanoparticles because they can easily be separated from water using a magnetic field. Separation using magnetic gradients, the so called high magnetic gradient separation (HGMS), is a process widely used in medicine and ore processing [79]. This technique allows one to design processes where the particles not only remove compounds from water but also can easily be removed again and then be recycled or regenerated. This approach has been proposed with magnetite (Fe_3O_4), maghemite ($\gamma-Fe_2O_3$) and jacobsite ($MnFe_2O_4$) nanoparticles for removal of chromium (VI) from wastewater [80, 81]. Water soluble CNTs have been functionalized with magnetic iron nanoparticles for removal of aromatic compounds from water and easy separation from water for reuse.

Nanofiltration

Nanofiltration membranes (NF membranes) are used in water treatment for drinking water production or wastewater treatment [82]. NF membranes are pressure driven membranes with properties between those of reverse osmosis and ultra filtration membranes and have pore sizes between 0.2 and 4 nm. NF membranes have been shown to remove turbidity, microorganisms and inorganic ions such as Ca and Na. They are used for softening of groundwater (reduction in water hardness), for removal of dissolved organic matter and trace pollutants from surface water, for wastewater treatment (removal of organic and inorganic pollutants and organic carbon) and for pre treatment in seawater desalination. Carbon nanotubes have been arranged to form a hollow monolithic cylindrical membrane [83], which was efficient for the removal of bacteria or hydrocarbons and that can easily be regenerated by ultrasonication or autoclaving.

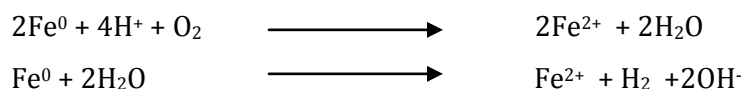
Degradation of pollutants

The semiconductor TiO₂ has been extensively studied for oxidative or reductive removal of organic pollutants [83]. Illumination promotes an electron to the conduction band, leaving a hole in the valence band. This process produces a potent reducing and oxidizing agent. In water, photo oxidation occurs primarily through hydroxyl radicals. Because TiO₂ requires ultraviolet light for excitation, it has been sensitized to visible light by dyes, through incorporation of transition metal ions.

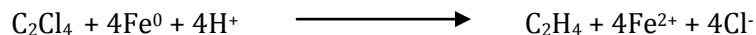
Pollution Prevention and Treatment Using Nanotechnology or by doping with nitrogen [45]. The degradation rate of several dyes by nanosized TiO₂ was found to be 1.6–20 times higher than for bulk TiO₂ particles. Several types of compounds such as dyes and organic acids have been shown to be rapidly degraded. A special type of TiO₂ photocatalysts are titania nanotube materials, which were shown to have superior activity [55-84].

Zerovalent iron

Laboratory research has established that nanoscale metallic iron is very effective in destroying a wide variety of common contaminants such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes, other polychlorinated hydrocarbons, pesticides and dyes [49]. The basis for the reaction is the corrosion of zerovalent iron in the environment:



Contaminants such as tetrachloroethane can readily accept the electrons from iron oxidation and be reduced to ethene:



However, nanoscale zerovalent iron (nZVI) can reduce not only organic contaminants but also the inorganic anions nitrate, which is reduced to ammonia, perchlorate (plus chlorate or chlorite), which is reduced to chloride, selenate, arsenate, arsenite and chromate [85,86]. nZVI is also efficient in removing dissolved metals from solution, e.g. Pb and Ni [87]. The reaction rates for nZVI are at least 25–30 times faster and also the sorption capacity is much higher compared with granular iron [88]. The metals are either reduced to zerovalent metals or lower oxidation states, e.g. Cr (III), or are surface complexed with the iron oxides that are formed during the reaction. Some metals can increase the dechlorination rate of organics and also lead to more benign products, whereas other metals decrease the reactivity. The reaction rates for nZVI can be several orders of magnitude faster on a mass basis than for granular ZVI [42]. Because the reactivity of ZVI towards

lightly chlorinated and brominated compounds is low and because the formation of a passivating layer reduces the reactivity with time, many approaches have been explored where the surface is doped with a catalyst (e.g. Pd, Pt, Cu, Ni) to reduce the activation energy. The same approach has also been tested for nZVI. Surface normalized reaction rates for such materials were found to be up to 100 times faster than for bulk ZVI [89].

The nanoscale iron particles can be produced either by a top down approach (e.g. milling of iron filings) or by direct chemical synthesis [45]. A common method for synthesis of iron nanoparticles is by reduction of an aqueous ferric solution by reducing agents such as sodium borohydride or sodium hypophosphite.

