Ecofriendly Application of Nanomaterials: Nanobioremediation

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Nanomaterials exhibit unique physical and chemical properties and, hence, they have received much attention from scientists and researchers in different areas of environmental sciences, specifically in bioremediation. Bioremediation provides a good clean-up strategy for some types of waste, but as it is expected, it will not be useful for all. For example, bioremediation may not provide a feasible strategy at sites with high concentrations of chemicals that are toxic to most microorganisms. These include heavy metals and salt. Further, the advancement in science and technology has increased standard of living which directly or indirectly contributesto the increase in waste and toxic material. Therefore, the remediation of contaminants by use of existing technology is not effective and efficient in cleaning up the environment. Hence, nanomaterials may be applied for bioremediation, which will not only have less toxic effect on microorganisms, but will also improve the microbial activity of the specific waste and toxic material which will reduce the overall time consumption as well as reduce the overall cost. In this paper we have briefly summarized the major types of nanomaterials that have been used so far in bioremediation of waste and toxic materials.

1. Introduction

There are various ecofriendly applications of nanomaterials (NMs) as far as environmental science is concerned, such as materials that provide clean water from polluted water sources in both large scale and portable applications and one that detects and cleans up environmental contaminants (waste and toxic material), that is, remediation [1, 2]. “Remediate” means to solve the problem and “bioremediation” means the process by which various biological agents, such as bacteria, fungi, protists, or their enzyme are used to degrade the environmental contaminants into less toxic forms [3]. The important benefit of bioremediation over conventional treatments is economical, high competence, minimization of chemical and biological sludge, selectivity to specific metals, no supplementary nutrient requirements, regeneration of biosorbent, and the possibility of metal recovery [4]. When bioremediation occurs on its own, then it is known as natural attenuation or intrinsic bioremediation and when it is incited to occur with the addition of fertilizers for the enhancement of bioavailability within the medium, then it is known as biostimulated bioremediation. Most common bioremediation technologies include bioventing, bioleaching, bioreactor, bioaugmentation, composting, biostimulation, land farming, phyto remediation, and rhizofiltration [5]. Bioremediation of a contaminated site typically works in one of two ways. In the first case various substances such as the right temperature, nutrients, and amount of oxygen are used to enhance the growth of whatever pollution-eating microbes (indigenous microorganisms) might already be living at the contaminated site. In the second, less common case, specialized microbes (exogenous microorganisms) are added to degrade the contaminants. But in both cases once harmful chemicals are cleaned up and microbes have eaten their available “food,” the microbes die. Therefore, bioremediation applications fall mainly into two broad categories: in situ or ex situ. In situ bioremediation treats the toxic material in the location in which it is found so it is less expensive because in this process
there is less release of contaminants, toxin or pollutant to the environment, as it is treated at the place where it is found therefor due to confinement of contaminants, toxin or pollutant less amount of NMs can treats large volume or area. However, it is slower and some time may be difficult to manage, whereas ex situ bioremediation processes require excavation of contaminated material or toxic substances before they can be treated. Ex situ techniques can be faster, easier to control, and are used to treat a wider range of contaminants and soil types than in situ techniques [6]. Types of NMs, synthesis methods, and examples are given in Table 1 [7].

