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MILESTONES OF NANOSCIENCE IN ENVIRONMENTAL BIOTECHNOLOGY- A REVIEW

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ABSTRACT

Nanotechnology is an emerging field that has the ability to consistently change and modify the properties of nanostructures by controlling their surface properties and structure at a nanoscale level. These valuable characteristics make nanoparticles highly attractive candidates for use in the field of environmental biotechnology ranging from fundamental scientific studies to commercially useable treatment technologies. Nanotechnology had played immense role in sensing and detecting various pollutants, pollution prevention and in vast number of remediation treatment technologies. It plays a vital role in the development of new methodologies to produce novelnano-products, to replace already existing equipment and to reformulate new chemicals and materials with enhanced performance and efficacy. All these improvements results in less energy consumption, detection and sensing of pollutants, environmental remediation, water, soil and air purification, cleaner production and prevention of food contamination and spoilage which in turns provides great human health and life style benefits. Environmental applications of nano science not only addresses the development of solutions to cope with existing environmental problems but also elaborate different preventive measures for various problems that may occur in the future. This review discusses the recent advances and application of nanotechnology in the field of environmental biotechnology. It sheds light on the process and pros and cons of almost all the nanomaterials such as metal oxides, metal nanoparticles, zeolites, carbon compounds, filtration membranes, nanoadsorbents, and photocatalysts for efficient environment treatment and remediation. Not only the beneficial properties but their comparisons with conventional processes are also reported. This review briefly illustrates the commercialization aspect together with the future prospects of nanotechnology related to environment, health and production process.

Keywords: Nanoscience, nanomaterials, pollutants, nanoadsorbents, photocatalysts nanoparticles, environmental remediation.

INTRODUCTION AND BACKGROUND

With rapid industrialization and enhanced anthropogenic activities, different grades of pollutants had been generated. Common pollutants are carbon monoxide (CO), chlorofluorocarbons (CFCs), heavy metals (arsenic, chromium, lead, cadmium, mercury and zinc), hydrocarbons, nitrogen oxides, organic compounds (volatile organic compounds and dioxins), sulphur dioxide and particulates. Major factors that are meant to be the cause of pollution in water include waste disposal, oil spills, and release of fertilizers, herbicides and pesticides, by-products of industrial processes and combustion and extraction of fossil fuels [1]. Gaseous and solid waste pollutants include molds, germs, viruses, mites, allergens, dust particles, pungent odor, toxicants, smoke and VOCs. Water is also contaminated by a number of pollutants including organic and inorganic wastes. Health effects of pollutants include respiratory problems, coughing, nausea, pulmonary congestion, asthma, reduced work capacity, cancer, premature death, influenza, visual impairment, cardiovascular problems, less manual dexterity along with stomach problems, liver toxicity and neurological disorders. For environmental cleanup process, different techniques have been used and the most recent one is nanotechnology. Nanotechnology is the understanding and management of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications [2]. Nanoscience is concerned with design, synthesis, characterization, evaluation and application of devices together with materials on nanoscale**.** Nanomaterials are highly reactive, have large specific surface area, high degree of functionalization and various size dependent characteristics. All these properties make them suitable for large number of applications in different areas. Nanoscience has played its great role in different environmental remediation and detection techniques and this review paper illustrates good examples of these techniques.

NANOTECHNOLOGY IN WASTEWATER TREATMENT

Any water which is contaminated by microorganisms, bacteria, industrial effluents, heavy metals and organic pollutants is termed as wastewater. Waste water comprises of proteins, carbohydrates, oils and fats, surfactants, bacteria, viruses and other microorganisms. The treatment process of wastewater is based on the composition of the wastewater. The conventional treatment of the wastewater consists of certain steps which are given in the figure 1. Introduction of the tertiary treatment process greatly ensures the purity of the wastewater after treatment [3]. Unfortunately it is too expensive that industries fails to find any interest in it.

