Chapter 15
Role of Nanoparticles in Remediation of Contaminated Soil

M. Trivedi, S. Kedari, and G. C. Nikalje

1 Introduction

Technology and inventions has led to the industrial development all over the world. Meanwhile, this expansion of industrialization has led to release of various hazardous contaminants like carbon monoxide, chlorofluorocarbons, lead (Pb), arsenic (As), cadmium (Cd) and others in the environment (Mandeep and Shukla 2020). The improper disposal of these materials has reduced the quality of soil, water and air (Cechin et al. 2016). Maintaining the quality of these natural resources has become difficult causing pollution and a risk to the human health as well as environment (Mueller and Nowack 2010). To overcome these problems, several methods of remediation are being introduced, viz. bioremediation, phytoremediation and chemical and physical remediation. Bioremediation and phytoremediation use living organisms like microbes, fungi and plants, respectively. Both these methods are time-consuming and take longer time for treatment; hence they cannot be applied for immediate remediation (Sarkar et al. 2019). In addition, utilization of nanotechnology for bioremediation, i.e. nanobioremediation, is emerging.

Nanotechnology is the design, production and application of structures, devices and systems by manipulation of size and shape at the nanometre scale. They have a high surface to volume ratio, making them a budding candidate for environmental cleanup. From the past few years, green technology being in vogue, synthesis of

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nanoparticles has become a crucial part to be explored. The use of nanoparticles in the environment can be for remediation, treatment, sensing pollutants and their prevention. The nanoparticles have few peculiar properties like their at least one dimension measuring between 1 and 100 nm, having high surface to volume ratio and catalytic and magnetic properties which make them worth for the use of remediation technology (Koul 2019). In order to remove heavy metals from wastewater, carbon nanoparticles (CNTs) are widely used. They don't create any kind of secondary pollution and can be used to remove heavy metal from contaminated sites. The enzyme-mediated remediation is gaining boom with the use of nanoparticles in it as they provide an inert microenvironment that doesn't interfere with the nature of enzymes; also the biological activity remains specific (Baruah et al. 2019).

The various industrial sectors like mining, agriculture and chemical factories have contributed to a great extent for causing the environmental pollution. The use of plants and microbes has been an inexpensive, eco-friendly and cost-effective approach in cleanup technology since Romanian times. Various species from bacteria and fungi have capability to remove heavy metals and convert them to less toxic compounds, for example, fungi from *Aspergillus*, *Allescheriella* sp., *Klebsiella oxytoca*, *Phlebia* sp. and *Stachybotrys* sp. (Dixit et al. 2015)

2 Biosynthesis of Nanoparticles

Microbes are the nano-factories for green synthesis of cadmium, gold, platinum, palladium, silver and titanium nanoparticles (Benjamin et al. 2019). The presence of certain enzymes in the bacteria helps in catalysing the reaction leading to synthesis of nanoparticles. Fungi are also a good source for synthesis of nanoparticles as they secrete more amounts of proteins as compared to bacteria for the synthesis of nanoparticles. These can be further purified by filtration. It provides a simple, rapid, eco-friendly and stable method (Yadav et al. 2017).

Another approach for green synthesis of nanoparticles is the use of plants called phyto-nanotechnology. It is a single-step biosynthesis of nanoparticles, using plants. Plants can be grown easily as well by using plant tissue culture, for yearlong availability. Plants also facilitate the nanoparticle synthesis at industrial scale (Kharissova et al. 2013). The plant-derived nanoparticles can be used in the environmental and biomedical sector. In addition, by using genetic engineering approaches, nanoparticle synthesis can be enhanced in both plants and microbes at large scale.

