

Tiny Nanotechnology Tools for Water Remediation

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Abstract

Nanotechnology is being involved in synthesis, characterization & applications of engineered devices and structures on the scale of nanometer, a point where alteration in bulk material properties arises due to quantum mechanical effects. Green Nanotechnology involves developing products that benefit the environment either directly or indirectly and offers the potential of novel nanomaterials for the treatment of surface water, groundwater and wastewater contaminated by toxic metal ions, organic and inorganic solutes and microorganisms. Due to their unique activity nanoscale particles increases the efficiency to absorb the contaminants and is comparatively inexpensive compared to traditional precipitation and filtration methods. The paper highlights that nanotechnology offers great promise for delivering new and improved remediation technologies to clean up the environment.

Keywords: Green Nanotechnology, Nanomaterial, Nanofiltration, Water Remediation.

Introduction

Green nanotechnology is considered to play a key role in the shaping of current environmental engineering and science & refers to the use of nanotechnology to enhance the environmental sustainability, minimize potential environmental and human health risks associated with the pollution and contamination by using nanotechnology products, and to encourage replacement of existing products with new nano-products that are more environmentally friendly throughout their lifecycle.

The nanoscale has stimulated the development and use of novel and cost effective technologies for remediation, pollution detection, pollution monitoring and remediation of pollutants. Some nano-scaled particles have properties that make them very suitable for treating water. They often have enhanced catalytic properties; due to their nanosize or their modification at the nanoscale. Nanocatalysts can chemically degrade pollutants including those that current technologies treat inefficiently and at great cost. For example, nanotitanium dioxide is a more effective catalyst than microscale titanium dioxide and can be used to treat water by chemically degrading organic pollutants that are harmful to the environment. Nanosilver also is used to disinfect drinking water. Both are successful adaptations to the nanoscale to serve a beneficial use (<http://www.nanowerk.com/spotlight/spotid=4662.php>).

A prime water resource application of nanotechnology is to further improve membrane technology. Nanofiltration membranes are already in use removing dissolved salts and micro pollutants as well softening water and treating wastewater. Meanwhile new classes of nanoporous materials are in the works with pores sufficiently small to filter out the tiniest micro-organism. Also, research is looking at the use of magnetic nanoparticles to bind with contaminants that are then removed by a magnet. Having large surface areas relative to their volume, magnetic nanoparticles readily bind with water-borne contaminants such as arsenic or oil. Another promising application of nanotechnology is its use to address water problems in developing countries by helping to resolve technical challenges to removing water contaminants. Nanotechnology holds promise for more varied, affordable, effective water treatment methods that are more adaptable to the needs of developing countries (<http://webarchive.nationalarchives.gov.uk>).

Nanoremediation Process

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. With respect to remediation of environmental contaminants, the range of nanotechnology applications mirrors the spectrum of non-nano strategies for contaminant remediation (B. Karn *et al.*, 2009). Two of the major distinctions that define types of conventional remediation technologies also apply

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to nanotechnologies for remediation: adsorptive versus reactive and in situ versus ex situ. Adsorptive remediation technologies remove contaminants (especially metals) by sequestration, whereas reactive technologies affect degradation of contaminants. In situ technologies involve treatment of contaminants in place, whereas ex situ refers to treatment after removing the contaminated material to a more convenient location (e.g. pumping contaminated groundwater to the surface and treatment in aboveground reactors) (Paul G. Tratnyek *et al.*,2006).

Ex-Situ Nanotechnology

A prominent example of a nanotechnology for contaminant remediation by adsorption is known as self-assembled monolayers on mesoporous supports (SAMMS) (Fryxell, G. E al). SAMMS are created by self-assembly of a monolayer of functionalized surfactants onto mesoporous ceramic supports, resulting in very high surface areas (~1000 m²/g) with adsorptive properties that can be tuned to target contaminants such as mercury, chromate, arsenate, and selenite. Dendritic polymers are another type of nanostructured material that has the potential for use in remediation. Recent examples of this approach include dendrimer-enhanced ultrafiltration to remove Cu (II) from water (New York, NY,2004) and soil washing to remove Pb (II) (Diallo, M. S., *et al.*,2005) contamination. Nanotechnologies that affect remediation by contaminant degradation – rather than adsorption – are particularly attractive for organic contaminants. A well-established approach for remediation of organic contaminants is photo-oxidation catalyzed by metal oxide nanoparticle such as TiO₂, and the potential benefits of quantum-sized (< ~10 nm) photocatalysts have long been recognized for contaminant degradation applications. Another method is based on injection of FeO nanoparticles into the groundwater through application wells. This technology is environmentally friendly and cost-effective compared to methods like pump & treat or gas extraction (venting) (Xu, Y, *et al.*,2006).

