

Biocompatible Nanomaterials for Pollutant Treatment Technologies

G.Vani Padmaja

University of Delhi, Delhi, India

Abstract: *Modern research trends are emerging out more on the polymer based nanomaterials which are widely applied in the active areas of pharmacology, drug designing, drug delivery systems, environmental remediation, energy storage and their conversions etc. This review shows the recent research developments in the use of nanomaterials for waste water treatments, specific adsorption mechanisms, improvements, control of toxicity and various techniques to control the hazardous pollutants present in the environment. Recent reports show different electrochemical sensors that incorporate biomolecules like enzymes, antibodies and aptamers as recognition elements for fabrication of simple, low cost, compact biosensors that can be extensively used for on-site, rapid environmental monitoring of deadly pollutants like pathogens, heavy metals, pesticides and explosives. Some new biohybrid nanomaterials had great potential as efficient novel antibacterial agents with high biocompatibility. Designing of hybrid nanocomposites by the conjugation of the natural and synthetic polymers with certain active elements like TiO₂, creates certain advanced materials with the desired (tailored) properties and functions. This paper mainly emphasizes on the particulate pollutants in the air which is growing tremendously with the rapid increase in the technologies and industries leading to so many chronic diseases and various the health hazards. Thus nanomaterials could be specifically functionalized and designed to act as a sensor prototype for certain toxin materials in the environment. Designed nanomaterials has the ability to treat particulate pollutants and can offer many advantages to improve existing environmental pollution remediation technologies and also gives pointers to create new technology that is better than current technology.*

Keywords: Nanomaterials, biohybrid, biocompatibility, nanocomposites, sensors, environment.

1. Introduction

Nanotechnology and its products “nanomaterials” are being widely used across fields as healthcare, industrial, electronics, cosmetics, pharmacology, bioclinical, biomedical fields and other areas. Nanomaterials often differ from those of bulk materials in their physical and chemical properties, so they call for specialized risk assessment. This also means monitoring health risks to workers, consumers to every individual and also potential risk to the environment [1-2]. To shape up the current environment engineering and science, the combination of environment science with nanotechnology can be used as an important tool in fabricating the desired nanomaterials. The small size of the nanoparticles has enunciated the development of new and low cost techniques for the pollutant sensors, pollutant detecting devices and monitoring, pollution remediation techniques etc. Nanocomposites and nanostructured materials are very effectively and efficiently used in various fields because of small size and highly active large surface areas. Thus these can be very extensively used as the toxic pollutant absorbants and adsorbants. The conventional methods of pollutant treatment methods include carbon adsorption, ozonisation, chlorination, ultrafiltration, sedimentation etc. The newly designed and synthesized biocompatible nanomaterials with exceptionally very high active and large surface areas could be great tool for the pollutant treatment techniques over traditional methods. Chemically designed and modified nanomaterials especially nanoporous materials are drawing a lot of attention because of their unique size, electronic properties and very active surface areas [3-5]. The incorporation of certain transition metals like Ti, Zn etc in the nanomaterials enhances the desired adsorption properties of the molecule. Using the concept of environmental nanoscience, depending upon the nature and complexity of the pollutants, specific biocompatible nanomaterials could be designed and

synthesized encapsulated by certain metal ions can be efficiently applied in the pollutant treatment technologies. Recent advances in the nanotechnology engineering have led to the production of reduced sized TiO₂ particles and such particles have applications in various environment treatment techniques. [5-7].

2. Nanomaterials

Nanotechnology involves designing and producing substances or structures at a very small or nano scale, 100 nanometres (100 millionth of a millimetre) or less to form nanomaterials. Nanomaterials are one of the important products of nanotechnologies such as nano-scale particles, tubes, rods, fibres etc. Nanoparticles are normally defined as being smaller than 100 nanometres in at least one dimension. Important features of nanomaterials include the average size of the particle, nature for clumping, size of the individual particles, description of the particle number size distribution (smallest to the largest particle present in the preparation), surface area, structure etc. Nanomaterials constitute an emerging interdisciplinary field of science that deals with the development of various methods for preparing nanoscopic bits of a desired material like polymers, semiconductors etc. Nanomaterials have manifold possible commercial and technological applications. A relatively new method is reported for preparing and developing nanomaterials is through membrane-based synthesis. In this method, the synthesis of the desired material is carried within the pores of a nanoporous membrane. As the membranes employed contain cylindrical pores of uniform diameter, monodisperse nanocylinders of the desired material, with controlled dimensions are obtained. These nanocylinders could be either hollow as a tubule or solid as a fibril or nanowires. Titania nanocomposites and nanospheres MTNSs have the excellent photocatalytic activities. The mixed phase TiO₂ nanocomposites and