2. The Science of Bioremediation with Nanomaterial

There are various reasons for different NMs to be used in bioremediation; for example, when the material is brought to nanoscale, surface area per unit mass of a material increases; hence, a larger amount of the material can come into contact with surrounding materials and this affects the reactivity. NMs show quantum effect; therefore less activation energy is required to make the chemical reactions feasible. Surface plasmon resonance is another phenomenon exhibited by NPs which can be used for the detection of toxic material. As far as shape and size are concerned various metallic and nonmetallic NMs of different shapes and sizes can be used for environmental clean-up. For example, it can use various single metal NPs, bimetallic NPs, carbon base NMs, and so forth, because (i) NPs can diffuse or penetrate into a contamination zone where microparticles cannot reach and (ii) they have higher reactivity to redox-amenable contaminants. It is observed that oxide-coated Fe\(^0\) can form weak and outer-sphere complexes with contaminants such as carbon tetrachloride (CT). Oxide coating increases the reactivity and hence, through electron transfer, CT can be broken down into methane, carbon monoxide, or format, whereas benzoxquinone, bytrichloroetheone, and other chlorinated aliphatic hydrocarbons can be broken down into chemicals with lower toxicities in batch experiments and field assessments [8]. In addition to field applications, TiO\(_2\) nanotubes can be used in a laboratory setting to degrade pentachlorophenol (PCP) through a photoelectrocatalytic reaction [9]. Single metal NPs can also be used as biocatalysts for reductive dechlorination. Palladium, Pd (0) NPs can be deposited on the cell wall and inside the cytoplasm of *Shewanella oneidensis* and can be charged with H\(^+\) radicals by adding different substrates such as hydrogen, acetate, and formate as electron donors in a bioreductive assay containing Pd (II). When these charged Pd (0)-deposited *S. oneidensis* cells are brought in contact with chlorinated compounds, the H\(^+\) radical on the Pd (0) can catalytically react with PCP, resulting in the removal of the chlorine molecule from the chlorinated compounds [10]. NPs can be further used to immobilize microbial cells that can degrade or biorecover specific chemicals. Unlike conventional cell immobilization on micron-sized media or a fixed surface, magnetic NPs (that is Fe\(_x\)O\(_y\)) have been functionalized with ammonium oleate and coated on the surface of *Pseudomonas delafeldii*. By applying an external magnetic field to these microbial cells, these magnetic NP-coated cells concentrated at a specific location on the reactor wall, separated from the bulk solution, and recycled for the treatment of the same substrate. These microbial cells have been added into a bioreactor at a high biomass concentration and were demonstrated to desulfurize organic sulfur from fossil fuel (that is dibenzothiophene) as effectively as non-NP-coated cells [11]. The specific NMs that will be discussed hereafter focus on remediation of various types of waste (Figure 1). These include applications for solid waste, groundwater and wastewater, petroleum and petroleum products (hydrocarbon), soil remediation, uranium remediation, and heavy metal pollution remediation. The ability of NMs to abate pollution production is in progress and could potentially catalyze the most revolutionary changes in the environmental field in the coming decades.

3. Nanoiron and Its Derivatives in Bioremediation

Nanoscale zero-valent iron (NZVI) was synthesized and tested for the removal of As (III), which is a highly toxic, mobile, and predominant arsenic species in anoxic groundwater [12]. Arsenic (V) has been also removed from groundwater using nanoscale zero-valent iron as a colloidal reactive barrier material [13]. The supported zero-valent iron NPs “ferragels” rapidly separate and immobilize Cr (VI) and Pb (II) from aqueous solution, reducing the chromium to Cr (III) and the Pb to Pb (0) while oxidizing the Fe to goethite (\(\alpha\)-FeOOH) [14]. Anionic, hydrophilic carbon (Fe/C), and poly (acrylic acid)-supported (Fe/PAA) zero-valent Fe-NPs were studied as a reactive material for the dehalogenation of chlorinated hydrocarbons in groundwater as well as in soils [15]. Iron can be used to construct a reactive wall in the path of a contaminated groundwater plume to degrade halogenated organic compounds [16]. High surface-area nickel-iron NPs...
Table 1: Type of NMs, their synthesis methods, and examples.

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Synthesis methods</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal nanoparticles (NPs)</td>
<td>Photochemical</td>
<td>Pt, Rh, Pd, Ir, Ag, Au, Cu, Co, Ni, FeNi, Cu$_3$Au, CoNi, CdTe, CdSe, ZnS</td>
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<tr>
<td></td>
<td>Electrochemical</td>
<td></td>
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<td></td>
<td>Biochemical</td>
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<td></td>
<td>Thermochemical</td>
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<tr>
<td>Carbon NMs</td>
<td>Arc-discharge</td>
<td>Cylindrical nanotube (SWNT, MWNT)</td>
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<td></td>
<td>Laser ablation</td>
<td>fullerences</td>
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<td></td>
<td>Chemical vapor deposition</td>
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</tr>
<tr>
<td>Metal oxide NPs</td>
<td>Hydrothermal</td>
<td>ZnO, Fe$_2$O$_3$, Fe$_3$O$_4$, MgO, BaCO$_3$, BaSO$_4$, TiO$_2$</td>
</tr>
<tr>
<td></td>
<td>Solvothermal</td>
<td></td>
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<tr>
<td></td>
<td>Sol-gel</td>
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<tr>
<td></td>
<td>Reverse micelles method</td>
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<tr>
<td></td>
<td>Electrochemical deposition</td>
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</tr>
<tr>
<td>Polymer NMs</td>
<td>Electrochemical polymerization</td>
<td>Nanowire of polypyrrole, polyaniline, poly</td>
</tr>
<tr>
<td></td>
<td>(3,4-ethylenedioxythiophane)</td>
<td>(PAMAM)</td>
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<tr>
<td>Nanocomposite</td>
<td>Innovative methods</td>
<td>Nanocomposite of polyethylene oxide and polyethyleneimine; CNT</td>
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<td></td>
<td></td>
<td>epoxy composites include hydrocarbon polymer composites, conjugated</td>
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<tr>
<td></td>
<td></td>
<td>polymer composites, CNTs with polycarbonates, floropolymers,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polyethylene glycol, polyester polyamides, and so forth</td>
</tr>
<tr>
<td>Bionanomaterials</td>
<td>Biological</td>
<td>Viruses, plasmids, and protein NPs</td>
</tr>
</tbody>
</table>

