Current trends in nanotechnology for bioremediation

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Abstract: Nanotechnology is an emerging field to produce nano-scale products with more efficient reactivity and larger surface area than its bulk phase. These unique attributes of nanoparticles offer immense potential for their application to clean up petroleum hydrocarbons, pesticides, and metal-contaminated sites. As compared to the conventional physicochemical methods of remediation of contaminated sites, the bioremediation has been drawing increasing attention due to its economic, eco-friendly and self-propelling attributes. Nanoparticles (NPs) can be either applied directly for removal of organic contaminants through adsorption or chemical modification. They can also serve as a facilitator in microbial remediation of contaminants either by immobilising or through the induced production of remediating microbial enzymes. The present review provides an overview of different types of nano-technologies with biological and plant-based bioremediation approaches.

Keywords: bioremediation; nanotechnology; genetic engineering; recombinant DNA technology.

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1 Introduction

The increase in population density and the need to increase agricultural production together with industrial advances and urbanisation were the main sources of environmental contamination during the 20th century. Industrialisation, wars and the use of intensive metals and organic components have leveraged environmental problems.

Faced with the problem of environmental pollution that grows every day, bioremediation becomes an alternative strategy to control the destruction of biodiversity. Numerous methods have been used for this control and technological advancement, among which nanobiotechnology has stood out as a promising alternative in the remediation of pollutants.

Currently, pollutants of concern include hydrocarbons, heavy metals, drugs, pesticides, and explosives. The effects of these pollutants can give a serious threat to human health and the ecosystem. Prolonged exposure may cause the development of mutagens and carcinogens, which break down slowly and remain in the environment for long periods. Among these pollutants, contamination of soils, residue, surface water and air with hazardous materials such as petroleum is a major problem facing the world today.

Although many conventional physicochemical techniques, such as precipitation, electrochemical treatment, electrocoagulation, and adsorption are now being practised, there is still an immediate requirement for the improvement of unique, effective, eco-friendly and cost-effective approaches for the remediation of the environmental contaminants (Fomina and Gadd, 2014).

Bioremediation technology uses microorganisms to remove pollutants using relatively low-technology and low-cost techniques. It depends on the presence of specific microorganisms and combination of appropriate natural conditions (Adams et al., 2015).

This increasingly innovative technology is very promising for treating waste compounds and media with the possibility to degrade components since it uses natural microbial activity mediated by different consortia of microbial strains. It may be any process that uses microorganisms, fungi, green plants or their enzymes to return the natural environment altered by contaminants to its original condition (El Amrani et al., 2015; Rathore et al., 2014).

As contaminants are mostly found as mixtures, there is a need for technologies that are capable of monitoring, recognising, and treating such a small amount of contaminants in air, water, and soil. In this context, there is a need for technology that can sense, reduce, prevent, and treat environment contamination. Nanotechnology has the potential to provide a sustainable solution to the global challenges related to protecting water, soil, and providing cleaner air. Nanoscience allows designing and manipulating materials at the atomic and molecular level. These materials can be fabricated with specific functionalities that can recognise a particular pollutant within a mixture. The small size of NPs, together with their high surface-to-volume ratio, can lead to very sensitive detection (Asztemborska et al., 2015; Das et al., 2015).

Nanomaterials used for water quality monitoring, notably those used for the detection of trace pollutants and pathogens include carbon nanotubes (CNTs), magnetic nanoparticles, noble metal nanomaterials and quantum dots (Kumari and Singh, 2016; Xue et al., 2016, 2017). Moreover, the use of elemental or zero-valent metals in nanoscale form, such as iron, nickel and palladium, has shown encouraging results towards contaminated sites with various types of toxic substances (Li et al., 2016b), primarily to stabilise transition metals such as chromium and arsenic and dehalogenation of persistent organic compounds (Rizwan et al., 2014; Thomé et al., 2015; Vena et al., 2016).

Although technology has gained wide attention and studies, there is the need to investigate the trends that have evolved in studying bioremediation in the past decade; some aspects of focus are comparability of available data, the applicability of available technology, availability or unavailability of technology for laboratory investigations, geographical diversity, shortage of expertise in the field, regulatory bottlenecks associated with extensive trials and a general skepticism or acceptance of the effectiveness of the technology which may have interfered (Adams et al., 2015). Nanotechnology associated with bioremediation is a field of science capable of exploring several aspects to help the environment become cleaner and conditions that favour the progress of life. The present review is an attempt to focus on the potential application of nanotechnology and its integration with various crucial processes associated with the bioremediation technology such as immobilisation of the hydrocarbon-degrading microorganisms, substrates and/or enzymes, solubilisation of the hydrophobic compounds and stimulation of microbes' degrading properties.

