

Nanotechnological Treatment of Water and Its Impact on Biota- An Overview

Namita Bhardwaj

Assistant Professor, Dr. C.V. Raman University,
Kota, Bilaspur (C.G.) India.

ABSTRACT

There is the huge hope that nanotechnological applications and products will lead to a cleaner and healthier environment [1], maintaining and re-improving the quality of water, so that the Earth will be able to support human and other life. 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 [2]. On the other hand, the discussion about the potential adverse effects of nanoparticle has increased steadily in recent years and is a top priority in agencies all over the world. When nanoparticle 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 effect. This paper will give a general overview of potential environmental applications of nanotechnology and nanoparticle and will also give a short overview of the current knowledge about possible risks for the environment.

Keywords: Nanotechnology, Degradation, Catalysis, pollutant, Nanoparticles.

I INTRODUCTION

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

II TREATMENT OF WATER BY USING SORBENTS

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 nanoparticle may have advantages over conventional materials due the much larger surface area of nanoparticle on a mass basis. In addition, the unique structure and electronic properties of some nanoparticle can make them especially powerful adsorbents. Many materials have properties that are dependent on size [3].

Hematite particles with a diameter of 7 nm, for example, adsorbed Cu ions at lower pH values than particles of 25 or 88 nm diameters, indicating the uniqueness of surface reactivity for iron oxides particles with decreasing diameter [4]. However,

another study found that normalized to the surface area the nanoparticle had a lower adsorption capacity than bulk TiO₂ [5]. Several types of nanoparticle 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, but also natural nanosized clays 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 [6].

Chemically modified nanomaterials have also attracted a lot of attention, especially nanoporous materials due to their exceptionally high surface area [7]. 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 [8]. TiO₂ functionalized with ethylenediamine was, for example, tested for its ability to remove anionic metals from ground water.

CNTs have attracted a lot of attention as very powerful adsorbents for a wide variety of organic compounds from water. Examples include dioxin [9], 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. 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. 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. Unlike the case with fullerenes, no adsorption-desorption hysteresis was observed, indicating reversible adsorption [10].

Fullerenes have also been tested for adsorption of organic compounds. Adsorption depends to a great extent on the dispersion state of the C60, which are virtually insoluble in water. 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. Fullerenes are only weak sorbents for a wide variety of organic compounds (e.g. phenol)

III WATER TREATMENT THROUGH MAGNETIC NANOPARTICLE

Magnetic nanoparticle 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 [11]. 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 (Fe₃O₄), maghemite (γ-Fe₂O₃) and jacobite (MnFe₂O₄) nanoparticle for removal of chromium (VI) from wastewater. 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.

IV WATER TREATMENT BY NANOFILTRATION

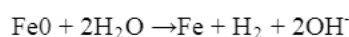
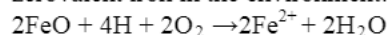
Nanofiltration membranes (NF membranes) are used in water treatment for drinking water production or wastewater treatment [12]. NF membranes are pressure-driven membranes with properties between those of reverse osmosis and ultrafiltration membranes and have pore sizes between 0.2 and 4 nm. NF membranes 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 [13], which was efficient for the removal of bacteria or hydrocarbons and that can easily be regenerated by ultrasonication or autoclaving.

V DEGRADATION OF POLLUTANTS BY NANOSIZED TiO₂

The semiconductor TiO₂ has been extensively studied for oxidative or reductive removal of organic pollutants. 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 or by doping with nitrogen. 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 [14] have been shown to be rapidly degraded. A special type of TiO₂ photocatalysts is Titania nanotube materials, which were shown to have superior activity [15].

VI WATER TREATMENT THROUGH ZEROVALENT IRON

Laboratory research has established that nanoscale metallic iron is very effective in destroying a wide variety of common contaminants such as chlorinated methane, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes, other polychlorinated hydrocarbons, pesticides and dyes [16]. The basis for the reaction is the corrosion of zerovalent iron in the environment:



Contaminants such as tetra chloroethane can readily accept the electrons from iron oxidation and be reduced to ethenes: However, nanoscale Zerovalent iron (nZVI) can reduce not only organic contaminants but also the inorganic anions nitrate, which is reduced to ammonia, per chlorate (plus chlorate or chlorite), which is reduced to chloride, selenate, arsenate, arsenite and chromate. nZVI is also efficient in removing dissolved metals from solution, e.g. Pb and Ni. The reaction rates for nZVI are at least 25–30 times faster and also the sorption capacity is much higher compared with granular iron. 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 [17].

