ENVIRONMENTAL NANOTECHNOLOGY

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Environmental Nanotechnology: An Introduction

1.1 Introduction

Nanoscience and nanotechnologies have enabled an understanding of matter and have profound implications in all sectors, i.e. agriculture and food, energy production efficiency, the automotive industry, cosmetics, medical and drugs, household appliances, computers and weapons. Nanoscience is multidisciplinary and interdisciplinary branch of science and technology, which has an impact on virtually every spectrum of human endeavour including communications, computing, textiles, cosmetics, sports, therapy, automotive, environmental monitoring, fuel cells and energy devices, water purification, food and beverage industry, etc. The tiny objects constructed atom-by-atom or molecule-by-molecule present one of the exciting prospects for research in nanoscience.

The Royal Society (2004) and Royal Academy of Engineering gives the following definitions of 'nano science' and 'nanotechnologies':

> *'Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where the properties differ significantly from those at a larger scale'.*
>
> *Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale.*

Nanomaterials are structured components with at least one dimension less than 100 nm. Materials have one dimension in the nanoscale and are extended in the other two-dimensional layers, such as graphene, thin films or surface coatings. Materials that are at nano scale having two dimensions and extended to one dimension include nanowires and nanotubes. Materials that are nano scale in three dimensions are particles. Nanocrystalline materials such as precipitates, colloids and quantum dots (tiny particles of semiconductor materials), made up of nanometre-sized grains, fall in this category.

Nanoparticles can be defined as material purposefully produced with one dimension in 1–100 nm range (as stated by the American Society for Testing and Materials (ASTM) Committee on Nanotechnology). The materials have unique properties compared to their bulk and atomic counterparts. The engineered nanoparticles are widely used by consumers as novel products. With the unique properties and characteristics such as their size and shape, it is possible that these materials have profound demand in the market. The use of nanoparticles in environmental technologies and the potential impact on the energy sector, potential effects on human health and the environment (adverse and beneficial) is reviewed by Biswas and Wu (2005). Environmental nanoparticles is a new and fast-growing field.

The principal factors that cause the properties of nanomaterials differ significantly from other materials: increased relative surface area and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30 nm has 5% of its atoms on its surface, that of size 10 nm, 20% of its atoms, and that of size 3 nm, 50% of its atoms. The nanoparticles have a much greater surface area per unit mass compared with larger particles, because growth and catalytic chemical reaction occur at surfaces, which means a given mass of material in the nanoparticulate form will be much more reactive than the same mass of material made up of larger particles. Nanomaterials can be nanoscale in one dimension (surface films), two dimensions (strands or fibres) or three dimensions (precipitates, colloids). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular and irregular shapes.

There is variety in the types of nanoparticles that have been fabricated, with almost every element in the periodic table, together with various alloys and compounds can form nanoparticles. Nanoparticles can be metallic, semiconducting or insulating and typically their properties are very different from those of the corresponding bulk materials. The seven main nanomaterial categories include carbon-based nanomaterials, nano-composites, nanometals and nano alloys; biological nanomaterials; nano-polymers; nano-glasses and nano-ceramics.

Due to their small dimension, nanomaterials have extremely large surface area to volume ratio, which gives rise to more 'surface'-dependent material properties. When the sizes of nanomaterial are comparable to length, the developed material will be affected due to surface properties of the nanomaterial. This will enhance or modify the properties of the bulk materials (e.g. metallic nanoparticles can be used as very active catalysts, chemical sensors and nanowires that enhance sensitivity and sensor selectivity). Different properties of nanomaterials have different applications in different areas (Table 1.1).