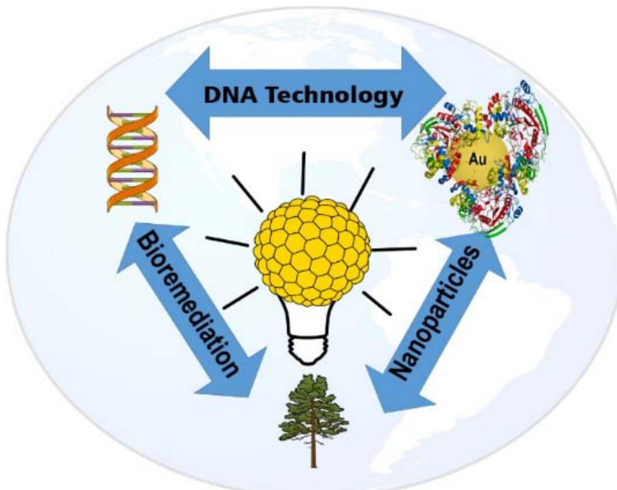
2 Background of nanotechnology

Nanotechnology is an emerging field to produce nano-scale products with more efficient reactivity and larger surface area than in the bulk phase. These unique attributes of nanoparticles offer immense potential for their application to clean up petroleum hydrocarbons, pesticides, and metal-contaminated sites. In recent years, the green processes for the synthesis of various nanoparticles have 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, which could be divided into three categories: treatment and remediation, sensing detection, and pollution prevention. The specific nanotechnologies discussed here focus on bioremediation in various fields.

3 Nanotechnology bioremediation

Nanomaterials comprise particles with at least one dimension measuring between 1–100 nm. Some specific characteristics like high surface-to-volume ratio, enhanced magnetic and special catalytic properties, etc. (Contado, 2015) make these nanoparticles (NPs) more worthwhile than their mass phase counterparts in the field of remediation technology. Distinctive subordinate properties of nanoparticles frequently exist, which are predominantly because of their high surface-to-volume ratio and can lead to very sensitive detection and their respective bulk material empowers them to remediate the contamination at a quick rate with a reduced measure of hazardous by-products. Nanoparticles formed by CNTs, nanoscale zeolites, dendrimer enzymes, metallic metal or metal oxides are other inorganic nanomaterials, which are used broadly to remove heavy metal ions in wastewater treatment. However, nanosized metals or metal oxides provide high surface area and specific affinity. Besides, metal oxides possess minimal environmental impact and low solubility and no secondary pollution, and have been adopted as sorbents to remove heavy metals from the polluted sites (Amin et al., 2014). The use of nanoparticles in enzyme-mediated remediation technology is gradually gaining ground because they provide a biocompatible and inert microenvironment which is least interfering with the native properties of the enzymes and helps in retaining their biological activities (Ferreira et al., 2015). Nevertheless, a choice of nanomaterials for the remediation process is a significant stride as they may be dangerous to the microorganisms required in the remediation process (Figure 1; Rizwan et al., 2014).

Figure 1 Pathway of nanobiotechnology for bioremediation (see online version for colours)



4 Role of biotechnology in bioremediation

Human footprint has created enormous environmental contaminants over the past century, including organic molecules from fuel and chemical spills, military activities, agriculture, industry, and forestry and naturally occurring inorganic contaminants that are mobilised and concentrated by mining, irrigation, and geochemical cycles. To overcome this problem, since the Roman times, the use of microbes and plants for remediation has been explored as non-invasive, cost-effective, and environmentally friendly options to clean up contamination sites.

Among the organisms utilised for bioremediation, microalgae have been widely utilised to treat wastewaters and bio-removal of heavy metal ions and are considered an environmentally and economically sustainable method to remove toxic metals from wastewaters (Jia and Yuan, 2016). Moreover, fungi have also emerged as potential biocatalysts to remove heavy metals from aqueous solution and transform them into less toxic compounds (Dixit et al., 2015). Several fungi such as *Klebsiella oxytoca, Allescheriella sp., Stachybotrys sp., Phlebia sp. Pleurotuspulmonarius,* *Botryosphaeriarhodina* have shown metal binding potential. However, even though these organisms have been used with a certain level of success, the development of the recombinant DNA technology demonstrated that desirable characteristics can be manipulated and improved in the diverse living bodies, especially plants. Using recombinant DNA technology, control of target genes expression has been achieved, bringing unimagined advancement in the use of plants for the benefit of the environment. Biotechnological approaches are currently being used for the phytoremediation of heavy metals and metalloids such as mercury (Hg) (Saleh et al., 2017; Iannazzo et al., 2017; Al Omar et al., 2017), cadmium (Cd) (Cahoon et al., 2015), lead (Pb) (Khasimsaheb et al., 2017), selenium (Se) (Dhillon and Bañuelos, 2017), copper (Cu), and arsenic (As). By genetically modifying plants(Ibañez et al., 2016), scientists have achieved plants with augmented resistance to harmful agents, enhanced product yield and increased adaptability for better survival, which is essential for bioremediation.

