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Review Paper

Nanotechnology: Remediation Technologies to clean up the Environmental pollutants

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Abstract

Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling the shape and size at the nanometer scale; Environmental nanotechnology (E-nano) products can be developed for a wide array of urgently needed environmental remediation. The nanoparticles / nanostructures made by mechanical and /or microbial action with fundamental building blocks are among the smallest human made objects and exhibit novel physical, chemical and biological properties; which has wider application for pollution prevention, detection, monitoring and remediation of pollutants. Environmental nanotechnology would be the new innovation to remediate and treat the contaminants to acceptable levels. Environmental scientists and engineers are already working with nanoscale structure to manipulate matter of the atomic or molecular scale that has cut across discipline of chemistry, physics, biology, and even engineering. The paper highlights that-nanotechnology offers great promise for delivering new and improved remediation technologies to clean up the environment.

Key words: Nanotechnology, environment, remediation, nanomaterials, nanostructure, environmental nanotechnology.

Introduction

Environmental nanotechnology is considered to play a key role in the shaping of current environmental engineering and science. The nanoscale has stimulated the development and use of noval and cost effective technologies for remediation, pollution detection, pollution monitoring and remediation of pollutants[1]. The nanostructured materials are used as biosensors for monitoring and detection of different compounds[2]. The use of nanoparticals may have advantage over conventional method due the much larger surface area of nanoparticles on a mass basis. The unique structure and electronic properties of some nanoparticles are adsorbent of pollutants. Many nano materials have properties of adsorbents, depend on size. Chemically modified nanamaterial have also attracted a lot of attention especially nanoporous materials due to their exceptionally high surface area[3]. The particle size of such materials is, however, not in the nano range but normally 10-100um. .Another option is to modify chemically the nanoparticle itself[4]. TiO2 functionalized with ethylenediamine as such, tested for its ability to remove anionic metals from contaminated groundwater[5].

The most common environmental remediation techniques traditionally used to treat large volumes of water intended for municipal water supplies include carbon adsorption, air stripping, oxidation through ozonation or chlorination and incineration, ultrafilteration and sedimentation[6,7]. These approaches are generally used for large scale pollutant removal. On a smaller scale, use of activated carbon adsorbents to remove organic contaminants at the point -of-use is being practiced.

Scientific and technical methods to mitigate environmental pollution rely on many approaches and vary for the cases of soil, water and air purification. The remediation approach chosen depends on the complexity and nature of the contaminated media and economic costs of the treatment. Environmental remediation plays a pivotal role in the decision to employ a particular technology[8].

Nanoparticles-Synthesis and Characterization

Research concerning nanocluster optical properties and photocatalysis has focused on a limited number of readily available materials such as TiO2, ZnO or ZnS. A nanoparticles is a microscopic particles whose size is measured in nanometers (nm). It defined as a particle with atleast one dimension<100 nm. Nanotech is expected to bring a fundamental change in manufacturing in the next few years, and will have an enormous impact on Environmental sciences for detection, monitoring and remediation of pollutants as well as life sciences including dry delivery, diagnostics, nutraceuticals and production of biomaterials Engineered nanoparticles NP (<100nm) are an important tool to realize a number of these applications. Some of the salient features are: Particles less than 100nm, Small size, High surface area, Easy to suspend in liquids, Particles smaller than 200nm can be easily sterilized by filteration with a 0.22 micron filter, Deep access to cells and organelles, Variable optical and magnetic properties

Synthesis

Milling of Large particles: for many particles a limit in grindability can be reached, where subject to further grinding, no decrease in particle size is observed. Hence, it is energy intensive to go down to nanoparticle size range. Most of the size reduction operations utilize high shear wet milling for production of nanoparticles. Typical operation for wet milling may require many hours to a few days. However one has to be aware of contamination problem due to milling media.

Precipitation of nanoparticles: nanomaterial is dissolved in solvent to achieve molecular solution. Then the nanoparticles is obtained either by removing the solvent rapidly or by mixing an antisolvent (non solvent) to the solution reducing its solubility strength. Initially, a nuclei is formed, which grow because of condentation and coagulation, thus giving final particle. If the desolubilization is slow then sticky nuclei or particles are formed that have a tendency of agglomeration giving large size particles

SCF Technology: Following methods are used utilizing liquid carbon di oxide: Rapid expansion of super critical solution for particles formation (RESS), RESS with co-solvent for nanoparticles (RESS-SC), Supercritical anti solvent process (RAS), SAS-EM process produces nanoparticles of controllable size, SCF exposure of pressure-quench technique can be employed to form porous structures or inclusion complexes and to remove residual solvents in pharmaceutical particulate systems, Safety and health issues are to be looked into with SCF tech.