TABLE 1.1

Nanoparticles Properties and Their Applications

Property	Application
Optical	Anti-reflection coatings. Tailored reflective index of surfaces. Light-based sensors for cancer diagnosis.
Magnetic	Increased density storage media. Nanomagnetic particles to create improved detail and contrast in MRI images.
Thermal	Enhance heat transfer from solar collectors to storage tanks. Improve efficiency of coolants in transformers.
Mechanical	Improved wear resistance. New anti-corrosion properties. New structural materials, composites, stronger and lighter.
Electronic	High performance and smaller components, e.g. capacitors for small consumer devices such as mobile phones. Displays that is cheaper, larger, brighter and more efficient. High conductivity materials.
Energy	High energy density and more durable batteries. Hydrogen storage applications using metal nanoclusters. Electrocatalysts for high efficiency fuel cells. Renewable energy, ultra high performance solar cells. Catalysts for combustion engines to improve efficiency, hence economy.
Biomedical	Anti-bacterial silver coatings on wound dressings. Sensors for disease detection (quantum dots). Programmed release drug delivery systems. 'Interactive' food and beverages that change colour, flavour or nutrients depending on a diner's taste or health.
Environmental	Clean-up of soil contamination and pollution, e.g. oil. Biodegradable polymers. Aids for germination. Treatment of industrial emissions. More efficient and effective water filtration.
Surfaces	Dissolution rates of materials are highly size dependant. Activity of catalysts. Coatings for self-cleaning surfaces, Pilkington's glass for example.
Personal care	Effective clear inorganic sunscreens.

1.2 Properties of Nanomaterials

1. *Electrical properties*: The electrical properties of nanomaterials vary between metallic and semiconducting materials and depend on the diameter of the nanomaterial. The very high electrical conductivity of nanomaterial is due to minimum defects in the structure.
2. *Thermal conductivity*: The thermal conductivity of nanomaterials is very high, due to the vibration of covalent bonds which is 10

times greater than the metal. The high thermal conductivity of nanomaterials is due to minimum defects in the structure.

3. *Mechanical properties*: Nanomaterials are very strong and withstand extreme strain. The synthetic method is used for producing nanomaterials that exhibit properties as result of their characteristic length scale being in the nanometre range (~1–100 nm). The synthetic method controls size in this range so that one property or another can be attained. Nanomaterials can be synthesized by two main methods 'bottom up' and 'top down'.

The bottom-up approach involves the constitution of nanomaterials atom by atom, molecule by molecule and cluster by cluster. The chemical or biological methods are involved in the synthesis of nanostructured building blocks (e.g. nanoparticles) and subsequently assembled into final forms of nanomaterial in the bottom-up approach. The advantage of bottom-up approach is the possibility of obtaining nanostructures with lesser defects and more homogeneous chemical composition.

In top-down approach physical, chemical or mechanical methods are involved, wherein the suitable starting material is reduced in size. However, top-down approach develops imperfection of the surface structure, such as defects in the surface structure have significant impact on physical properties and surface chemistry.

1.3 Major Applications in Nanotechnology

Nano tools: Tools and techniques for synthesizing nanomaterials, manipulating atoms and fabricating device structures, and for measuring and characterizing materials and devices at the nanoscale.

Nano devices: Making devices at the nanoscale is important in microelectronics and optoelectronics at the present time, and at the interface with biotechnology with the aim of mimicking the action of biological systems such as cellular motors.

1.4 Type of Nanoparticles

Ultra-fine particles: Often referred to as nanometre-diameter particles that are not intentionally produced (less than 100 nm size), such as naturally airborne particles or incidental products of processes involving combustion (e.g. carbon black, smoke, welding fumes).

Engineered nanomaterial: Intentionally manufactured material, containing particles (unbound state, aggregate or agglomerate) and 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm.

Nano powder: A mass of dry nanoparticles.

Nano aerosol: A collection of nanoparticles suspended in a gas.

Nano fibre: A nano-object with two similar external dimensions at the nano scale and the third dimension significantly larger. A nano-fibre can be flexible or rigid. The two similar external dimensions are considered to differ in size by less than three times and the significantly larger external dimension is considered to differ from the other two by more than three times. The largest external dimension is not necessarily in the nano scale.

Nano platelet: A nanoparticle having a 'platelet' morphology (a minute flattened body) that presents only one dimension at the nanoscale (they have a very thin but wide aspect ratio).

High aspect ratio nanoparticles (HARNs): Particles with one or two dimensions at the nanoscale are much smaller than the others. Nano-fibres and nano platelets are considered as HARNs.

Agglomerate: A group of nanoparticles held together by relatively weak forces (van der Waals, electrostatic or surface tension).

1.5 Types of Engineered Nanoparticles

Carbon-Based Particles: Nanoparticles, which are commonly composed of carbon and having shapes in the form of spheres, ellipsoids and tubes. The spheres are known as fullerenes and the tubes are known as carbon nanotubes.