Soil and groundwater remediation

The use of nZVI for groundwater remediation represents the most widely investigated environmental nanotechnological technique. Granular ZVI in the form of reactive barriers has been used for many years at numerous sites all over the world for the remediation of organic and inorganic contaminants in groundwater (see Figure 1). With nZVI, two possible techniques are used: immobile nZVI is injected to form a zone of iron particles adsorbed on the aquifer solids or mobile nZVI is injected to form a plume of reactive Fe particles that destroy any organic contaminants that dissolve from a DNAPL (dense non aqueous phase liquid) source in the aquifer. With this technique, the formation of a pollutant plume is inhibited. The successful results of field demonstrations using nZVI have been published, with reported reductions in TCE of up to 96% after injection of 1.7 kg of nanoparticles into the groundwater [90]. A larger test was conducted where 400 kg of nZVI was injected and significant reductions in TCE soil concentration (>80%) and dissolved concentrations (57–100%) were observed [53]. To date approximately 30 projects are under way in which nZVI is used for actual site remediation. Whereas most research using nZVI has been devoted to groundwater, much less has been published about soil remediation. These studies have mostly been done in soil slurries and efficient removal of PAHs by nZVI has been reported [91]. For PCBs, a removal of only about 40% was attained, caused by the very strong adsorption of PCBs to the soil matrix and limited transfer to the nZVI particles. nZVI has also been used to immobilize Cr (VI) in chromium ore processing residue. Because the iron particles have a strong tendency to aggregate and adsorb on surfaces of minerals, much effort has been directed towards methods to disperse the particles in water and render them mobile. In one approach, water soluble starch was used as a stabilizer, and in another, hydrophilic carbon or poly (acrylic acid) delivery vehicles were used [92]. Modified cellulose, sodium carboxymethyl cellulose (CMC), was found to

form highly dispersed nZVI and also several polymers have been tested and found to be very effective. In this stabilized form the nZVI was up to 17 times more reactive in degrading trichloroethene than non stabilized material. However, for other stabilizing agents a decrease in reactivity of up to 9 or 2–10 fold was observed. To deliver the nZVI to the oil/water interface in the case of DNAPL contamination, a copolymer was used to increase colloid stability and at the same time increase phase transfer into the organic phase [93].

Environmental risks

Behavior in the environment

The use of nanoparticles in environmental cleanup applications will inevitably lead to the release of nanoparticles into the environment. Assessing their risks in the environment requires an understanding of their mobility, bioavailability, toxicity and persistence. Whereas air borne particles and inhalation of nanoparticles have attracted a lot of attention nowadays, still very much less is known about the possible exposure of aquatic and terrestrial life to nanoparticles in water and soils. Nanoparticles agglomerate rapidly into larger aggregates or are contained within other materials (e.g. polymers). Cations, for example, are able to coagulate acid treated CNTs with critical coagulation concentrations of 37 mM for Na, 0.2 mM for Ca and 0.05 mM for trivalent metals (e.g. La³⁺). Aggregation of CNTs added as a suspension to filtered pond water has been reported [94]. Sedimentation and therefore removal from water can be expected under such conditions. The coagulation and interception by surfaces also determine the fate of nanoparticles in porous media and rapid removal has been observed in many, but not all, cases. However, a recent research shows that humic and fulvic acids are able to solubilize CNTs under natural conditions and that stable suspensions are obtained [95]. Most nanoparticles in technical applications are functionalized and therefore studies using pristine nanoparticles may not be relevant for assessing the behaviour of the actually used particles. As mentioned above in section 1.5 on groundwater remediation, functionalization is often used to decrease agglomeration and therefore increase mobility of particles. Very little is known to date about the influence of functionalization on the behavior of nanoparticles in the environment.

Ecotoxicology

A consistent body of evidence shows that nanosized particles can be taken up by a wide variety of mammalian cell types, are able to cross the cell membrane and become internalized [96]. The uptake of nanoparticles is size dependent. Most of the toxicological studies have been carried out with mammalian cells and therefore were carried out in a cell culture medium containing a mixture

of proteins and other biological compounds. In this medium, nanoparticles are coated with proteins and have a negative surface charge irrespective of the charge of the pristine particles [97]. Results from such studies therefore cannot be directly transferred to environmental conditions.

Ecotoxicological studies show that nanoparticles are also toxic to aquatic organisms, both unicellular (e.g. bacteria or protozoa) and animals (e.g. daphnia or fish). Whereas bulk TiO_2 is considered to have no health effects on aquatic organisms, this is clearly not the case for nanosized TiO_2 . This was found both for inorganic nanoparticles such as TiO_2 [98], CeO_2 and ZnO and for carbon containing particles such as fullerenes and CNTs. The observed effects ranged from higher activity of certain stress related genes, lipid peroxidation and glutathione depletion and antibacterial activity (growth inhibition) for microorganisms to increased mortality and reduced fertility at high particle concentrations. Inorganic nanoparticulate TiO_2 had a toxic effect on bacteria and the presence of light was a significant factor increasing the toxicity. In copepods purified CNTs did not show any effect whereas unpurified CNTs with all their by-products increased mortality [99]. Organisms are able to use a lipid coating of CNTs as a food source and therefore alter the solubility and toxicity of the CNT in the organism.

