Journal of Materials and
Environmental Sciences
ISSN : 2028-2508

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JMES, 2017 Volume 8, Issue 2, Page 740-757

http://www.jmaterenvironsci.com /

A Review of Nanobioremediation Technologies for Environmental Cleanup: A Novel Biological Approach

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Received 20 Sep 2016,
Revised 27 Oct 2016,
Accepted 31 Oct 2016

Keywords

- ✓ Nanotechnology,
- ✓ Nanobioremediation,
- ✓ Biosynthesis,
- ✓ Nanofactories,
- ✓ Environment.

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Abstract

The challenging task of the 21st Century is to clean up the contaminants of the environment by ecofriendly, sustainable and economically adoptable technologies. Nanobioremediation is a new emerging technique for remediation of pollutants using biosynthetic nanoparticles. It is still a new area but growing rapidly in to the field of nanotechnology. The present review speculates on biosynthesis of nanoparticles from plants, bacteria, yeast and fungi which are emerging as nanofactories and potential application in environmental cleanup. The majority of the biogenic nanoparticles that have been tested have yielded very good results. The biosynthetic route of nanoparticle synthesis could emerge as a better and safer alternative to conventional methods.

1. Introduction

The emergence of nanotechnology has been the subject of extensive research in recent years, by intersecting with various other branches of science and involving all forms of life [1]. The concept of nanotechnology was first postulated by Richard Feynman in 1959 [2] and is among the fastest growing areas of scientific research and technology development worldwide. The area is often referred to as the ‘‘Next Industrial Revolution’’ [3]. In recent years, the green processes for the synthesis of various nanoparticles has evolved into an important branch of nanotechnology and created substantial interest in the areas of chemical, electronic, and biological sciences. Nanotechnology presents a number of potential environmental benefits. This could be divided into three categories: treatment and remediation, sensing and detection, and pollution prevention. The specific nanotechnologies discussed here focus on site remediation and wastewater treatment. Besides the applications for soil, groundwater, and wastewater, a number of nanotechnologies for air remediation are also in development. Smaller particle size enables the development of smaller sensors, which can be deployed more easily into remote locations. The ability of nanotechnology to minimize pollution is in progress and could potentially catalyze the most revolutionary changes in the environmental field [4]. The applications of nanotechnology, such as nanoscale filtration techniques, adsorption and breakdown of contaminants by nanoparticle catalysts, in the cleanup of contaminated water could be summarized by Smith [5]. Wastewater remediation using nanoparticles is one of the areas of concentration among the various applications of the nanotechnology [6]. Biosynthesis of nanoparticles using microorganisms has emerged as rapidly developing research area in green nanotechnology across the globe, with various biological entities being employed in synthesis of nanoparticles constantly forming an impute alternative for conventional chemical and physical methods. Optimization of the processes can result in synthesis of nanoparticles with desired morphologies and controlled sizes, quickly and cleanly [7]. Nanotechnologies are pervasive solution vectors in our economic environment. It is necessary to develop new methods to assess development for better understanding of nanotechnology- based innovation.

2. Nanoparticles

Nanotechnology is characterized by the use of very small manufactured particles (<100 nm), called nanoparticles (NPs) or ultrafine particles. Nanoparticles (nano-scale particles = NSPs) are atomic or molecular aggregates with dimension between 1 and 100 nm that can drastically modify their physico-chemical properties compared with the bulk material. Nanoparticles can be made from a variety of bulk materials and they can act depending on chemical composition, size or shape of the particles. They are more reactive and more mobile in nature.

Nanoparticles are broadly in two groups of organic and inorganic nanoparticles. Organic nanoparticles include carbon nanoparticles (fullerenes) while some of the inorganic nanoparticles include magnetic nanoparticles, noble metal nanoparticles (e.g. gold and silver) and semiconductor nanoparticles (e.g. titanium dioxide and zinc oxide). Ruffini-Castiglione and Cremonini [8], identified three types of NSPs: natural (e.g. volcanic or lunar dust, mineral composites), incidental (resulting from anthropogenic activity, e.g. diesel exhaust, coal combustion, welding fumes) and engineered. The latter includes metal-based materials quantum dots, nanogold, nanozinc, nanoaluminium, TiO_2, ZnO and Al_2O_3 [9]. Smaller particle size enables the development of smaller sensors, which can be deployed more easily into remote locations. Recently, nanomaterials (NMs) have been suggested as efficient, cost-effective and environmentally-friendly alternatives to existing treatment materials, in both resource conservation and environmental remediation [10-12]. Biological synthesis of nanoparticles has grown markedly to create novel materials that are eco-friendly, cost effective and stable with great importance in wider application in the areas of electronics, medicine and agriculture [13]. Although nanoparticles can be synthesized through an array of conventional methods, the biological route of synthesizing advantageous because of ease of rapid synthesis, controlled toxicity, control of size characteristics, low cost, and eco-friendly approach [14]. Nanoparticles are extensively used for removal of biological contaminants (such as bacteria) and chemical contaminants including organic pollutants [15].