3 Nanobioremediation

In the past few decades, a large number of contaminants including organic and inorganic pollutants have been persisting in the soil and water ecosystem. Organic pollutants include pesticides, aromatics, hydrocarbons and chlorinated solvents, while heavy metals contribute to the inorganic pollutants in the soil. Various materials like graphene-based materials, nanoparticles and bio-sorbents have been developed for remediation of soil (Chugunov et al. 2000; Wang and Yuan 2014; Gu et al. 2016). Nanobioremediation is the removal of pollutants (e.g. heavy metals, organic and inorganic toxins etc.) by enhancing microbial activity using nanoparticles synthesized by plants, fungi and microbes with the assistance of nanotechnology (Singh et al. 2016). Nanoparticles utilized for bioremediation of water and soils are summarized in Table 15.1. A combined approach of nanotechnology and biotechnology could be more effective in remediation by consolidated effect of microbes and plants together. Many nanomaterials such as bimetallic nanoparticles, carbon fibres, enzymes, nanotubes and zeolites have been successfully used for remediation purpose (Khin et al. 2012).

Soil is one of the valuable assets on this earth, which is now contaminated with heavy metals and agrochemicals. Such contamination leads to loss in biodiversity and affects the geochemical cycles. The irreversible agglomeration of calcium peroxide nanoparticles can be avoided by a simple surface modification technique which is based on hydrolysis-precipitation using calcium chloride as precursor (Khodaveisi et al. 2011). This technique involves use of polyethylene glycol 200 as surface modifier. In addition, it has ability to synthesize new reagents in nanosize with enhanced quality of in situ chemical oxidation. The need for cost-effective new technologies for the decontamination of contaminated sites has increased. In this regard, nanoscale zerovalent iron (nZVI) is widely used for degradation of chlorinated pollutants in soil as an alternative to, e.g. permeable reactive barriers or excavation. A study conducted by El-Temsah et al. (2016) compared two types of nZVI (type B made using precipitation with borohydride and type T produced by gas phase reduction of iron oxides under H_2) for efficient degradation of DDT, as well as the ecotoxicity of soil and water was tested on plants (barley and flax), earthworms (*Eisenia fetida*), ostracods (*Heterocypris incongruens*) and bacteria (*Escherichia coli*). Both types of nZVI effectively degraded DDT in water and had a negative impact on the tested organisms, with nZVI-T giving least adverse effects.

Another entity used for decontamination of soil and groundwater is zerovalent iron (ZVI). The development of stable nanoscale ZVI (nZVI) products has gained a boom. In a study conducted by De Gisi et al. (2017), the effectiveness of nZVI treatment for the decontamination of marine sediments polluted by heavy metals, using the commercial product Nanofer 25s, was evaluated. Two kinds of experiments labelled as (i) sediment at low dosage (2, 3 and 4 g nZVI per kg of SS) and (ii) sediment at high dosage (5, 10 and 20 g nZVI for every kg SS) were performed on sieved sediment with a size <5 mm. According to their results, nZVI is more suitable to be used for specific element removal rather than to be applied for a generalized contamination, meaning that a mix of techniques can be suggested for whole sediment remediation.

It was supposed that when hydroxyapatite (HAP) was used for remediation of heavy metal-contaminated soils, its effectiveness seemed likely to be affected by its particle size. In the study by Li et al. (2014), a pot experiment was conducted to evaluate the efficiency of two particle sizes of HAP: nanometre particle size of HAP

Table 15.1 Applications of nanoparticles for bioremediation of toxic contaminants

Contaminant	Nanoparticles	Results	References
14C-2,4-DCP	CNTs	CNTs inhibited 14C-2,4-DCP mineralization and degradation in soil; SWCNTs had a higher effect than MWCNTs on 14C-2,4-DCP biodegradation	Xia et al. (2010)
2,4-Dichlorophenoxyacetic acid (2,4-D)	Fe_3O_4	These nanoparticles combined with soil indigenous microorganisms induced higher 2,4-D degradation efficiency; they also reduced the half-lives of 2,4-D and resulted in the increased soil microbial populations	Fang et al. (2012)
Aroclor 1242	PAA-coated nZVI	The soil microflora was changed with the PAA-coated nZVI that reduced chloroaromatic mineralizing microorganism's activity	Tilston et al. (2013)
Arsenic	GO	Arsenic uptake was enhanced by GO and amplified which could be proved by phytotoxicity in wheat indicated by decreasing plant biomass and root numbers and increasing the oxidative stress	Hu et al. (2014)
Cd	GO	GO enhanced Cd toxicity with increased ROS production, suppressed plant growth in the *Microcystis aeruginosa*	Tang et al. (2015)
	TiO_2 NMs	TiO_2 NMs increased plant Cd uptake, decreased Cd stress in the plants in soybean In *Chlamydomonas reinhardtii* TiO_2 NMs reduced free Cd ion contents, lowered Cd bioavailability, alleviated Cd-induced growth inhibition	Singh and Lee (2016), Yang et al. (2012)