(1:3 Ni:Fe) have been studied as a reagent for the dehalo-
genation of trichloroethylene (TCE) [17]. The disappearance of pentachlorophenol (PCP) from aqueous solutions in con-
tact with zero-valent metals (ZVMs) may be due to dechlo-
oration reactions or sorption to ZVM-related surfaces [18].
The capability of powdered zero-valent iron to dechlorinate
DDT and related compounds at room temperature has been
investigated. Specifically, DDT, DDD [1,1-dichloro-2,2-bis(p-
chlorophenyl)ethane], and DDE [2,2-bis(p-chlorophenyl)-1,
1-dichloroethylene] transformation by powdered zero-valent
iron in buffered anaerobic aqueous solution was studied at
20°C, with and without the presence of nonionic surfactant
Triton X-114. The iron has been successful at dechlorinating
DDT, DDD, and DDE. Table 2 lists many of the pollutants
potentially remediated by nanoiron technology [19].

4. Dendrimers in Bioremediation

The word "dendrimers" is derived from the Greek words
where "dendri" means like a branch of tree and "meros" means part of tree. Dendrimers highly branched and
monodisperse macromolecules are the recently recognized
members of the polymer field, with the first dendrimers
report published in the 1980s by the groups of Buhleier
et al. [20], Tomalia et al. [21], and Newkome et al. [22].
Technically, a dendrimer is a polymer, which is a large
molecule comprised of many smaller ones linked together. Dendrimers
have some proven applications and numerous potential appli-
cations. Dendrimers are relatively monodispersed and highly
branched macromolecules with controlled composition and
architecture consisting of three components (Figure 2(a)): a
central core, interior branch cells or radial symmetry, and ter-
mental branch cell or peripheral group [23]. Dendrimers have
many void spaces for their interaction of other substances
Figure 2(b) [24]. Therefore, dendrimers-NPs composite can
be prepared and can be used to enhance catalytic activity. This
type of developed composite will be used in water treatment
and dye treatment industries due to more reactivity and more
surface area and less toxicity. Therefore, the researcher has
also proposed its application in clean water recovery unit.
PAMAM dendrimers with special structure and properties
are used in water treatment. It is efficient and innoxious as
a water treatment agent. The researcher has also developed
simple filtration unit for the removal of organic pollutants
by utilizing TiO$_2$ porous ceramic filters of which the pore
was impregnated with an alkylated poly(propylene imine)
dendrimer, poly(ethyleneimine) hyperbranched polymer, or
β-cyclodextrin, thus resulting in hybrid organic/inorganic
filter modules of high mechanical strength and high surface
area [25].
5. Nanocrystals, Carbon Nanotubes, and So Forth in Bioremediation