Recent biotechnological approaches for phytoremediation include biosorption, phytostabilisation, hyperaccumulation, dendroremediation and biostimulation, which majorly depend on enhancing or preventing specified genes activities. For example, AtPHR1 gene introduction into garden plants *Torenia, Petunia*, and *Verbena* changed their ability for Pi absorption. The authors genetically engineered *Torenia, Petunia* and *Verbena* using a plasmid containing a fragment of the AtPHR1 gene mediated by *Agrobacterium tumefaciens*. AtPHR1 is effective in other plant species, such as *Torenia, Petunia*, and *Verbena* (Matsui et al., 2013) but posttranscriptional modification of the endogenous AtPHR1 counterpart might be inhibited by overexpression of AtPHR1.

In another example, genetically engineered (GE) plants have been applied to the expression of metal chelators with the goal of enhancing mercury (Hg) phytoremediation. Tobacco plants were genetically modified via the nuclear genome to express the ppk gene and have increased polyphosphate production and enhanced tolerance and accumulation of Hg up to 10 μM (Nagata et al., 2006). Also, the expression of the *merP* gene in the nuclear genome of transgenic *Arabidopsis thaliana* provided similar resistance of up to 10 μM Hg (Hsieh et al., 2009). More recently, it was reported the development of a chloroplast transformation approach to express the mouse metallothionein gene (*mt1*), which accumulated mercury in high concentrations within plant cells. By using transplastomic plants, resistance up to 20 μM Hg and maintained high chlorophyll content and biomass were obtained. Although the transgenic plants accumulated high concentrations of mercury in all tissues, leaves accumulated up to 106 ng of Hg, indicating active phytoremediation and translocation of mercury. Such an accumulation of mercury in plant tissues facilitates proper disposal or recycling (Ruiz et al., 2011).

Recombinant DNA technology has also proven to be effective in eliminating arsenic particles that are considered as serious contaminants in soil (Khan et al., 2016). In an attempt to enhanced tolerance to arsenic (As), by expressing PvACR3 in Arabidopsis (Chen et al., 2013) seeds of plants genetically engineered with PvACR3 germinated and grow in the presence of a higher quantity of as than the normal generally lethal dose to wild-type seeds. In this case, the arsenic was reduced by Arsenate reductase present in *Arabidopsis thaliana*.

Another important strategy used for heavy metal detoxification is the use of phytochelatins (PC). Directed evolution of *Arabidopsis thaliana* phytochelatin synthase (AtPCS1) yields mutants that confer levels of cadmium tolerance and accumulation greater than anexpression of the wild-type enzyme in Saccharomyces cerevisiae, Arabidopsis, or *Brassica juncea* (Cahoon et al., 2015). Surprisingly, the AtPCS1 mutants that enhance cadmium tolerance and accumulation are catalytically less efficient than the wild-type enzyme. Metabolite analyses indicate that transformation with AtPCS1, but not with the mutant variants, decreases the levels of the PC precursors, glutathione, and γ-glutamyl cysteine, upon exposure to cadmium. Selection of AtPCS1 variants with diminished catalytic activity alleviates depletion of these metabolites, which maintains redox homeostasis while supporting PC synthesis during cadmium exposure. These results emphasise the importance of metabolic context for pathway engineering and broaden the range of tools available for environmental remediation.

The explosive 2,4,6-trinitrotoluene (TNT) is a highly toxic and persistent environmental pollutant where plants could be used for remediation. Recently it has been revealed that its phytotoxicity is caused by the reduction of TNT in the mitochondria, forming a nitro radical that reacts with atmospheric oxygen, generating reactive superoxide. The reaction, which is catalysed by monodehydroascorbate reductase 6 (MDHAR6), can be reduced in Arabidopsis by downregulating MDHAR6 and consequently enhancing TNT tolerance. This new discovery is contributing toward the remediation of TNT contaminated sites (Johnston et al., 2015). Table 1 provides a summary of the genes and target plants for phytoremediation.

