

1

Pollution Prevention and Treatment Using Nanotechnology

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1.1

Introduction

Environmental nanotechnology is considered to play a key role in the shaping of current environmental engineering and science. Looking at the nanoscale has stimulated the development and use of novel and cost-effective technologies for remediation, pollution detection, catalysis and others [1]. However, there is also a wide debate about the safety of nanoparticles and their potential impact on environment and biota [2, 3], not only among scientists but also the public [4, 5]. Especially the new field of nanotoxicology has received a lot of attention in recent years [6, 7]. Nanotechnology and the environment – is it therefore a Janus-faced relationship? There is the huge hope that nanotechnological applications and products will lead to a cleaner and healthier environment [8]. Maintaining and re-improving the quality of water, air and soil, so that the Earth will be able to support human and other life sustainably, are one of the great challenges of our time. The scarcity of water, in terms of both quantity and quality, poses a significant threat to the well-being of people, especially in developing countries. Great hope is placed on the role that nanotechnology can play in providing clean water to these countries in an efficient and cheap way [9]. On the other hand, the discussion about the potential adverse effects of nanoparticles has increased steadily in recent years and is a top priority in agencies all over the world [10, 11]. Figure 1.1 shows the hits for a search for “risk” related to nanotechnology in the Web of Science. Publications that deal in one way or other with “risk” have skyrocketed in the last few years since 2002.

The same properties that can be deleterious for the environment can be advantageous for technical applications and are exploited for treatment and remediation. Figure 1.2 shows a few examples of this Janus face of nanotechnology: engineered particles with high mobility are needed for efficient groundwater remediation, but at the same time this property will render a particle more difficult to remove during water treatment. The toxicity of some nanoparticles can be used for water disinfection where killing of microorganisms is intended, whereas the same property is unwanted

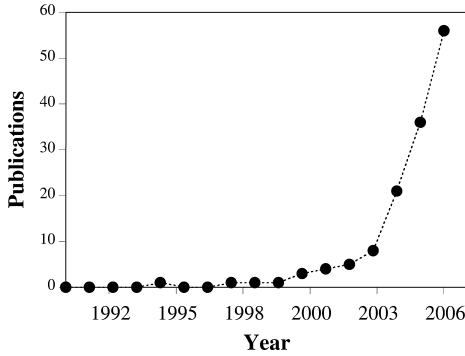


Figure 1.1 Hits in the Web of Science for the search terms “(nanotechnol* OR nanopart* OR nanotub*) AND risk” for the years 1990–2006.

when nanoparticles eventually enter the environment. The catalytic activity of a nanoparticle can be advantageous when used for the degradation of pollutants, but can induce a toxic response when taken up by a cell. The high sorption capacity of certain nanoparticles is exploited for the removal of organic and inorganic pollutants while this property may also mobilize sequestered pollutants in the environment. The engineering of nanoparticles that are easily taken up by cells will have a huge impact on medicine and pharmacological research, but the dispersion of such particles in the environment can lead to unwanted and unexpected effects. Also the

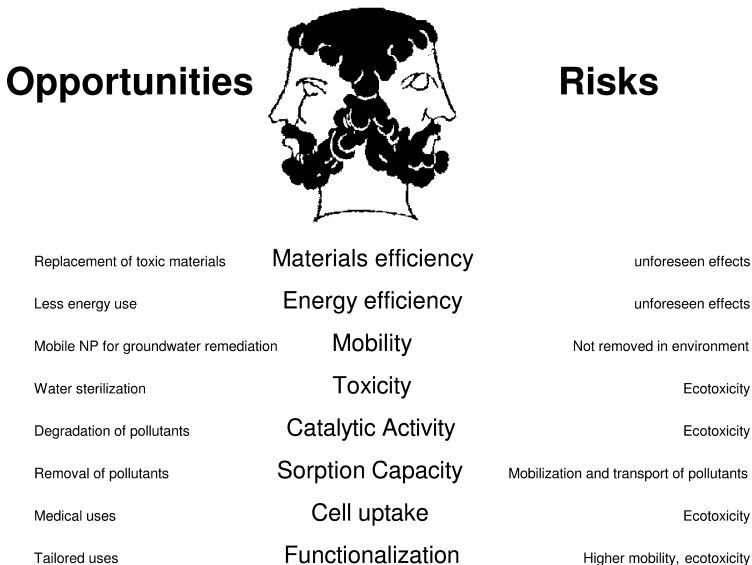


Figure 1.2 The Janus face of nanotechnology.

fact that many engineered nanoparticles are functionalized and therefore have a different surface activity from pristine particles is pivotal for many applications where a tailored property is needed, but such particles may behave in a completely different way from standard particles in the environment and may, for example, be much more mobile or show an increased (or decreased, as the case may be) toxicity. This short list of properties exemplifies the fact that engineered nanoparticles or nanotechnological applications make use of the same properties that are looked for by environmental scientists.