The exceptional and tunable properties of carbon-based nanomaterials such as nanocrystals and carbon nanotubes (CNTs) enable new technologies to identify and solve a broad range of environmental applications: sorbents, high-flux membranes, depth filters, antimicrobial agents, environmental sensors, renewable energy technologies, and pollution prevention strategies [26]. Such as NMs like single-walled carbon nanotubes (SWCNTs) multiwalled carbon nanotubes (MWCNTs) and hybrid carbon nanotubes (HCNTs) has been evaluated as the removal of ethylbenzene from aqueous solution. The equilibrium amount removed by SWCNTs was higher than that by MWCNTs and the SWCNTs performed better for ethylbenzene sorption than the HCNTs and MWCNTs. Isotherms study indicates that the BET isotherm expression provides the best fit for ethylbenzene sorption by SWCNTs. CNT, specially SWCNTs, are efficient and rapid adsorbents for ethylbenzene which possess good potential applications to maintain high-quality water. Therefore, it could be used for cleaning up environmental pollution to prevent ethylbenzene borne diseases [27]. Recently, cyclodextrins (CD) and CNTs have been included in water treatment and pollutant monitoring application. For example, CD-co-hexamethylene-/toluene-diisocyanate polyurethanes and CNT-modified equivalents have been developed and have been successfully applied in removing organic contaminants from water to very low levels. Calixarenes, thiacalixarenes, and CNT-based polymeric materials incorporating these molecules have been synthesized, characterized, and tested for removing both organic pollutants (p-nitrophenol) and inorganic pollutants (Cd$^{2+}$, Pb$^{2+}$) from water. An environmental friendly adsorbent, CNTs immobilized by calcium alginate (CNTs/CA) have been prepared and their copper adsorption property has been investigated via equilibrium studies. Experimental results showed that copper removal efficiency of CNTs/CA is high and reaches 69.9% even at a lower pH of 2.1. The copper adsorption capacity of CNTs/CA can attain 67.9 mg/g at a copper equilibrium concentration of 5 mg/L [28]. MWCNTs can be used to remove nickel ions from water [29] and magnetic-MWCNT nanocomposites have been applied to remove cationic dye from aqueous solution [30].

6. Single-Enzyme NPs in Bioremediation

Enzymes are proteins which are specific and effective, which function as biocatalysts in bioremediation. However, the lack of stability and relatively short catalytic lifetimes of enzymes may limit their usefulness as cost-effective alternatives to synthetic catalysts. Enzymes lose their activity due to oxidation, which results in less stability and a shorter lifetime thereby rendering them less efficient. An effective way to increase the stability, longevity, and reusability of the enzymes is to attach them to magnetic iron NPs. If enzymes are attached to the magnetic iron NPs then we can easily separate the enzymes from reactants or products by applying a magnetic field. With this purpose, two different catabolic enzymes, trypsin and peroxides, have been used to uniform core-shell magnetic nanoparticles (MNPs). The reported study indicates that the lifetime and activity of enzymes increase dramatically from a few hours to weeks and that MNP-enzyme conjugates are more stable, efficient, and economical.
The study shows that MNPs shield the enzymes preventing them from becoming oxidized. This results in an increased lifetime of the enzymes. Because of the high magnetization of MNPs, NP-enzyme conjugates can efficiently be magnetically separated, making enzymes more productive [31].

7. Engineered Polymeric NPs for Bioremediation of Hydrophobic Contaminants

Sorption of hydrophobic organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), to the soil has been shown to limit their solubilization rate and mobility. In addition, sequestration of contaminants by sorption to soil and by partitioning in nonaqueous phase liquids (NAPLs) reduces their bioavailability. Polymer nanonetwork particles have been demonstrated to increase the “effective” solubility of a representative hydrophobic organic contaminant, phenanthrene (PHEN), and to enhance the release of PHEN from the contaminated aquifer material. Poly(ethylene)glycol modified urethane acrylate (PMUA) precursor chain has been developed in enhancing the bioavailability of PHEN. PMUA NPs are shown to increase the mineralization rate of PHEN crystal in water. PHEN sorbed on aquifer material, and PHEN dissolved in a model NAPL (hexadecane) in the presence of aquifer media. These reported results show that PMUA particles not only enhance the release of sorbed and NAPL-sequestered PHEN but also increase its mineralization rate. The accessibility of contaminants in PMUA particles to bacteria also suggests that particle application may be an effective means to enhance the in situ biodegradation rate in remediation through natural attenuation of contaminants. In pump-and-treat or soil washing remediation schemes, bioreactors could be used to recycle extracted NPs. The properties of PMUA NPs are shown to be stable in the presence of a heterogeneous active bacterial population, enabling them to be reused after PHEN is bound to the particles and has been degraded by bacteria [32].