Table 1 Selected examples of transferred genes and target plants for phytoremediation

Transferred genes	*Gene products*	*Target plants*	*Related functions*	*Treatments*	*Duration*	*References*
PCS1	Phytochelatin synthase	*Oryza sativa*	Biosynthes is of metal ligands	15–100 µM arsenic	10 days	Shri et al. (2014)
NRAMP1	Natural resistance associated macrophage protein	*Arabidopsis thaliana*	Xylem loading of metals	5–10 µM arsenic; 10–25 µM cadmium	10–20 days	Tiwari et al. (2014)
ECS	γ-glutamyl cysteine synthetase	*Populustremul a and Populus. alba*	Biosynthes is of metal ligands	100 µM cadmium	80 days	He et al. (2015)
At5g05600	β-glucuronidase (GUS)	Arabidopsis thaliana	PAH	0.2 mM phenanthrene	14 days	Hernández-Vega et al. (2017)

5 Biosynthesis of bio-nanoparticles

Nanoparticles (NPs) can be synthesised by ‘green’ approaches by microbes, which is an efficient way to exploit microorganisms as convenient nano-factories (Mishra et al., 2015). Recently, phytonanotechnology has provided new avenues for the synthesis of nanoparticles and is an eco-friendly, simple, rapid, stable, and cost-effective method. Phytonanotechnology has advantages, including biocompatibility, adaptability, and the medical applicability of integrating nanoparticles utilising the universal solvent, water, as a reducing medium. In this way, plant-derived nanoparticles produced by promptly accessible plant materials and the non toxic nature of plants are appropriate for satisfying the high demand for nanoparticles with applications in the biomedical and environmental areas. Recently, gold and silver nanoparticles were effectively integrated utilising the leaf and root extracts from the medicinal herbal plant *Panax ginseng* (Singh et al., 2015). Additionally, different plants have been used for the synthesis of metal nanoparticles (Table 2).

Table 2 Denotes the use of various plants for the synthesis of metal nanoparticles

Metal nanoparticles	*Plant*	*References*
Gold	*Camellia sinensis* (Green tea), *Juniperus communis* (Zimbora tea)	Geraldes et al. (2016)
	Sesbania grandiflora L.	Das and Velusamy (2014)
	Eucommia ulmoides	Guo et al. (2015)
Silver	*Tephrosia tinctoria*	Rajaram et al. (2015)
	Grewia flaviscences	Sana et al. (2015)
	Clerodendrum serratum	Priyadharshini Raman et al. (2015)
Platinum	Azadirachtaindica	Thirumurugan et al. (2016)
	Quercus glauca	Karthik (2016)
	Azadirachta indica	Thirumurugan et al. (2016)
Palladium	*Chlorella vulgaris*	Arsiya et al. (2017)
	Origanum vulgare L.	Shaik et al. (2017)
	Anogeissus latifolia	Kora and Rastogi (2015)

6 Nanobioremediation

The removal of pollutants by enhancing microbial activity (for example, heavy metals, organic and inorganic toxins) using nanoparticles/nanomaterials shaped by plants, fungi, and microbes with the assistance of nanotechnology is called nanobioremediation (NBR) (Singh and Walker 2006). Nanotechnology helps to build phytoremediation productivity, where nanoparticles can be utilised for remediation of soils, water tainted with substantial metals, natural and inorganic toxins (Table 3). Nanoparticles in compound-based bioremediation can be utilised as a part of a blend with phytoremediation. A consolidated approach including nanotechnology and biotechnology could beat this constraint: complex natural mixes would be contaminated into fewer complex mixes by nano-encapsulated chemicals, which thus would be quickly corrupted by the joint exercises of microorganisms and plant (Pillai and Kottekottil, 2016).

7 Environmentally remediation by CNTs

Over the past years, numerous studies have extensively explored the CNTs as a new adsorbent for the removal of a number of heavy metals from water. CNTs have been used to remove cadmium (Ihsanullah et al., 2015; Wang et al., 2016b), chromium (Duan et al., 2017), lead (Iannazzo et al., 2017), nickel (Iannazzo et al., 2017), copper (Matos et al., 2017), mercury (Al Omar et al., 2017; Iannazzo et al., 2017; Saleh et al., 2017), arsenic (Aranda et al., 2016), zinc (Jiang et al., 2016) and cobalt (Gupta et al., 2016). The results of these studies confirmed that CNTs are an excellent adsorbent for the removal of heavy metal from aqueous solutions.