In- Situ Nanotechnology

In situ degradation of contaminants, when feasible, is often preferred over other approaches because it has the potential to be more cost effective. However, in situ remediation requires delivery of the treatment to the contamination at on site position and this has proven to be a major obstacle to expanded development of in situ remediation technologies. With respect to this issue, nanotechnology has special relevance because of the potential for injecting nanosized (reactive or adsorptive) particles into contaminated porous media such as soils, sediments, and aquifers (Paul G. Tratnyek *et al.*,2006). Although a variety of types of nanoparticle might be applicable to in situ remediation (e.g. nonionic amphiphilic polyurethane or alumina-supported noble metals by far the greatest interest is currently in nanoparticles that contain nZVI. (Hoffmann, M. R., *et al.*,1995). A common type of in situ or below-ground

remediation method used for cleaning up contaminated groundwater is the permeable reactive barrier (PRB). PRBs are treatment zones composed of materials that 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 (C.S. Rajan *et al.*,2011).

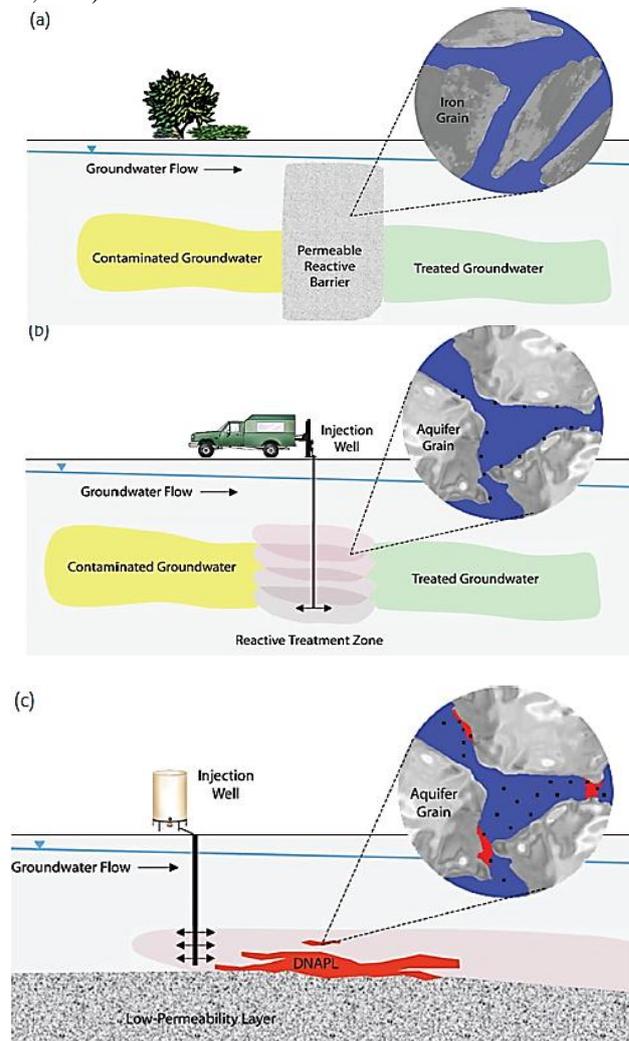


Fig.1 Three approaches to application of Fe particles for groundwater remediation: (a) a conventional permeable reactive barrier made with millimeter-sized construction-grade granular Fe; (b) a reactive treatment zone formed by sequential injection of nanosized Fe to form overlapping zones of particles adsorbed to the grains of native aquifer material; and (c) treatment of non-aqueous phase liquid contamination by injection of mobile nanoparticles. In (b) and (c), nanoparticles are represented by black dots and zones that are affected by nanoparticles are represented as pink plumes (Xu, Y, *et al.*,2006).