3. Unique properties of nanoparticles

The last decade witnessed significant focus on nanoparticles and nanomaterials because of their unique size-dependent physical and chemical properties. Nanoparticles exhibit a number of special properties relative to bulk material and often have unique visible properties because they are small enough to confine their electrons and produce quantum effects. Nanoparticles such as gold are widely used in various fields such as photonics, catalysis, electronics and biomedicine due to these unique properties. Bioremediation of radioactive wastes from nuclear power plants and nuclear weapon production, such as uranium, has been achieved using nanoparticles. Cells and S-layer proteins of *Bacillus sphaericus* JG-A12 have been found to have special capabilities for the cleanup of uranium contaminated wastewaters [16]. Biological systems possess a unique ability to be self-organized and to synthesize molecules that have highly selective properties. A unique study on plants suggests that some nanomaterials may inhibit seed germination and root growth [9].

4. Biogenic production of various nanoparticles

Traditionally, nanoparticles were produced only by physical and chemical methods. The need for biosynthesis of nanoparticles arose due to the high cost of physical and chemical processes. In the search of cheaper pathways for nanoparticle synthesis, microorganisms (Fig.1) and then plant extracts were used for synthesis. Biosynthesis of nanoparticles is a bottom-up approach where the main reaction occurring is reduction/oxidation. The microbial enzymes or the plant phytochemicals with antioxidant or reducing properties are usually responsible for reduction of metal compounds into their respective nanoparticles. The production of nanomaterials is currently estimated to be in the millions of tons worldwide and is expected to increase dramatically in the near future [17]. The term ‘nanomaterial’ is used generally to describe specifically engineered materials that have at least one dimension between 1 and 100 nm. Not only vascular plants, but also microorganisms such as bacteria, yeasts, algae, fungi and actinomycetes can be used for biosynthesis of nanoparticles [18].

4.1 *Nanoparticles produced by plants*

Green synthesis of nanoparticles by plants is gaining importance now-a-days because of single step biosynthesis process, absence of toxicants and occurrence of natural capping agents [19]. The advantage of using plants for the synthesis of nanoparticles is that they are easily available, safe to handle and possess a broad variability of metabolites that may aid in reduction.

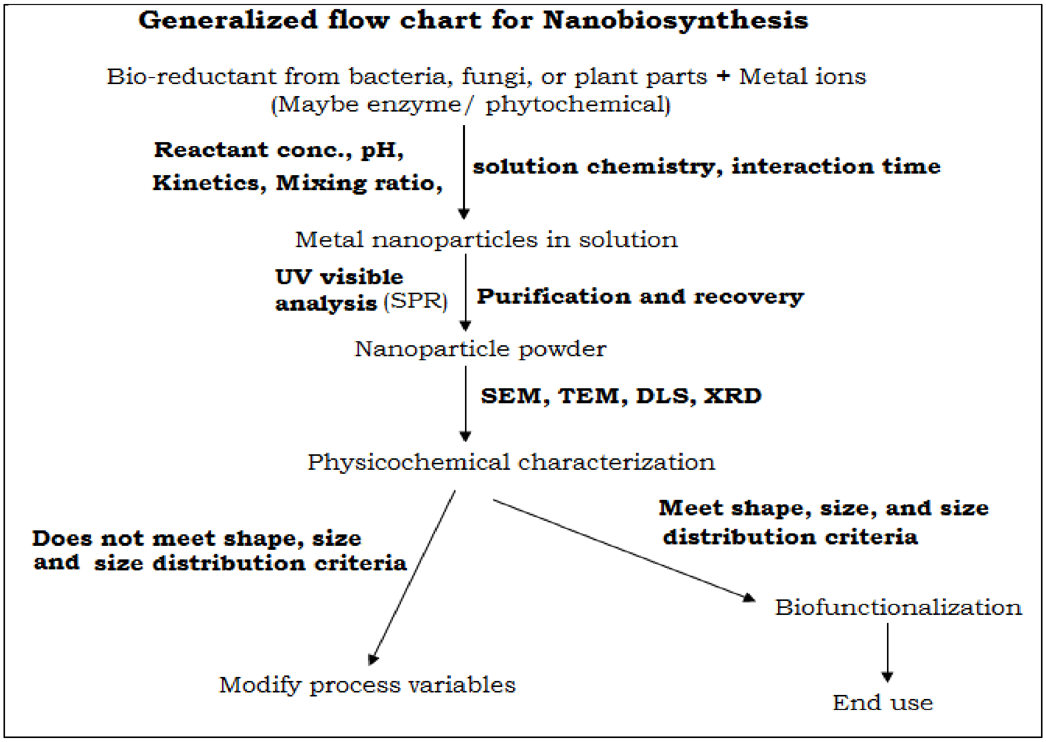


Figure 1: Flowchart outlining the biosynthesis of nanoparticles

A number of plants are currently being investigated for their role in the synthesis of nanoparticles (Table 1). While fungi and bacteria require a comparatively longer incubation time for the reduction of metal ions, water soluble phytochemicals do this in a much lesser time. Therefore, compared to bacteria and fungi, plants are better candidates for the synthesis of nanoparticles. Taking use of plant tissue culture techniques and downstream processing procedures, it is possible to synthesize metallic as well as oxide nanoparticles on an industrial scale once issues such as the metabolic status of the plant are properly addressed. It is evident from compiled information that effect of nanoparticles varies from plant to plant and depends on their mode of application, size, and concentrations [20]. The review reveals that the research on nanoparticles, essentiality for plants, is in the early stages; more rigorous study is needed to understand physiological, biochemical, and molecular mechanisms of plants in relation to nanoparticles and further work is needed to explore the mode of action of NPs, their interaction with biomolecules, and their impact on the regulation of gene expressions in plants.