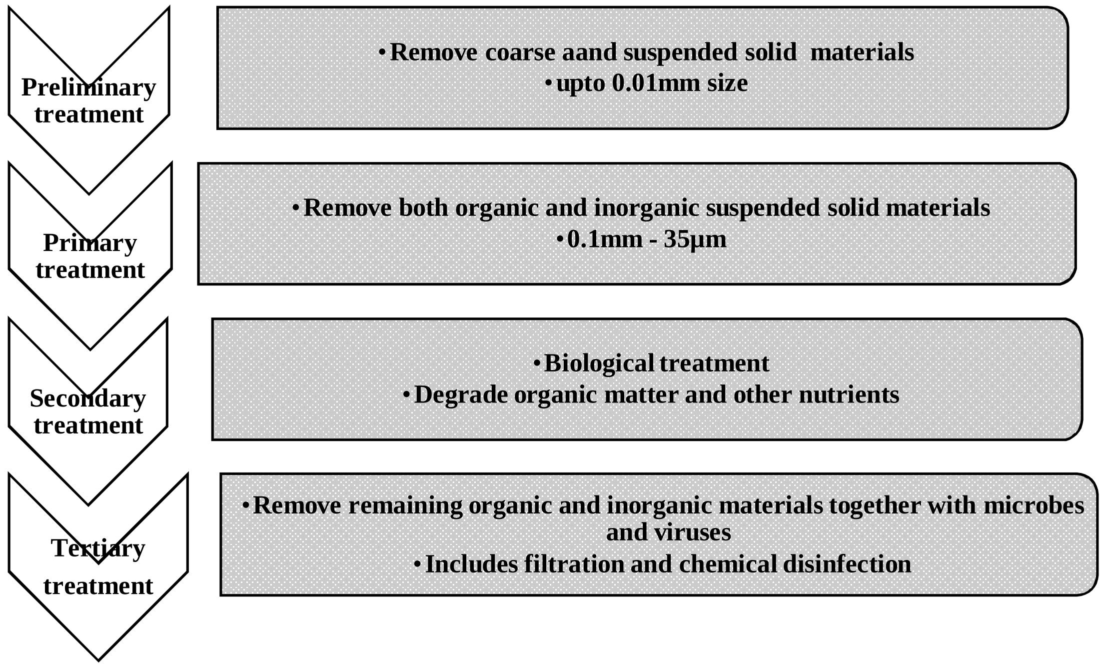

Figure 1: Scheme of conventional wastewater treatment process

Industrial wastewater contains a wide variety of effluents depending upon its source like wastewater from agriculture, steel, iron, food and mining industry. Uncontrolled human population and increased industrialization without planning disturbed the natural processes of water purification and there is a scarcity of water on the Earth. In the developing countries approximately 90% of the diseases are caused by the usage of contaminated water [4]. Therefore it is necessary to treat and purify the water before its consumption. But the conventional methods were not efficient in the wastewater treatment to such an extent that it can be called as safe for human consumption. So, it has been a great challenge to find out such a cost effective and efficient wastewater treatment processes. Nanotechnology offers a great potential for this purpose.

Nanotechnology for efficient wastewater treatment:

Recently, different techniques and tools have been developed by nanotechnology, in order to purify water and provides new alternatives for wastewater treatment in more efficient and cost effective way [3]. Some of the important features of nanomaterials that made them so important are:

a. They are very small and highly reactive in their action.
b. They provides precise and accurate results.
c. Nanomaterials are cost effective and environment friendly.

Different Nano-science based treatment technologies are available for wastewater treatment [5] including Nanosorbents, Photocatalysis and Nanofiltration.

Nanosorbents:

There are two salient features of nanosorbents which make them more effective. a) They have high specific surface areas which helps in increased affinity towards the greater number of target contaminants. b) Their pores are of nano size so, efficient sorption of contaminants takes place. It has been illustrated that 3D flowerlike iron oxide(self-assembled) nanostructures can efficientlyabsorb organic dyes and remove heavy metal ions from the wastewater [6]. Nanoparticles are magnetic in nature. So, it is easy to separate and regenerate them by magnetic separation and catalytic combustion respectively. Some of the important nanomaterials which serves as sorbents are given in the Table# 1.

Photocatalysis:

Photocatalysis is one of the important treatment technology used for wastewater. It uses nanostructured catalyst medium (light active) for the degradation of a range of pollutants in the water. It is a surface phenomenon and involves a complex mechanism comprising of 5 different steps illustrated in figure 2.

Figure 2: Basic steps involved in photocatalysis

An ideal photocatalyst should be highly photoactive, biologically and chemically inert, non-toxic, photo-stable and cost effective [7]. Titanium dioxide, ferric oxide, zinc oxide, cadmium sulfide and zinc sulfide are commonly used examples of nano-structured semiconductor photo-catalysts. It has been greatly used to degrade harmful organic contaminants, heavy metals (recovery of gold, platinum, rhodium & removal of mercury & cadmium) and microbes (*Escherichia coli* & *Staphylococcus aureus*) from the waste water [5].