Metal-Based Particles: These nanoparticles include metal oxides (e.g. TiO_2, ZnO, CeO_2), quantum dots (semiconductor devices with chemical composition of CdSe or ZnS) and zero-valence metals (e.g. zero-valence Fe, colloidal silver and gold). They consist of closely packed metals with particulate sizes of a few nanometres to a 100 nm in diameter. These particles also have size-sensitive optical properties.

Dendrimers: These nanoparticles are synthesized polymers with many side branches with different functional groups on the surface of these dendrimers. Dendrimers are used for different functions and applications and they have cavities inside that can host other types of molecules.

Composites: These are nanoparticles combined with other nano or bulk materials. A composite material (also called a composition material) is a material made from two or more constituent materials with significantly different physical or chemical properties, when combined, produce a material with characteristics different from the individual. Some examples include using nanoparticles in a wide variety of merchandise to improve their current properties (i.e. nano clays including mineral silicates, montmorillonite, bentonite, kaolinite, hectorite and hallosite).

1.6 Properties

One-dimensional nanomaterials: They are extended in the other two dimensions and are known as layers (e.g. thin film or surface coatings).

Two-dimensional nanomaterials: They are extended in one dimension only and are known as wires (e.g. nanowires or carbon nanotubes).

Three-dimensional nanomaterials: All three dimensions are in the nanoscale and they are known as nanoprecipitates (e.g. nanoparticles or quantum dots).

Research and technology in nanotechnology including development at the atomic, molecular or macromolecular levels in the length scale of approximately 1 to 100 nm range is intended to provide a fundamental understanding of materials at the nanoscale, to create and use structures, devices and systems that have novel properties and functions. Nano technology is now being created and evolving a wide range molecular synthesis, manipulation and manufacturing of materials and devices for specific purposes so as to design innovative methods for the new technology to be applied for sustainable development. Nanotechnology includes design, characterization, production and application of structure, device and system on controlling the shape and size at the nanoscale. It is possible to control fundamental characteristics of a material by creating nanometre-scale structure that changes melting point, magnetic properties and colour without changing its chemical composition. The goal of nanotechnology goal is to form the desired structure or pattern with novel functionality from direct atoms and molecules. The physical, chemical and biological properties of nanoparticles differ in fundamental and valuable means from the properties of individual atom and molecular or bulk matter. Research and development in nanotechnology is directed towards the understanding and creating of improved materials, devices and systems that exploit approximately the new field of nanotechnology from multidisciplinary directions, viz. physical, chemical and biological engineering. The approximation of active nanostructures and nano systems may bring significant changes in various fields, viz. industry, agriculture, medicine, quality of life and the environment.

Environmental nanotechnology (E-nano) is considered to play a key role in the shaping of current environmental science and engineering. Environmental nanotechnology products already exist in a wide array for environmental protection. Nanotechnology pollution prevention technology refers to reduction in the use of raw materials, water or other resources and the elimination or reduction of waste and use of more energy-efficient products. In clean and green technology, the production of nanoparticles for nanotechnology will lead to a great reduction in waste generation, less hazardous chemical synthesis, improved catalysis and faster technology.

In nano sciences, nanoscale deals with the smaller parts of matter that can be manipulated at the nanoscale that the resulting materials often have different optical or electrical properties from the same material at the micro or macro scale (e.g. nano titanium oxide is a more effective catalyst than microscale titanium oxide). Magnetic nanoparticles and nano catalysts are often examples of using these materials for the treatment of polluted water for drinking, sanitation and irrigation. Nano-catalysts can chemically degrade pollutants. Zeolites can also be fabricated to separate harmful dynamic form of water to remove heavy metal ions. Naturally occurring altapulgite clays (Khider et al., 2004) and zeolite are also used in nano filtration technology. Researchers are developing new classes of nano porous materials that are more effective than conventional filters.