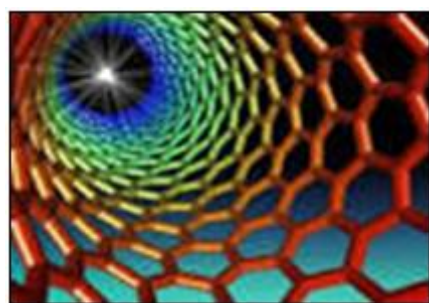
nanoparticles have improved photo catalytic and photovoltaic activities. Cellulose nanoparticles and composites produced with specific physico-chemical properties can be widely used broad areas [8-12]. Specific important features of nanomaterials include the following:

Physical properties:

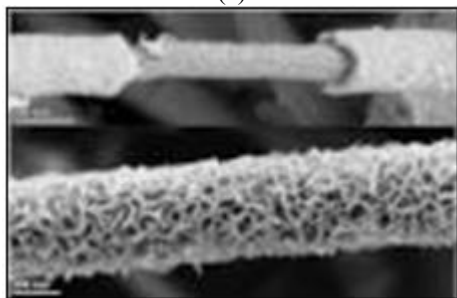
- 1) Size, shape and ratio of width and height
- 2) Specific surface area
- 3) Property to stick together (agglomeration process)
- 4) Number size distribution
- 5) Nature of the surface (smooth or rough)
- 6) Structure of the nanomaterial (crystal structure and any crystal defects)
- 7) Solubility.

Chemical properties:

- 1) Structure of the nanomaterial (molecular)
- 2) Composition of the nanomaterial, including purity, additives and known impurities.
- 3) Physical state (solid, liquid or gas)
- 4) Surface chemistry of the nanomaterial
- 5) Molecular interaction of the nanomaterial with different solvents.



(a)



(b)

Figure 1: a) Nanomaterials b) Hybrids and nanocomposites

Nanomaterials include many class of substances which includes:

- 1) Metal based substances like metal oxides like Titanium oxides, Silver Oxides, nanogold, nanosilver etc. and also quantum dots whose optical properties vary with size have the ability to absorb light and re-emit it. Carbon nanotubes which are formed by structures such as C-60 fullerenes and other carbon based materials.
- 2) Dendritic molecules or dendrimers are the polymeric structures constructed by different branching units. These have hollow spheres or cavities in which the desired metal or its oxide could be incorporated depending upon the desirable properties of the molecule.

- 3) Bio- inorganic nanocomposites and certain metal composites are used to treat diseases. Besides these, various manufactured nanomaterials have very wide range of applications like structural applications, skin care products, information and communication technologies, biotechnology, environment technology etc.

3. Characterization

The physicochemical characterization for the nanomaterials identified as important for environmental studies includes measures of aggregation/agglomeration/dispersability, size, dissolution (solubility), surface area, surface charge, surface chemistry/composition, assuming that the chemical composition already be known. Various methods and techniques to analyze and characterize the nanoparticles or nanomaterials are as below:

To analyse the size and surface areas of nanomaterials microscopic techniques include SEM (scanning electron microscopy), Atomic force microscopy (AFM), Optical Microscopy, NMR, X-Ray diffraction, DSC, Turbidimetry, Filtration, Electrophoresis, Hydrophobic interaction chromatography, Field flow fraction, Single particle optical sensing, Zeta potential analyzer, Malven particle analyzer etc. The interactive surface size, shape and morphology with surface area and porosity, chemical compositions are measured by TOF-MS (Mass spectrometry), Electron microscopy, Atomic force microscopy (AFM). Hydrated surface analysis is done by Epiphaniometer, BET (Braunauer, Emmet and Teller method). The porosity of the nanomaterials could be studied by Mercury porosimetry, Electron, Atomic force and tunnel microscopy, Small angle X-Ray diffraction etc [12-18]. The wettability of the nanoparticles is studied by the capillary penetration methods, Power tablet methods, microsphere tensiometry methods, gel trapping techniques.

