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7. Use of Nanotechnology in Remediation of Environmental Pollutants

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7.1 Introduction:

Environmental pollution is one of the highly concerned global issues as affected the whole planet. Although numerous laws are made to control environmental pollution, but there is no improvement has been seen in recent years. The quality of air degraded day by day and it became toxic several part of the earth. Specifically air pollution causes severe illness, even snatch away the lives of people. Environmental pollution not only destroyed our environment but also cause serious health problems in humans. Heavy metals, particulate matter, pesticides, herbicides, fertilizers, oil spills, toxic gases, industrial effluents, sewage and organic compounds are some of the contaminants that polluted our environment. Intensive agriculture, industrialization and various land activities contaminate water, soil and air as well as with toxic pollutant. Waste discharge from pulp, dyeing, petrochemical and textile industries and the partial degradation of phenoxy contaminants in various remediation processes produce phenolic components. These may have deleterious consequences on the health and well-being of plant and animal biota. So there is an urgent need to control environmental pollution to restore the health of the environment. During recent years various technologies have been used to eliminate pollutants from the environment. New technologies are constantly explored for the remediation of the air, water and soil contaminants. Salvaging basic resources, along with remediating toxic pollutants and contaminants, by adopting latest technologies is a challenging priority. So nanotechnology is emerging to provide a state of art solution to these problems.

Nanotechnology involves the creation and manipulation of materials at the nanometer scale, either by scaling up from single groups of atoms or by refining or reducing bulk materials. This technology has gained a lot of attention in the past decades due to the unique physical properties of nanoscale materials or nanoparticles. Nanoparticles are wide the class of materials that include particulate substances, which have one dimension less than 100 nm at least. Nanoparticles possess unique physical and chemical properties due to their high surface area and nanoscale size. Their size, shape and structure determine their reactivity, toughness and other properties. Due to these properties nanoparticles can be used in various domestic and commercial applications that include catalysis, imaging, and medical application as well as environmental applications. It was found that nanomaterials have enhanced reactivity and better effectiveness than their bulkier counterparts.

Various types of materials can be employed in environmental remediation. Since environmental pollutants are the mixture of different compounds of high volatility, and low reactivity, it is challenging to the capture and degrades these pollutants.

Due these complexities, recent studies have focused on the use of nanomaterials for the development of new environmental remediation technologies. As compared to traditional approaches nanomaterials or nanoparticles has more potential due to their unique surface chemistry, because they can functionalized or grafted with functional groups that can target specific molecules of interest for efficient remediation. Moreover, due to their specific physical properties and chemical composition, they provide additional advantageous characteristics that directly affect the material for contaminant or pollutant remediation. The rich surface modification chemistry along with the unique physical parameters of the nanoparticles offers significant advantages over traditional methods for controlling environmental contamination.

The larger exposed area of nanoparticles reflects in higher number of atoms being stationed at the surface and these are readily available for several reactions including catalysis. Nanoparticles can detect and treat existing environmental contaminants and prevent new pollution. They can be used in the treatment of various contaminated media by chemically transforming contaminants or they act as super adsorbent. Nanoparticles also play vital role in the development of environmental sensor which can detect pollutant at molecular level. Nanoparticles can be used to improve water quality. Bioactive nanoparticles, Nano adsorbents and nanostructured catalytic membranes have enormous application in water purification. They serve as high capacity ligands for the toxic metal ions, organic and inorganic solutes and remove them from contaminated water. Soil pollution is also major problem that faced by our over growing population. Due to growing population the amount of solid and plastic waste has increased and it affects adversely the soil health and fertility. In this case, nanotechnology solution can be used for bioremediation and phytoremediation to remove contaminants.