Table 3 A selection of microorganisms used to synthesise bio-nanoparticles

Microorganism	*Nano particle*	*Size (nm)*	*Extracellular/intracellular*	*References*
Algae				
Bifurcaria bifurcata	Copper oxide	5 to45 nm	Intra	Abboud et al. (2014)
Bifurcaria bifurcata	Gold	30 to 0.25 nm	Intra	Venkatesan et al. (2014)
Sargassum plagiophyllum	Silver chloride	18 to 42 nm	Intra	Stalin Dhas et al. (2014)
Bacteria				
Bacillus strain CS 11	Silver	42 to 92 nm	Extra	Das et al. (2014)
Deinococcus radiodurans	Gold	43.75 nm	Extra	Li et al. (2016a)
Pseudomonas putida KT2440	Selenium	70 to 360 nm	Extra	Avendaño et al. (2016)
Fungus				
Aspergillus fumigatus AA001	Zinc oxide	12.56 nm	Extra	Srivastava et al. (2016)
Aspergillus japonicus AJP01	Gold	15 to 20 nm	Extra	Bhargava et al. (2015)
Macrophomina phaseolina	Silver	16 to 20 nm	Extra	Bhargava et al. (2015)

Recently, cyclodextrins (CD) and CNT(s) have been used as cost-effective materials in wastewater treatment and removing pollutants. For example, multiwalled CNTs/iron oxides modified by -cyclodextrin (MWCNTs/iron oxides/ -CD) was proposed using 1,6-diisocyanatohexane as cross-linker have been developed and have been successfully applied in removing organic pollutants. Experimental results showed that p-nitrophenol removal efficiency of CNTs/CD is high and reaches 70%.The recyclability studies suggest that MWCNTs/iron oxides/β-CD has an excellent regeneration capacity and can support use as a cost-effective material in wastewater treatment (Liu et al., 2014).

8 Application of carbon nanoparticles in bioremediation

8.1 Nanoscale zero-valent metals

Nano-scale zero-valent iron (nZVI) is a type of iron nanoparticle that has been investigated for deployment for *in situ* remediations, i.e., within the subsurface, as a groundwater and aquifer treatment.Generally, zero-valent metals (Fe^0, Zn^0, Ti^0, Ni^0, Pd^0, Mg^0, Al^0, etc. (Lu et al., 2015; Li et al., 2016b) have emerged as a low-cost and viable chemical medium for removal of environmental contaminants. They have significantly strong chemical reducibility, high efficiency and a large specific surface and thus the most promising applications in environmental remediation (Fan et al., 2017; Cao et al., 2018). nZVI is the most frequently utilised nanomaterial in Europe and in the USA for soil and groundwater remediation. Owing to its small size, nZVI has a higher reactivity towards a wide scope of contaminants, including halogenated mixtures, nitrate, phosphate, and polycyclic hydrocarbons, and a higher versatility contrasted with its microscale partner. The conceivable method for NZVI to trigger mutagenicity would be because of consolidation in cells and its reactive oxygen species (ROS) producing properties (Fu et al., 2014). The toxicity of nZVI under oxic conditions is essentially lower than under anoxic conditions, or, in other words, the arrangement of an iron oxide layer came about because of the surface oxidation. Thus, nZVI is viewed as a promising remediation procedure appropriate to an extensive scope of applications and ubiquitous environmental problems especially in hydrophilic organic compounds (HOCs) and PAHs (polycyclic aromatic hydrocarbons) (Binh et al., 2016).

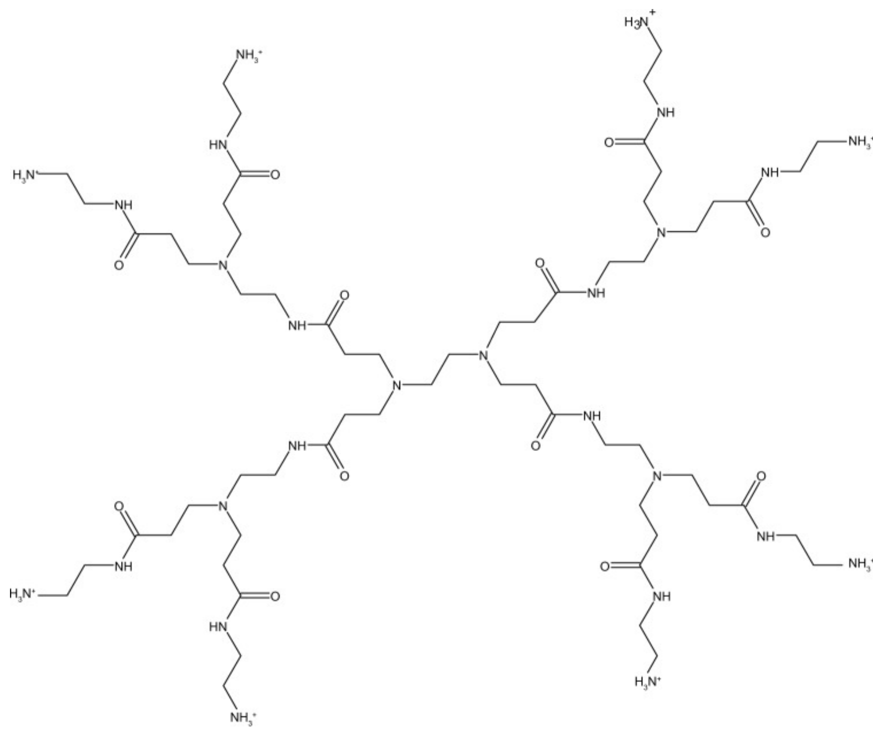
Nano-phytoremediation for degradation and removal of 2,4,6-trinitrotoluene (TNT), trichloroethylene, benzene, toluene, and radionuclides from contaminated soil is obviously more effective than either nanoremediation or phytoremediation (Shi et al., 2015). Regarding these points, the highest remediation efficiency of Endosulfan, an organochlorine pesticide, was achieved over 120 days of nano-phytoremediation (Pillai and Kottekottil 2016).