The reaction rates for nZVI can be several orders of magnitude faster on a mass basis than for granular ZVI. 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. Surfacenormalized reaction rates for such materials were found to be up to 100 times faster than for bulk ZVI. The nanoscale iron particles can be produced either by a top-down approach (e.g. milling of iron filings) or by direct chemical synthesis. A common method for synthesis of iron nanoparticle is by reduction of an aqueous ferric solution by reducing agents such as sodium borohydride or sodium hypophosphite [18].

VII 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. 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. 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. To date approximately

VIII RISK FACTOR IN USE OF NANOPARTICLES FOR WATER TREATMENT

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, 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. 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 study shows that humic and fulvic acids are able to solubilize CNTs under natural conditions and that stable suspensions are obtained [19].

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.

IX 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. 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. 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 TiO₂ is considered having no health effects on aquatic organisms, this is clearly not the case for nanosized TiO₂. This was found both for inorganic nanoparticle such as TiO₂, CeO₂ 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 nanoparticle TiO₂ 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 byproducts increased mortality. 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 [20].

Nanosized CeO₂ 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. 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.

X CONCLUSION

This paper 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.

REFERENCES

- [1] T. Masciangioli, W. X. Zhang, Environ. Sci. Technol. 2003, 37, 102A. M. F. Hochella, Geo chim. Cosmo chim. Acta 2002, 66, 735.
- [2] 35A. S. Madden, M. F. Hochella, T. P. Luxton, Geochim. Cosmochim. Acta 2006, 70, 4095.
- [3] 36D. E. Giammar, C. J. Maus, L. Y. Xie, Environ. Eng. Sci. 2007, 24, 85.
- [4] 37S. Pacheco, J. Tapia, M. Medina, R. Rodriguez, J. Non-Cryst. Solids 2006, 352, 5475.
- [5] 38E. A. Deliyanni, E. N. Peleka, K. A. Matis, J. Hazard. Mater. 2007, 141, 176.
- [6] 39G. D. Yuan, L. H. Wu, Sci. Technol. Adv. Mater. 2007, 8, 60.
- [7] 40P. Liang, Q. Ding, F. Song, J. Sep. Sci. 2005, 28, 2339.
- [8] 41C. Lu, C. Liu, J. Chem. Technol. Biotechnol. 2006, 81, 1932.
- [9] Y. S. Chen, J. C. Crittenden, S. Hackney, L. Sutter, D. W. Hand, Environ. Sci. Technol. 2005, 39, 1201.
- [10] 93H. M. Zhang, X. Quan, S. Chen, H. M. Zhao, Environ. Sci. Technol. 2006, 40, 6104.
- [11] 94W. X. Zhang, J. Nanopart. Res. 2003, 5, 323.
- [12] 95K. Sohn, S. W. Kang, S. Ahn, M. Woo, S. K. Yang, Environ. Sci. Technol. 2006, 40, 5514.
- [13] 96Y. H. Liou, S. L. Lo, W. H. Kuan, C. J. Lin, S. C. Weng, Water Res. 2006, 40, 2485.
- [14] 97J. S. Cao, D. Elliott, W. X. Zhang, J. Nanopart. Res. 2005, 7, 499.
- [15] 98K. Mondal, G. Jegadeesan, S. B. Lalvani, Ind. Eng. Chem. Res. 2004, 43, 4922.
- [16] 99S. R. Kanel, J. M. Greneche, H. Choi, Environ. Sci. Technol. 2006, 40, 2045.
- [17] 100G. Jegadeesan, K. Mondal, S. B. Lalvani, Environ. Prog. 2005, 24, 289.
- [18] 101S. R. Kanel, B. Manning, L. Charlet, H. Choi, Environ. Sci. Technol. 2005, 39, 1291.
- [19] 102S. M. Ponder, J. G. Darab, T. E. Mallouk, Environ. Sci. Technol. 2000, 34, 2564.
- [20] 103B. A. Manning, J. R. Kiser, H. Kwon, S. R. Kanel, Environ. Sci. Technol. 2007, 41, 586.