Nanofiltration:

Filtration is the most common and older technology and had passed through a number of changes with reference to pore size and filtering material with the passage of time. Conventional filtration, microfiltration and then even ultrafiltration fails to remove some of the contaminants from the wastewater. So, scientists move towards a better option, nanofiltration. In this separation technique pressure-driven membrane is used to purify the water by high permeation rate and repulsion property based on charge. It uses minimum energy and is much popular in the developed countries. It gains importance in different industries like pharmaceuticals, petrochemical industry textiles, dairy industry and many more. It can not only filter out the organic and inorganic contaminants but also the microbes because of various membrane [8].

Carbon nanomaterials are often studied and used because of their high mechanical robustness, ease of preparation and excellent ability to reject contaminants. Their pore size ranges from 1-10µm. So, only water can pass through it. Metal oxides are also used as another low cost alternative for the fabrication of nano-filter membranes. Common metal oxides used are TiO_2, ZnO, SiO_2 and ZrO_2 [5].

Zeolites also find enormous applications in nanofiltration because of their chemical and thermal stability. They are microporous crystalline aluminosilicate materials and their pore sizes ranges from sub-nanometer to nanometer scale [8, 9].

Table 1: Some important nanomaterials as sorbents

Nanosorbents	Principle	Properties	Uses (Removal/ reduction)	References
Biosorbents DNA matrix -Triolein-embedded biosorbents -Chitosan-based sorbents -Bio-sorbent from black liquor	Derived from agricultural& biological materials. Used for the removal of pollutants which are present in minute quantities in water.	↓cost, ↑efficiency, ↓biological&agricultural sludge, no need of additional nutrient &regenerative	Derivatives of dioxins. Organic contaminants. Heavy metals Pb(II), Cu(II), Cd(II), Zn(II) & Ni(II)	[10] [11] [12] [13]
Carbon nanotubes (CNTs)	Adsorption of pollutants depends upon the morphology & surface status of CNTs.	highly specific,chemically and thermally stable, reactivity can be varied by functionalizing their surface	1, 2-dichlorobenzene with Cd & Pb. Dyes.	[14, 15]
Nano zero valent iron	Newly discovered for the removal of a wide range of organic & inorganic pollutants from water.	Highly reactive and short lifetime, surface-modified, emulsified, bimetallic, better distribution on carbon support	Heavy metals (Cu, Ag reduced & Zn, Cd adsorbed). Precipitation &adsorption for As, Cr, Cu, Pb, Ba, Co & U ions.	[16] [17]
Metal Oxide Nanosorbents -Iron and silicon oxides -Tungsten oxide	Metal oxides are used as adsorbent materials.	Materials used are of low cost. Easily functionalized to tune adsorption capacity and selectivity.	Organic pollutants Heavy metals Organic dyes	[18, 19, 20]
Carbon Nanosorbents	Carbon nano-materials are used for the adsorption of different organic &inorganic pollutants present in water.	↑adsorption capacity, ↑thermal stability,↑resistance against attrition losses ↓cost.	Benzene & toluene. Hg(II), Co(II), Ni(II), Cu(II) Cd(II), Pb(II), Cr(III) & Cr(VI)	[21]

NANOTECHNOLOGY IN GASEOUS TREATMENT

Nanotechnology also plays an important role in cleaning toxic gases from the environment. Different treatment technologies are available for the removal of germs, molds, viruses, allergens, mites, dust particles, specific odor, toxicants, smoke and volatile organic compounds including High Efficiency Particulate Air Filters, Electrostatic Filters, Ozone gas, Ultraviolet radiations and many others. But the complete removal or excellent results can only be observed by using the nanotechnology (photocatalyst).

Applications of nanotechnology in comparison with conventional treatment methodologies

Polychlorinated biphenyls, dioxins and polychlorinated dibenzofuran are extremely toxic and stable pollutants. Adsorbents like γ-aluminum oxide, clay, zeolites and even activated carbon were unable to remove these toxic compounds [22]. So, Long and coworkers explores the use of carbon nanotubes for their complete removal or degradation [23].

Continuous efforts had been made to find out the treatment technologies for the removal of oxides of nitrogen, sulphur and carbon from air. Various adsorbents were used for nitrogen oxides and carbon dioxide removal like zeolites, ferric oxy-hydroxide (FeOOH), activated carbon [24] and zeolite, activated carbon and silica respectively. But they are unable completely remove these oxides and also cause some hazardous problems[25]. Use of chemically modified CNTs, and a nanocatalyst containing platinum and cobalt particles provides astonishing results. Baden Aniline and Soda Factory (BASF), a chemical company along with different universities prepared a photocatalyst using solar energy to convert CO_2 into ethanol and explains its potential use as fuel.