Nanoparticles from emulsions: Polymers or protein based nanoparticles can be produced by emulsification solvent evaporation process. With the recent development in the homogenization, very fine emulsions can be created that can yield nanoparticles. The size, zeta potential, hydrophilicity and the loading of the nanoparticles can be controlled by various parameters including the amounts of emulsifier and polymer, the intensity and duration of homogenization and the particle hardening profile. Hardening of polymer particles is achieved by solvent removal, whereas hardening of proteins such as albumin can be done by cross linking. The single emulsion method is suitable for hydrophobic methods, whereas double emulsion is needed for hydrophilic method. Both the processes are relatively simple and have been widely used for a variety of nanoparticles formation from emulsion.

Biogenic synthesis of nanoparticles using microorganisms: Numerous microorganisms are reported to biosynthesize gold and silver nanoparticles by NADPH-dependent reductase enzymes that reduce metal salts to nanoparticles through electron shuttle enzymatic metal reduction process table 1.

Characterization of Nanoparticles

Following methods are used to characterize the nanoparticles

Measurement of size: Microscopy- SEM, Optical Micriscopy, Atomic Force Microscopy (AFM), Single Particle Optical Sensing, DLS (Dynamic Light Scattering), NMR, DSC, X-raydiffraction, Turbidimetry, Filteration, Field flow fraction, Hydrophobic interaction chromatography, Electrophoresis, Isopygnic centrifugation, Zeta potential Size distribution can be checked by Coulter counter or other instruments like Malven Particle Analyzer.

Characterization: Characterization of nanoparticles goes hand in hand with their design and production. It is important to advance the appropriate analytical science as it is to progress manufacturing technology: i) deriving information from concentrated system when quantities of sample are present. ii) surface characterization such as charge and morphology both in solid and wet state. iii) Improving ability to characterize nanoparticles in the solid, state, particularly when isolated in a matrix material as is with spray drying or liophilization. iv) PAT Process Analytical Technology) and it is deserves research.

Many analytical techniques available today that can provide data on nano engineered materials. These techniques are accepted and well established, although their application to new materials may not be widely known. Development of analytical tools specifically for nanotechnology is underway, yet used a new measurement with a new technology may result in many question or unexpected variables in contrast to trusted data with considerable historical context. The costs of instruments development are also extremely high in term of time and capital. The use of proven analytical tools that include TEM, SEM, XPS, XRD, Auger and TOF-SIMS to characterize products of nano andmicro technology are reported. A full understanding of product behaviour and characteristic throughout the manufacturing process and subsequent lifetime of the product is required for both production and safety reasons.

Nanotechnology: Environmental Applications

The pollution detection nanostructures and/or devices are being used for a variety of environmental applications. The nanopstructure material developed for detection of pollution monitoring and remediation is highlighted in table 2.

Table-1
Biogenic synthesis of gold and silver nanoparticles by various microorganisms

Microbe	Location	Size range (nm)
Silver (Ag) nanoparticles		
Bacteria		
Pseudomonas stutzeri	Intracellular	200
Morganella sp.	Extracellular	20-30
Lactobacillus strains	Intracellular	
Plectonema boryanum (Cyanobacteria)	Intracellular	1-10,1-100
Klebsiella pneumonia	Extracellular	5-32
Stenotrophomonas maltophila		
Yeast		
MKY3	Extracellular	2-5
Fungi		
Phoma sp.3.2883	Extracellular	71.06-74.46
Verticillium	Intracellular	25+- 12
Aspergillus fumigates	Extracellular	5-25
Trichoderm asperellum	Extracellular	13-18
Phaenerochaete chrysosoporium	Extracellular	50-200
Gold (Au) Nanoparticles		
Bacteria		
Lactobacillus strains	Intracellular	-
Shewanella alga	Intracellular, pH 7	10-20
Extracellular,pH1		1-50
Escherichia coli DH5α	Intracellular	25-33
Thermomonospora sp.	Extracellular	8
Rhodococcus sp.	Intracellular	5-15
Fungi		
Fusarium oxysporum	Extracellular	20-40
Algae		
Sargassum wightii	Extracellular	8-12
Chlorella vulgaris	-	9-20