4.2 *Nanoparticles produced by bacteria*

Bacteria are capable of mobilization and immobilization of metals and in some cases, the bacteria which can reduce metal ions show the ability to precipitate metals at nanometre scale. Bacteria are considered as a potential ‘biofactory’ for the synthesis of nanoparticles like gold, silver, platinum, palladium, titanium, titanium dioxide, magnetite, cadmium sulphide, and so forth.The use of bacteria as a source of enzymes that can catalyze specific reactions leading to inorganic nanoparticles is a new rational biosynthesis strategy and use of enzymes, microbial enzymes, vitamins, polysaccharides, biodegradable polymers, microorganisms, and biological systems for synthesis of nanoparticles [7]. Extracellular secretion of enzymes offers the advantage of producing large quantities of nanoparticles of size 100 – 200 nm in a relatively pure state, free from other cellular proteins. The further purification of nanoparticles is successfully achieved by filtering. The special metal binding abilities of the bacterial cells and S-layers make them useful for technical applications in bioremediation and nanotechnology.

Table 1: Denotes the use of various plants for the synthesis of nanoparticles

Nanoparticles	**Plant**	**Reference**
Silicon-Germanium (Si-Ge) nanoparticles	*Freshwater diatom* *Stauroneis sp.*	[21]
Gold and silver nanoparticles	*Citrus sinensis*	[22]
	Diopyros kaki (Persimmon)	[23]
	Pelargonium graveolens	[24]
	Hibiscus rosa sinensis	[25]
	Coriandrum sativum	[26]
	Emblica officinalis	[27-28]
	Phyllanthium	[29]
	Mushroom extract	[30]
Silver nanoparticles	*Elettaria cardamomom*	[31]
	Parthenium hysterophorus	[32-33]
	Ocimum sp.	[34]
	Euphorbia hirta, Nerium indicum	[35]
	Azadirachta indica	[36-39]
	Brassica juncea	[40]
	Pongamia pinnata	[41]
	Clerodendrum inerme	[42]
	Gliricidia sepium	[43]
	Desmodium triflorum	[44]
	Opuntia ficus indica	[45]
	Coriandrum sativum	[46]
	Carica papaya (fruit)	[47]
	Pelargoneum graveolens	[36]
	Aloe vera extract	[48]
	Capsicum annum	[49]
	Avicennia marina	[50]
	Rhizophora mucronata	[51]
	Ceriops tagal	[52]
	Rumex hymenosepalus	[53]
	Pterocarpus santalinus	[54]
	Sonchus asper	[55]
Gold nanoparticles	*Terminalia catappa*	[56]
	Banana peel	[57]
	Mucuna pruriens	[58]
	Cinnamomum zeylanicum	[59]
	Medicago sativa	[60]
	Magnolia kobus and Dyopiros kaki	[26], [28]
	Allium cepa L.	[61]
	Azadirachta indica A. Juss.	[39]
	Camellia sinensis L.	[62]
	Chenopodium album L.	[63]
	Justicia gendarussa L.	[64]
	Macrotyloma uniflorum (Lam) Verde	[65]

	Mentha piperita L. *Mirabilis jalapa L.* *Syzygium aromaticum (L)* *Terminalia catappa L.* *Amaranthus spinosus*	[21] [66] [67] [56] [68]
Nanoparticles of silver, nickel, cobalt, zinc and copper	*Brassica juncea, Medicago sativa and Helianthus annuus*	[69]
Platinum nanoparticles	*Diopyros kaki* *Ocimum sanctum L.*	[70] [71]
Palladium nanoparticles	*Cinnamomum zeylanicum Blume.* *Cinnamomum camphora L.* *Gardenia jasminoides Ellis.* *Soybean (Glycine Max) L.*	[72] [73] [74] [75]
Lead Nanoparticles	*Vitus vinifera L.* *Jatropha curcas L.*	[76] [77]
Magnetic Nanoparticles	*Aloe vera*	[78]

In this section, most of the bacterial species used in nanoparticle biosynthesis are shown (Table 2). The properties of nanoparticles are controlled by optimization of important parameters which control the growth condition of organisms, cellular activities, and enzymatic processes (optimization of growth and reaction conditions).Thus, more elaborate studies are needed to understand the exact mechanisms of reaction and identify the enzymes and proteins which involve nanoparticle biosynthesis. The large-scale synthesis of nanoparticles using bacteria is appealing because it does not need any hazardous, toxic, and expensive chemical materials for synthesis and stabilization processes [7].