Removal of VOCs especiallytoluene, hexane and acetaldehyde can be efficiently done by manganese oxide (highly porous) with gold nanoparticles as compared to the conventional catalyst methods [26].

In 2014 Prof Tony Ryan (scientist) and Prof Simon Armitage (poet) from University of Sheffield, UK had made a poster coated with nanoparticles (titanium dioxide) which can clean the air from different sized dust particles and nitrogen dioxide as well [27].Different industries using nanotechnology based approaches to clean the environment along with their potential benefits are given in the Table 2.

Table 2: Companies, products and their benefits for the treatment of wastewater and air by nanotechnology

Product/year launch	Company	Benefits [References]
Capillary ultrafiltration membrane technology (2003)	University of Stellenbosch &Water Research Commission (South Africa)	Cost effective,excellent removal of Fe, Al & Mn oxides from industrial, sea & wastewater[28]
Nano-composite catalyst (2004)	NanoStellar (United States)	Low cost technology due to less use of platinum [29]
Nanofiltration membrane (2006)	Saehan Industries (Korea)	Used in China & Iran. Requires less energy than reverse osmosis [30]
Manganese Oxide nanopowder (2006)	American Elements (United States)	Removal of VOCs from industrial emissions in the air [29]
Nanorust or *CBEN's arsenic-removing technology (2009)	Rice University (United States)	low-cost technology to remove arsenic from water [30, 31]
Virus-free water (2009)	Rice University (United States)	Silicone &TiO_2 were used to disinfect water in min. than hours [32, 33]
Membranes based on nanotube (2009)	Poriferia (Greece)	Efficient removal of carbon dioxide [29]
Quad-Nano Extreme (a metal catalyst) (2006)	Air OasisAir Purifiers (United States)	Air clarifier, reduces ozone in the environment to a safer level [34]

Gens Nano (a photocatalyst) (2009)	**Green Earth Nano Science Inc. (Canada)**	**Removes formaldehyde, NOx, benzene, VOCs & automobiles exhaust [35]**
Elbegast (2012)	**Goldemar (United States)**	**Low cost as compared to platinum & removes VOCs, CO, SOOT, HCs & NOx [36]**

***CBEN- Center for Biological and Environmental Nanotechnology**

APPLICATION OF NANOTECHNOLOGY FOR TREATMENT OF CONTAMINATED SOILS

Various organic chemicals which are resistant to biodegradation are mainly contributing to the contamination of surface and subsurface soils. These are posing a serious threat to safety of living organisms and their natural habitats as many of these are of toxic and mutagenic nature. These persistent chemicals include polycyclic aromatic hydrocarbons (PAHs) comprising heavier fractions of petroleum with two or more benzene rings and relative stability. Due to their hazardous nature, U.S. Environmental protection Agency (EPA) has enlisted 16 of these PAHs as priority pollutants. Some of these chemicals are used to manufacture different kind of stuff like dyes, explosives, medicinal drugs etc. However exposure of soil to these pollutants may be caused by industrial activity including oil leaks, improper disposal and incomplete combustion (Chang et al., 2005). In addition, several sites are also found which are heavily contaminated with halogenated organic compounds like pentachlorophenol, trichloroethylene, trichloroethane, dinitrotoulene, and trinitrotoluene. These chemicals are also placed in the EPA list of priority pollutants. As these carcinogenic contaminants are also immune to biodegradation and persist in the environment (Vogel et al., 1987).

Remediation techniques

Different remediation techniques have been used for the soils contaminated with PAHs. These include various chemical and biological approaches like Fenton reaction for pyrene removal (Chang et al., 2003). Moreover, treatment of surface and subsurface soils with different surfactants is also tested. As four column experiments have been conducted to evaluate the potential of aqueous surfactants for tertrachloroethylene extraction from sand particles. In addition, separation of phenanthrene from soil by using different surfactants is also reported (Pennell et al., 1994). However, Wilson and Jones (1993) found that use of in situ techniques for removal of most of the PAHs from contaminated soil do not give sufficient results. Therefore, more effective techniques are required to effectively remove PAHs.