Nanotechnological remediation processes from Lab Scale to End User Applications for the Restoration of a Clean Environment (NANOREM) is designed to unlock the potential of nano-remediation and support both the appropriate use of nanotechnology for *in situ* remediation. This effort is being undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of nanoparticles, market demand, overall sustainability, and stakeholder perceptions (Bardos et al., 2015).

8.2 Dendrimers

Technically, the dendrimer is a polymer, which is an extensive molecule composed of many smaller ones linked together and capable of removing both organics and heavy metals. Therefore, the dendrimers-NPs composite can be prepared and used to improve catalytic activity. This type of developed composite could be used in water treatment and dye treatment industries due to more reactivity and larger surface area and less toxicity. Polyamidoamine (PAMAM) dendrimers with extraordinary structure and properties are used as efficient and non-toxic water treatment agents (Figure 2). Researchers have developed a simple filtration unit for the expulsion of organic pollutants by using TiO_2 porous ceramic filters of which the pore was immobilised with an alkylated poly(propylene imine) dendrimer, poly(ethyleneimine) hyperbranched polymer, or β-cyclodextrin, therefore resulting in hybrid organic/inorganic filter modules of high mechanical strength and high surface area (DeFever et al., 2015; Hayati et al., 2016).

Figure 2 Chemical structure of generation 1 polyamidoamine (PAMAM) dendrimer



8.3 Engineered polymeric NPsfor bioremediation

Throughout the past decades, ENPs (engineered polymeric NPs) have been widely used for land and groundwater remediation. Polypyrrole (PPy) is considered as one of the most effective adsorbent materials applied to sorption of toxic heavy metals, the developed PPy/MAA (mercaptoacetic acid) composite achieved the environmental benefit of remediating (Ag^{+}) from polluted water (Das et al., 2017). Polymer nanonetwork particles have been shown to expand the "effective" solubility of a representative hydrophobic organic contaminant, phenanthrene (PHEN) (Kalantary et al., 2014), and to improve the release of PHEN from the contaminated aquifer material.

8.4 Strategies for nanoparticles to control the pollution

In recent years, significant research has been devoted to a specific way to remove the toxic pollutants from contaminated water. The combinations of the expanding demand for clean water and rising utilisation of nanotechnology have been made us put numerous endeavours to examine different parts of water treatment by nanomaterials (Table 4). Nano filtered (NF) membrane process is a productive strategy to purify large volumes of contaminated water to high-quality consumable water. During degradation, pesticides are rarely mineralised into carbon dioxide, water, and other inorganic materials; in most cases, they are just converted into a number of transformation products (TPs) (Sinclair et al., 2006). Recently, Madsen and Søg (Henrik and Madsen, 2014) studied the applicability of NF membrane filtration for the treatment of groundwater contaminated with pesticides and pesticide transformation products (PTPs). It has been observed that NF99HF membrane was able to remove the regular pesticides about 90%; however, it has a smaller size and so it is easy to employ low-pressure reverse osmosis (RO) membrane to obtain satisfactory removal of PTPs.