The semi-conductor photocatalytic process has shown a great potential as a low cost, environmental friendly and sustainable treatment technology to align with the 'zero' waste scheme in the water/waste water industry. The advanced oxidation methods have been widely demonstrated to remove persistent organic compound microorganisms in water. Various material engineering solutions devices include composite photo catalysts within a carbon nanotube (Yu et al., 2005), dyed sensitizer (Vinodgopal et al., 1996), noble metals of metal ion incorporation (Ni et al., 2007), transition metals (Litter, 1999) and nonmetal doping (Fujishima et al., 2008). In material engineering, the strategie is to balance both the half reaction rate of the photocatalytic reaction by adding an electron acceptor, or modifying the structure and composition of the catalyst.

The field of nanotechnology is opening new doors to water decontamination, purification and desalinization and provides improved detection of harmful water-borne substances. Iron nanoparticles have a high surface area for reactions and can be used to detoxify carcinogenic chlorinated hydrocarbon in groundwater. They can also render heavy metals like lead and mercury insoluble, reducing their contamination. Dendrimers, with their sponge-like molecular structure, can clean up heavy metals by trapping metal ions in their pores. Nanoscale filters have a changed membrane, enabling them to treat both metallic and organic contaminant ions via both steric filtrations based on the size of opening and Donnan filtration based on electrical charge. Gold nanoparticles coated with palladium have proved better than palladium alone for removing trichloroethylene from groundwater. Titanium dioxide can be used to decontaminate bacteria-ridden water when exposed to bacterial cell membrane, bacteria like *E. coli* Xiuchun (Lin et al., 2014). Water purification filtration can also be achieved through nanoscale polymer 'branches' coated with molecules that can capture and remove poisons metals, protein and germs.

The understanding and control of matter at dimensions of roughly one to one hundred billionths of a meter is bringing dramatic changes to the materials and processes of science and technology worldwide. By working at the molecular level, nanotechnology opens up new possibilities in material design. The nanoscale materials used for treatment can change colour, shape, and phase much more easily than at the macroscale. The fundamental properties like strength, surface-to-mass ratio, conductivity and elasticity can be designed in to create dramatically different materials. Nanoparticles have unique mechanical, electrical, optical and reactive properties distinct from larger particles. Nanoscience and manipulation (nanotechnology) also open up the convergence of synthetic and biological materials to explore biological systems that are configured to the nanoscale. The traditional boundaries between living and non-living systems allows for the design of new materials. Advances in biomaterials and biocomposites converge with advances in nanotechnology and increase their application in the future.

The interaction of nanoscale particles with the environment has led to caution and concern about toxicology, worker health and safety and regulation. Regulations specific to nanomaterials and products have been slow to emerge, partly due to the inherent difficulty in regulating materials based on particle size, as well as lack of public outcry in favour of stiffer regulation and the success so far of self-regulation by industry and the avoidance of any nano-disasters.

The manipulation of matter at the molecular scale is bringing new materials and new possibilities to industries as diverse as electronics, medicine, energy and aeronautics. The ability to design new materials from the bottom-up is impacting the building industry as well. New materials and products based on nanotechnology can be found in building insulation, coatings and solar technologies. Research work underway in nanotech labs will soon result in new products for lighting, structures and energy. In the building industry, nanotechnology has already brought to market self-cleaning windows, smog-eating concrete and many other advances. The currently available products are minor compared to those incubating in the world's nanotech labs today. The R&D is in the process of illuminating walls that change colour with the flip of a switch, Nano composites as thin as glass yet capable of supporting entire buildings, and photosynthetic surfaces making any building façade a source of free energy.