This chapter will give a general overview of potential environmental applications of nanotechnology and nanoparticles and will also give a short overview of the current knowledge about possible risks for the environment.

1.2 More Efficient Resource and Energy Consumption

Pollution prevention by nanotechnology refers on the one hand to a reduction in the use of raw materials, water or other resources and the elimination or reduction of waste and on the other hand to more efficient use of energy or involvement in energy production [1]. The implementation of green chemistry principles for the production of nanoparticles and for nanotechnological applications in standard chemical engineering will lead to a great reduction in waste generation, less hazardous chemical syntheses, improved catalysis and finally an inherently safer chemistry [12]. However, there are very few data that actually show quantitatively that these claims are true and that replacing traditional materials with nanoparticles really does result in less energy and materials consumption and that unwanted or unanticipated side effects do not occur.

Nanomaterials can be substituted for conventional materials that require more raw material, are more energy intensive to produce or are known to be environmentally harmful [8]. Some new nanocatalysts can be used at much lower temperatures than conventional catalysts and therefore require less energy input [13]. The capacity of nanocatalysts to function at room temperature opens the way for broad applications of nanomaterials in many consumer products. Another example of how nanotechnology can reduce energy costs is nanomaterial coatings on ships, which are expected to realize fuel savings on the order of \$460 million per year for commercial shipping in the USA [13]. Nanodiamonds are expected to increase the life expectancy of automotive paints and therefore to reduce material costs and expenditure [14]. Nanotechnology may also transform energy production and storage by providing alternatives to current practices. One example is nanoparticulate catalysts for fossil fuels [15], which will lead to reduced emissions or better energy efficiency, higher storage capacity for hydrogen [16, 17], biohydrogen production [18] and more effective and cheaper solar cells or coatings on windows that reduce heat loss [19]. Nanoparticles can increase the storage capacity of batteries and rechargeable batteries [20–22] or are used in flat screens where they reduce the amount of heavy metals [8].

1.3

Pollution Detection and Sensing

Various nanostructured materials have been explored for their use in sensors for the detection of different compounds [23]. An example is silver nanoparticle array membranes that can be used as flow-through Raman scattering sensors for water quality monitoring [24]. The particular properties of carbon nanotubes (CNTs) make them very attractive for the fabrication of nanoscale chemical sensors and especially for electrochemical sensors [25–28]. A majority of sensors described so far use CNTs as a building block. Upon exposure to gases such as NO_2 , NH_3 or O_3 , the electrical resistance of CNTs changes dramatically, induced by charge transfer with the gas molecules or due to physical adsorption [29, 30]. The possibility of a bottom-up approach makes the fabrication compatible with silicon microfabrication processes [31]. The connection of CNTs with enzymes establishes a fast electron transfer from the active site of the enzyme through the CNT to an electrode, in many cases enhancing the electrochemical activity of the biomolecules [27]. In order to take advantage of the properties of CNTs, they need to be properly functionalized and immobilized. CNT sensors have been developed for glucose, ethanol, sulfide and sequence-specific DNA analysis [27]. Trace analysis of organic compounds, e.g. for the drug fluphenazine, has also been reported [32]. Nano-immunomagnetic labeling using magnetic nanoparticles coated with antibodies specific to a target bacterium have been shown to be useful for the rapid detection of bacteria in complex matrices [33].

1.4

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; nano-sized zerovalent iron used for the removal of metals and organic compounds from water; and nanofiltration membranes.

1.4.1

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 [34]. 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 [35]. However, another study found that normalized to the surface area the nanoparticles had a lower adsorption capacity than bulk TiO₂ [36]. 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 [37, 38] but also natural nanosized clays [39] have been investigated. Also, oxidized and hydroxylated CNTs are good adsorbers for metals. This has been found for various metals such as Cu [40], Ni [41, 42], Cd [43, 44] and Pb [45, 46]. Adsorption of organometallic compounds on pristine multi-walled CNTs was found to be stronger than for carbon black [47].