Nanomaterials as Remediation Agent

Titanium Dioxide (TiO₂) Based Nanoparticles

Titanium dioxide (TiO₂) is one of the popular materials used in various applications because of its semiconducting, photocatalytic, energy converting,

electronic and gas sensing properties (Tungittiplakorn, *et al*,2005). Many researchers are focused on TiO₂ nanoparticle and its application as a photocatalyst in water treatment. Nanoparticles that are activated by light, such as the large band-gap semiconductors titanium dioxide (TiO₂) and zinc oxide (ZnO), are frequently studied for their ability to remove organic contaminants from various media. These nanoparticles have the advantages of readily available, inexpensive, and low toxicity. The semiconducting property of TiO₂ is necessary for the removal of different organic pollutants through excitation of TiO₂ semiconductor with a light energy greater than its band gap, which could generate electron hole pairs. These may be exploited in different reduction processes at the semiconductor/solution interface. It is known that, the semiconducting properties of TiO₂ materials is responsible for the removal of various organic pollutants, but the rapid recombination of photo-generated electron hole pairs and the non-selectivity of the system are the main problems that limit the application of photocatalysis processes (U. Diebold, *et al*,2003).

It was suggested that, replacing adsorbed solvent molecules and ions by chelating agents, i.e. surface modification, changes the energetic situation of surface states and considerably alters the chemistry, which is taking place at the surface of titanium dioxide (TiO₂). The effect of surface modification of nanocrystal TiO₂ with specific chelating agents such as arginine, lauryl sulfate, and salicylic acid has been reported. Paek *et al*. (O.V. Makarova, *et al*,2000), fabricated mesoporous photocatalysts with delaminated structure with high surface area which are able to provide simple accessibility and more chances for guest molecules and light to receive by the active sites. The exfoliated layered Titanate in aqueous solution was reassembled in the presence of Anatase TiO₂ nanosol particles to make a large number of mesopores and eventually a large surface area TiO₂ photocatalysts. Another approach for enhancing photocatalytic activity of TiO₂ nanoparticle is its surface modification by metals like gold and platinum. The reason is that the presence of metals helps to keep the electrons and holes from recombining in the semiconductor and thereby increasing the efficiency of photocatalysis.

In recent years, the technology of ultrasonic degradation has been studied and extensively used to treat some organic pollutants. The ultrasound with low power was employed as an irradiation source to make heat-treated TiO₂ powder. This method was used for decomposition of parathion with the nanometer Rutile titanium dioxide (TiO₂) powder as the sonocatalyst after treatment of high-temperature activation (S.M. Paek, *et al*,2006).

Nanoscale Iron Nanoparticle (nZVI)

Nanoparticles could provide very high flexibility for both in situ and ex situ remediations. For example, nanoparticles are easily deployed in ex situ slurry reactors for the treatment of contaminated soils, sediments, and solid wastes. Alternatively, they can be anchored onto a

solid matrix such as carbon, zeolite, or membrane for enhanced treatment of water, wastewater, or gaseous process streams. Direct subsurface injection of nanoscale iron particles, whether under gravity-feed or pressurized conditions, has already been shown to effectively degrade chlorinated organics. Iron nanoparticles are an attractive component for nanoremediation.

Iron at the nanoscale was synthesized from Fe (II) and Fe (III), using borohydride as the reductant (J. Wang, *et al*,2006). 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. nZVI are generally preferred for nanoremediation because of large surface area of nanoparticles and more number of reactive sites than micro-sized particles and it possess dual properties of adsorption and reduction (X. Q. Li, *et al*,2006). Zero-valent iron removes aqueous contaminants by reductive dechlorination, in the case of chlorinated solvents, or by reducing to an insoluble form, in the case of aqueous metal ions. Iron also undergoes "Redox" reactions with dissolved oxygen and water.

