Chapter 7
Nano-bioremediation: An Innovative Remediation Technology for Treatment and Management of Contaminated Sites

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Abstract As every method has its own benefits and setbacks, the integration of remediation methods could be thought of as a solution to tackle remediation problems. Integrated approaches could overcome the disadvantages of individual technologies and provide a better alternative to conventional remediation methods. Nano-bioremediation is one of such kind of methods which received a lot of attention in the past few years. It aims at reducing the contaminant concentrations to risk-based levels, alleviating the additional environmental impacts simultaneously. This method brings the benefits of both nanotechnology and bioremediation together to achieve a remediation that is more efficient, less time taking, and environment friendly than the individual processes. The present chapter provides a brief account of nanotechnology and variety of nanostructured materials reported for removing organic and inorganic contaminants from environmental matrices followed by detailed description of nano-bioremediation technique, its process, and applications.

Keywords Environmental contamination · Nano-bioremediation · Nanoparticles · Pollutants removal · Environmental safety

1 Introduction

The increasing rate of industrialization, urbanization, and modernization has brought down unsustainable pollution load on the environment. The toxic pollutants are increasing at alarming levels in the environment which are deteriorating the quality of environment, disturbing the ecosystem, and adversely impacting the human health. As per the Outlook on the Global Agenda 2015 report, the problem of rising pollution in developing countries is the sixth most significant global trend,

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and in Asia, it is third (World Economic Forum). In response to this, several in situ and ex situ technologies were proposed by different groups of researchers for taking up large-scale clean-up of contaminated sites. However, certain limiting factors such as high operational and maintenance cost, high energy requirements, destructive methodologies, time constraints, etc. restrict their widespread application (Zelmanov and Semiat 2008).

In the past few decades, nanotechnology application has occupied various sectors of our life such as medicine, textiles, pharmaceutics, electronics, optics, cosmetics, sports, and many more. The area of environmental remediation also has not been left untouched by nanotechnology. It is evident from the research ongoing and number of articles published in this field that nanotechnology could take up remediation tasks and challenges efficiently (Tratnyek and Johnson 2006; Mueller and Nowack 2010; Singh and Misra 2014; 2016; Patil et al. 2016). Recently, the concept of sustainable remediation has acquired a great importance, as it essentially aims at reducing the contaminant concentrations to risk-based levels and alleviating the additional environmental impacts. Recent development made in this arena has incorporated multiple technologies together in single system so that a complete solution could be provided that can decontaminate the site economically in a time efficient manner as well as improve the quality of the site through restoration. Among restoration methods, bioremediation is one which could combat contamination issues in an economic and environment-friendly way. Bioremediation essentially uses the microorganisms to remediate the pollutants present in water and soil matrices (Saxena et al. 2019; Bharagava et al. 2017a, b; Gautam et al. 2017; Saxena et al. 2016; Chandra et al. 2015; Saxena and Bharagava 2017; Saxena and Bharagava 2015; Perelo 2010; Mosa et al. 2016). According to the EPA, bioremediation is a "treatment that uses naturally occurring organisms to break down hazardous substances into less toxic or non toxic substances." It has several advantages over physicochemical methods such as high selectivity, specificity, cost and energy efficiency, minimal requirement, etc. However, bioremediation has its limitation too, that is, it takes a long period of time for carrying out degradation of a toxic compound, typically several months to over a year. Moreover, its application becomes restricted in cases of sites severely contaminated with highly toxic and hazardous pollutants (Azubuike et al. 2016).

As every method has its own benefits and setbacks, the integration of remediation methods could be thought of as a solution to tackle remediation problems. Nano-bioremediation is one of such kind of methods which received a lot of attention in the past few years. Nano-bioremediation exploits the benefits of nanotechnology together with advantages of bioremediation. The present chapter provides a brief account of nanotechnology and variety of nanostructured materials reported for removing organic and inorganic contaminants from environmental matrices followed by detailed description of nano-bioremediation technique, its application processes, and methods.