8. Engineered Polymeric NPs for Soil Remediation

Hydrophobic organic groundwater contaminants, such as polynuclear aromatic hydrocarbons (PAHs), sorb strongly to soils and are difficult to remove. Amphiphilic polyurethane (APU) NP has been synthesized for use in remediation of soil contaminated with PAHs. The particles are made of polyurethane acrylate anionomer (UAA) or poly(ethylene glycol), modified urethane acrylate (PMUA) precursor chains that can be emulsified and cross-linked in water. The resulting particles are of colloidal size (17–97 nm as measured by dynamic light scattering). APU particles have the ability to enhance PAH desorption and transport in a manner comparable to that of surfactant micelles, but unlike the surface-active components of micelles, the individual cross-linked precursor chains in APU particles are not free to sorb to the soil surface. Thus, the APU particles are stable, independent of their concentration in the aqueous phase. Here APU particles have to be engineered to achieve desired properties and experimental results show that the APU particles can be designed to have hydrophobic interior regions that confer a high affinity for phenanthrene (PHEN) and hydrophilic surfaces that promote particle mobility in soil. The affinity of APU particles for contaminants such as PHEN can be controlled by changing the size of the hydrophobic segment used in the chain synthesis. The mobility of colloidal APU suspensions in soil is controlled by the charge density or the size of the pendant water-soluble chains that reside on the particle surface. The ability to control particle properties offers the potential to produce different NPs optimized for varying contaminant type and soil condition [33].

9. Biogenic Uraninite NPs and Their Importance for Uranium Remediation

Geoscientists have great interest in biogenic uranium due to its importance in bioremediation strategies and due to its small particle size and biological origin. Recent researchers have found the chemical/structural complexities of this important natural NMs and have begun to illuminate the chemical/structural complexities of this important natural NMs. Intriguingly, in spite of its incredibly tiny size, the molecular-scale structure, energetics, and surface-area-normalized dissolution rates of hydrated biogenic uraninite appear to be similar to those of coarser-particle, abiotic, stoichiometric UO₂. These findings have important implications for the role of size as a moderator of NP aqueous reactivity and for the bioremediation of subsurface U (VI) contamination [34].

10. Bioremediation (Phytoremediation) of Heavy Metal Pollution by NPs of Noaea Mucronata

Many countries are facing environmental pollution with heavy metal and in the last two decades a great effort has been made to minimize the pollution sources and to remediate the polluted soil and water resources. A field study was conducted in a dried waste pool of a lead mine to find the native accumulator plants. Using flame absorption atomic method concentration of heavy metal had been determined both in the soil and the plants that were grown in dried waste pool. The concentration all the toxic metals (Cu, Zn, Pb, and Ni) were found to be higher than it is found in the natural soil. The experimental result shows that six dominant vegetation, namely, Gundelia tournefortii, Centaurea virgata, Reseda lutea, Scariola orientalis, Eleagnrum angustifolia, and Noaea Mucronata, accumulated heavy metals. Based on the results, the study concluded that Noaea mucronata belonging to Chenopodiaceae is the best Pb accumulator and also a good accumulator for Zn, Cu, and Ni, but the best Fe accumulator is Reseda lutea and the best one for Cd is Marrubium vulgare. The bioaccumulation ability of nanoparticles prepared from N. mucronata was evaluated in experimental water containers. Experiment shows that the
amount of heavy metals decreases many-fold during three days bioremediation [35].

11. Conclusion

Salient features of NMs of different types such as metal NMs, oxide NMs, carbon NMs, polymer NMs, nanocomposite and biological NMs, their synthesis method, and examples are given. This paper mainly focuses on the importance of NMs in degradation of waste and toxic material, which will also decrease the cost of degradation of waste and toxic materials. NMs not only directly catalyze degradation of waste and toxic materials, which is toxic to microorganism, but also it also helps enhance the efficiency of microorganisms in degradation of waste and toxic materials. This also shows that phytoremediation can be applied in the removal of heavy toxic metal from contaminated soil. Therefore, based on the above discussion, it can be said that, like its applications in various other fields of sciences, it has immense applications in bioremediation too. Due to its powerful potential, it is expected that their application will increase at a great leap in the near future, and it will play a critical role in sustainable development.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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