Table-2
Pollution Detection and sensing- nanostructure material

Nanostructure material	Function
Silver nanoparticle array membranes	Water quality monitoring
Carbon nanotubes (CNTs)	Electrochemical sensors
CNTs as a building block	Exposure to gases such as NO2, NH3 or O, the electrical resistance of CNTs changes dramatically, induced by charge transfer with the gas molecules or due to physical adsorption
CNTs with enzymes	Establish 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
CNTs sensors	developed for glucose, ethanon, sulphide and sequence- specific DNA analysis
Magnetic nanoparticles coated with antibodies	Useful for the rapid dection of bacteria in complex matrices

Sensors: The characterization of environmental sensors is based primarily on the physics involved and their operating mechanisms. For example, chromatography relies on the separation of complex mixtures by percolation through a selectively adsorbing medium with subsequent detection of compounds of interest. Electrochemical sensors include sensors that detect signal changes (e.g. resistance) caused by an electric current being passed through electrodes that interact with chemicals. Mass sensors rely on disturbances and changes to the mass of the surface of the sensors during interaction with chemicals. Optical sensors dectet changes in visible light or other electromagenetic waves during interactions with chemicals. Within each of these categories, some sensors may exhibit characteristic that overlap with those of other categories. For example, some mass sensors may rely on electrical excitation or optical settings.

Types of sensors: Biosensors, Electrochemical Sensors, Mass Sensors, Optical Sensors, Gas Sensors

Nanotechnology and pollution control: Pollution results from resource production and consumption, which in their current state are very wasteful. Nanofabrication holds much potential for effective pollution control, but it currently faces many problems that prevent it from mass commercialization-particularly its high cost. Nanotechnology plays a vital role in air and water pollution control.

Air Pollution: Air pollution can be remediated using nanotechnology in several ways. One is through the use of nano-catalysts with increased surface area for gaseous reactions. Catalysts work by speeding up chemical reactions that transform harmful vapors from cars and industrial plants into harmless gases. Catalysts currently in use include a nanofiber catalyst made of manganese oxide that removes volatile organic compounds from industrial smokestacks. Other methods are still in development.

Another approach uses nanostructured membranes that have pores small enough to separate methane or carbon dioxide from exhaust (Jhu etal 2008). John Zhu of the University of Queensland is researching carbon nanotubes (CNT) for trapping greenhouse gas emissions caused by coal mining and power generation. CNT can trap gases up to a hundred times faster than other methods, allowing integration into large-scale industrial plants and power stations. This new technology both processes and separates large volumes of gas effectively, unlike conventional membranes that can only do one or the other effectively.

Water Pollution: As with air pollution, harmful pollutants in water can be converted into harmless chemicals through chemical reactions. Trichloroethene, a dangerous pollutant commonly found in industrial wastewater, can be catalyzed and treated by nanoparticles. Studies have shown that these "materials should be highly suitable as hydrodehalogenation and reduction catalysts for the remediation of various organic and inorganic groundwater contaminants"[9].

Nanotechnology eases the water cleansing process because inserting nanoparticles into underground water sources is cheaper and more efficient than pumping water for treatment. The deionization method of using nano-sized fibers as electrodes is not only cheaper, but also more energy efficient. Traditional water filtering systems use semi-permeable membranes for electrodialysis or reverse osmosis. Decreasing the pore size of the membrane to the nanometer range would increase the selectivity of the molecules allowed to pass through. Membranes that can even filter out viruses are now available.

Also widely used in separation, purification, and decontamination processes are ion exchange resins, which are organic polymer substrate with nano-sized pores on the surface where ions are trapped and exchanged for other ions[10]. Ion exchange resins are mostly used for water softening and water purification. In water, poisonous elements like heavy metals are replaced by sodium or potassium. However, ion exchange resins are easily damaged or contaminated by iron, organic matter, bacteria, and chlorine.

Recent developments of nano-wires made of potassium manganese oxide can clean up oil and other organic pollutants while making oil recovery possible[11]. These nanowires form a mesh that absorbs up to twenty times its weight in hydrophobic liquids while rejecting water with its water repelling coating. Since the potassium manganese oxide is very stable even at high temperatures, the oil can be boiled off the nanowires and both the oil and the nanowires can then be reused[11].