2 Nanotechnology

Applications of nanoparticles can be seen in almost every field of science like automobiles, cosmetics, agriculture, food, textiles, space, defense, engineering, medical fields, and environment. According to the US National Nanotechnology Initiative (NNI), nanotechnology is defined as "the understanding and control of matter at dimensions between approximately 1–100 nanometres, where unique phenomena enable novel nanotechnology applications." Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale. In the past few years, use of nanotechnology in contaminant removal has become prominent due to its small particle size, high surface area to volume ratio, easy injection to the site of action, flexibility for in situ and ex situ application, etc.

2.1 Shapes, Sizes, and Structures

Nanotechnology basically deals with particles having dimensions within 1–100 nm range and forms the functional systems that can be used to solve a problem or perform a specific function. Different properties of nanoparticles like its reactivity, magnetism, stability, and optical characteristics depend on the distinctive size, shape, and structure of the nanoparticles. These characteristics of nanoparticles make them suitable candidates in different fields of application like drug delivery, textiles, cosmetics, water purification, food packaging, and several other industrial uses. The nanoparticles can be synthesized in different shapes like rods, spheres, cubes, triangles, polygons, etc., and depending on their shapes, the nanoparticles are named as nanospheres, nano-rods, nano-cubes, etc. (Wu et al. 2016). The structure of the nanomaterials can be organized with respect to their dimensions. The nanomaterials are mostly found in zero dimension, e.g., fullerenes, atomic clusters; one dimension, e.g., nanofibers and nanowires; or two dimensions, e.g., nanodisks, nanolayers, etc. (Benelmekki 2015).

2.2 Synthesis and Characterization

There are mainly two approaches for the synthesis of nanoparticles. One is top-down approach and the other is bottom-up approach. When a larger system breaks down to form nanosized particles, it is known as top-down approach such as high energy ball milling, grinding, etching, laser pyrolysis, lithographic techniques, etc., whereas in bottom-up approach, atoms combine to form clusters, and these clusters aggregate to

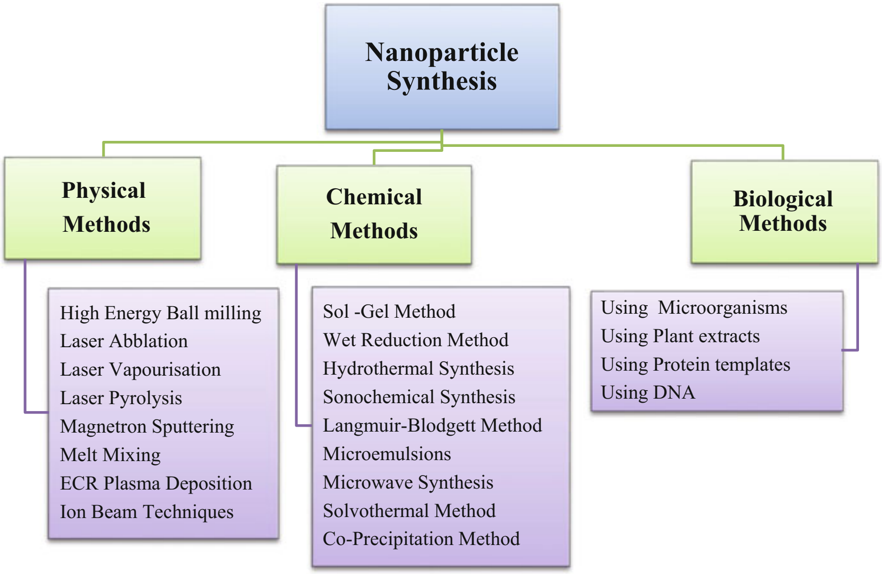

Fig. 7.1 Methods of nanoparticle synthesis

give rise to nanoparticles. Examples of bottom-up approach include coprecipitation, chemical reduction, etc. (Singh and Misra 2014). The methods for synthesis of nanoparticles can be classified into physical, chemical, and biological methods. Figure 7.1 shows various ways/methods of nanoparticle synthesis falling under physical, chemical, and biological methods. After synthesis, characterization of the nanoparticle is imperative for the purpose of identification of its size and shape, surface charge, morphology, crystallographic nature, etc. This characterization can be done through multiple techniques such as scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning tunneling microscopy (STM), nuclear magnetic resonance (NMR), etc. (Sun et al. 2006; Nurmi et al. 2005; Ramamurthy and Eglal 2014).