4.3 *Nanoparticles produced by yeast and fungi*

Fungi are an excellent source of various extracellular enzymes which influence nanoparticle synthesis. They have been widely used for the biosynthesis of nanoparticles and the mechanistic aspects governing the nanoparticle formation have also been documented for a few of them (Table 3). In addition to monodispersity, nanoparticles with well-defined dimensions can be obtained using fungi. Compared with bacteria, fungi could be used as a source for the production of larger amounts of nanoparticles. This is because of fungi secrete a greater volume of proteins which directly translate to higher productivity of nanoparticle formation [79]. Instead of fungi culture, isolated proteins have also been used successfully in nanoparticle production. The use of specific enzymes secreted by fungi in the synthesis of nanoparticles is promising. Understanding the nature of the biogenic nanoparticle is equally important. Microbiological methods generate nanoparticles at a much slower rate than that observed when plant extracts are used. In the biosynthesis of metal nanoparticles by a fungus, enzymes are produced which reduce a salt to its metallic solid nanoparticles through the catalytic effect [80]. This is one of the major drawbacks of biological synthesis of nanoparticles using microorganisms and must be corrected if it is to compete with other methods. For industrial applications, fungi should have certain properties which include high production of specific enzymes or metabolite, high growth rate, easy handling in large-scale production and low-cost requirement for production procedures which provides advantages over other fungus methods [81]. Fungi have an edge over other biological systems due to wide diversity, easy culture methods, reducing time and increasing cost-effectiveness. This, in turn provides an eco-friendly approach for nanoparticle synthesis. Genetic engineering techniques can be employed to improve the particle properties in near future [82]. In synthesis of numerous enzymes and rapid growth with the use of simple nutrients, yeast strains possess certain benefits over bacteria and the synthesis of metallic nanoparticles employing the yeast is being considered [83].

Table 2: Denotes the use of various bacteria for the synthesis of nanoparticles

Nanoparticles	**Bacterium**	**Reference**
Silver nanoparticles	*Bacillus cereus* *Oscillatory willei NTDMO1* *Escherichia coli* *Pseudomonis stuzeri* *Bacillus subtilis* *Bacillus sp.* *Bacillus cereus* *Bacillus thuringiensis* *Lactobacillus strains* *Pseudomonas stutzeri* *Corynebacterium* *Staphylococcus aureus* *Ureibacillus thermosphaericus*	[84] [85] [19] [86-88] [89] [90] [91] [92] [93] [94] [95] [96] [97]
Magnetic nanoparticles	*Magnetosirillium magneticum* *Sulphate reducing bacteria*	[87] [98]
Palladium nanoparticles	*Desulfovibrio desulfuricans NCIMB 8307*	[99]
CdS nanoparticles	*Clostridicum thermoaceticum* *Klebsiella aerogens* *Escherichia coli*	[100] [100] [101]
Gold nanowires	*Rhodopseudomonas capsulate*	[102]
Gold nanoparticles	*Alkalothermophilic actinomycete* *Thermomonospora sp.* *Pseudomonas aeruginosa* *Lactobacillus strain*	[18] [18] [103] [93]
As-S nanotubes	*Shewanella sp.*	[104-105]
ZnS nanoparticles	*Sulphate reducing bacteria of the family Desulfobacteriaceae*	[100], [106-110]

5. Nanobioremediation (NBR)

The removal of environmental contaminants (such as heavy metals, organic and inorganic pollutants) from contaminated sites using nanoparticles / nanomaterial formed by plant, fungi and bacteria with the help of nanotechnology is called nanobioremediation. NBR is the emerging technique for the removal of pollutants for environmental cleanup. Current technologies for remediation of contaminated sites include chemical and physical remediation, incineration and bioremediation. With recent advances, bioremediation offers an environmentally friendly and economically feasible option to remove contaminants from the environment [111]. Three main approaches of bioremediation include use of microbes, plants and enzymatic remediation. Nanotechnology increases phytoremediation efficiency, Nanoparticles can also be used for remediation of soils, water contaminated with heavy metals, organic and inorganic pollutants. Recent studies have shown that organic contaminants such as atrazine, molinate and chlorpyrifos can be degraded with nanosized zerovalent ions [112-113]. Nanoparticles in enzyme-based bioremediation can also be used in combination with phytoremediation [114-115]. For example, several complex organic compounds, such as long-chain hydrocarbons and organochlorines, are particularly resistant to microbial and plant degradation. A combined approach involving nanotechnology and biotechnology could overcome this limitation: complex organic compounds would be degraded into simpler compounds by nanoencapuslated enzymes, which in turn would be rapidly degraded by the joint activities of microbes and plants.