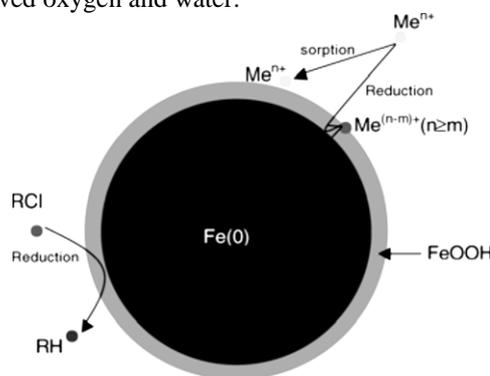


Fig.2 Schematic diagram of Zero-valent Iron (X. Q. Li, *et al*,2006)

Nanoclay

Nanoclays are natural nanomaterials that occur in the clay fraction of soil, among which montmorillonite and allophane are the most important species. Montmorillonite is a crystalline hydrous phyllosilicate (layer silicate). Recently Organically modified montmorillonites or organoclays are develop in the form of polymer-clay nanocomposite. Clays are layered minerals with space in between the layers where they can adsorb positive and negative ions and water molecules. Clays undergo exchange interactions of adsorbed ions with the outside too. Although clays are very useful for many applications, they have one main disadvantage i.e. lack of permanent porosity. To overcome this problem, researchers have been looking for a way to prop and support the clay layers with molecular pillars. Most of the clays can swell and thus increase the space in between their layers to accommodate the adsorbed water and ionic species. The composite structures, known as pillared clay, could stabilize TiO₂

particles and give access of different molecules to the surface of TiO₂ crystals. Ooka *et al.* (S. M. Ponder *et al.*, 2000) prepared four kinds of TiO₂ pillared clays from Montmorillonite, saponite, fluorine hectorite and fluorine mica serves as nanoclay for water remediation. They have tested the surface hydrophobicities and performances of clays in adsorption-photocatalytic decomposition & It was found that surface hydrophobicity can be enhanced by the presence of polyethylene oxide (PEO) surfactants (C. Ooka *et al.*, 2004). It resulted in forming larger precursors of TiO₂ nanoparticles and condensing them on the fragmented pieces of the silicate. Introducing PEO surfactants into the synthesis process significantly enhanced the porosity and surface area of the composite solid.

Nanoclays found potential application in petroleum industry for removing hydrocarbons from refinery process water and also been tested for treating ground and surface water and for other toxic organic chemicals from pharmaceuticals and pesticides industries. Nanomer® and Cloisite® are the popular nanoclays available in the market. Nanomer® is a nanoclay product developed by Nanocor/AMCOL International Corporation, and Cloisite® nanoclays are produced by Southern Clay Products, Inc., of Texas, USA.

Nanotubes

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). Carbon nanotubes act like as nanosorbent, and hold tremendous potential for applications because of their unique properties, such as strong antimicrobial activity, higher water flux than other porous materials of comparable size, tunable pore size and surface chemistry, high electrical & thermal conductivity, special adsorption properties and their ability to be attached to a functional group to increase the affinity towards the target molecule (H.Y. Zhu *et al.*, 2005) makes CNTs as a promising material for water remediation. Some studies showed that unfunctionalized 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 re-use, are functionalized with various functional groups (e.g. hydroxyl, carboxyl, amines, etc.) to increase their water solubility and biocompatibility. To increase the absorption capacity of MWCNTs, it is oxidized with nitric acid, this creates reactive sites in either on tip of nanotube or either by creating defects site on the side wall of the tube, resulting to which a higher level of adsorption was achieved due to high reactivity.

The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface have a strong interaction (In most cases, several driving forces act simultaneously, including hydrophobic effect, π - π interaction, π - π electron-donor-

acceptor interaction, electrostatic interaction, and hydrogen bonding) with other molecules or atoms, which make CNTs a promising adsorbent material substituted for activated carbon in many ways. They are utilized for the removal of heavy metals like Cr³⁺, Pb²⁺, and Zn²⁺ (N. Savage *et al.*, 2005), metalloids such as arsenic compounds, organics, biological impurities, and removing many kinds of organic and inorganic pollutants such as dioxin and volatile organic compounds (G. P. Rao *et al.*, 2007).