2.3 *Environmental Remediation via Nanotechnology*

Since the environment is deteriorating day by day by pollution, a promising technology must be developed to remove the harmful pollutants from it. Although there are a lot of technologies applied for contaminant removal, nanotechnology became prominent for its high removal efficiency, less time period, and being economical in comparison to several other technologies.

There are different varieties of nanomaterials applied for eliminating contaminants from environmental matrices (Goutam et al. 2018). These nanomaterials can be classified into nanotubes, nanofibers, nanoshells, nanoclusters, and nanocomposites depending on their shape, size, structure, and composition. These nanomaterials have demonstrated successful removal of hazardous pollutants from ground/surface water, soil, and sediments. For instance, carbon nanotubes are reported to successfully remove organic contaminants and metal ions from wastewater through adsorption process (Hadavifar et al. 2014). Nanofibers have also shown their potency in removing toxic compounds. Nylon 6 electrospun nanofibers not only remove estrogens from aqueous solution but could be repeatedly used as long as seven times for removal purposes (Qi et al. 2014). Titanate nanofibers also demonstrated 96% of phenol degradation (Barrocas et al. 2017). Nanoshells referred to spherical particles having a dielectric core and a thin metallic shell. Among nanoshells, Ag nanoshells have been applied efficiently to catalyze the degradation of organic dyes in industrial effluents (Vellaichamy and Periakaruppan 2016). Nanomaterials like nanoclusters and nanocomposites have also shown their efficiency in environmental remediation. The degradation efficiency of nonylphenol was found to be 96.2% within 120 min with initial dosage of 0.4 g/L and 5 mM persulfate by nZVI nanocomposite (Hussain et al. 2017). Heavy metals like Ni, Zn, Pb, Cd, and Cr are also reported to be successfully removed from water bodies using nanostructured graphite oxide and silica/graphite oxide nanocomposite (Sarkar et al. 2018).

One of the significant advantages of using nanoparticles is that it can be used for both in situ and ex situ remediation of harmful pollutants. In ex situ remediation, the contaminated soil and water are brought to the treatment plants and treated with nanoparticles methodically removing the toxic contaminants, whereas in in situ treatment methods, nanoparticles are either directly injected to the contaminated site or are introduced inside a permeable reactive barrier (PRB) where it successfully treats the contaminant plume and removes it (Karn et al. 2009).

Nanoscale zerovalent iron (nZVI) has shown enormous potential in contaminant reduction and can be successfully used in groundwater remediation either through direct injection or through permeable reactive barriers (PRBs) (Singh et al. 1998; Oh et al. 2001). A case study in Czech Republic reported that when nZVI was injected into a metal fabrication industrial area contaminated with chlorinated ethylenes, it showed 50% removal of the contaminant within 5–6 months (Lacina et al. 2015). When an aquifer contaminated with trichloroethylene (TCE) was treated with nZVI, it successfully removed 95.7% of TCE within 1 month without generating any chlorinated intermediates. It was also found that nZVI can be reused several times even after being aged for 5 months (Ahn et al. 2016).

Since the nanoparticles tend to agglomerate easily and oxidize fast, the surface of nanoparticles can be coated with suitable stabilizers to increase its stability and reduce agglomeration (Sakulchaicharoen et al. 2010). The surface coatings increase the adsorbing capacity of nanoparticles decreasing their agglomeration. A report showed that phosphate can be efficiently removed from water with humic acid-coated magnetite nanoparticles (Rashid et al. 2017). Titania-coated silica nanoparticles degraded 93.29% of safranin-O dye from aqueous solution at optimal conditions (Ekka et al. 2016). Another research shows that gold nanoparticles with surface coatings can be reused for 6 times with more than 90% conversion efficiency and keep high activity even after exposing in air for 1 month (Guo et al. 2016). Table 7.1 enlists few other contaminants which have been studied for their remediation using nanoparticles.