Chemically modified nanomaterials have also attracted a lot of attention, especially nanoporous materials due to their exceptionally high surface area [48]. The particle size of such materials is, however, not in the nano-range but normally 10–100 μm. Another option is to modify chemically the nanoparticle itself [49]. TiO₂ functionalized with ethylenediamine was, for example, tested for its ability to remove anionic metals from groundwater [50].

CNTs have attracted a lot of attention as very powerful adsorbents for a wide variety of organic compounds from water. Examples include dioxin [51], polynuclear aromatic hydrocarbons (PAHs) [52–54], DDT and its metabolites [55], PBDEs [56], chlorobenzenes and chlorophenols [57, 58], trihalomethanes [59, 60], bisphenol A and nonylphenol [61], phthalate esters [62], dyes [63], pesticides (thiamethoxam, imidacloprid and acetamiprid) [64] and herbicides such as sulfuron derivatives [65, 66], atrazine [67] and dicamba [68]. 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 [69]. It was found that purification (removal of amorphous carbon) of the CNTs improved the adsorption [54]. 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 [70]. Unlike the case with fullerenes, no adsorption–desorption hysteresis was observed, indicating reversible adsorption [70].

Fullerenes have also been tested for adsorption of organic compounds. Adsorption depends to a great extent on the dispersion state of the C₆₀ [71], which is virtually insoluble in water [72]. Because C₆₀ 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 [70, 73]. 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) [74].

An interesting application is oxide–CNT composites, which have been explored for the removal of metals [75] and also of anions such as arsenate and fluoride [76, 77]. Specially designed polymers and dendrimers are exploited for their potential removal of metals and organics [78, 79].

1.4.2

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 [80]. 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 ($\gamma\text{-Fe}_2\text{O}_3$) and jacobite (MnFe_2O_4) nanoparticles for removal of chromium(VI) from wastewater [81–83]. Water-soluble CNTs have been functionalized with magnetic iron nanoparticles for removal of aromatic compounds from water and easy separation from water for re-use [84].

1.4.3

Nanofiltration

Nanofiltration membranes (NF membranes) are used in water treatment for drinking water production or wastewater treatment [85]. NF membranes are pressure-driven membranes with properties between those of reverse osmosis and ultrafiltration 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 pretreatment in seawater desalination.

Carbon nanotubes have been arranged to form a hollow monolithic cylindrical membrane [86], which was efficient for the removal of bacteria or hydrocarbons and that can easily be regenerated by ultrasonication or autoclaving.

1.4.4

Degradation of Pollutants

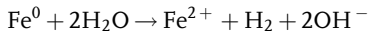
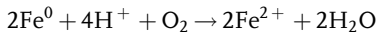
The semiconductor TiO_2 has been extensively studied for oxidative or reductive removal of organic pollutants [49, 87]. Illumination promotes an electron to the conduction band, leaving a hole in the valence band. This process produces a potent reducing and oxidizing agent. In water, photo-oxidation occurs primarily through hydroxyl radicals. Because TiO_2 requires ultraviolet light for excitation, it has been sensitized to visible light by dyes, through incorporation of transition metal ions [49]

or by doping with nitrogen [88]. The degradation rate of several dyes by nanosized TiO_2 was found to be 1.6–20 times higher than for bulk TiO_2 particles [89]. Several types of compounds such as dyes [88, 90] and organic acids [91] have been shown to be rapidly degraded. A special type of TiO_2 photocatalysts are titania nanotube materials, which were shown to have superior activity [92, 93].

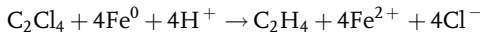
1.4.5

Zerivalent 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 [94]. 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 [95, 96], perchlorate (plus chlorate or chlorite), which is reduced to chloride [97], selenate [98], arsenate [99, 100], arsenite [101] and chromate [102, 103]. nZVI is also efficient in removing dissolved metals from solution, e.g. Pb and Ni [102, 104]. The reaction rates for nZVI are at least 25–30 times faster and also the sorption capacity is much higher compared with granular iron [105]. 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 [106].

The reaction rates for nZVI can be several orders of magnitude faster on a mass basis than for granular ZVI [107]. 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 [108–111].

The nanoscale iron particles can be produced either by a top-down approach (e.g. milling of iron filings) or by direct chemical synthesis [105]. 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 [49].