1.7 Nanotechnology: Environmental Applications

1.7.1 Air Purification

Nanotechnology is contributing towards indoor air quality on all of these fronts. Samsung Electronics has launched new nano e-HEPA (for electric high efficiency particulate arrest) filtration system. The system sifts the air to filter particles, eliminate undesirable odours and kill airborne health threats. It uses a metal dust filter that has been coated with 8 nm silver particles. The Kitasato Research Centre of Environmental Sciences in Japan found the nonfilter killed 99.7% of influenza viruses. Up to 98% of odours were eliminated, and another nonfilter eliminated all noxious VOC fumes from paint, varnishes and adhesives. Donaldson Filtration Systems uses ultra-web nanofibre media from a layer of nanofibres that encourage dust particles to rapidly accumulate on the filter surface building a thin, permeable dust-stopping filter cake. Ultra-Web cleans the air better by filtering even submicron contaminants. This filter has an efficiency of 0.3 micron filtrate and eliminates larger particles by capturing them on the surface of the media, solving premature filter plugging and making contaminants easier to pulse off compared to depth-loading 80/20 blend or cellulose commodity media. Independent lab tests concluded that 80/20 and cellulose media have lower MERV efficiency ratings and are not suitable for capturing submicron particulate matter. ConsERV brand energy recovery ventilator products that are claimed by their manufacturer, Dais Analytic Corporation, to improve heating, ventilating and air conditioning systems in buildings, have been promoted as reducing the energy required to heat, cool and dehumidify, working best when outdoor weather is extreme and energy demand is highest, and bringing in the freshness of outdoors while controlling uncomfortable humidity and moisture that can lead to mold. Unlike other energy recovery products, ConsERV uses patented polymer membranes in a highly efficient and reliable solid state enthalpy exchange core that has no moving parts. Another product, the Nano Breeze room air purifier, utilizes a patented fluorescent light tube coated with phosphor to produce UVA radiation and blue light. The outside of the tube features a fibre-glass mesh where each strand is coated with a thin layer of 40-nm semiconductor crystals, the air circulating over the light tubes cleaned by photocatalytic oxidation.

1.7.2 Water Purification

Nano science and nanotechnology also open new doors for water decontamination, purification and desalinization, and providing improved detection of harmful water-borne substances. Nanomaterials will become critical components of industrial and public water purification systems, said Dr. Mamadou Diallo, director of Molecular Environmental Technology at the California Institute of Technology, recipient of an EPA grant for nanotechnology research. Research reported that iron nanoparticles have a high surface area and reactivity and can be used to detoxify carcinogenic chlorinated hydrocarbons in groundwater. Photocatalysis is a rapidly expanding technology for wastewater treatment. The effects of adsorption, temperature, intensity of light, pH, and the presence of anions, cations, etc have been described by Bhatkhande et al., 2001.

The synthesis and fabrication of functional nanomaterials with predictive, rational strategies is a major focal point of research for many groups worldwide. In practice, this effort has entailed the design, production and characterization of a myriad of nanostructures including nanoparticles, nano cubes, nano rods, nanowires, and nanotubes, which maintain fundamentally interesting size dependent electronic, optical, thermal, mechanical, magnetic, chemical and other physical properties. From the perspective of applications, these structures have wide-ranging utility in areas as diverse as catalysis, energy storage, fibre engineering, fuel cells, biomedicine, computation, power generation, photonics, pollution remediation and sensing. In recent years, semiconductor photocatalytic process has shown a great potential as a low-cost, environmental friendly and sustainable treatment technology. Engineered-photocatalysts, photo-reactor systems, process optimizations and modellings of the photooxidation processes for water treatment is throughly reviewed by Chong et al., 2010.

A simple technology for arsenic removal from drinking water using synthetically prepared clay material, hydrotalcite (HT), for the removal of arsenite (As(III)) and arsenate (As(V)) from drinking water as a economic solution was analyzed by Gillman 2006.