Table 4 Different nanomaterials used for the removal of pollutants from contaminated water by adsorption

Pollutant	*Nanoparticles adsorbent*	*Removing capacity*	*References*
As(III)	Mt-nZVI	59.9 mg/g	Bhowmick et al. (2014)
As(V)	nZVI-RGO	29.04 mg/g	Wang et al. (2014)
As(V)	δ-Fe2OOH	37.3 mg/g	Faria et al. (2014)
Cd(II)	S-nZVI	83.19%	Su et al. (2015)
	nZVI	30.2%	
Cd(II)	AgNPs	4.67 mg/g	Zuo et al. (2015)
Cr (VI)	nZVI	30 mg/L	Myllymäki et al. (2017)
Cr (VI)	Magnetic MWCNTs	16.234 mg/g	Huang et al. (2015)
Hg(II)	Pristine MWCNTs	79.8 mg/g	Gupta et al. (2014)
	Oxidised MWCNTs	151.5 mg g^{-1}	
Rhodamine B	MWCNTs	65–90%	Jung and Kim (2014)
Amoxicillin	PVA/TiO_2/graphene-MWCNT	22.9 mg/g	Mohammadi et al. (2015)

Soil, a critical asset on planet Earth, is being degraded from a variety of sources. Contamination such as heavy metals and pesticides may result in the loss of biodiversity and functioning of soil like nutrient cycling etc. During the last two decades many nanoscale materials have been researched for remediation, such as zeolites, nanometal oxides, nanotubes and carbon fibre, enzymes, and bimetallic nanoparticles (Table 5).

Table 5 Application of different nanomaterials in environment remediation

Metal nanoparticles	*Remediation*	*References*
Zinc	Direct red 23	Kumar et al. (2014)
	Malachite green	Khezami et al. (2015)
Gold	Methylene blue	Suvith and Philip (2014)
	4-Nitrophenol	Shen et al. (2017)
Copper	Methylene blue	Sinha and Ahmaruzzaman (2015)
	Methyl orange	Soomro et al. (2015)
Silver	Organic dyes (methyl violet, saffranin, eosin methylene blue, methyl orange)	Muthukrishnan et al. (2015)
Titanium dioxide	Rhodamine B	Alshammari et al. (2014)

8.5 Green nanoremediation

Recently, nano-remediation has become a major subject of research and development with great potential for contaminated site cleanup and protecting the environment from pollution (Dixit et al., 2015). It enables remediation in deeper soils and is compatible with other technologies like bioremediation and is an expanding tool for contaminant cleanup (Huang et al., 2016). The development and use of nanofertiliser (bio stimulation and bioaugmentation), nanominerals (bio stimulation) or green synthesised nanooxidisers (PAH oxidation) could be explored to properly exploit the massive significance of nano-remediation in PAH removal (Nkansah et al., 2012; Jin et al., 2016; Lawal, 2017).

Transgenic approaches and advances in protein and genetic engineering techniques have opened up new avenues for the development of genetically modified microorganisms (GMOs) and plants to function as 'exclusive biocatalysts' in which certain desirable enzymes or degradation pathways from the diverse organism are brought together in a single host with the aim to perform specific reactions. Even the use of genes that encode the biosynthetic pathway of biosurfactants could improve the rate of biological degradation by increasing the pollutant bioavailability in the natural ecosystem. Also, the genes conferring resistance to critical stress factors enhance both the survival and performance of the designed catalyst. Further, coupled green approaches such as mixed cell culture system with biosurfactant flushing or rhizoremediation, vermicomposting with bioaugmentation and nano-remediation with phytotechnologies, etc. can be aimed to counteract the current challenges and upgrade the existing and emerging technologies.

9 Future prospects

Recently, electrokinetic remediation (EK), enzyme-mediated bioremediation, phyto bioremediation, and biosensors have been utilised for the treatment of contaminated soils. Electrokinetic remediation is useful for the treatment of low hydraulic permeability soils, where other techniques such as natural attenuation are not adequate. This technique involves the application of a low-intensity direct current through the soil between appropriately distributed electrodes. Ionic pollutants are transported to the oppositely charged electrode by electromigration (Villen-Guzman et al., 2015). Currently, the permeable reactive barrier (PRB) with EK treatment (electrokinetic) is the main innovation technique to the removal of heavy metals or organic compounds from polluted soils (Ramírez et al., 2015).

Development of electrochemical biosensors by coupling with the metallic (mono/bi) nanomaterials such as nanowires (Gunti et al., 2015), nanorods and nanospheres offers distinct advantages such as high sensitivity and real-time detection of heavy metals. Another area of microbial biosensors reveals potential applications in pesticide and heavy metal detection (Gutiérrez et al., 2015) in which eukaryotic microorganisms have an edge over prokaryotic cells. This is primarily due to the advantage of developing whole cell biosensors (Gutiérrez et al., 2015) with selective and sensitive applications related to the detection of heavy metal and pesticide toxicity. In the future, these microbial biosensors (Sun et al., 2015) will have wider applications in monitoring environmental metal pollution and sustainable energy production.