Nanosized CeO_2 particles were adsorbed on the cell wall of *E. coli* but the microscopic methods were not sensitive enough to discern whether internalization had taken place [99]. Nanosized ZnO was internalized by bacteria. Nanoparticles that damage bacterial cell walls have been found to be internalized, whereas those without this activity were not taken up. CNTs have been shown to be taken up by a unicellular protozoan and they induced a dose dependent growth inhibition. The CNTs were localized with the mitochondria of the cells. These results from ecotoxicological studies show that certain nanoparticles will have effects on organisms on the environment, at least at elevated concentrations. The next step towards an assessment of the risks of nanoparticles in the environment will therefore be to estimate the exposure to the different nanoparticles.

Conclusion

Nanotechnology is the engineering and application of atoms, molecules, and particles whose sizes are on the nanometer scale (1-100 nm). Studies have shown that nanoparticles (NPs), most especially the nano metal oxides have improved and/or unusual physico chemical properties when compared with the corresponding bulk materials. Thus, these unique properties make NPs very useful in different fields like medicine, electronics, biomaterials, energy production, water and wastewater treatment, etc. Different methods such as the gas phase synthesis (gas condensation processing, chemical vapour condensation, microwave plasma processing, and combustion flame

synthesis), ball milling, co-precipitation, sol gel, micro emulsion, and surfactant have been widely reported in literature over the years for the production of NPs. There are few conventional technologies which are affordable and can be produced locally for effective removal of contaminants from water and wastewater. However, there are several challenges with regards to the cost and the removal efficiency of certain pollutants, most especially, the persistent organic pollutants and endocrine disruptors by these conventional technologies. Environmental nanotechnology vis nanotechnology and/or nanotechnology combined with conventional technologies are able to treat organic and inorganic contaminants to acceptable levels. There is currently intense scientific interest in nanotechnology for water and wastewater treatment; nevertheless, there are concerns about the toxicity and environmental impact of NPs.

Nano titanium dioxide, zerovalent iron, zinc oxide, silver oxide, carbon nanotube, and composites have been extensively used as photo catalysts, membranes and adsorbents in water and wastewater treatment. Chemically modified NPs have also attracted a lot of attention. The combination of NPs with other treatment processes such as the physical, chemical, biological, and advanced oxidation processes similarly yielded enhanced outcome. The application of nanotechnology for the removal of toxic pollutants such as the pharmaceutical and personal care products, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalates, furans and dioxins, agrochemicals and pesticides, volatile organic compounds, viruses and bacteria, dyes, inorganic pollutants, etc., has been widely reported by several investigators in the field of nanotechnology. Some of the recently reported investigations include; the use of copper NPs in paper filters for point of use water purification by Dankovich and Smith; 2014 [100], the adsorption of methylene blue onto synthesized nanoscale zerovalent iron bamboo and manganese bamboo composites by Shaibu et al., 2014 [101], the use of synthesized nano silver bioconjugate material for the treatment of organophosphorus pesticide reported by Das et al., 2012 [102], the removal of boron from water using iron oxide/hydroxide based NPs (NanoFe) and Nano Fe-impregnated granular activated carbon as adsorbent by Zelmanov and Semiat, 2014 [103], and the application of green nano iron particles for the adsorptive removal of As (III) and As (V) from aqueous solution reported by Prasad et al., 2014. Moreover, the article by Cai et al., 2014 [104], focused on the desalination of seawater by nano Ag and Ag@C on graphene. A detailed review on the catalytic applications of Au/TiO₂ NPs for the removal of water pollutant was presented by Ayati et al., 2014 [105], while Ayanda et al., 2013 [106]; and Fatoki et al., 2014 [107], evaluated the potential of nano oxides and composites for the remediation of organotin compounds (tributyltin and triphenyltin chlorides). Interestingly, results have shown that environmental nanotechnology could be

effectively utilized for the removal of organic and inorganic contaminants from drinking water, sewage, municipal, industrial and process wastewater. The limitation to the use of nanotechnology in water and wastewater treatment is that the NPs might be difficult to separate from the treated solution, which may result to loss of the NPs. Nevertheless, this problem could be reduced by immobilization of the NPs on appropriate substrate. The toxicity and environmental impact of NPs are also currently being investigated to understand their impact on human health and the environment.

Nanotechnology, the manufacturing and skill of controlling matter at the nanoscale (1–100 nm), offers the prospective of new nanomaterials for treatment of groundwater, surface water and wastewater polluted by poisonous organic and inorganic solutes, metal ions and microorganisms [108, 109]. Owing to their unique activity toward unmanageable contaminants and application flexibility, many nanomaterials are under dynamic research and development. For that reason, literature about existing research on different nanomaterials (nanostructured catalytic membranes, nanosorbents, nanocatalysts, and bioactive nanoparticles) and their application in water treatment, purification and disinfection is reviewed in this article [110]. Moreover, knowledge regarding toxicological effects of engineered nanomaterials on humans and the environment is presented [111]. There is no doubt in saying that the quality of groundwater is decreasing day by day and there is an immense need for adopting a new and advanced technique for the remediation of groundwater. In India, there is a great need for adopting such a technique to remediate groundwater and a lot of further scope in research and development is still there to be worked on.

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