7.2 Nanobioremediation:

It is estimated that around 10 million tons of toxic compounds are released by industry. These toxic chemical compounds further react to form chemicals like polychlorinated dibenzo-p-dioxine which is a by-product of certain chemical processes involving chlorine. These compounds have variable physical and chemical property. They have cytotoxic effects and their interaction with biotic and abiotic environmental components have complicated the remediation processes. So to overcome such problems nanoparticles can be useful tool. The use of nanoparticles in remediation processes can help to avoiding process intermediate and increases the speed of degradation. Apart from physical and chemical remediation technologies, biological treatment of pollutant have become relevant because of its low cost and wide range of application. Bioremediation involves the process of bioaccumulation, biotransformation and biostabilization. In recent years, nanoparticles have been integrated with biological processes to accelerate and enhance the removal of toxic compounds from the environment. The term nanobioremediation was first used by Cechin and his co-workers for the processes where nanoparticles, microorganisms and plants are used to remove contaminants. Further El-Ramady and his colleagues named these types of practices according to the nature of organisms utilized for the remediation. Thus the processes like phyto-nanoremediation, microbial nanoremediation and zoo-nanoremediation are named after the organisms used in the remediation process. There is a proper interaction between nanoparticles and living organism in case of nanobioremediation, which help to eradicate contaminants from environment.

According to some researcher the physical and chemical interaction between nanoparticles, biota and contaminants depends on various parameters which includes the size of nanoparticles, its shape, surface coating, chemical nature of the nanoparticles and contaminant, the type of the organisms, media, pH as well as temperature. For example pH and temperature of media play an important role in the proper development of living organisms or microorganisms.

In turn these parameters also influence the stability of nanoparticles and contaminants. For example gold nanoparticles are stable in milio water and buffer, but they lose their stability at pH of 4, 7, 8 and 10. It is also proved that different synthetic methods influenced the thermal stability of copper nanoparticles.

For remediation of contaminants, specific temperature and pH has synergistic effect on nanoparticles and living organisms in nanobioremediation. Sorption is an essential part of nanobioremediation. This process involves adsorption and absorption. In adsorption, the interaction between the pollutant and the sorbent occurs at a surface level. In the second one, the pollutant penetrates deeper layers of the sorbent to form a solution. In case of adsorption a chemical reaction occurs whereas in absorption only physical forces are involved.

In sorption process, the contaminants can be immobilized, sequenced and concentrated. Numerous study and research has been conducted to understand the nature of the adsorption process using nanomaterials or nanoparticels. So mechanistic, thermodynamic as well as kinetic studies are needed for describing the nanomaterial when this material enters into contact with the contaminants.

The degradation of contaminants occurred by photocatalytic process that depends on the nature of nanoparticles or nanomaterials. The product that is produced after degradation further bio transformed by the biotic system and reduce the concentration of pollutant or contaminant in the media. In addition to this, some enzymes produced by living organisms may degrade a variety of pollutant or contaminants. Nanoparticles are able to enter contaminated zones due to their small size, where entry of other particle is not possible.

That’s why nanobioremediation technologies can be used in different field. This aspect represents an advantage over other remediation techniques. But the standardization of protocols is necessary to evaluate the toxicity of nanoparticles and nanoparticles in soil and water, elucidation of their interactions with biotic and abiotic elements. A regulatory frame is also required where these materials could be applied.

By extension, methods that are developed as a combination of several different materials (hybrids/composites), gathering specific desired properties from each of its components, are potentially more efficient, selective, and stable than methods based upon a single Nano platform. For instance, adhering nanoparticles to a scaffold can be an alternative way to increase the stability of the material when compared to the use of nanoparticles alone.

Functionalizing material with specific chemicals responsible for targeting contaminant molecules of interest can help increase the selectivity and efficiency of the material.

7.3 Commonly Used Nanoparticles in Remediation of Contaminats:

Different metal-based nanomaterials or nanoparticles have been described for the remediation of numerous contaminants. Metal and metal oxide nanomaterials are highly efficient adsorbents exhibiting advantages such as fast kinetics and high adsorption capacity.

7.3.1 Silver Nanoparticles (Ag NPs):

These are well known for their significant antibacterial, antifungal, and antiviral activity, and thus applied as water disinfectants. For instance, Ag NPs of less than 10 nm in diameter were found to be highly toxic to Escherichia coli and Pseudomonas aeruginosa. They can also prevent viruses from binding to host cells by preferentially binding to the virus' glycoproteins.