Currently, the metagenomic-based molecular technique is viewed as the novel technique to investigate the diversity of microbes, an accurate way to reveal the genetic content in extremely high concentration arsenic and antimony contaminated under complex environment conditions (Luo et al., 2014). Geoengineering methods have recently been involved in harmful cyanobacterial bloom (HCB) remediation. To date, Li and Pan (2015) developed the [modified local sand/soil (MLS) with chitosan] flocculation-capping technology (MLS-FCT) by embedding a MC-degrader isolated via novel technique in capping layer to degrade MCs (90%) eluted from algae floc in 40 days.

Some recent advances in innovative remedial approaches that are mostly biological and expected to give rise to an 'era of green biotechnology' in the near future are nano-remediation, transgenic approaches, and photo-hetero microbial systems. These emerging technologies have successfully remediated a number of organic and inorganic pollutants (Kuppusamy et al., 2016). However, their potential to remediate organically contaminated soils is still unexplored and hence could be the focus of future research in order to develop a rapid, reliable, low-cost and low risk-based contaminant cleanup strategy. To overcome the microbe-related limitations at real contaminated sites in the presence of mixed high contaminant levels, 'engineering microbial consortia' could be developed and used in the near future. Use of algae bacterial consortia is much more beneficial than bacterial consortia, or bacterial fungal consortia in the remediation of pollutants. This is because cyanobacteria or microalgae release a variety of lightweight compounds and extra polymeric compounds composed of nucleic acids, lipids, proteins, excretion products, and fermentation products that serve as microbial growth substrates which, in turn, enhance the degradation potential of aliphatic and aromatic contaminants by the bacteria. Hence future research can focus on the development and testing of the algal-bacterial groups of strains that are able to degrade metal effect and PAH-contaminated environment.

Among the applications of NMs, the utilisation of nZVI is becoming one of the most prominent examples of a rapidly emerging technology with extensive potential advantages, numerous uncertainties, and misconceptions regarding the fundamental components of this innovation, but it difficult to design applications for optimal performance. For example, currently there are three basic fundamental uncertainties associated with the application of nZVI, such as

1 high concentrations of nZVI aggregate to produce micron size clusters which do not exhibit 'true' nanosize effects

2 the mobility of bare or uncoated nZVI will be less than a few metres under almost all relevant conditions

3 the potential risk to human or ecological health remains largely unknown.

These uncertainties highlight that our understanding of the basic processes involved in this technology is still evolving and incomplete.

The major environmental concern is that the tiny nanoparticles could end up in environmental bodies such as in drinking water sources, thus harming the health of humans and animals. Nanoparticles present potential risks in terms of:

1. ability to disperse in the environment including potential long-range transport
2. ecotoxicity ability to cause adverse effects to organisms in the environment
3. persistency ability to remain in the environment
4. bioaccumulation ability to bioaccumulate or bioconcentrate in higher order organisms
5. reversibility ability for removal or to reverse their original introduction from environment (Bardos et al., 2015).

In general, because nanotechnology is likely to represent a beneficial replacement of current practices for site remediation, research into health and environmental effects of nanoparticles is urgently required.

The strategic approach to sustainability is to apply the preparation of green synthesis of nanoparticles from plants, microbes and use the nZVI particles. However, the environmental implications using development of analytical biomarkers to monitor nanoparticle dispersion, and develop and prepare green nano initiative particles needs to be assessed. There is an urgent need to assess the ecological risk and consequences caused by nanoparticles and a thorough understanding of the environmental fate of these nanoparticles will be a must.

10 Conclusions

Application of nanotechnology offers additional advantages in the field of bioremediation of contaminated sites. Simultaneously, this technology is also being used in different fields like agriculture in the form of nano fertiliser, decontamination of organic wastes and water purification systems. Various types of nanoparticles are being utilised to accomplish productive microbial degradation of pollutants in the environment, as they act upon a number of bioremediation steps that otherwise hinder the process and impose kinetic limitations on the system. The state-of-art in bioremediation technology still needs to be augmented in the light of fast developing field of nanotechnology. However, there is an urgent need to assess the ecological risk and consequences of these nanoparticles as they can influence the living biota including human health. Further researches on bio-accumulators of nanoparticles as well as toxicokinetics of nanoparticles must be evaluated to prevent the adverse effect of these nanoparticles on the flora and fauna. A better understanding of the environmental fate of these nanoparticles needs to be investigated before they are applied at the field scale. Besides, the successful and sustainable application of nanotechnology will depend upon the selection of low cost, environmentally safe nanotechnology, with another diverse spectrum of human life such as biomedicine, agriculture, and bioremediation.

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