Table 7.1 Nanoparticle-mediated remediation of contaminants

Nanoparticle	Contaminant	Remarks	References
Fe/Ni bimetallic nanoparticles	Tetracycline (TC)	Removal efficiency of TC showed a decreasing trend with time due to the aging of Fe/Ni nanoparticles. The main aging products are found to be magnetite and maghemite	Dong et al. (2018)
Magnetic nanoparticle adsorbents, (Mag-PCMA-T)	PAHs and metal contaminants	Mag-PCMA-T could simultaneously remove PAHs and metal contaminants from water with efficiency greater than 85%	Huang et al. (2016)
Hematite nanoparticles	Carbamazepine	Hematite nanoparticles can be used to adsorb carbamazepine from water samples which showed an increasing trend with time up to 2.5 h. After 2 h 90% of carbamazepine got desorbed	Rajendran and Sen (2018)
Al_2O_3 nanoparticles	Arsenite	Al_2O_3 nanoparticles adsorbed maximum arsenite from groundwater at normal pH and temperature	Prabhakar and Samadder (2018)
Activated carbon nanoparticles (ACNPs)	Sulfate and copper	ACNPs increased surface hydrophilicity of nanofiltration membranes thereby escalating removal of sulfate and Cu ions from water	Hosseini et al. (2018)
Polystyrene nanoparticle	Estrone hormone	The efficiency of polystyrene nanoparticles in estrone removal were found to be lower than most nanofiltration/reverse osmosis (NF/RO) systems, that is around 40% but its final permeability was five times higher than other filtration systems	Akanyeti et al. (2017)
CTAB modified magnetic nanoparticles	Chromium (VI)	The CTAB modified Fe_2O_3 nanoparticles can efficiently remove Cr (VI) from water at acidic pH in 12-h contact time	Elfeky et al. (2017)
nZVI	Cu, Pb, Sb	nZVI increased the soil washing efficiency showing selective removal for Cu, Pb, and Sb	Boente et al. (2018)

(continued)

Table 7.1 (continued)

Nanoparticle	Contaminant	Remarks	References
Manganese oxide nanoparticles	17β-estradiol	MnO_2 nanoparticles removed 88% of estrogens from soil. The decreased injection velocity and increased concentration of nanoparticles elevated the estrogen degradation	Han et al. (2017)
Palladium nanoparticles	Pentachlorobiphenyl	The stabilized Pd nanoparticles coupled with supercritical fluid CO_2 are able to remove all PCBs from soil at 200 atm and all existing temperature ranges	Wang and Chiu (2009)
Reduced graphene oxide silver nanoparticles (rGO-Ag)	Phenol, bisphenol A, and atrazine	The rGO-Ag shows photocatalytic degradation of these organic compounds. When the reaction is carried out under visible light, significant decrease in contaminants is seen promoting oxidative degradation	Bhunia and Jana (2014)
Zinc oxide nanoparticles	Benzophenone-3 (BP-3)	ZnO nanoparticles showed successful degradation of benzophenone-3 (BP-3) which is a highly persistent EDC	Rajesha et al. (2017)
TiO_2 nanoparticles	EDCs (diclofenac, metoprolol, estrone, and chloramphenicol)	The photocatalytic activity of TiO_2 nanoparticles were able to degrade the EDCs arising from PPCPs. However the large particle size of the nanoparticle and presence of rutile decrease the photodegradation efficiency	Czech and Rubinowska (2013)
CuO nanoparticles	Arsenic(As)	CuO nanoparticles adsorb considerable amount of As from water showing potential to be applied in field applications	Reddy et al. (2013)
Cerium oxide nanoparticles	Cadmium (II), lead (II), and chromium (VI) ions	CeO_2 nanoparticles were effectual in removing the three toxic heavy metals from aqueous system. The removal efficiencies were found highest at pH 5 and 7	Contreras et al. (2015)