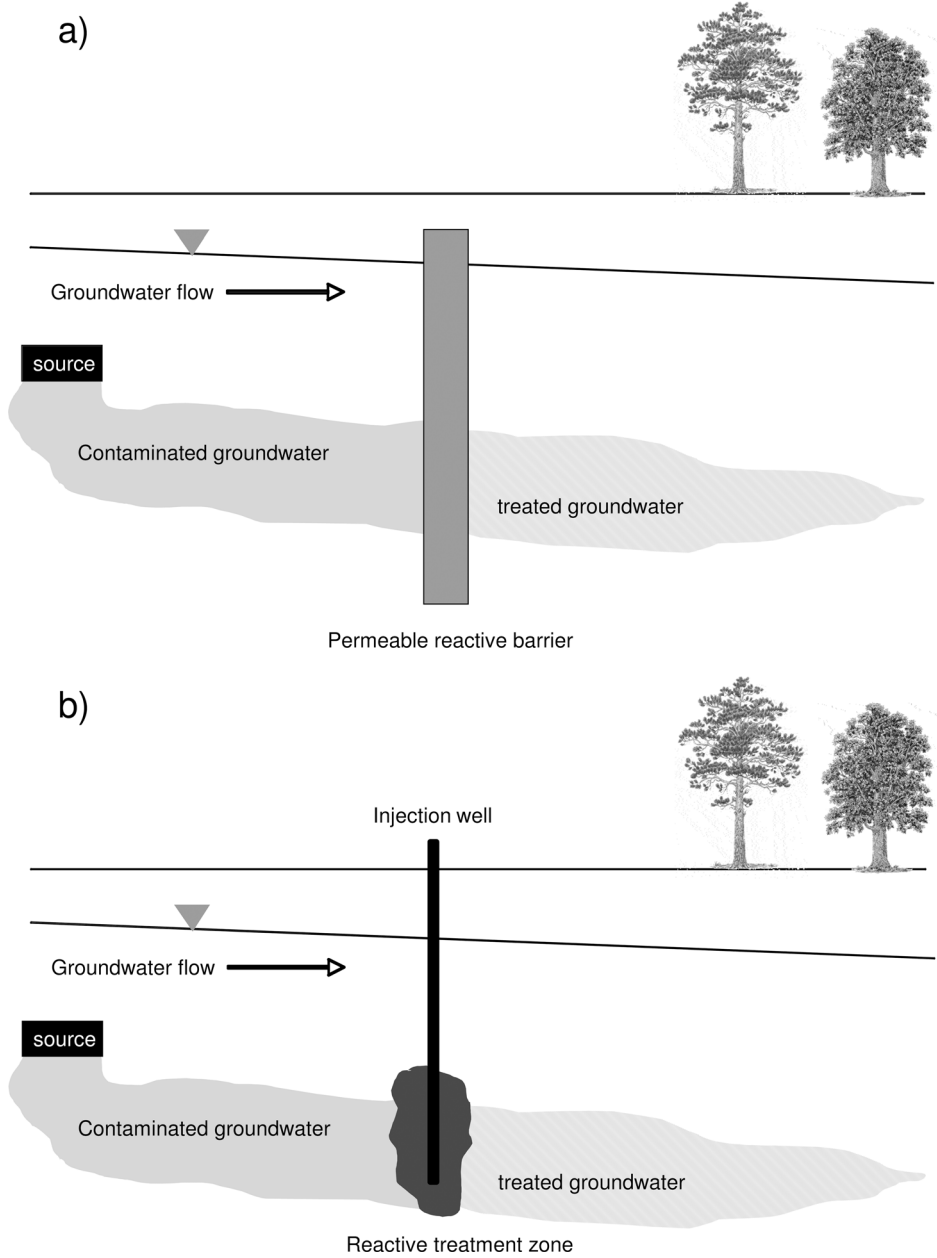


Figure 1.3 Three approaches to application of ZVI for groundwater remediation: (a) conventional reactive barrier using granular ZVI; (b) injection of nZVI to form an immobile reaction zone; (c) injection of mobile nZVI. Modified after [107].