Permeable reactive barrier (PRB) technology

The traditional methods for treatment of halogenated contaminants like soil washing, thermal desorption and bioremediation are considered less effective due to their high cost, secondary waste production and slow rate. Permeable reactive barrier (PRB) technique is effectively used to treat ground water contaminated with various compounds like chlorinated ethylenes, halomethanes, nitroaromatic compounds, pentachlorophenol, chlorinated pesticides such as DDT, polychlorinated biphenyls, atrazine etc. (Reddy, 2010). It involves use of zero-valent iron Fe° as reactive medium for de-halogenation of contaminants as they react with iron and are reduced into non-toxic form (Sharma and Reddy, 2004). Possible reductive reactions between zero-valent iron and a halogenated compound are given as following;

Reactions of zero-valent iron (Fe0) with a halogenated organic compound (RX) in water

Reaction	Mechanism
Anaerobic corrosion of iron	$Fe + 2H_2O = Fe^{2+} + H_2 + 2\ OH^-$
Aerobic corrosion of iron	$2Fe + O_2 + 2H_2O = 2Fe^{2+} + 4OH$
Possible reductive reactions of iron with RX	
Reaction of RX with ferrous ion in the aqueous phase	$RX + 2Fe^{2+} + H^+ = 2\ Fe^{3+} + RH + X$
Reaction of RX at the surface of the metal (electron transferreaction)	$RX + Fe + H^+ = RH + Fe^{2+} + X$
Adsorption of RX to the metal surface and the	$Fe = Fe^{2+} + 2e^-$
subsequent surface reaction of the organic radical R*	$RX + e^- = R^* + X^-$ $R^* + H^+ + e^- = RH$

Limitations of PRB

Although PRB technique has advantage of being relatively economical due to low cost of Fe°, easy handling and operational activity. However, its efficiency is compromised by following factors;

i) Formation of oxide surface film which reduces the reactivity of Fe°.

ii) Air contact reduces the ability of iron to reduce halogenated compounds.

iii) Variation in reactivity of zero-valent iron for different compounds thus reaction rate is not predictable.

These limiting factor reduce the effectiveness of PRB for long term in situ remediation (Reddy, 2010).

Use of Nano-scale iron particles (NIP) for soil treatment

Nanotechnology has equipped the remediation techniques with the tool of nanoscale zerovalent iron particles (NIP) which can be used for treatment of various non-degradable organic compounds from soil and groundwater. These particles are more effective than PRB due to following properties;

i) Higher reducing ability and rate of reaction as compared to PRB technique.
ii) In situ detoxification of compounds by direct injection of NIP into contaminated soil as compared to PRB in which contaminated water passes through the PRB.
iii) Increased surface to volume ratio which makes the NIP more reactive.

Moreover, several studies have reported the effectiveness of nanoscale iron particles as compared to iron fillings which is used in permeable reactive barrier method (Cao et al., 2005).

Though several nanoscale metal oxides are considered suitable for use for soil treatment. However, some of these like ZnO and AgO_2 are avoided due to their toxicity. In contrast, nanoscale iron particles are widely used due to their environment friendly nature, low cost, easy injecting procedure and fast reaction which results in production of less toxic waste products.

Reactivity of NIP

Reaction time, concentration of both NIP and contaminant act as limiting factors for reactivity of NIP. Whereas, rate of reaction is affected by pH, temperature and absence or presence of oxygen etc. The reaction involves following steps;

a) Halogenated contaminants move from solution towards iron particles.
b) Absorption of these compounds at surface of iron.
c) Reduction reactions resulting in de-halogenation of compounds.
d) Desorption of compounds from iron particles.
e) Movement of reduced products back into the solution (Shih et al., 2008).

Modification of NIP to increase the reactivity and stability

Increased reactivity and stability are achieved by modification of NIP. Reactivity is increased by synthesis of composite nanoparticles/ bimetallic particles which involves combining NIP with a noble metal e.g. Ag/Fe, Cu/Fe, Ni/Fe. The noble metal protects the iron core against oxidation reactions and acts as a catalyst (Li et al., 2006). Since these particles are prone to clustering due to magnetic properties and van der walls attractions. Furthermore, these have greater density as compared to water which results in quick settlement. Thus the rate of NIP delivery to contaminated zone is compromised due to clustering and sedimentation. This problem can be solved by increasing the stability of iron particles by using different modifiers like polyacrylic acid, potato starch, guar gum etc. which modify the surface of NIP and increase both their reactivity and movement towards contaminated sites (Saleh et al., 2007).

Soil treatment with NIP and modified NIP

Soils can be directly injected with NIP slurry due to their small particle size. However, reaction rate is slower in soil as compared to aqueous media (Varanasi et al., 2007). Reaction rate can be increased by both increasing the concentration of NIP and reaction time. Use of NIP has been proved to remove 60% of pyrene from soils in Taiwan (Chang et al., 2007). However modification may compromise the transport and reactivity of NIP which can be avoided by using suitable modifier like lactate modification and appropriate delivery system. It is considered effective in soils with high permeability when used with pressurized delivery system. Whereas, soils with low permeability need electro kinetic delivery system for effective transport of lactate modified NIP (Reddy, 2010).