3 Nano-bioremediation: An Integrated Approach Toward Environmental Clean-up

Nano-bioremediation is an integrated technology that applies both nanotechnology and bioremediation together to achieve a remediation that is more efficient, less time taking, and environment friendly than the individual processes. Integrated approach could overcome the disadvantages of individual technologies and can provide better remediation results. For instance, incorporation of microbial strains in nZVI helps in more efficient remediation of pollutants. Chlorinated aliphatic hydrocarbons (CAH) are recalcitrant compounds which can neither be removed completely by nZVI nor organochlorine respiring bacteria (ORB). Koenig et al. (2016) combined both the technologies for removal of CAHs and showed that at appropriate dosage, a wide range of CAHs can be treated efficiently. They further suggested that the spent nZVI can be regenerated by certain minerals like cysteine and vitamins which remains available in bacterial environments. A reductive-oxidative strategy consisting of nZVI and an aerobic bacterium (*Sphingomonas* sp. PH-07) found to be effective for degradation of polybrominated diphenyl ethers (PBDEs) in aqueous solution. The nZVI particles break down the complex PBDEs like deca-BDE to lower BDEs through reductive debromination which were then degraded easily by microbes (Kim et al. 2012). Under optimal conditions, nZVI-CA beads showed 91.35% Cr (VI) removal, and for biofilm-coated nZVI-CA beads, the removal percentage was found to be 97.84%. When the efficiency of beads was investigated in column experiments, increased Cr (VI) removal was observed as compared to the free beads. The height of the column increases the reactive sites of the beads, which in turn enhance the removal of the toxic metal from the contaminated water. However in case of real samples, the efficiency of removal got decreased which may be attributed to the presence of colloidal particles present in the samples (Ravikumar et al. 2016). It is suggested by a report that permeable reactive Fe^0 barriers might be an effective approach to degrade RDX plumes and that treatment efficiency could be enhanced through bioaugmentation. When nZVI and white rot fungi were applied simultaneously, a substantial increase in RDX degradation as compared to the individual approach was observed. In addition to that, nZVI corrosion produces hydrogen gas which favors the growth and metabolic activities of the fungi further promoting RDX removal (Oh et al. 2001).

Hydrogen is considered as highly favorable electron donor for microorganisms carrying out biotransformation of contaminants in environmental substrates. The possibility of using cathodic hydrogen (produced during corrosion of nZVI under anaerobic conditions) as an electron donor for contaminant-degrading microbes, has been explored by many researchers (Weathers et al. 1997; Liu et al. 2005). Xiu et al. (2010b) demonstrated that the degradation of chlorinated solvent can be boosted by using nZVI as reducing agent along with bacteria that utilize cathodic depolarization and reductive dechlorination as metabolic niches. In another study wherein carboxymethyl cellulose (CMC) stabilized bimetallic nanoparticles (CMC-Pd/nFe^0) was integrated with *Sphingomonas* sp. strain NM05 for studying degradation of γ-HCH, synergistic effect on γ-HCH degradation was reported in case of integrated system, which further indicate that stabilized nanoparticles have some kind of biostimulatory effect on cell growth (Singh et al. 2013). Shin and Cha (2008) also observed biostimulatory effect of nFe^0on nitrate reducing microbial culture. In addition, nZVI supported microbial reduction was found to remain indifferent to fluctuating low temperatures, which otherwise is a major disadvantage with abiotic nitrate reduction.