(continued)

Table 15.1 (continued)

Contaminant	Nanoparticles	Results	References
Chlordane and DDx	MWCNT and C60	C60 increased chlordane accumulation in *Solanum lycopersicum* and *Glycine max* and suppressed DDx uptake, while MWCNT decreased chlordane and DDx accumulation in all the plants	De La Torre-Roche et al. (2013)
Cr	Silicon NMs	Silicon NMs reduced the Cr accumulation, and ROS production in the *Pisum sativum* silicon NMs improved plant growth, protein, nitrogen, carotenoids and chlorophyll contents and antioxidative enzymes activities	Tripathi et al. (2015)
	CMC-stabilized nZVI	These nanoparticles suppressed Cr uptake in rape and Chinese cabbage by 61 and 36%. Also reduced Cr leachability, bioaccumulation and bioavailability	Wang et al. (2014)
Diuron	CNT	Diuron bioavailability was increased by CNTs; stronger diuron toxic effect on the photosynthetic activity of *Chlorella vulgaris* was observed	Schwab et al. (2013)
Phenanthrene	MWCNTs	MWCNTs adsorbed phenanthrene MWCNTs increased the phenanthrene biodegradation	Xia et al. (2010)
Phenol	Ni/Fe	The *Bacillus fusiformis* growth was prompted by nZVI and Ni/Fe nanoparticles aided in the biodegradation of phenol	Kuang et al. (2013)
PCE	Air-stable nano iron	Dechlorination of tetrachloroethane was demonstrated in synthetic aqueous medium and in polluted groundwater	Andreas et al. (2009)

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Table 15.1 (continued)

Contaminant	Nanoparticles	Results	References
DDT	Nanosized zerovalent iron: type B and type T	Both types of nZVI effectively degraded DDT in water, but showed lower degradation of aged DDT in soil. Both types of nZVI had negative impact on the tested organisms. Negative effects were mostly due to oxidation of nZVI, resulting in O_2 consumption and excess Fe(II) in water and soil	El-Temsah et al. (2016)
Pb, Zn, Cu and Cr	Hydroxyapatite (HAP): nanosized (nHAP) and micro-sized (mHAP)	Both nHAP and mHAP were able to reduce the bioavailability and reduced the uptake of Pb, Zn, Cu and Cr. Also convert them from nonresidual to residual forms	Li et al. (2014)
Pb and Cd	nZVI, nZVI-bentonite, nanoalginite and nano carbon	The tested nanoparticles proved high efficiency in immobilizing Cd and Pb in polluted soils. The best nanomaterials recommended to be used for remediation of Cd- and Pb-polluted soils are nZVI, bent-nZVI and nanoalginite, with special preference for nZVI	Helal et al. (2016)
Polychlorinated biphenyls (PCB)	Iron oxide, V_2O_5/TiO_2 nanoparticles	Iron oxide and V_2O_5/TiO_2 are very good oxidation catalysts, and maximum destruction of PCBs was obtained with iron oxide as catalyst in the presence of air	Varanasi et al. (2007)
Pb and Cd	nZVI	nZVI and cellulosic waste were used to reduce the bioavailability of Pb and Cd in a contaminated soil. Application of nZVI showed higher heavy metal removal efficiency than cellulosic waste	Tafazoli et al. (2017)
Cd	CMC stabilized and non-stabilized nZVI	Both nanoparticles showed maximum removal of Cd at pH 6 in 45 min	Nasiri et al. (2013)