Removal of Pollutant by Adsorbant: The nanoparticles have been investigated as adsorbant for removal of organic and inorganic contaminants. The nano size metal oxides and natural nanosized clays have been investigated for the removal of metals and inorganic ions. Besides oxidized and hydrooxylated CNTs are good absorbers for metals such as Cu, Ni, Cd and Pb. Pristine multiwalled CNTs has been found to be stronger adsorber materials for organometallic compounds.

CNTs has also been been found as a powerful adsorbant for a wide variety of organic compounds from aquatic environment, which include: dioxin, polynuclear aromatic hydrocarbons (PAHs), DDT and its metabolites, PBDEs, chlorobenzenes and chlorophenoles, trihalomethanes, bisphenol A and nonyphenol, phthalate easters, dyes, pesticides, and herbicides such as sulfuron derivatives, atrazine and dicamba. Nanoporous polymers which has cross linked and copolymerized with fuctionalized CNTs have been demonstrated for a high sorption capacity for a variety of organic compounds such as p- nitrophenol and trichloroethylene.

Degradation of Pollutants Using Semiconductors-TiO2 and ZnO: The semiconductor-TiO2 nanoparticles have been extensively studied for oxidative transformation of organic and inorganic contaminants[4,12]. There are now used in a variety of products such as self-cleaning glass, disinfectant tiles, and filters for air purification[13]. TiO2 electrodes have the capacity to determine the chemical oxygen demand of water and are used as sensors for monitoring contaminated water[14]. TiO2 nanoparticles can be immobilized on different supports which are used for the solar detoxification of water and air. These engineered nanoparticles are known for their interaction with organic, inorganic and biological contaminants such as heavy metals, organochlorine pesticide, arsenic and phosphates in water, induced by ultravilot light. TiO2 leads to pollutant degradation through two everyday chemical reactions: reduction and oxidation. Once excited by UV and TiO2 electron-hole pairs develop. These electrons have sufficient oxidizing potential to oxidize pollutants in wastewater[15]. Interestingly, the combination of UV and TiO2 generates bactericidal activity, which attacks several types of bacteria. This approach thus provides a comprehensive treatment procedure since chemical species and pathogens can be removed from wastewater simultaneously.

Other nanoparticles with semiconducting properties, such as ZnO,ZnS,F2O3 and CdS can be used for photocatalysis oxidation. TiO2 is biologically and chemically inert and has demonstrated great resistance to corrosion along with the capacity to be used repetitively without substantial loss of catalytic activity and it is therefore inexpensive to use. In light of these properties, TiO2, is potentially more attractive for environmental applications than other oxidative nanoparticles[16]. However, TiO2 requires ultraviolet light and consequently, is effective only for treatment of transparent wastewater. Several research groups have attempted to overcome this limitation by extending the nanoparticle excitation into visible light with the doping of TiO2 with transition metal ions or sensitizing dye such as Ru (II) polypyridyl complex, or investigated an approach involving a tube reactor production based on hollow glass tubes[17]. The tubes are extremely coated with TiO2 and UV-Light passes through the hollow tubes. Preliminary results suggested that combining ultrasound processes such as sonolysis and photocatalysis improves pollutant oxidation and could be an effective approach. Several pilot projects are under way to evaluate the potential of solar reactors to generate the energy required for TiO2 excitation and detoxification of polluted water. If these attempts are successful sunlight could play an economic and ecologically part in the treatment of wastewater.

Unlike TiO2, semiconductor nanoparticles such ZnO are able to emit strongly in the visible region, and the visible emissions of ZnO are usually very sensitive to hole scavengers such as phenols or iodide ions[18]. ZnO particles thus seem good candidates for use as sensors for chemical compounds. It has been claimed that sensor system based on ZnO could reach a detection sensitivity of 1ppm. Furthermore, ZnO has the ability to induce contaminant degradation under ultraviolet light[17]. Consequently, use of ZnO can be considered as a promising way to simultaneously sense and destroy toxic chemicals. It has been reported that nanostructured ZnO films could simultaneously detect and degrade organic compounds in water. Such a catalyst system is useful to induce contaminant degradation where the system senses a targeted molecule, thus avoiding destruction of inoffensive molecules present in the environment.