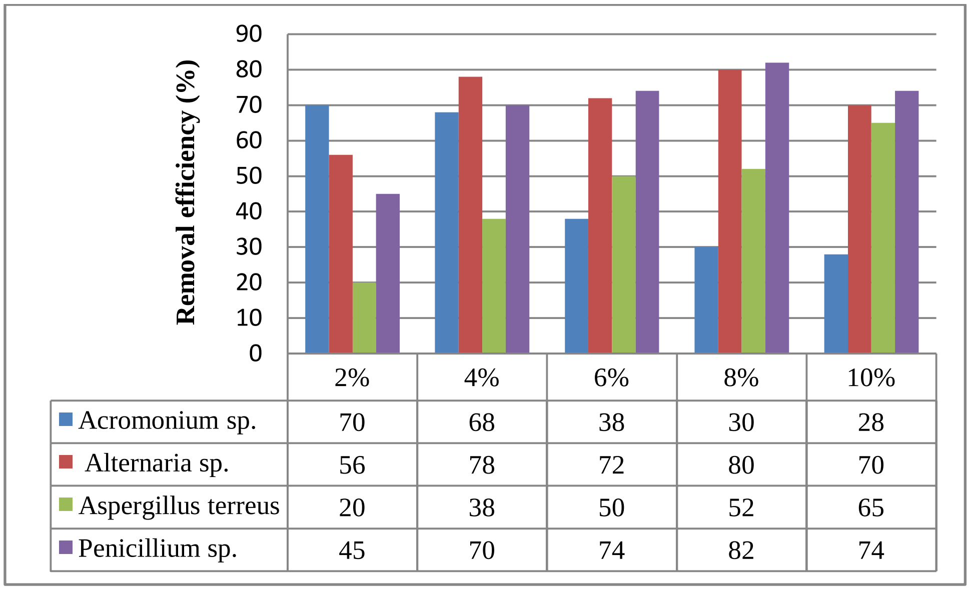
Table 3: Denotes the use of various yeast and fungi for the synthesis of nanoparticles

Nanoparticles	Yeast and Fungi	Reference
PbS nanoparticles	*Torilopsis species* *Rhodospiridium dibovatum*	[116] [117]
CdS quantum dots	*Schizosacharomyces pombe*	[116]
CdS nanoparticles	*Candida glabrata* *Schizosaccharomyce pombe*	[118]
Ag nanoparticles	*Silver tolerant yeast strains MKY3* *Cladosporium cladosporioides* *Coriolus versicolor* *Fusarium semitectum* *Fusarium oxysporum* *Phaenerochaete chrysosporium* *Aspergillus flavus* *Extremophillic yeast* *Aspergillus niger* *Aspergillus oryzae* *Fusarium solani* *Pleurotus sajor-caju* *Trichoderma viride*	[116] [119] [120] [121] [122-123] [124] [125] [126] [127] [128] [129] [130] [131]
Stable silver nanoparticles	*Aspergillus flavus, A. furnigatus* *A. terreus, A. nidulans*	[132] [133]
Gold and silver nanoparticles	*Verticillium sp. and Fusarium oxysporum*	[134]
Bioactive nanoparticles	*Lichen fungi (Usneea longissima)*	[135]

CeO_2 and ZnO nanoparticles have increased root and shoot growth in edible plants such as soybean, wheat, corn and alfalfa [136-137], suggesting that nanotechnology can significantly enhance the efficiency of phytoremediation. Several studies [138-142] have shown that nano-sized TiO_2 can have a positive effect on growth of spinach when administered to the seeds or sprayed onto the leaves. Nano-TiO_2 was shown to increase the activity of several enzymes and to promote the adsorption of nitrate and accelerate the transformation of inorganic into organic nitrogen. Table 1 shows the use of plant nanoparticles in the field of bioremediation of heavy metals, whereas fungal nanoparticles (in Fig. 2) efficiently remove petroleum pollutants.

Table 4: Some plant nanoparticles used in bioremediation of heavy metals

Plant Species used for Forming Nanoparticles	Best Bioremediation of Heavy metals	Reference
Noaea mucronata	Pb (98%), Zn (79.03%), Cu (73.38%), Cd (72.04%) and Ni (33.61%)	[143]
Euphorbia macroclada	Pb (92%), Zn (76.05%), Cu (74.66), Cd (69.08%) and Ni (31.50%)	[144]



	2%	4%	6%	8%	10%
🟦 Acromonium sp.	70	68	38	30	28
🟥 Alternaria sp.	56	78	72	80	70
🟩 Aspergillus terreus	20	38	50	52	65
🟪 Penicillium sp.	45	70	74	82	74

Figure 2: Some fungal nanoparticle used in bioremediation of initial concentration with 2%, 4%, 6%, 8%, 10% petroleum oil [145].

Both of the case studies (Table 4 and Fig. 2) show the significant removal of heavy metals and oil pollutants by use of biogenic nanoparticles. The *Aspergillus niger* silver nanoparticle (*A. niger* grow in the presence of $AgNO_3$) effectively decolorized 85.8% of dye within a 24 hour incubation cycle and the dye was fully decolorized within 48 hours of incubation. Whereas the plain culture of *Aspergillus niger* was able to degrade only 76% of Congo red dye in the same incubation conditions and complete decolorization was only observed after a full 48 hour incubation [146].

6. Remediation of pollutants using nanotechnology

In response to a growing need to address environmental contamination, many remediation technologies have been developed to treat soil, leachate, wastewater and groundwater contaminated by various pollutants, using in-situ and ex-situ methods [147]. Remediation has grown and evolved, continually developing and adopting new technologies and improving the remediation process. The small particle -size of nano iron (1-100 nm) facilitates a high level of remedial versatility. Nano-scale iron particles and their derivatives offer more alternatives to many remediation technologies. (Table. 5) shows the lists of many pollutants potentially remediated by nano iron [135].