(continued)

Table 15.1 (continued)

Contaminant	Nanoparticles	Results	References
Estradiol	CMC-stabilized MnO_2 nanoparticles	CMC-stabilized MnO_2 nanoparticles hold the potential to degrade various emerging contaminants soil and groundwater	Han et al. (2015)
Polycyclic Aromatic hydrocarbons (PAHs)	Amphiphilic polyurethane (APU) nanoparticles	APU particles have the ability to enhance PAH desorption and transport	Tungittiplakorn et al. (2004)
PAHs	nZVI particles	Both the micro- and nanoscales of ZVI were capable of removing the target compound in soil, but the higher removal efficiencies were by nanoscale ZVI because of the massive specific surface area	Chang and Shu (2005)
Zn and lindane	nZVI particles	The application of nZVI reduced lindane and extractable Zn concentrations following a dose-dependent pattern	Anza et al. (2019)
Zn^{2+}, $Cu^{2+}$and Cr^{3+}	NiO and MgO nanoparticles	NiO-MgO silica-based nanoparticles can be employed for the adsorptive of these metals repeatedly without impacting the adsorption capacity indicating their sustainability	Abuhatabab et al. (2020)
Pesticide-metolachlor	Zerovalent iron	Zerovalent iron can be used for on-site, field-scale treatment of pesticide-contaminated soil	Comfort et al. (2001)
Chlorinated pesticide	nZVI	Use of NZVI has capability for partial or complete dehalogenation of the organochloro pesticides	Singh et al. (2009)
Trichloroethylene (TCE) and Cr(VI)	Nano zerovalent iron (nZVI), emulsified nano zerovalent iron (EZVI), micro zerovalent iron (MZVI)	nZVI achieved a higher reduction of TCE than the other two particles	Jagupilla et al. (2009)

(nHAP) and micrometre particle size of HAP (mHAP) induced metal immobilization in soils. Both mHAP and nHAP were assessed for their ability to reduce lead (Pb), zinc (Zn), copper (Cu) and chromium (Cr) bioavailability in an artificially metal-contaminated soil. The results indicated that both mHAP and nHAP had significant effect on reducing the uptake of Pb, Zn, Cu and Cr by pakchoi (*Brassica chinensis L.*). Furthermore, both mHAP and nHAP were efficient in covering Pb, Zn, Cu and Cr from non-residual into residual forms. The results suggested that mHAP had the better effect on remediation of multiple metal-contaminated soils than nHAP and was more suitable for applying in situ remediation technology.

The ecosystem can be balanced by mine soil reclamation that minimizes adverse environmental impacts and also creates additional lands for agricultural use which indirectly enhances the carbon (C) sequestration (Liu and Lal 2014). A study by De Gisi et al. (2017) proposes a practical and economical approach to apply nanotechnology for mine soil reclamation which suggests adding small amounts of nanoparticles to the conventional soil amendment materials and then applying the mixtures for soil quality improvements.

4 Mechanism of Nanobioremediation

Nanotechnology is a new emerging field with numerous applications in environmental cleanup. Recently, it is being used in the decontamination of various contaminated sites (Pérez et al. 2018). The behaviour of nanoparticles depends on their size, surface area, chemical composition and its reactivity. The morphology, particle size distribution, specific surface area, surface charge and crystallographic characterization are the important characteristics that help to understand the behaviour of the nanoparticles (Thome et al. 2015). Before applying nanomaterials for bioremediation of soil ecosystem, their interaction with soil and pollutants needs to be understood. The nanomaterials used for cleanup are selected depending upon their reactivity with different pollutants present on the contaminated site.