1.7.3 Nano Monitoring

1.7.3.1 Nano Biosensors for Pesticide Detection

Research studies conducted for the development of analytical tools for pesticide residue determination. In parallel with typical chromatography, immunochemical assays based on biomolecules were employed as an alternative for pesticide measurement by virtue of its high selectivity, sensitivity and reliability as well as its rapidity (Gabaldon et al., 1999). Traditional immunoassay is performed as discrete tests, that is, one assay for one analyte and several detecting runs for all of the components in a complex system. Nanomaterial applications adds further advantages to such systems, such as further miniaturization, measurement of more variables, greater sensitivity, less sample material required, faster detection rates, read-outs in real time and application of novel detection methodologies (e.g. electronic, colorimetric, fluorometric and mass changes). Nanomaterial-based unit-molecular and array types of biosensors are being developed for the detection of pesticides. The bio-sensors varies from free biomolecules to those conjugated to a substrate such as NPs, nanowires, nanotubes and thin films. Interaction of the target with the biosensor can be measured either directly or indirectly by recording the changes in colour, fluorescence or electrical potential. In array technologies, multiple biomolecules are fixed to a substrate allowing multiple analytes to be measured simultaneously. A gold NP (30 nm)-based dipstick competitive immuno-assay with a sensitivity of $27\,ng\,ml^{-1}$ was developed to detect organochlorine pesticide such as DDT (Lisa et al., 2009). Gold NPs have the property of agglomeration associated with colour production, which was used for pesticide detection. Development of a colour signal aided easy visual detected when gold NP-labeled antibodies were bound to the pesticide residues. The NP (gold)-based dipstick technique was suitable for the detection of several toxins in food and environmental samples and can be applied for rapid on-site testing of pesticides (Lisa et al., 2009). Vinayaka et al. (2009) used cadmium telluride quantum dots (CdTe QDs), semiconductor fluorescent NPs, in a fluor immunoassay to detect 2, 4-dichlorophenoxyacetic acid (2, 4-D), a herbicide. It was possible to detect 2,4-D up to 250 pg l^{-1}. Wang et al. (2009) developed a zirconium oxide NP (~50 nm)-based immunoassay for sensitive detection (0.02 nM) of organophosphate pesticides using phosphorylated enzyme acetylcholinesterase as a potential biomarker. Joshi et al. (2005) developed a disposable, sensitive biosensor for organophosphorus pesticides (0.5 nM) based on acetylcholinesterase binding on multi-wall carbon nanotubes modified thick film strip electrode.

1.7.3.2 Nano Biosensors for Plant Pathogen Detection

Recently, several methods of microbial identification and typing are available for most plant pathogens. Methods based on traditional culture are time-consuming (Fletcher et al., 2006). Techniques based on biochemical profiles for identification are limited by the population of characterized strains in the databases. The specific serological techniques such as ELISA and indirect fluorescent antibody staining depend on the titre and specificity of the antibody either monoclonal or polyclonal (Lister, 1978; Uddin et al., 2003; Yuen et al., 1998). Cross-reactivity among closely related strains prevents their clear identification (Cho and Goodman, 1979; Jain et al., 1992). Costly nucleic-acid-based polymerase chain reaction methods such as restriction fragment length polymorphism, DNA fingerprinting and amplification of the internal transcribed spacer region from rRNA gene increase specificity of identification (Bariana et al., 1994; Doorn et al., 2007; Gao et al., 2004; Schaad et al., 2002). Currently, a novel microbial detection technology based on NPs is being developed. Silica-based NPs (60 nm) were filled with a fluorescent dye and conjugated to an antibody specific to a surface antigen of the microbe of interest (Zhao et al., 2004). Detection of a single bacterial cell was possible using this technique (Zhao et al., 2004). This method has potential for the sensitive detection of plant pathogens. Recent advances in the development and application of biosensors for environmental analysis and monitoring are reviewed (Rodriguez-Mozaz et al., 2006).

1.7.4 Nano Bioremediation

1.7.4.1 Pesticide Degradation

Treatment on pesticide-contaminated soil and water ranges from conventional methods such as incineration, phytoremediation and photochemical processes to innovative methods such as ultrasound-promoted remediation and other advanced oxidation processes (Bhatkhande et al., 2001; Chaudhry et al., 2002; Farre et al., 2007; Hee Joo and Cheng, 2006; Hoffmann et al., 1995). Degradation of bio-recalcitrant pollutants using NPs is another promising approach (Hee Joo and Cheng, 2006; Zhang, 2003). Research studies showed that pesticides such as atrazine, molinate and chlorpyrifos are susceptible to degradation with nanosized zerovalent iron (ZVI, 1–100 nm). Nanosized ZVI had a greater reactivity than granular ZVI, and their direct injection into the groundwater plume to minimize installation costs was suggested (Zhang, 2003). Applications of ZVI structures and iron oxide NPs were found for the removal of humic material and toxins (Giasuddin et al., 2007; Waychunas et al., 2005). However, little is known about the long-term performance of these nanoparticles/colloidal systems. The application of NPs such as biopolymer-stabilized FeS (200 nm) are in scavenging and degradation of lindane, a persistent organic pollutant found in drinking water as well as in food (Paknikar et al., 2005). The approaches for photocatalytic decomposition of pesticide residues using titania doped with Fe_2O_3 or other metals sprayed directly on crops or even incorporated into the pesticide formulation are promising (Sasson et al., 2007). Layer-by-layer surface (LbL) nano-engineering is a novel strategy for direct surface modification of colloidal entities, which utilizes sequential adsorption of oppositely charged polyelectrolytes to form a complex assembly via electrostatic interactions (Yang et al., 2005). Guan et al. (2008) directly encapsulated microcrystals of the insecticide imidacloprid (IMI) by LbL assembly using polysaccharides chitosan and sodium alginate followed by the addition of photocatalytic NPs. Photocatalytic degradation and mineralization of the IMI by TiO_2 NPs ($\sim$30 nm) and silver and sodium dodecyl sulfate modified TiO_2 NPs were reported.