Slightly larger particle sizes (i.e., 11–23 nm) afford lower bactericidal activity. In addition, triangular Ag NPs exhibited better antibacterial effects than Ag nanorods and Ag Nano spheres, emphasizing the importance of not only size, but Ag NPs have been coupled with several other materials such as metal oxides and polymers with the goal of improving the overall efficiency of the resulting nanocomposite.

7.3.2 Titanium Oxide Nanoparticles (TiO2 NPs):

Another frequently investigated metal-based material for environmental remediation is titanium oxides. TiO2 NPs have been extensively studied for waste treatment, air purification, self-cleaning of surfaces, and as a photocatalyst in water treatment application due to their characterized low-cost, nontoxicity, semiconducting, photocatalytic, electronic, gas sensing, and energy converting properties. TiO2 NPs are activated by light, and thus frequently studied for their ability to remove organic contaminants from various media. TiO2 NPs are capable of producing highly reactive oxidants like hydroxyl radicals that serve as a disinfectant for microorganisms such as fungi, bacteria, viruses, and algae. Since TiO2 exhibits a rather limited photocatalytic capability, the material is typically doped with another transition metal ion to increase performance. Therefore, several studies have investigated metal-doped TiO2 NPs. The synthesis of TiO2 nanofibers (control) and Ag-doped TiO2 Nano fibers can be performed by a sol–gel electrospinning technique. These materials were as photocatalyst for the photocatalytic degradation of 2-chlorophenol under UV irradiation. Ag-doped TiO2 nanofibers presented increased photodegradation when compared to the TiO2 nanofibers.

The increase was attributed to four possible factors, including, adequate amount of Ag on the surface that effectively captured photo induced electrons and holes, quick transfer of photo induced electrons to the adsorbed oxygen present on the surface of the nanofibers, increased amount of surface hydroxyl groups, and expanded response range to light to the visible region. In addition to titanium oxide materials, titanates (i.e., inorganic compounds of titanium oxide) have also been reported for the removal of contaminants. The fabrication of basic, acidic, and neutral titanate nanotubes (TNTs) by a hydrothermal method, and these materials were evaluated for the catalytic reduction of NO with ammonia.

Manganese oxides were loaded to the three TNT formulations to yield Mn-doped titanate nanosheets, titanate nanorods, and titanate nanotubes (i.e., Mn/TNTs) in the case of basic, acidic, and neutral pH media, respectively.

7.3.3 Mixed Oxide Material Nanoparticles:

Moreover, mixed oxide materials have also been investigated. TiO2 SiO2 binary mixed oxide materials using bamboo as a silica source and titanium isopropoxide or titanium butoxide. The materials were evaluated for the photocatalytic degradation of methylene blue dye. The results showed a significant photo activity as indicated by the degradation rate of methylene blue at varied treatment times. The composite may have potential applications in smaller-scale industrial wastewater treatment systems. These mixed oxide materials have enhanced abilities to remove a wide variety of pollutants. Despite the fact that these binary mixed oxides show better activity than pure TiO2 materials in most instances, their utilization is limited for the mineralization of selected pollutant.

7.4 Silica Nanomaterials:

Due to their versatility, mesoporous silica materials have gained attention for various applications, such as adsorption and catalysis. Mesoporous silica materials possess a number of beneficial features for environmental remediation applications including: high surface area, facile surface modification, large pore volumes, and tunable pore size. Due to their exquisite performance as adsorbents, a variety of studies have reported the use of these materials for contaminant remediation in the gas phase. Furthermore, different surface modifications of mesoporous silica materials have been reported in many publications.

7.4.1 Carbon-Based Nanomaterials:

The structural composition of elemental carbon and its mutable hybridization states account for the unique physical, chemical, and electronic properties of carbonaceous materials compared to metal-based nanomaterials. Mutable hybridization states can yield different structural configurations such as fullerene C60, fullerene C540, single-walled nanotubes, multi-walled nanotubes, and graphene.