Table 5: Pollutants remediated by Nano iron technology

Acid Orange	Dichlorobenzenes	Orange II
Acid Red	Dichloromethane	Pentachlorobenzene
Arsenic	Cis-Dichloroethene	Pentachlorophenol
Bromoform	Trans- Dichloroethene	Perchlorate
Cadmium	1,1- Dichloroethene	PCBs
Carbon tetrachloride	Dichromate	Silver
Chloroform	DDT	Tetrachlorobenzenes
Chloromethane	Hexachlorobenzene	Tetrachloroethene
Chlorobenzene	Lindane	Trichloroethene
Chrysoidine	Mercury	Trichlorobenzenes
Dioxine	Nickel	TNT
Dibromochloromethane	Nitrate	Tropaeolin
Dichlorobromomethane	NDMA	Vinyl Chloride

Theron et al. [148] have undertaken a thorough review of nanotechnology and, the engineering and art of manipulating matter at the nanoscale (1–100 nm), highlighting the potential of novel nanomaterials for treatment of surface water, ground water, and waste water contaminated by toxic metal ions, organic and inorganic solutes, and microorganisms (Table 6) and (Table 7). Polypyrrole-polyaniline (PPy-PANI) nanofibres can be considered as an alternative adsorbent for the removal of Cr (VI) from aqueous solution [149]. Nanotechnology promises to make current waste water treatment processes more energy efficient by utilizing single-stage treatment methods that can remove biological and chemical contaminants in treated wastewater [150]. Treatment processes incorporating nanotechnologies could be undertaken more safely, by negating the need to use toxic chemicals such as chlorine and ozone and the potential further improvement in quality of treated waste water increases the potential for beneficial reuse.

Table 6: Choice of nanoparticles for removing specific contaminant

Nature of the contaminant	**Contaminant to be removed**	**Nanoparticles**
Metal/Non-metal	Pb (II)	Ca-alginate iron oxide magnetic nanoparticles
	Hg (II)	Carboxy-methylated chitosan ferromagnetic nanoparticle
	Hg	Thiol-functionalised silica ferromagnetic nanoparticle
	Heavy metals	Thiol-functionalized super-paramagnetic nanoparticles
	Arsenic	Zinc oxide nanoparticles
	Cobalt and iron	Iron nanoparticles
	Metal ions	Carbon nanoparticles
	Lead	Polyacrylic acid - stabilized zero-valent iron nanoparticles (PAA- ZVIN).
	Arsenic and copper metal	Iron nanoparticles
	Zerovalent iron nanoparticles	Hexachlorocyclohexanes
Organic/Inorganic	Methylene blue	Geothite nanoparticle
	Tri-chloroethane (TCE)	Metallic gold nanoparticle coated with palladium
	Chlorinated ethane	Metallic gold nanoparticle coated with palladium
	Chlorinated methane	Metallic gold nanoparticle coated with palladium
	Inorganic-mercury	Gold nanoparticle supported on alumina
	Methylene blue	Goethite nanoparticle
	Trihalomethanes (THM)	α-Fe_2O_3 sintered in zeolite form
	Chlorpyrifos and Malathion	Silver and gold nanoparticle
Microorganism	Pathogenic bacteria	Silver nanoparticles
	Escherichia coli	CeO_2 nanoparticles
	Escherichia coli and *Bacillus megaterium*	MgO nanoparticles
	Bacillus subtillus	Magnesium nanoparticles
	E. coli, Staphylococcs aureus	Silver nanoparticles

Table 7: Examples of nanoparticles and nanomaterials for use in water remediation [148]

Nanoparticle/Nanomaterial	**Pollutant**
Nanocrystalline zeolites	Toluene, NO_2
Carbonaceous nanomaterials CeO_2-Carbon nanotubes (CNTs) Activated carbon fibres (ACFs) CNTs functionalized with polymers CNTs functionalized with Fe Single-walled carbon nanotubes Multi-walled carbon nanotubes	Heavy metal ions Benzene, toluene, ethylbenzene, xylene p-nitrophenol benzene, toluene, dimethylbenzene Heavy metal ions Trihalomethanes (THMs) Heavy metal ions THMs chlorophenols Herbicides Microcystin toxins
Self-assembled monolayer on mesoporous supports (SAMMS) Anion-SAMMS Thiol-SAMMS HOPO-SAMMS	Inorganic ions Heavy metal ions Actinides and lanthanides
Biopolymers	Heavy metal ions
Zero-valent iron nanoparticles (nZVI)	Polychlorinated biphenyls (PCBs) Inorganic ions Chlorinated organic compounds Heavy metal ions
Bimetallic nanoparticles Pd/Fe nanoparticles	PCBs Chlorinated ethane Chlorinated methanes
Ni/Fe nanoparticles Pd/Au nanoparticles	TCE and PCBs Dichlorophenol Trichlorobenzene Chlorinated ethane Brominated organic compounds (BOCs)
Nanocrystalline TiO_2 Nitrogen (N)-doped TiO_2 Fe (III)-doped TiO_2 Supported TiO_2 nanoparticles TiO_2 based p-n junction nanotubes	Heavy metal ions Azo dyes Phenol Aromatic pollutants Toluene