1.7.5 Soil Structure and Remediation

Soil clays are sub-micrometric soil particles. Common clays are layered phyllosilicate materials, with a polymeric silicate base, which are nano dimensional in one plane. Advanced instrumentation such as transmission electron (TEM) and high-resolution transmission electron (HRTEM) microscopy showed that clays are composed of stacked tetrahedral and octahedral sheets (Wilson et al., 2008). Other inorganic nanomaterials such as the tubular aluminosilicate imogolite and its non-tubular precursor called protoimogolite are soil components (Farmer et al., 1983). NPs such as iron and silica originate from natural weathering of bedrocks. Other naturally occurring NPs are iron oxides (2–5 nm length), as colloidal phases of ferrihydrite, associated with organic matter in river-borne material (Allard et al., 2004).

1.7.6 Future Prospects

Nanomaterials, owing to their increased contact surface area, might have toxic effects that are not apparent in the bulk materials, especially in open agricultural ecosystems (Nel et al., 2006). The selection of nanomaterials for application in the field may be critical as materials that are nontoxic, biocompatible and biodegradable in agriculture. The food and nutrition products that contain nanoscale additives already in the market, such as iron in nutritional drink mixes, micelles that carry vitamins, minerals and phytochemicals in oil and zinc oxide in breakfast cereals (Hoyt and Mason, 2008). Advancements in agriculture based on nanotechnology to promote 'precision farming' allowing optimum use of the natural resources with judicious farming practices.

Different sensor and controlled delivery technologies would change the face of agriculture farming. The sensors, global positioning system, global information system and actuators throughout an agricultural area could measure (data and statistics) and report on several different environmental, crop and pest variables. The technology already exists to measure each of variables in agroecosystem. However, measurement requires technical expertise, is labour-intensive and can take days, by which time the opportunity for optimal intervention could be missed. By providing robust, portable or remote in situ nanotechnology-based sensing and monitoring, backed up with analytical software, farmers can begin to make their own informed choices, in real-time, and apply agrochemicals or engage expert help only when necessary.

In recent agricultural scenario, the extensive use of agrochemicals to boost agricultural production has polluted not only the top soil, but also groundwater. Agricultural productivity increase to feed large population is essential, but keeping the in mind the damage to the ecosystem new approaches need to be considered. Nano-based material use is increasingly important for the agricultural sector. Promising results and applications are already being developed in the areas of delivery of pesticides, bio pesticides, fertilizers and genetic material for plant transformation. Nanomaterial use for delivery of pesticides and fertilizers is expected to reduce the dosage and ensure controlled slow delivery. A main contribution anticipated is the application of nanoparticles to stabilize biocontrol preparations that will go a long way in reducing the environmental hazard. A major hurdle in the removal of harmful contaminants from soil was its detection in the field, which was costly with conventional methods. Nanotechnology, by exploiting the unique properties of nanomaterials, has developed nano sensors capable of detecting pathogens at levels as low as parts per billion. Apart from detection, nanotechnology has also solutions for degrading persistent chemicals into harmless and sometimes useful components. Agro nano-based technology takes advantage of the powerful tools of nanotechnology for the benefit of humankind. Indiscriminate use of pesticides and fertilizers causes environmental pollution, emergence of agricultural pests and pathogens, and loss of biodiversity. Nanotechnology, by virtue of nanomaterial related properties, has potential agro-biotechnological applications for alleviation of these problems (Ghormade et al., 2011). Nanotechnology tools can be employed to address the urgent issues of environmental protection and pollution. Nanotechnology can endeavour to provide and fundamentally streamline the technologies currently used in environmental detection, sensing and remediation.

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