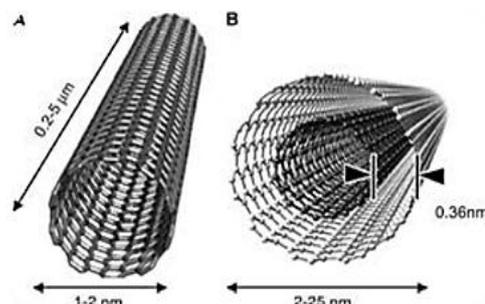


Fig. 3 Schematic Representation of Single walled Carbon Nanotube and Multi walled Carbon Nanotube (H.Y. Zhu *et al.*, 2005)

Magnetic Nanoparticles

One of the major applications of magnetic particles is in the area of magnetic separation. In this case, it is possible to separate a specific substance from a mixture of different other substances. The separation time is one of the important parameters in the magnetic separation method. Separations using magnetic gradients, such as “High Magnetic Gradient Separation” (HGMS), are now widely used in the fields of medicine, diagnostics and catalysis. In HGMS, a liquid phase containing magnetic particles is passed through a matrix of wires that are magnetized by applying a magnetic field (X. Peng *et al.*, 2005). The particles are held onto the wires and at the conditions that the field is cut off, they can be released. If these particles are used in order to be fixed to specific molecules, the latter can be isolated from waste water or slurries. It is well known that Cr (VI) is toxic to animals and plants, while Cr (III) is considered to be less harmful. Hu *et al.* (A.F. Ngomsik *et al.*, 2005) developed an innovative process combining nanoparticle adsorption and magnetic separation for the removal and recovery of Cr (VI) from wastewater. They produced ten nanometer modified MnFe₂O₄ nanoparticles as a new adsorbent using a co-precipitation way followed by a surface redox reaction. The results exhibited that surface-modified MnFe₂O₄ nanoparticles were efficient adsorbents for the rapid removal of Cr (VI) from aqueous solutions.

Nanomembrane

A membrane is a semi-permeable and selective barrier between two phases (retentive and permeate) through which only selected chemical species may diffuse. Membrane filtration is frequently employed for the separation of dissolved solutes in a fluid or the separation

of a gas mixture (J. Hu *et al*,2005). Historically, membrane technology has had wide application in wastewater treatment and desalination via reverse osmosis. In this method, a pressure difference across a membrane is employed to overcome the osmotic pressure gradient. The smaller water molecules are literally pushed through the membrane while the large solute species are retained behind (M. Alborzfar *et al*,1998). Among different classes of membranes, reverse osmosis (RO) filtration is a well-known process in the desalination of seawater and ultrafiltration (UF) is a well-established process in the fractionation of Natural Organic Matter (NOM).

Nanofiltration (NF) is a process with membrane permeability between RO and UF. Another membrane design is emulsion liquid membrane (ELM). An ELM is formed by first encapsulating an aqueous "receiving" or strip phase within a hydrophobic membrane liquid. This emulsion is then further dispersed within the continuous aqueous feed phase. This technology was used for the extraction of phenols, removal of heavy metal cations such as zinc, cadmium, chromium, copper, lead, palladium and mercury from wastewater and also removal of alkali metal cations such as Na⁺, K⁺, Li⁺ and Cs⁺, radioactive fission products, such as Cs-137, Sr-90, Ce-139 and Eu-152 and anions, such as chlorides, sulfate, phosphate and chromate (M. Alborzfar *et al*,1998). Ultrafiltration has been applied in most membrane separation processes. The hydrophilicity of the membrane and its porous structure play important roles in these processes. An appropriate porous membrane must have high permeability, good hydrophilicity and excellent chemical resistance to the feed streams. In order to obtain high permeability, membranes should have high surface porosity, and good pore structure. Polyvinylidene fluoride (PVDF) is a material that can form such asymmetric membranes, since it is thermally stable and resistant to corrosion by most chemicals and organic compounds. PVDF-based membranes exhibit outstanding anti-oxidation activities, strong thermal and hydrolytic stabilities and good mechanical properties (S.E. Kentish *et al*,1998).

Conclusion

There is a growing threat of water-borne infectious diseases, especially in the developing world. This threat is rapidly being exacerbated by demographic explosion, a global trend towards urbanization without adequate infrastructure to provide safe drinking water, increased water demand by agriculture that draws more and more of the potable water supply, and emerging pollutants and antibiotic-resistant pathogens that contaminate our water resources. The aim of this review is to give an overall perspective of the use of nanoparticles to solve potential issues such as treatment of contaminated water for drinking and reuse more effectively, than through conventional means. Nanoremediation has the potential to

clean-up large contaminated sites in-situ, reducing clean up time and eliminating the need for removal of contaminants and hence reducing the contaminant concentration to near zero. The success of the technique in field conditions is a factor of interdisciplinary work that is involved. The collaboration of chemistry, material science and geology is one of the key challenges of this research.

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