The process of remediation involves various steps: synthesis of nanoparticles; transport of nanoparticles to the site; and injection of nanoparticles and their reaction with the target pollutant. Due to their small size, nanoparticles can easily penetrate into the porous medium like soil and reach the pollutants. The small size of nanoparticles allows to be easily transported in the subsurface, via injection or direct push in slurry form to contaminated zones under pressure or gravity in the view of treatment (Caliman et al. 2010; Noubactep and Care 2010). For a successful remediation, it is necessary for nanoparticles to reach the contaminants. But nanoparticles have clustering tendency and agglomerate rapidly; hence the distribution to the target zone is uneven. The surface of NPs is modified, by coating it with a stabilizer like polymer, e.g. CMC (carboxymethyl cellulose), which reduces the agglomeration and enhances dispersion and transport. The key mechanism for heavy metal removal by zerovalent iron nanoparticles is adsorption and redox reaction which converts toxic heavy metal to less toxic in nature (De Gisi et al. 2017).

4.1 Adsorption

Adsorption is a surface-based phenomenon where solutes adhere to the surface of the adsorbent and form a thin film (Bushra et al. 2017). Nanoparticles have higher surface area to volume ratio which makes them a good adsorbent for remediation. Whereas iron oxides can adsorb heavy metal from soil, hence nanoscale iron oxides are added to the soil. Iron oxide nanoparticles can bind to arsenic and adsorb it from soil. The nanoscale magnetite particles can effectively immobilize phosphate from soil by adsorption (Pan et al. 2010). However, the adsorption depends upon the pH, size of particles and surface morphology. A study of adsorption of phenol from aqueous solution was carried out by using alginate stabilized silver nanoparticle (AgNP) and gold nanoparticle (AuNP) beads as adsorbents.

This study showed that the adsorption efficiency and removal of phenol depends upon various parameters like initial concentration, contact time, pH and adsorbent dosage. The alginate stabilized AgNP and AuNP beads were found to be good adsorbent for adsorption of phenol from aqueous solution (Pal et al. 2014). The removal of arsenic species including As (III) and As(V) from drinking water using magnetic iron oxide nanoparticles coated on sand (MIONCS) was studied by Afzali et al. (2015). The results showed maximum adsorption capacity of arsenic is 0.285 mg g^{-1} at pH 7, which is higher than most of the available arsenic adsorbents. It concluded that the adsorption property of MIONCS has a higher efficiency for arsenic removal from drinking water. Mehrizad et al. (2012) investigated removal of 4-chloro-2 nitrophenol (4C2NP) from pharmaceuticals and pesticide industries using titanium dioxide nanoparticles as an adsorbent. The adsorption capacity was increased as the concentration and temperature of 4C2NP increases. Titanium dioxide nanoparticles recorded a maximum capacity of 86.3 mg.g^{-1} at optimal conditions.

4.2 Redox Reaction

Redox reaction involves reduction and oxidation in which electrons are transferred from one compound to other which results in oxidizing one compound and reducing the other (Tandon and Singh 2015). This transfer of electrons results in change in the oxidation state of the element. Redox reaction can stabilize or immobilize toxic contaminants and convert them to non-toxic or less toxic form which is the motive of remediation. Iron is a strong reducing agent and most commonly used for remediation. ZVI effectively dechlorinates many halogenated hydrocarbon compounds (Gillham and O'Hannesin 1994). The degradation is based on redox reactions, in which iron donates electrons to the contaminants, reducing them to fewer toxic compounds (Mueller and Nowack 2010). The reactivity of nZVI is more than ZVI; hence it is widely used for removing heavy metals like mercury (Hg), nickel (Ni), cadmium (Cd), lead (Pb) and chromium (Cr) from soil (Fig. 15.1).