In a variety of investigations determining the suitability of carbon nanotubes and graphene for environmental remediation applications, it has been reported that surface treatments, activation, or functionalization of the pristine carbon material is first required. Multi-walled and single walled carbon nanotubes (MWCNTs and SWCNTs) have been the subject of many studies. The adsorption properties of these materials make them particularly useful for the removal of organic and inorganic pollutants from air and from large volumes of aqueous solution.

Carbon based nanomaterials are also employed to remediate contaminants through photocatalytic approaches. Under UV irradiation, photons of energy greater than or equal to the band gap of the nanotubes promote the generation of valence band holes (h+) and conduction band electrons. The holes are responsible for the formation of hydroxyl radicals that take part in the oxidation of chlorinated organic compounds.

The electrons form superoxide radicals that take part in the reduction of heavy metal contaminants. Several studies have been reported that describe the use of graphene to fabricate photocatalytic nanocomposites. Graphene composites containing TiO2 NPs show increased photocatalytic activity when compared to bare TiO2- NPs due to an increase in conductivity.

7.4.2 Carbon Nanotubes (CNTs):

Most notably, efforts have been undertaken to open the closed ends of pristine CNTs in order to enhance their adsorption properties. Generally, single walled carbon nanotubes (SWCNTs) are arranged in a hexagonal configuration (i.e., one nanotube surrounded by six others), thus forming bundles of aligned tubes with a heterogeneous, porous structure. For a typical open-ended CNT bundle, adsorption can take place in four different available sites, which are of two types: those with lower adsorption energy, localized on external surfaces of the external CNTs composing the bundle; and those of higher adsorption energy, localized either in between two neighboring tubes or within an individual tube. Adsorption on external sites reaches equilibrium much faster than adsorption on internal sites due to the direct exposure of the external sites to the adsorbing material. Multi walled carbon nanotubes (MWCNTs) do not usually exist as bundles, except when specific methods of preparation are used to create such configurations.

Many researcher have demonstrated in their nitrogen adsorption studies that different types of pores (i.e., inner and aggregated) create a multi-stage adsorption process. Aggregated pores were shown to be more significantly responsible for the adsorption properties of these materials than the less accessible inner pores.

7.4.3 Polymer-Based Nanoparticles:

Although the large surface area-to-volume ratio of nanomaterials contributes to higher reactivity with concomitant improved performance, the occurrence of aggregation, non-specificity, and low stability can limit the use of these nanotechnologies due to the lack of functionality. An alternative to enhance stability of nanoscale materials is to employ the use of a host material, the purpose of which is to serve as a matrix or support to other types of materials. Polymers are mostly used for the detection and removal of contaminant chemicals (e.g., manganese, nitrate, iron, arsenic, heavy metals, etc.), gases (e.g., CO, SO2, NOx), organic pollutants (e.g., aliphatic and aromatic hydrocarbons, pharmaceuticals, or VOCs) and a wide array of biologics (e.g., bacteria, parasites, viruses, etc.). Polymeric hosts (e.g., surfactants, emulsifiers, stabilizing agents, and surface functionalized ligands) are often employed to enhance stability and overcome some of the limitations of pristine nanoparticles as well as to impart other desirable properties such as enhanced mechanical strength, thermal stability, durability, and recyclability of the material in question. Amphiphilic polyurethane (APU) NPs have been developed for the remediation of polynuclear aromatic hydrocarbons (PAHs) from soils, thus validating the hypothesis that organic NPs can be engineered with desired properties. The hydrophilic surface of the nanoparticles promotes mobility in the soil, while the hydrophobic interior of the material confers affinity for the hydrophobic organic contaminants. APU NPs removed phenanthrene from contaminated aquifer sand (i.e., 80% recovery).