Degradation of Pollutants Using Iron nanoparticles: 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 etenes, chlorinated benzenes, other polychlorinated hydrocarbons, pesticides and dyes[19]. The basis for the reaction is the corrosion of zerovalent iron in the environment. Contaminants such as tetrachloroethene can readly accept the electros from iron oxidation and be reduced to ethane.

However, nanoscale zerovalent iron (nZVI) can reduce not only organic contaminants but also the inorganic anions nitrate, which is reduced to ammonia[20,21] perchlorate (plus chlorate or chlorite) and then reduced to chloride[22], selenate[23], arsenate[24], arsinite[25] and chromate[26,27]. nZVI is also efficient in removing dissolved metals from solution, eg Pb and Ni[28]. The reaction rates for nZVI are atleast 25-30 times faster and also sorption capacity is much highercompared with granular iron[29]. The metals are either reduced to zerovalent metals or lover oxidation states, eg Cr (III), or are surface complexed with the iron oxides that are formed during the reaction. Some metal can increase the dechlorination rate of organics and also lead to more benign products, whereas other metals decrease the reactivity (Lien etal 2007). The most of the research using nZVI has been devoted to groundwater and soil remediation.

Nanotech for Hazardous waste clean-ups: Nanoscale materials can make a huge difference in the cleanup of hazardous waste. There are two reasons for the optimism: firstly, the size of nano materials lets them penetrate otherwise impossible- to-reach ground water or soil and secondly, their engineered coatings allow them to stay suspended in groundwater, a major asset in cleanups. If practically feasible, nanomaterials could slash clean-up prices by avoiding the extraordinary costs and risks of hauling waste away for burning or burial. Most nano-remediation research projects undertaken by the department of defence are focused on cleaning up ground water contaminated by chlorinated solvents like trichloroethylene. Research shows that results have been promising in most demonstrations with most of the contaminant being destroyed – a finding that has been replicated by researchers elsewhere. However, there are complications. For one, iron also reacts with non-targeted materials, making it to degrade too quickly, before remediation is comparticles clump after their release, making it difficult for them to travel beyond where they are injected.

Scientists are trying coatings that might enable nanoparticles to travel. They are also trying to learn how to make the nano-iron react only with target contaminants as well as to get it to self-destruct after it has done its job. Such "smarter" nanomaterials will ultimately make the technology won't be a silver bullet for clean ups because most contaminated sites are fouled by more than a single contaminant and a phased approach will be needed.

Nanoparticles in Waste Water: The environmental management of nanoparticle waste could greatly improve following a new study into substances found in wastewater. Researchers from several scientific institutions around the world collaborated on the study have focused on the behaviour of potentially hazardous nanoparticles in sewage treatment plants, particularly silica-shelled nanoparticles. During the course of the studies, it was discovered that coating these nanoparticles with a commercial surfactant enabled their separation from the water together with other waste particles. The scientists say that if the nanoparticles were allowed to "settle out" in this way, then they could be stopped from passing on to the subsequent stage of the waste treatment process, which would help prevent industrial accidents.

Remediation technologies to clean up Environmental Pollutants

Environmental cleanup has promoted the development of highly efficient photocatalysts that can participate in detoxification reactions. Environmental remediation by photocatalysts comes with several advantages: direct conversion of pollutants to non toxix by products without the necessity for any other associated disposal steps; use of oxygen as oxidant and elimination of expensive oxidizing chemicals; potential for using free and abundant solar energy; self regeneration and recycling of photocatalyst, etc. A significant amount of research on semiconductor-catalyzed photooxidation of organic chemicals has been carried out during the past 15 years. The ability to catalyse the destruction of a wide variety of organic chemicals and complete oxidation of organics to CO_2 and dilute mineral acids in many cases, lack of inherent toxicity and resistance to photodegradation at low cost render this process highly suitable for environmental remediation.

Environmental protection and pollution issues are frequently discussed worldwide as topics that need to be addressed sooner rather than later. Nanotechnology can strive to provide and fundamentally restructure the technologies currently used in environmental detection, sensing, remediation and pollution removal. Some nanotechnology applications are near commercialization: nanosensors and nanoscale coatings to replace thicker, more wasteful polymer coating that prevent corrosion, nanosensors for dectection of aquatic toxins, nanoscale biopolymers for improved decontamination and recycling of heavy metals, nanostructured metals that break down hazardous organics at room temperature, smart particles for environmental monitoring and purification, nanoparticles as novel photocatalyst for environmental cleanup.

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