Nanomaterials and Pollution Control

Contaminants and deadly pollutants are mostly found mixed in air, water and soil. Thus, there is an urgent need of technology that is able to monitor, sense and, if possible, purify the contaminants from the air, water and soil. In this context, nanotechnology offers a broad range of possibilities and technologies to improve the quality of existing environment. In treatment and remediation of pollutants of the soil and groundwater, minute nanomaterials are being extensively used to convert (respective break down of) pollutants on site. The process can also be employed with contaminants that have been hard to fight up to now, for example through heavy metals or the hazardous, carcinogenic softener PCB. However, in various remediation projects (reclamation of contaminated sites), nanomaterials and nanoparticles have only been used selectively since an effective reliable, low cost, economical and eco-friendly applications are not yet mature. The potential risks and challenge for the environment is difficult to assess. The nano-remediation and the nanotechniques for pollution control are comparatively expensive due to the high manufacturing costs of manufactured nanomaterials (MNMs) and nanoparticles. Nanotechnology offers multiple advantages to improve existing environmental pollution technologies and create new methodologies that are much

better than current technology. Thus, nanotechnology can be applied in the fields of environment which include:

- a) The cleanup (remediation) and purification,
- b) the detection of contaminants (sensing and detection), and
- c) the pollution prevention.

Water pollution control

Water pollution is caused by various factors, including industrial waste disposal, oil spill, herbicides and pesticides, leakage of fertilizers, by-products of industrial processes, combustion and extraction of fossil fuels. The harmful pollutants in the environment can be converted into harmless ones by certain degradation reactions. In recent years, water pollution has become an important issue, and it is quite difficult to solve the problems related to it. The development of nanotechnology can be used to improve water quality and we can use nanotechnology as reactive media for separation and filtration, bioremediation and disinfection etc. Some of the examples of nanoparticles and nanomaterials that can be used for remediation of water are carbon nanotubes (CNTs) zeolites, biopolymers, self-assembled monolayers on mesoporous supports, single-enzyme nanoparticles, nanoparticles of zero valent iron etc. Recent studies showed that cellulose nanomaterials' play a very beneficial role in environmental remediation and membranes for water filtration because of their high surface area-to-volume ratio, high strength, functionalizability, sustainability and low environmental impact. Using the nanotechnology and inserting the nanoparticles in the polluted and contaminated water the process is much cheaper and efficient than the other conventional methods. By reducing the pore size in nanometer range of the semipermeable membrane for water filtration methods, filtration can be made more sensitive, selective and efficient. The deionization of water using nanofibers as the electrodes is very efficient and much economical. Several methods that can use nanotechnology use reactive media for separation and filtration, bioremediation and disinfection.

Fe- Nanomaterials

Fe- nanomaterials could be used by direct injection into the soil, sediment or solid waste for pollution treatment. In this process nanoparticles are mixed with water to form slurry. The nanoparticles are injected and will remain in the form of a suspension thereby a treatment zone is formed. The other way is to attach the nanoparticles to a solid matrix or surface such as activated carbon and has also been found to be very efficient. Fe-nanomaterials could be substituted with other metals such as Zn and Sn which have the ability to reduce contaminants such as iron. Metal alloys such as iron and iron-nickel-copper have been widely used to degrade trichloroethene and trichloroethane [19-25]. Recent studies showed ferritin has the ability to remediate toxic metals and chlorocarbon under visible light or sun radiation. The advantages of ferritin are that it does not react under photoreduction and it is also more stable than that of Fe catalyst.

Nanosemiconductors:

Compounds such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron (III) oxide (Fe_2O_3) and tungsten oxide (WO_3) nanoparticles act as photocatalysts. With respect to

environmental pollution and remediation, photocatalysts oxidize organic pollutants into nontoxic materials. The use of TiO_2 in advanced methods of photochemical oxidation for the remediation of water for organic and inorganic contaminants is because of its very low toxicity, high photoconductive nature, and high photostability, easily available and low cost material. The surface of TiO_2 developed into nanotubes is proven to be more effective at transformations of the organic and inorganic contaminants. TiO_2 electrodes are showed to be very effective to determine the chemical oxygen demand of water and thus can be employed as sensors for detecting the level of contaminants in water. ZnO photocatalysts are currently being developed as nanomaterials and nanoparticles which are likely to have two functions: to detect and remediate contaminants. ZnO could be considered to be potentially more efficient in sensing and eliminating toxic substances from water [26-30].