An analysis of different formulations indicated that the APU nanoparticle affinity for phenanthrene increased when the size of the hydrophobic backbone was also increased. Furthermore, increasing the number of ionic groups on the precursor chain contributed to a reduction in APU particle aggregation in the presence of polyvalent cations. While the application of these materials in the environment could be beneficial for contaminant remediation, there is no report on the biodegradability of such materials, which contributes to concerns regarding their fate after application. Poly (amidoamine) or dendrimers (PAMAM) have been utilized in wastewater remediation for water samples contaminated with metal ions such as Cu2+. Those dendritic nanopolymers contain functional groups such as primary amines, carboxylates, and hydroxamates which are able to encapsulate a broad range of solutes in water, including cations (e.g., Cu2+, Ag+, Au+ etc). They are used as chelating agents and ultrafilters to bind with metal ions thus facilitating water purification. These materials have also been used as antibacterial/antivirus agents. The key feature of the dendritic nanopolymers is that they have a lower tendency to pass through the pores of ultrafiltration membranes compared to linear polymers of similar molecular weight polymers due to their lower polydispersity and globular shape. Therefore, they have been employed to improve ultrafiltration (UF) and microfiltration (MF) processes for the recovery of dissolved ions from aqueous solutions. First, a solution of functionalized dendritic nanopolymers is mixed with contaminated water and then the bound nanopolymer-contaminants are transferred to UF or MF units to recover the clean water. They can be separated from each other by changing the acidity (pH) of the solution and then the recovered concentrated solution of contaminants is collected for disposal and the nanopolymers may be recycled.

7.4.4 Biological Response during the use of Nanoparticles in Bioremediation:

The bacteria and plants which are used in bioremediation are capable of immobilizing metals and transforming both organic as well as inorganic contaminants. It is reported in recent years that the combine use of nanoparticels and bioremediation technologies showed promising results to eliminate contaminants or pollutant from the environment. The combination of nanopartilcles with electrokinetic remediation, chemical oxidation and bioremediation has significant effects in the removal of contaminants from heavily polluted sites. Toxic compounds like polychlorinated byphenils (PCBs) which create a global environmental problem due to their persistence, long range atmospheric transport and slow degradation as well as biocculation.

These compounds are used in electrical capacitors, transformers, hydraulic fluids as wells lubricants. Although these compounds have various uses in preparing numerous useful products but they are very harmful to our environment. To degrade these toxic compounds nanoparticles can be used along with bioremediation.

Researchers have developed a nano/bio treatment for these compounds by using the bimetallic nanoparticles Pd/nFe and *Burkholderia xenovorans* LB400, bacteria. It is also reported that by using carbon nanotubes and *Anthrobacter* sp. PCBs can be degraded. Studies also showed that using of magnetic nanoparticles along with *Rhodococcus rhodochrous* bacteria can degrade compounds like chlorophenal. Likewise the combined effect of phyto and nanoparticles are also provided evidence of successful removal of contaminant from soil and water.

Bometallic nanoparticles along with plants like tobacco are used to degrade compounds such as hexabromocyclododecane (HBCD). This compound is act as a flame retardant additive for preparing thermoplastic polymers and used in insulation, textiles, and electronics. But it has toxic effect to the environment and carcinogenic in nature.

The nanobioremediation technology thus helps to eliminate the toxic effect of hexabromocyclododecane from the environment. So it is found that nanoparticles along with microorganisms and plant gives a significant result in degrading toxic compounds and helps to eliminate the harmful effects of these compounds from the environment.

7.5 Conclusion:

As we are facing the global problem of environmental pollution, new technologies are emerging to control it and help in removing the toxic effect of pollutant. Nanotechnology is one the modern technology which shows promising results in controlling pollution. Use of nanoparticles in nanotechnology helps to remove contaminants from soil and water. Combination of nanoparticles with microorganisms and plants provides significant effect in pollutants eradication. The physical properties and chemical nature of nanoparticels or nanomaterial enables them to remove tough molecules of pollutant from the environment. Thus nanotechnology would help us to restore our environment by removing toxic compounds.

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