As the toxicity of nanoparticles for microorganisms is well documented in literature (Li et al. 2010; Diao and Yao 2009), the dosage of nanoparticles in integrated system plays a significant role. In case of CAH treatment by nZVI and ORB, nZVI showed lethal effect on bacteria over 0.5 g/L, but it was found to have positive impact on ORB activity below 0.1 g/L (Koenig et al. 2016). The issues of nanoparticle toxicity toward bioagent can be addressed by modifying the surface of nanoparticles through coating, stabilization, or entrapment. The coating prevents the adhesion of nanoparticles on microbial cells, which in turn result in enhanced remediation of contaminants. Li et al. (2010) compared bactericidal effect of bare nZVI with polyelectrolyte (polystyrene sulfonate and polyaspartate) and natural organic matter adsorbed nZVI on *E. coli* and found that surface modification diminishes the toxicity of nZVI for exposure concentrations below 0.1–0.5 g/L. The study reported that surface modification diminishes the toxicity of nZVI for exposure concentrations below 0.1–0.5 g/L. An et al. (2010) while investigating nitrate reduction with bimetallic nanoparticles and chitosan/sodium oleate modified iron nanoparticles also observed reduced toxicity of modified nanoparticles toward microbes. The oxidation of nanoparticles with time or aging of nanoparticles is also reported to decrease the toxicity of nanoparticles (Phenrat et al. 2009). Apart from preventing the direct contact of nanoparticle with microbial cell, coating is also observed to enhance the expression of dechlorinating genes in *Dehalococcoides* spp., which in turn accelerates the degradation efficiency of TCE in sequential nano-bio treatment system Xiu et al. (2010a).

Le et al. (2015) investigated polychlorinated biphenyls (PCBs) removal by the nano-bio approach and found that the sequential treatment of PCB with Pd/Fe nanoparticles followed by bioremediation with *B. xenovorans* could effectively transform PCBs to less toxic and innocuous compounds. They further investigated the toxicity level of PCBs in *Escherichia coli DH5α* before and after treatment using toxic equivalent values and reported lower cytotoxicity of residual PCBs toward *E. coli* after treatment. When nZVI and whey both were injected into groundwater contaminated with Cr (VI), Němeček et al. (2016) observed 97–99% of Cr (VI) removal in an integrated system having nZVI and whey generated microbes. Besides removing the contaminants, microbes were also found to regenerate the oxidized Fe^0 nanoparticles which further increased the rate of remediation reducing the dosage of nanoparticles.

Multi-walled carbon nanotubes (CNTs) along with bioremediation are also successfully used for contaminant removal. In a study, *Shewanella oneidensis MR-1*, a facultative Gram-negative bacterium, was immobilized in calcium alginate beads containing carbon nanotubes to reduce Cr (VI) to Cr (III) in wastewater. The study demonstrated four times higher reduction rates in cells immobilized over CNTs containing beads in comparison to the free cells and the beads without CNTs (Yan et al. 2013). The reason for enhanced reduction was ascribed to enhanced electron transfer by the CNTs. Similarly, Pang et al. (2011) immobilized *P. aeruginosa* in polyvinyl alcohol (PVA), sodium alginate, and CNTs matrix for carrying out Cr (VI) reduction. The study showed that CNT-modified immobilized cells reduce Cr (VI) contaminant more efficiently and can be reused effectively up to nine times.

Pd nanoparticles have also shown their efficiency in integrated system. Chidambaram et al. (2010) reported in situ synthesis of Pd nanoparticles using *C. pasteurianum* BC1 cells, wherein *C. pasteurianum* reduced the Pd (II) ions to Pd nanoparticles which were retained in the cell wall and cytoplasm of the cells in the form of bio-Pd. This bio-Pd system successfully catalyzed the reduction process of Cr (VI) to insoluble Cr (III) species. One added benefit of bio-Pd system mediated reduction was the production of hydrogen gas which provides an alternative to the costly addition of molecular hydrogen to above ground pump and treat systems. MgO nanoparticles in combination with yeast *Candida* sp. SMN04 have been studied for treating Cefdinir in aqueous medium (Adikesavan and Nilanjana 2016). The half-life of Cefdinir in nano-bio system was observed to reach less than half of the time taken by the individual yeast cell. Incorporation of MgO nanoparticles in the system was reported to increase the permeability of cell membrane allowing more amount of contaminant to get access to the cells, thereby accelerating degradation rate in comparison to individual system. Table 7.2 presents nano-bioremediation methods reported for a variety of environmental contaminants.