Polymeric nanomaterials:

Nowadays, polymeric nanomaterials are much in light in the field of environmental pollution control. Molecularly imprinted polymers (MIPs) are synthetic polymers which possess specific cavities designed for target molecules. Because these polymeric molecules are of predetermined selectivity, these can be used as ideal materials in the wastewater treatment and specifically MIP-based composites offer a wide range of applications in wastewater treatment. Photocatalytic degradation of diary effluents (environmentally toxic) was studied using novel polyurethane (PU)-based membranes. Silver-titanium dioxide nanofibers (AgTiO_2 NFs) and silver-titanium dioxide nanoparticles (AgTiO_2 NPs) were individually incorporated in PU electrospun nanofibers. The PU- AgTiO_2 nanoparticles and PU- AgTiO_2 nanofibres were found to be effective in the degradation of dairy effluents, a maximum degradation upto 75% and 95% [31-32]. Nanoparticles containing CeO_2 , zero-valent iron nanoparticles (nZVI), ZnO , carbon nanotubes and SAMMS (self-assembled monolayer on a mesoporous support) were found to be used efficiently to remove heavy metals from water by sorption phenomena. SiO_2 and TiO_2 , amorphous titanium phosphate and silica monolith aerogels with different degrees of hydrophobicity contain several functional groups (e.g. -OH moieties) at the surface enabling the sorption of organic pollutants. Metals and metal oxides such as TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, ZnO act as photocatalyst for the degradation of organic pollutants such as phenolic compounds, chlorinated organic compounds. Bimetallic particles (e.g. Pt/Fe, Pd/Fe, Au/Pd) can be very extensively used for the dechlorination of organic contaminants such as chloroalkanes. Amphiphilic polyurethane (APU) nanoparticles have good prospects as remediation agent where polyurethane acrylate anionomer (UAA) and poly (ethylene glycol)-modified urethane acrylate (PMUA) act as the reactant/precursor chains. Antimicrobial nanotechnology can be of great use to kill germs in water. Several nanomaterials showed strong antimicrobial properties through various mechanisms, such as photocatalytic production of reactive oxygen species which destroys cell components and viruses (e.g. TiO_2 , ZnO and fullerol), interruption of energy transduction (e.g. Ag and aqueous fullerene nanoparticles), compromising the bacterial cell envelope (e.g. peptides, chitosan, carboxyfullerene, CNTs, ZnO and silver nanoparticles), and

inhibition of enzyme activity and DNA synthesis (e.g. chitosan) [33-36].

Nanobiocides:

Research studies shows that the proliferation of bacteria that cause membrane fouling and eventually contamination of water can be inhibited by the surface-modified nanofibres. Polyvinyl alcohol (PVA), polyacrylonitrile (PAN) and poly ethylene oxide (PEO) nanofibres containing Ag nanoparticles have excellent antimicrobial activity with PVA nanofibres. Its been reported that PVA nanofibres reduces bacteria by 91-99% and PAN nanofibres reduces by 100%. Nanobiocides (antimicrobial nanoparticles) can be categorized into: Metal and metal oxides, engineered and synthesized nanomaterials, natural antibacterial substances etc.

Nanofiltration:

Currently, nanofiltration has become the newest and most leading-edge technology in water treatment. Nanofiltration (NF) is a relatively modern development in membrane technology with characteristics which lie in between ultrafiltration and reverse osmosis (RO). The various applications of NF membranes in the water and wastewater industry including water softening and color removal, industrial wastewater treatment, water reuse, and desalination has been reported [38-41]. NF is applied in varieties of water and waste water treatment and industrial applications for the selective removal of ions and organic compounds. Some other examples of nanotechnology applied in water remediation are: self-assembled monolayers on mesoporous silica (SAMMS),

- Dendrimers or polymeric dendrimers;
- single nanoparticle enzyme (SEN)
- bioactive polymers
- nanocrystalline zeolites, etc.

Air pollution control:

One of the most important applications of nanotechnology is the adsorption of toxic and hazardous pollutant gases in the atmosphere by the carbon nanotubes and by Au nanoparticles. Nanomaterials like single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) are unique macromolecules which have a one dimensional structure, thermal stability and exceptional chemical properties and have huge potential as superior adsorbents to remove different types of organic and inorganic pollutants present in the environment. The highly efficient adsorption capacity of pollutants by CNTs is because of its pore structure and the presence of a broad spectrum of surface active functional groups of CNTs that is achieved by the optimum chemical or thermal treatment. to design the CNTs to have optimal performance for a particular purpose. Current researches have proved the fact that some scientific products using TiO₂ nanomaterials such as active filters of photo-catalyst covered by TiO₂ on silica cotton and on Al₂O₃ fibers are used as air cleaners. Also studies showed that TiO₂/Apatite paint to kill bacteria was very successfully achieved. Research studies showed that interaction of dioxin with CNTs is found to be nearly three times stronger than the interaction of dioxin with activated carbon. Long and Yang reported that CNTs were significantly better than activated carbon and γ -Al₂O₃ for removing dioxins is because of the