NANOTECHNOLOGY IN ENVIRONMENTAL MONITORING

Anthropogenic activities particularly industrialization and extensive utilization of chemicals in `agriculture have caused pollution in soil, water and air. Monitoring pollution and contaminants in air, water and soil are very important to assess risks in environment. Detection of environmental pollutants is required for the safety of living organisms [50]. Environmental monitoring includes various aspects including monitoring emissions in air and drinking water, aquatic environment, air quality and depositions. Conventional chromatography and spectroscopic techniques for environmental monitoring like (GC/MS) and (HPLC/MS) are time consuming, expensive and requires a lot of expertise. For water samples it is difficult to carry out these activities outside laboratory [50, 51]. Instead of relying on conventional procedures, electrochemical and immunoassay techniques is gaining importance for developing biosensors with rapid and on-site monitoring [52]. Recently different types of biosensors have been utilized for the purpose of environmental monitoring. Biosensors can be defined as the analytical devices with a biological material incorporated in them and it is linked with a physiochemical transducer which can be optical, electrochemical, magnetic, micromechanical, thermometric or piezoelectric detector [53]. Biosensors can be classified on the basis of biological signal (enzyme, antibody, DNA, cell based and biomimetic) or transducer (electrochemical, piezoelectric, calorimetric and optical). Many of the biosensors are commercially available Biosensors field has flourished to an extent that it has allowed to develop biochip for real time monitoring with low costs [54].

In the search of perfection, quest of developing next generation biosensors has led us to the point where incorporation of nano-materials in biosensors takes place and reveals a great state of the art technology with bright prospects.

ROLE OF NANO-SENSORS IN ENVIRONMENT

Size of nano-materials is smaller than 100 nm. Nano-materials exhibit properties different form other materials as they are smaller than solids but larger than individual atoms and molecules. High dispersity of nano crystalline systems and size quantization of nano materials are the key factors due to which nano-materials exhibit very different properties. Laws of absolute quantum chemistry or classical physics are not followed by nano-materials [55]. As nanoparticles are smaller than characteristic length they exhibit new chemistry, new physics and thus new properties which is largely influenced by the size [56]. Nanotechnology has revolutionized the scientific industry and nano-materials have been utilized in many different commercial industries. Nano-materials find immense applications in the field of sensing technology. It has a promising role in pollution sensing field due to the unique properties of nano-materials [57].Large surface area, great catalytic efficiency, high surface reactivity and strong adsorption capacity makes nano-materials ideal candidates for sensing devices [58].Because of high sensitivity and great recognition, nanosensors are labeled as “smart devices” [59]. Nanosensors can possess the capability of detecting pollutants, toxins and microorganisms in minute amounts [57]. There are many advantages of nano-material enabled biosensors including sensitivity, selectivity, small size, low cost and fast response time [52, 45]. Varieties of nanomaterial have been employed for environmental monitoring with different modifications. Some of the nanosensors with their specifications used within the last ten years have been described in **Table 3**.