4 Application Methods and Process

There are two ways which have been reported for application of integrated nano-bio process in treatment system. First is sequential method wherein the contaminant is subjected to nanoparticles first and later on bioagent is added to carry out further process. The second method is concurrent or combined method where both nanoparticle and biological agent are added to the system simultaneously. The examples of both methods along with their process are given below:

4.1 Sequential Method

Bokare et al. (2010) developed a sequential hybrid treatment system with bimetallic nanoparticle (Pd/nFe) and an enzyme for studying degradation of triclosan (TCS) which is an antimicrobial agent used widely in personal care products. In the first step, triclosan (5 mg/L) was reduced with Pd/nFe nanoparticles (1 g/L) under anaerobic conditions which resulted in dechlorination of TCS to 2-phenoxyphenol. In the next step, nanoparticles were separated from the system, and the dechlorinated product was subjected to oxidation by laccase enzyme isolated from *Trametes versicolor* in presence of syringaldehyde (a natural redox mediator). The study reported complete transformation of TCS through redox process to nontoxic oligomers. Similar kind of reductive-oxidative hybrid strategy was successfully employed to demonstrate degradation of polybrominated diphenyl ethers (PBDEs) in aqueous solution using nZVI along with diphenyl ether-degrading bacteria *Sphingomonas* sp. PH-07 (Kim et al. 2012). Debromination of deca-BDE (5 g/L) was carried out

Table 7.2 Remediation of environmental contaminants using nano-bioremediation

Nanoparticle	Bioagent	Contaminant	Remark	References
Fe_3O_4 nanoparticles/ gellan gum gel beads	*Sphingomonas* sp. strain XLDN2–5 cells	Carbazole	The microbial cells immobilized in Fe_3O_4 nanoparticles/gellan gum gel beads degraded higher carbazole than the free cells and the non-magnetically immobilized cells. This integrated system showed progressive increase in degradation when being recycled	Wang et al. (2007)
Pd/nFe	Laccase derived from *Trametes versicolor*	Triclosan	The remediation of triclosan was solely achieved by Fe nanoparticles. However the degraded by-products were further converted to nontoxic compounds by the laccase secreted from *T. versicolor* strain	Bokare et al. (2010)
Bio-Pd nanoparticle	*C. pasteurianum* BC1	Cr(VI)	*C. pasteurianum* reduced the Pd(II) ions to Pd nanoparticles which stayed in the form of bio-Pd in the cell membrane and cytoplasm of the organism. It successfully catalyzed the Cr(VI) reduction reaction and also produced hydrogen gas	Chidambaram et al. (2010)
Pd/nFe	*Sphingomonas wittichii* RW1 (DSM 6014)	2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TeCDD	The highly toxic dioxin isomer is recalcitrant in nature and its degradation could not be acquired easily through a single technique. The degradation was accomplished by using the Pd/nFe nanoparticles and the *Sphingomonas* strain sequentially	Bokare et al. (2012)
Pd/nFe	*Burkholderia xenovorans* LB400	Polychlorinated biphenyl (PCB) Aroclor 1248	Pd/nFe nanoparticles efficiently dechlorinated the bi-, tri-, tetra-, penta-, hexa-chlorinated biphenyls into biodegradable intermediates which were then easily degraded by *Burkholderia xenovorans*	Le et al. (2015)
nZVI-C-A beads	*Bacillus subtilis*, *E. coli*, and *Acinetobacter junii*	Cr(VI)	The thin biofilm covering the nZVI entrapped calcium alginate beads removed around 92% of Cr (VI) showing enhanced removal by the combined technology	Ravikumar et al. (2016)

(continued)

Table 7.2 (continued)