7. Recent research trends and advances reported in bioremediation

Results from treatment of sites contaminated with chlorinated solvents [151] suggest that the reductive treatment of chlorinated solvent with nano-scale zero-valent iron particles might be enhanced by the concurrent or subsequent participation of bacteria that exploit cathodic depolarization and reduction. Bioremediation by biosorption of washing water from cotton fabric processing, by silver nanoparticles with the bacterium Chromobacterium violaceum [152] found that the bacteria were morphologically altered following the process, but a new culture was completely restored subsequently. The process also allowed recovery of silver leached into the effluent for reutilization, avoiding any effect to the environment and reducing cost. In reduction and adsorption of Pb^{2+} in aqueous solutions [153], the nano-zero-valent iron was produced by a reduction method and compared with commercially available zero-valent iron powder for Pb^{2+} removal from the aqueous phase. In comparison with Fluka, zero-valent iron has much higher reactivity towards Pb^{2+} and within 15 minutes, 99.9% removal could be attained. Nano-zero-valent iron material has thus been demonstrated to have great potential for heavy metal removal from wastewater. Bacterial degradation of organophosphates (OP_S) [154] determined the *Stenotrophomonas sp*. Strain YC1, a native soil bacterium that produces methyl parathion hydrolase (MPH), was genetically engineered to possess a broader substrate range (OPs). Results indicate that the broader substrate specificity, in combination with rapid degradation rate, makes this engineered strain a promising candidate for in situ remediation of contaminated sites. Fungal degradation of oily sludge-contaminated soil [155] using a novel yeast strain, *Candida digboiensis* TERI ASN6, was capable of degrading 40 mg of eicosane in 50 ml of minimal salts medium in 10 days and 72% of heneicosane in 192 h at pH 3. The degradation of alkanes yielded monocarboxylic acid intermediates while the polycyclic aromatic hydrocarbon pyrene found in the acidic oily sludge yielded the oxygenated intermediate pyrenol. The strain C. digboiensis could efficiently degrade the acidic oily sludge on site because of its robust nature, probably evolved through prolonged exposure to the contaminants. Hence, the potential of Candida digboiensis TERI ASN6 to bioremediate hydrocarbons is high. Elliott et al [156] proposed a technique using Zero-valent Iron Nanoparticles, for treating water contaminated with Hexachlorocyclohexanes. More than 95% of the HCHs were removed from solution with 2.2 to 27.0 gL–1 iron nanoparticles within 48hrs. Then ZVI particles were synthesized by mixing equal volumes of 0.50 mol L−1 sodium borohydride (98.5%) and 0.28 molL−1 ferrous sulphate heptahydrate solutions. Sharifabadi et al. [157] used the modified surfactant sodium dodecyl sulphate and no bacterium was detected in the output water when the Ag/ cation resin substrate was used as a filter system. Low bacterial removal by Ag/zeolite, Ag/sand, Ag/ fibrelass and Ag/anion resin filter systems was observed, which led to the conclusion that these systems are not ideal systems for the disinfection of drinking water. Ulucan et al [158] studied α-Fe_2O_3 sintered in zeolite form for the removal of Trihalomethanes (THMs) from drinking water dichlorobromomethane, dibromochloromethane and bromoform were ordered. The absorption capacity of zeolite was increased due the nanoparticle in zeolite form.

Nanotechnology offers great promise to stabilize and protect enzymes against mechanical and biotic degradation and therefore increases their half-life and enables recirculation in their use while reducing the cost of bioremediation strategies. Encapsulation of xenobiotic-degrading enzymes in nanoparticles (1–100 nm) improves both stability and protection against degradation. Enzymes that bind to nanoparticles are more stable and, therefore, less vulnerable to mechanical shearing and loss of three-dimensional structure. At the same time, because enzymes are encapsulated inside the nano-structure, protease attack can be prevented. As a result, enzymes remain stable and can be reused several times. The utility of this approach was demonstrated in a 100-day trial where a nanofibre-esterase enzyme complex remained functional in both repeated batch and continuous long-term operation [104]. Immobilization of enzymes using such approaches provides an excellent opportunity to extend the half-life and reusability of enzymes and therefore reduce the cost of operation. However, the true progress of emerging technologies could be realized only if all of the approaches discussed here are integrated at a conceptual stage.

8. Soil and groundwater remediation with nanoparticles

Nanoparticles can potentially be used for the remediation of soil and groundwater. Environmental remediation methods can be classified as adsorptive or reactive and as in-situ or ex-situ [159-160]. In an effort to combat the problem of water pollution, rapid and significant progresses in wastewater treatment have been made, including photocatalytic oxidation, adsorption/separation, disinfection, membranes processing and bioremediation [161-165]. These unique properties of nanomaterials, for example, high reactivity and strong sorption, are explored for application in water/wastewater treatment based on their functions in unit operations as highlighted in (Table 7) [166] Nanoparticles, having high absorption, interaction, and reaction capabilities, can behave as colloid by mixing mixed with aqueous suspensions and they can also display quantum size effects [167-168]. They can penetrate deeper and thus can treat water/wastewater which is generally not possible by conventional technologies [169]. Nanoscale calcium peroxide has recently been used for the clean-up of oil spills [170] and Nanoscale zero-valent iron for soil and groundwater remediation. Biopolymer-stabilized iron nanoparticles effectively degrade lindane [171]. Conventional remediation technologies include ex situ soil washing and pump-and-treat operations, and in situ thermal treatment, chemical oxidation and use of reactive barriers with iron [160].