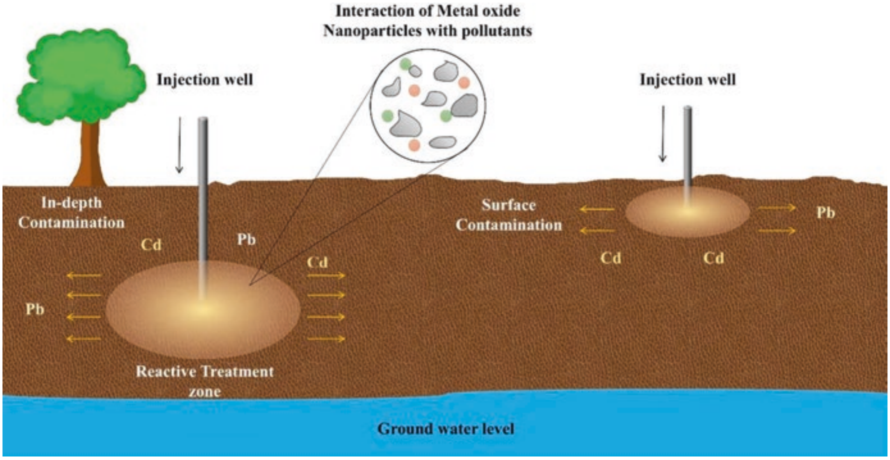

Fig. 15.1 Nanobioremediation of soil. Stabilized nanoparticles are transported in the form of slurry for proper distribution to the contaminated area. For in-depth contamination, the NPs are injected at deeper layers via injection well. For topsoil contamination, the nanoparticles are injected on the surface layer of soil. A reactive zone is created near the injection point through which the soil and pollutants interact with the nanoparticles. The incorporation of NPs with toxic heavy metal pollutants like lead (Pb), chromium (Cr) and cadmium (Cd) converts them to nontoxic or less harmful

5 Factors Affecting Reactivity of Nanoparticles

5.1 Mobility

Nanosize particles are much more mobile than larger sizes. The mobility of particles is less in solid medium like soil compared to aqueous medium like water; hence the degradation rate is also less. The mobility of natural or synthetic nanoparticles in the natural environment is strongly depend on whether the nanoparticles remain completely dispersed, aggregate and settle or form mobile nanoclusters (Karn et al. 2009). Soil composition also affects the dispersion of particles. For remediation, the particles should reach the contaminant zone, but their movement is disturbed by Brownian motion, density of particles, molecular interactions and also magnetic forces (Scott et al. 2011). Sometimes the particles get deposited on the surface of soil or in soil pores, which blocks the pores thus preventing the particles from reaching deeper layers. Nanoparticles are denser than water; due to this it gets settled in fluid; this also blocks the path (Cechin et al. 2016). To improve mobility, different surface coatings of polymers like carboxymethyl cellulose (CMC), polyethylene glycol (PEG), gum, etc. are being developed. These stabilizing agents promote easy distribution of particles through soil and enhance reactivity. Nasiri et al. (2013) evaluated the effect of stabilized and non-stabilized nZVI on the removal of Cd from soil. This resulted in nZVI being a suitable adsorbent for removal of Cd as both nZVI showed maximum adsorption. However, CMC stabilized nZVI had more colloidal stabilization and diffusion which increased its mobility and sustainability in comparison to non-stabilized nanoparticles.

5.2 Aggregation

Nanoparticles have a self-aggregation property which alters their dispersion. The interaction between soil and nanoparticles depends upon the surface chemistry of particles, ionic strength and porosity of soil and flow velocity (Karn et al. 2009), while the reaction between the nanoparticles and pollutants depends on the contact between them. Stable dispersion of particles in soil is essential for proper delivery in deep layers. But nanoparticles aggregate and form clusters which limit their migration and affect reactivity (Karn et al. 2009). Nanoparticles in concentrated solution aggregate more than in dilute solution; therefore, dilute solution is more stable than concentrated solution (He et al. 2008; Baalousha 2009). To prevent aggregation and loss of reactivity, stabilization of particles is necessary. Coating the particles with a stabilizing agent not only prevents agglomeration but also enhances reactivity and mobility. The principle of these stabilizers is that it creates a negatively charged layer on the surface of particles which induce repulsion with negatively charged soil, thus preventing agglomeration (Mueller and Nowack 2010).

If distribution of particles is achieved, surface reactivity increases thus enhancing the remediation. Polymer coating can also serve as a food or energy source for microorganisms (Galdames et al. 2020). Various natural and synthetic polymers or surfactants are used for coating NPs. Han et al. (2015) synthesized stabilized MnO_2 nanoparticles using carboxymethyl celluloses (CMC) as a stabilizer and tested their effectiveness for degrading aqueous and soil-sorbed estradiol. Non-stabilized MnO_2 particles rapidly aggregated and were unable to travel through soil column thus losing its mobility, whereas CMC-stabilized nanoparticles remained fully dispersed in aqueous solution without aggregating for months. CMC being a low-cost green stabilizer proved to be good for synthesizing birnessite (d-MnO_2) nanoparticles.