nanotube curved surface compared with those for flat sheets which gives stronger interactive forces between dioxin and CNTs [42-44]. Studies show that CNTs can be used as an adsorbent for the removal of NO_x, SO₂ and CO₂ on the highly porous manganese oxide with gold nanoparticles grown into it researchers have developed materials that are very effective for removing VOCs (volatile organic compounds), nitrogen and sulfur oxides from air at room temperature [45].

Nanobiosensors:

A nanocontact sensor has the potential to detect some metal ions without any preconcentration required and can be made in miniature size and automatic mode so that they can be handled easily. Besides these, the use of these sensors is economic (cost-effective) because they are synthesized with conventional microelectronics manufacturing equipments using simple electrochemical techniques. Recently nanobiosensors which are used extensively for assessing environmental pollution and water quality monitoring are mainly involved with the principle of the use of Biological Recognition Element and its interaction with the Signal Transducers. It was reported that the use of lux-based biosensors for rapid diagnosis of pollutants in arable soils was very well correlated with the conventional methods of detection. Nanotechnology-based biosensors employ those kinds of biomaterials such as portable biosensors which are able to easily detect affected people who have been exposed to chemicals by using the electrochemical immunoassay method. Research studies showed that SWNTs (single walled nanotubes) have a faster response and higher sensitivity than the conventional probes which are currently used in the detection of gas molecules such as NO₂ and NH₃. It is based upon the principle that gas molecules are directly bonded to the surface of SWNTs and influence the electrical resistance of the sensor. Another important advantage of SWNTs as sensors is the ability to achieve high sensitivity at room temperature whereas conventional solid sensors are operated at temperatures as high as 200–600°C [46-50].

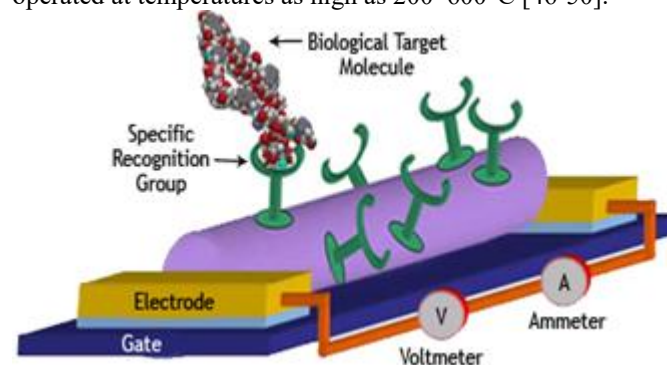


Figure 2: Biosensors

4. Conclusions

Nanomaterials being smaller in size can be highly reactive because of their large surface area to volume ratio and presence of active sites. These properties of nanoparticles can be applied very well for solving potential environmental issues such as air, water, soil contamination and their remediation. The science of nanotechnology is able to create an eco- friendly substances or materials which when applied can easily replace the used toxic material(s). For

example, nowadays the much used liquid crystalline display (LCD) computer screens are more energy efficient and less toxic and have largely replaced the screen cathode ray tubes (CRTs) which contains many toxic materials. Similarly, the use of CNTs in computer screens further reduces the impact on environment by eliminating toxic heavy metals, reducing the material and energy requirement as well as improving performance according to desired needs.

In this manuscript, the application of nanotechnology in the environmental field to prevent pollution, which includes the synthesis of green materials, nanocoatings, nanobiocides, nanosensors etc. and ways to prevent the release of hazardous substances into the environment have been discussed. Nanotechnology could be considered as an important platform to restructure the various methodologies and techniques employed for solving the existing and pressing environmental issues such as detectors, sensors, remediation, pollution control and prevention. The issue of environmental pollution and its prevention can be easily resolved by the interdisciplinary collaboration of many sciences like chemical sciences, physical sciences, material sciences, geological sciences etc. Also, keeping in mind the risk of toxicity of nanoparticles on the human health and environment, the applications of nanoparticles and nanomaterials should be done judiciously to avert any health and environmental risks.

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