Table 3. Nanosensors and their specifications

Signal transduction method	Recognition element	Type of Nano-particle employed	Comments	Ref.
Electrochemical Change in sensor resistance	Solids-state Gas sensor coupled with GIS modeling	Metal oxide is coated with electrodes on substrate, incorporation of GIS modeling	Gas adsorption and sensitivity increased at nanoscale	[60}
Optical properties (color/ refractive index) changes when exposed to organic vapors	Volatile organic compounds	Vapochromic complex is used as a sensing material and ESA (electrostatic self-assembly) method to build nano-cavities on optical fiber by depositing ionic monolayers doped with vapochromic complex	High reproducibility, efficient, nano-cavity sensitive to alcoholic vapors	[61]
Chemosensor for colorimetric recognition, Color change	Mercury ions	Chemically synthesized azochromophores fabricated with compact nanopore compact discs available as strips	Visual detection of ultra-trace Hg^{II} ions, Cost effective, energy saving system and ecofriendly, analysis can be done on site and in-situ without need of complex sample treatments	[62]
Electrochemical, AC voltage and frequency	Humidity sensor	LiCl doped TiO_2electrospunnanofibers	Highly sensitive, stable, can measure humidity at room temperature, good reproducibility	[63]
Multiple depending on particular type e.g., fluorescence, colorimetric	Small organic molecules, proteins, metal ions	Aptamer (oligonucleotide) functionalized Nano-biosensors, a number of nano-materials can be employed most successful are silver and gold nanoparticles	Highy selective interaction of oligonucleotide (DNA/RNA) with sample, high amplification signal, pH, viscosity ionic strength affects oligonucleotide	[64]
Photoluminescence	Hydrogen gas sensing at room temperature	Single ZnO nanowire sensor invented utilizing focused ion beam instrument	Possible to tune gas response and selectivity	[65]
Change in Refractive index/ color detection by optical spectroscopy	DNA, proteins, enzymatic activity	LSPR-based nano-biosensors, metal nanoparticles prepared by nanolithography incorporated to sensor moiety	Refractive index sensitivity of metal nanoparticles can be influenced by size and shape, combining SPR in metal films and LSPR by nanostructures enables detection of biochemical interactions inside nanoholes	[66]
Electrical current and sensor resistance	Selective and sensitive detection of NO_2gas	Nanosensor based on tungsten-oxide mesocages, hollow spheres and nanowires	Inexpensive, scalable synthesis method, significant response at low concentration	[67]
Fluorescence/ magnetic fluorescence/ surface plasmon resonance/ Surface enhanced Raman spectroscopy	Pathogens detection in water	Quantum dots, metals, carbon nanotubes, magnetic nanoparticles, dye doped nanoparticles	Whole cell detection of water borne pathogens, differentiation of viable from non-viable cells and detection of viable but non-culturable cells is still a challenge	[68, 69]
Electrochemical	Microorganisms, toxins, small organic molecules	Single walled carbon nanotubes	High response, magnificent sensing behavior, rapid, label-free	[70]
Electrochemical detection, Oxidation, reduction current of enzymatic products, change in pH	Organophosphorus pesticides and nerve agents	Gold nanoparticles and chemically reduced graphene oxide nanosheets	Stability, trace pesticide detection, optimization for broad substrates required	[65]

It can be stated explicitly that a variety of nanosensors have been employed in a number of studies for environmental monitoring. Design of nanosensors differs according to the type of nanoparticle used, signal transduction method and type of recognition element which it has to detect. Nanosensors allow more rapid and sensitive detection of analyte as compared to the conventional methods of detection. Thus, structure of nanosensors largely depends on the function it will be carrying out. Efforts are underway to design advanced and modernizednanosensors that can accumulate present advantages of nanosensors with the provision of environmental monitoring on site with naked eye.

IMPACT OF NANOTECHNOLOGY ON ENVIRONMENT

With the advancement in nanotechnology its impacts on environment and public health need to be considered. Vast research is needed in this regard to identify the environmental problems, different opportunities to eradicate that problem and to evaluate the impact of nanotechnology in environment. For cleanup of environment nanomaterials are used that include nanoscale zeolites, metal oxides, carbon nanotubes and fibers, enzymes, various noble metals [mainly as bimetallic nanoparticles (BNPs)], and titanium dioxide. One of the most commonly used nanomaterial is zero-valent iron (nZVI).

Table 4: Environmental Nanoparticles: Advantages and Disadvantages

Compound	Advantages	Disadvantages	References
TiO_2 based nanoparticles	• Non-toxic • photo-stable • water insoluble	Large volume of sludge generation • Difficult recovery • Costly	[71]
Iron based nanoparticles	Soil & water insitu remediation • Safe • Cost effective • removal persistent organic compound such as hexachloroccyclohexane	• Hard recovery • Sludge generation • Sludge disposal is expensive • Negative health impacts DNA damage, lipid peroxidation, and oxidative damage of proteins	[72-74]
bimetallic nanoparticles	Highly reactive in redox reactions	• Hard recovery • Sludge generation • Difficult disposal • Production of toxic products	[75]
Nanoclays	• low cost • unique structures • Highly stable • Reusable • high sorption capacity • easy to recover • large surface area	large amount of sludge generation • poor porosity	[75, 76]
Nanotube	• Adsorption of heavy metals, anions and organic pollutants • high thermal and electrical conductivity • Rigid and stable	• high operational cost • generation of sludge • difficult to recover • poses health problems	[77]
Dendrimes	• renewable	Conformational dynamics and 3-D	[78]

	• large binding capacity • cost-effective • pollutant reduction	structure are not well understood	
magnetite nanoparticles	adsorb organic pollutants and heavy metals less sludge generation	Requires external magnetic field for separation • Highly expensive.	[75]
Carbon nanotubes	• highly specific, thermally & chemically stable	• Lung diseases • Cancer • Alzheimer's disease	[2]

GREEN SYNTHESIS FOR ENVIRONMENT

With the advancement in nanotechnology, green chemistry and green technology are working on finding ways to eliminate toxic ingredients from the manufacturing processes in order to reduce their release in environment. Such processes need to be established that require low temperature, consume less energy and use renewable resources wherever possible. Green nanotechnology is trying to incorporate these ideas and aims to not only contribute to lessen the environmental problems, but also to synthesize such nanomaterials and products that have minimum negative impact on the environment and human health. If all the aforementioned prerequisites are full filled precisely, green nanotechnology should results in environmentally friendly and energy efficient manufacturing processes [79].