5.3 Stabilizers

The challenges like loss in mobility and transport of NPs to the site faced during remediation due to aggregation of particles are overcome by using stabilizing agents or stabilizers. These stabilizers are mostly polymers which can be synthetic or natural. Most of the synthetic polymers are negatively charged poly-electrolytes since they are capable of forming a poly-electrolyte layer that induces strong electrostatic repulsions (Hydutsky et al. 2007; Sirk et al. 2009). Some of the synthetic polymers are polyethylene glycol (PEG), polyacrylic acid (PAA), polystyrene sulphonate (PSS), polyoxyethylene sorbitan monolaurate, poly methacrylic acid and di-/tri-block copolymers which have been used as NZVI coatings and tested against different pollutants (Galdames et al. 2020). TCE (Schrick et al. 2004) and lindane (Román et al. 2013) have been degraded with PAA-coated nanoparticles. De Gisi et al. (2017) studied the efficiency of nZVI for treatment of marine sediments polluted with heavy metals by using commercial product Nanofer 25s coated with polyacrylic acid (PAA).

Natural polymers like carboxymethyl cellulose (CMC), starch, xanthan gum or guar gum have been used for coating which could enhance degradation, they can also serve as a food or energy source for microorganisms involved in bioremediation processes, and also, they are biodegradable (Galdames et al. 2020). Starr et al. (2009) investigated the effects of CMC-stabilized Fe3O4 nanoparticles on four pure cultures of bacteria, i.e. *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Enterococcus faecalis*. They hypothesized that CMC prevents nanoparticle aggregation as well as interactions between cells and nanoparticles. This study showed that stabilized nanoparticles may interact with bacterial surfaces without showing any toxicity or inhibitory effect to the tested organisms, thus concluding CMC-stabilized nanoparticles are non-toxic to bacteria. Table 15.2 shows different polymers used for stabilizing nanoparticles.

5.4 Longevity

Ageing is the factor for loss of reactivity of nanoparticles. Nanoparticles have limited lifespan; due to this, the reaction rate gets lesser day-by-day. Remediation with nZVI may be inefficient because nZVI particles may react with non-target substances, including dissolved oxygen, sulphate, nitrate and water. This also implies that nZVI will have a limited lifetime in porous media, and multiple injections of nZVI may be required, thereby making the treatment more costly (Tratnyek and Johnson 2006). Zerovalent iron nanoparticles have high surface area and get easily oxidized with the atmospheric oxygen due to which their functioning gets affected and reactivity decreases soon. Rapid oxidation results in formation of oxide layers on particles which may block the nZVP surface active sites and decrease the reactivity (Cullen et al. 2011). Encapsulation of nZVPs in a hydrophobic coating protects the core of nanoparticles from oxidation in air (Andreas et al. 2009).

6 Nanoparticles and Their Associated Risks

Studies have shown that nanoparticles are effective in bioremediation, but during this process there are few risks associated with them, major being impact on the microorganisms. Many studies have reported that nanoparticles have inhibited the growth of *E. coli* and *S. aureus* (Soni and Prakash 2015). Soil is rich in microbes that play vital roles in the biogeochemical cycles. The nanoparticles such as nano-iron can produce reactive oxygen species and disrupt the cell, leading to reduction

Table 15.2 Types of polymers used as stabilizing agents to prevent mobility and aggregation