Nanoparticle	Bioagent	Contaminant	Remark	References
Carbon nanotubes	*Shewanella oneidensis* MR-1	Cr(VI)	The MR-1 strain immobilized by CNT infused CA beads could remove four times higher Cr (VI) than the free cells or CNTs or CA beads	Yan et al. (2013)
nZVI	*Dehalococcoides* spp.	TCE	This study showed that nZVI stimulated the metabolic activity of methanogens but deactivated the dechlorinating bacteria, but after a lag phase the dechlorinating bacteria could again remove TCE producing ethene as by-product	Xiu et al. (2010b)
Pd(0) nanoparticles	*Shewanella oneidensis* MR-1	PCBs	The bio-Pd formed from the microbial reduction effectively dechlorinated around 90% of PCBs producing less toxic by-products	Windt et al. (2005)
Fe_3O_4 nanoparticles	*Sphingomonas* sp. XLDN2-5 cells	Carbazole	The Fe_3O_4 nanoparticles bound to the surface of the bacterial strain showed no increased degradation than the free cells but showed amazing reusability. Another advantage of using magnetic nanoparticles is it can be separated from the microorganism using an external magnet source	Li et al. (2013)
Magnetic Fe_3O_4 nanoparticles	*Pseudomonas delafieldii*	Dibenzothiophene	The magnetic nanoparticle coated microbial cells showed greater biodesulfurization of dibenzothiophene than the free cells or cells coated with celite. It is also observed that it can be reused more than five times	Shan et al. (2005)
nZVI	*Paracoccus* sp. *strain YF1*	Nitrate	Lower conc. of nZVI (50 mg/L) enhanced denitrification process along with slight microbial toxicity, while higher conc. (1000 mg/L) significantly reduced denitrification rate	Liu et al. (2014)

with nZVI (100 mg) under anaerobic condition in 15 ml glass test tube. After 20 days, PH-07 strain was added in reaction mixture and incubated for 4 days. The sequential system was found to be effective for degradation of deca-BDE showing reduction up to 67%. The debrominated products were further treated with PH-07 strain to study their mineralization. He et al. (2009) also reported sequential treatment of 2, $2'$4, 5, $5'$-pentachlorobiphenyl with an anaerobic nZVI reaction and successive aerobic transformation with bacterium H1.

4.2 Concurrent/Combined Method

In a microcosm study, Xiu et al. (2010a) investigated the effect of nZVI on dechlorinating microorganism using trichloroethylene (TCE) as model compound. For experiments, 100 mg of nZVI (1 g/L) and 4 ml of inoculation culture (*Dehalococcoides* spp.) along with mineral salt medium were added simultaneously in reaction vials containing TCE (20 g/L). The reaction mixture was then put over shaker at 200 rpm. Two other experiments were also carried out under similar conditions, one with nZVI alone and another with *Dehalococcoides* spp. only. Initially, nZVI was observed to inhibit microbial dechlorination, but later on it was found to have biostimulatory effect on dechlorinating bacteria which in turn could enhance the overall rate of contaminant degradation. The reason ascribed to this was the hydrogen which is evolved from nZVI during cathodic corrosion can be utilized as electron donor by dechlorinating bacteria. In another combined study, nanoparticle (nFe^0/Pd) was coated with a polymer (carboxymethyl cellulose, CMC) to avoid direct contact of nanoparticle with bacterial cells, as their direct contact inhibits the growth of bacteria cells (Singh et al. 2013). The study demonstrated degradation of γ-HCH in individual and combined system of CMC-Pd/Fe^0 and *Sphingomonas* strain NM05. The results revealed that γ-HCH degradation efficiency in combined system was ~1.7–2.1 times greater as compared to system containing either NM05 strain or CMC-Pd/nFe^0 alone.

5 Conclusion

Integration of nanoremediation with bioremediation either sequentially or concurrently appears to be a feasible alternative to conventional remediation technologies. More studies and development actions are still needed for bringing down these kinds of technologies to the marketplace for full-scale implementation. Moreover, the effect of environmental factors like pH, temperature, ionic strength, presence of competing or inhibitory substances, etc. on remediation efficacy of nano-bioremediation method is also needed.

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