Table 8: Examples of the use of nanoparticles in remediation

Process exploited	Target compounds	Nanomaterials used	Some of novel properties	Reference
Adsorption	Heavy metals, organic compounds, arsenic, phosphate, Cr (IV), mercury, PAHs, DDT, Dioxin	Iron oxides, Carbon-based nanomaterials such as dendrimers and polymers, Carbon nanotubes (CNTs)	High specific surface area and assessable adsorption sites, selective and more adsorption sites, short intra-particle diffusion distance, tunable surface chemistry, easy reuse, and so forth	[149], [172-176]
Photocatalysis	Organic pollutants, NO_X, VOCs, Azo dye, Congo red dye, 4-chlorophenol and Orange II, PAHs	TiO_2, ZnO, Species of iron oxides (Fe III, Fe_2O_3, Fe_3O_4)	Photocatalytic activity in solar spectrum, low human toxicity, high stability and selectivity, low cost, and so forth	[177-182]
Redox reactions	Halogenated organic compounds, metals, nitrate, arsenate, oil, PAH, PCB	Nanoscale zero-valent iron (nZVI), nanoscale calcium peroxide	Electron transfers such as photosynthesis, respiration, metabolism, and molecular signaling, nature of their redox centers	[112], [159], [183-187]
Disinfection	Diamines, phenols, formaldehyde, hydrogen peroxide, silver ions, halogens, glutaraldehyde, acridines	Nanosilver/titanium dioxide (Ag/TiO_2) and CNTs	Strong antimicrobial activity, low toxicity and cost, high chemical stability ease of use, and so forth	[188-189]
Membranes	Chlorinated compounds, polyethylene, 1,2-dichlorobenzene, organic and inorganic solutes, halogenated organic solvents	NanoAg/TiO_2/Zeolites /Magnetite and CNTs	Strong antimicrobial activity, hydrophilicity, low toxicity to humans, high mechanical and chemical stability, high permeability and selectivity, photocatalytic activity, and so forth	[188-189]

Literature abounds with studies on utilization of nanoparticles for adsorption of various pollutants, mostly metals and dyes [178, 190-197]. Adsorption procedures combined with magnetic separation has, therefore, been used extensively in water treatment and environmental cleanup [198-199]. Iron oxide NMs are promising for industrial scale wastewater treatment, due to their low cost, strong adsorption capacity, easy separation and enhanced stability [191, 200-201]. Photocatalysis could be used in a pump-and-treat operation to purify groundwater. In situ technologies, using - nZVI to treat polluted groundwater and soils, including: (1) injection of nZVI to form a reactive barrier; (2) injection of mobile nZVI to form an nZVI plume; (3) incorporation of NP into topsoil to adsorb or degrade pollutants [159, 183]. Photo catalysis, one of the advanced physico-chemical technologies applicable in photo degradation of organic pollutants [202], has attracted much attention in recent years.

9. Conclusion

Nanotechnology has the potential to revolutionize existing technologies used in various sectors, including pollution control. Nanotechnology plays a major role in the development of new products to substitute existing production processes, with improved performance, resulting in potential environmental and cost savings. Reduced consumption of materials is also beneficial. Moreover, nanotechnology provides the potential to organize and develop production processes in a more sustainable way, eventually as close to a zero-emissions approach as possible. It is clear from the reviewed literature that, while much attention has been focused on the development and potential benefits of nanomaterials in water treatment processes, concerns have also been raised regarding their potential human and environmental toxicity. Nanotechnology may provide effective solutions for many pollution- related problems such as heavy metal contamination, adverse effects of chemical pollutants, oil pollution, and so on. Nanotechnology could provide eco-friendly alternatives for environmental management without harming the natural environment. Several plants, fungi and bacteria with greater efficacy in accumulating very large concentrations of metals have been identified and are known as-‘hyper accumulators’. Such plants, fungi and bacteria are potentially useful for bioremediation of heavy metal pollution. Nanomaterials in different forms can be used for removal of other environmental pollutants. Nanoparticles (nano-scale particles = NSPs) obtained from such plants, fungi and bacteria, have had actual application in removing some heavy metals from polluted sites. Nanoparticles from plants, fungi and bacteria are useful for detoxification and bioremediation of soil, water and other environments in highly polluted conditions. In future, modification and adaptation of nanotechnology will extend the quality and length of bioremediation. The breath of anticipated opportunities, cross- disciplinary nature, potential for innovation, historical track record and the impact of the potential advantages of nanotechnology leads to the recognition of this area as of increasing importance.

Conflict of Interests- The author declares that there is no conflict of interests regarding the publication of this paper.

Acknowledgements- The authors appreciate the very helpful review of this paper and comments by Richard Chadd, Environment Agency of England, Senior Ecologist, Stepping Stone Walk, Winfrey Avenue, Spalding, Lincolnshire. PE11 1DA. UK.

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