Type of coating polymer	Polymers	Nanoparticles	Pollutants	References
Synthetic polymers	Polyethylene glycol 200 (PEG 200).	Amphiphilic polyurethane (APU) nanoparticles	Polycyclic Aromatic hydrocarbons (PAHs)	Tungittiplakorn et al. (2004)
	Polyethylene glycol 200	nZVI	Lindane	Román et al. (2016)
	Polyacrylic acid (PAA)	nZVI	Lindane	Román et al. (2013)
	Trichloroethylene (TCE)			Schrick et al. (2004)
	Polyvinylpyrrolidone (PVP)	nZVI	Trichloroethylene (TCE)	Sakulchaicharoen et al. (2010)
Natural polymers	Carboxymethyl cellulose (CMC)	nZVI	DDT	El-Temsah et al. (2016)
	CMC	Magnetite nanoparticle	Phosphorous	Pan et al. (2010)
	CMC	nZVI	Chromium	Chen et al. (2020)
	Chitosan	nZVI	Methylene blue (synthetic dye), aniline (aromatic primary amine)	Sravanthi et al. (2018)
	Xanthan gum	nZVI	–	Xue and Sethi (2012)
	Guar gum	nZVI	Trichloroethylene (TCE)	Sakulchaicharoen et al. (2010)

in beneficial microbes of soil (Morrison et al. 2002). Nanoparticles from heavy metals can hinder the movement of essential ions via the membrane indirectly inhibiting the growth of the microbe (Mashrai et al. 2017). The organic polymers can be coated to nanoparticles in order to reduce their toxic effects (Zhang et al. 2012). Very limited studies have been conducted till date on the impact of nanoparticles on the fungal growth, with most of them advocating a neutral effect on their growth (Tratnyek and Johnson 2006).

The smaller size of nanoparticles makes them an ideal candidate for bioremediation, but at the same time decrease in particle size and more reactivity make a substance more toxic. There are various studies related to the toxicity of nanoparticles. Nanoparticles may be ingested, inhaled or taken up through the skin (Oberdörster et al. 2007). Factors like the particle aggregation/disaggregation potential, partition coefficient, water solubility, composition, structure, molecular weight, the melting/boiling point, etc. (Vishwakarma et al. 2010) also play role in imparting toxicity to the nanoparticles; however toxicity studies need to be conducted on the mammals and the environment for the same.

A significant reduction in glutathione in the gills and lipid peroxidation in the brain was reported in largemouth bass (*Micropterus salmoides*) which was exposed to nC60 (1 ppm) (Oberdorster 2004). A study by Beddow et al. (2014) demonstrated nanosilver had an impact on *Nitrosomonas* sp. and *Nitrosococcus* species reflected by the inhibition to their nitrification rates. In another study on nitrifying bacteria, the impact of AgNPs [50-nm uncoated and 15-nm polyvinylpyrrolidone (PVP)-coated AgNPs]) to soil nitrification kinetics was studied. The results showed uncoated AgNPs exhibited more toxicity to nitrifying bacteria (Masrahi et al. 2014). The nickel manganese cobalt oxide (NMC) nanoparticle in quantity as low as 5 mg. L^{-1} is lethal for growth and respiration of soil bacterium *Shewanella oneidensis* MR-1 (Hang et al. 2016). Based on the toxic effects of various nanomaterials on the microbes, there is an urgent need to develop an alternative assessment procedure which is more efficient for evaluation. Further computational methods to predict properties, reactivity and mechanisms of actions for various molecular systems. Methods such as molecular dynamics simulations and quantum chemical calculations can be used to manage the potential risks associated with nanomaterials.

7 Conclusion and Future Prospects

Nanoparticles can profoundly be used for the remediation of soil. The small particles are highly reactive and have great absorption capacity. However, there are still a few challenges, such as the delivery of the particles to the target area, that need to be addressed. There are also concerns regarding the human and ecological toxicity caused due to these particles that requires extensive toxicity studies. Currently use of biosensors is viable option for soil bioremediation. Biosensors based on electrochemical properties such as high sensitivity and detection of heavy metals in real time can be developed in the form of nanowires, nanospheres and nanorods. Further whole-cell biosensors can be synthesized having better sensitivity with the help of eukaryotes for detection of heavy metals and agricultural chemicals that contaminate the soil. Such biosensors can be useful for monitoring of in situ pollution.

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