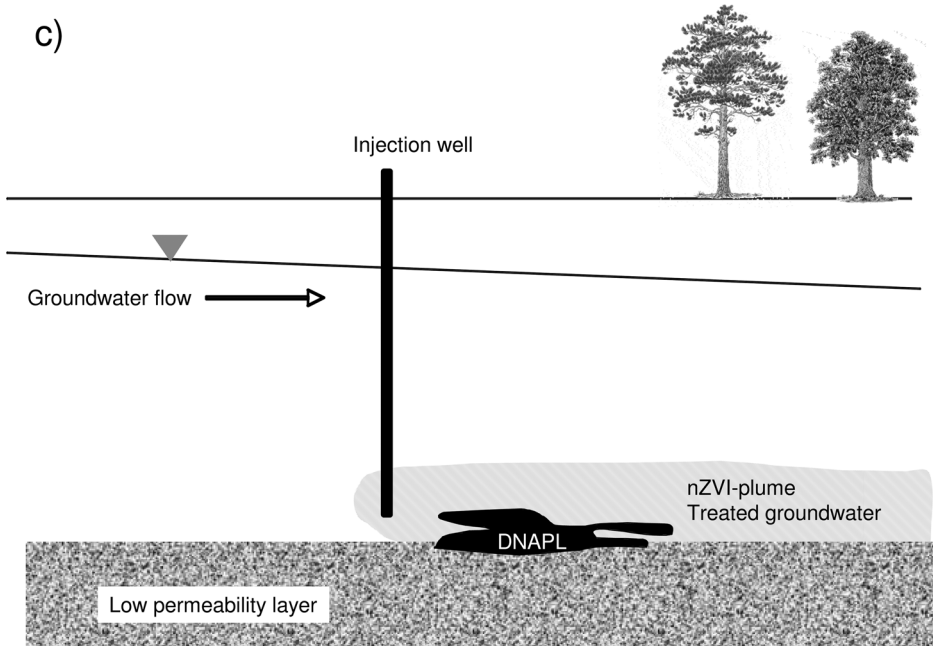


Figure 1.3 (continued)

1.5 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 1.3a). With nZVI, two possible techniques are used: immobile nZVI is injected to form a zone of iron particles adsorbed on the aquifer solids (Figure 1.3b) 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 (Figure 1.3c). 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 [112]. 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 [113]. To date approximately 30 projects are under way in which nZVI is used for actual site remediation [105].

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 [114, 115]. 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 [116]. nZVI has also been used to immobilize Cr(VI) in chromium ore processing residue [117].

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 [118], and in another, hydrophilic carbon or poly(acrylic acid) delivery vehicles were used [119]. Modified cellulose, sodium carboxymethylcellulose (CMC), was found to form highly dispersed nZVI [120] and also several polymers have been tested and found to be very effective [121]. 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- [121] or 2–10-fold was observed [121]. 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 [122].

1.6

Environmental Risks

1.6.1

Behavior in the Environment

The use of nanoparticles in environmental 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 [123], much less is known about the possible exposure of aquatic and terrestrial life to nanoparticles in water and soils [2]. 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. La^{3+}) [124]. Aggregation of CNTs added as a suspension to filtered pond water has been reported [125]. 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 [126, 127]. However, a recent study shows that humic and fulvic acids are able to solubilize CNTs under natural conditions and that stable suspensions are obtained [128].

Most nanoparticles in technical applications are functionalized and therefore studies using pristine nanoparticles may not be relevant for assessing the behavior 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.

1.6.2

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 [6, 7, 129–131]. The uptake of nanoparticles is size dependent [132, 133]. 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 [132]. 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 [134]. This was found both for inorganic nanoparticles such as TiO_2 [134–136], CeO_2 [137] and ZnO [136, 138] and for carbon-containing particles such as fullerenes [139–143] and CNTs [144]. 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 [136]. In copepods purified CNTs did not show any effect whereas unpurified CNTs with all their byproducts increased mortality [144]. 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 [145].

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 [137]. Nanosized ZnO was internalized by bacteria [138]. Nanoparticles that damage bacterial cell walls have been found to be internalized, whereas those without this activity were not taken up [146]. CNTs have been shown to be taken up by a unicellular protozoan [125] 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.

1.7

Conclusions

This chapter was intended to give an overview of the various aspects of nanotechnology and the environment, mainly looking at it from the side of applications rather than from the risk side. It should have become clear that nanotechnology in general

and nanoparticles in particular will have important impacts on various fields of environmental technology and engineering. However, we should always keep in mind that nanotechnology has a Janus face and that each positive and desired property of nanomaterials could be problematic under certain conditions and pose a risk to the environment. A careful weighing up of the opportunities and risks of nanotechnology with respect to their effects on the environment is therefore needed.

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