Bromothymol blue is a dye and it can cause skin and eye irritation. It is also associated with ingestion problems and May cause gastrointestinal irritation with nausea, vomiting and diarrhea. In some cases respiratory problems and allergies were also reported so scientists tried to degrade it with the help of nano-particles.Most frequently iron and magnetic nanoparticles were synthesized using different plants extracts. Tea extract was most commonly used plant resource for the synthesis of iron nanoparticles. Hoag with his coworkers synthesized iron based nanparticle from Camellia sinensis (green tea) extract. Tea polyphenols act as reducing agents. They have iron chelates, used for bromothymol blue degradation [80].

Another study used three different types of tea extracts, namely, green tea (GT), oolong tea (OT), and black tea (BT) to synthesize iron nanoparticles. These nanoparticles were tested for their capacity to act as a catalyst for Fenton-like oxidation of monochlorobenzene (MCB). It is a solvent and a chemical intermediate. Its acute inhalation exposure to animals produced narcosis, restlessness, muscle spasms and tremors. Long-term exposure to humans affects the central nervous system. Signs of neurotoxicity in humans include cyanosis, numbness, muscle spasms and hyperesthesia.Highest (69%) removal of MCB was observed with green tea based iron nanoparticles. Green tea based iron nanoparticles were also able to oxidatively degrade 81% of MCB along with a 31% reduction in chemical oxygen demand [81].

Huang et al also used Oolong tea extract for synthesizing iron nanoparticles to efficiently degrade Malachite green dye (75.5% in 60 minutes) which is otherwise difficult to degrade [82].

Eucalyptus globules leaf extract was used as a bio-reducing agent to synthesize nZVI. Plant extract contain polyphenolic compound named oenothein B which is responsible for synthesis and stabilization of iron nanaoparticle. These nanoparticles were found to be stable even after two months and a very small quantity was sufficient to remove a huge amount of (98.1%) hexavalent chromium just within 30 minutes [83].

Iron nanoparticles were synthesized using pomegranate leaf extract and were coated on the two strains of heat-killed yeast cells Yarrowia lipolytica. This bionanocomposite was used to degrade hexavalent chromium. The sorption capacity of magnetically modified yeast cells was three times more than that of unmodified yeast cells [84].

Banana peel ash extract was also utilized to produce iron oxide nanoparticles, and aqueous extract of Colocasia esculenta leaves was used to reduce graphene oxide. Nanohybrids of iron oxide/reduced graphene oxide were synthesized and they were able to remove 10 ppm of tetrabromobisphenol A in 30 minutes, lead and cadmium in 10 minutes at optimum experimental conditions [85]**.**

Plantain peel extract was used by Venkateswarlu et al. for synthesis of magnetite nanoparticles as a low-cost bio-reducing agent. The structure of nanaoparticle is mesoporous, possess ample surface area (11.31 m2/g) and have high saturation magnetization. Due to these properties these nanoparticles can be used in the field of environmental remediation for the removal of toxic metals and dyes [86].

CONCLUSION AND FUTURE PROSPECTS

With rapid increase in population, urbanization and industrialization, huge list of pollutants is contaminating the environment so, past efforts and treatment methods are not sufficient to sequester them. So, there is a need of technologies that can make pollution free environment. With emerging technology like phytoremediation, nanotechnology offers great deals to treat contaminants. Nanoengineered materials offers great potential for new treatment technologies that can be adapted by the consumers. Most of the nanotechnology applications are either compatible with the conventional methods or even much better. Nano-materials are advantageous to already existing treatment methods for-example different kind of nano- based membranes that can retain different size particles and eliminate contaminants. Nanomaterials havehigher process efficiency because of their distinctive characteristics, like high specificity and increased reaction rate. However, there are many drawbacks that have to be eliminated. Materials coated with nanoparticles have various risk potentials. They might release into the environment where they can be accumulated for long duration. Up until now, nanotechnology based treatments are applicable on small scale experiments. So, there is a need to use the spectra of nanotechnology on large scale. Nanotechnology will become a fundamental component of industrial treatment systems in the future as more progress is made in terms ofdevelopment of eco-friendly technology which would be economically beneficial.

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