Chapter 13
Interaction of Nanoparticles to Soil Pollutants

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1 Introduction

The industrialization has been propagating over a few years, which has brought processes of urbanization involving manufacturing, production, transportation, refining, mining, etc. The pesticides; phenols; heavy metals like lead, arsenic, cadmium, mercury, etc.; and hydrocarbons are produced and used every day, which adds to the list of contaminants that harm the environment (Chaplygin et al. 2021; Medvedeva et al. 2020). The soil and water are gravely affected parts of the environment. The contaminants contribute to the depletion of natural resources by producing hazardous wastes, which in turn threaten human health, causing diseases like cancer, chronic obstructive pulmonary disease, heart diseases, stroke, etc. These are taken up by humans in one way or another from ingestion, absorption, to inhalation. Bioaccumulation of toxic compounds like persistent organic pollutants (Bayen et al. 2005; Kelly et al. 2007; Houde et al. 2008), heavy metals, etc. (Smical et al. 2008; Kumar et al. 2011; Yap et al. 2011) sublimates in the food chains right from the fishes, and biota again pose a risk to human life as well as wildlife.

The requisition for modern technologies and methods to quicken the process of decontamination and the consequent reduction of their costs is growing exponentially. The employment of the technology working on a nanometric scale involving nanomaterials, like zinc, titanium oxide, and iron-based nanoparticles, particularly, has received great attention as an innovative method for remediation. However, several studies have been conducted on nanomaterials, but their behaviour in the soil pores, interaction with the soil biota, adsorption on mineral particles, and their

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interaction with the contaminants have not been discussed yet. The different processes used for synthesizing several kinds of nanomaterials having distinctive traits include photocatalytic deposition (PD), chemical solution decomposition (CSD), deposition-precipitation (DP), chemical vapour decomposition (CVD), ultrasonic irradiation, hydrothermal and thermal processes, etc. (Khajeh et al. 2013).

The basic property that has brought nanoparticle into such light and has made it such an upcoming field for its applications in remediation and various other fields is that despite their small size, nanoparticles offer a very large surface area to volume ratio, when compared to bulk material, which provides better interaction. Nanoparticles exist naturally in nature and can also be manufactured as by-products of combustion reactions or produced through engineering techniques, since nanoparticles can be easily generated and programmed for particular roles that find their functions in various domains. This large surface area allows diffusion across membranes that are allowing molecules, ions, heat, etc. to diffuse through the particles that is in and out, at very high rates. The entire particle reaches homogenous equilibrium in a very short time due to the small diameter keeping it stable during diffusion.

The objective of this chapter is to elaborate the prospects of various nanomaterials and their interaction with the soil pollutants. The viability of amalgamating remediation technologies like bioremediation, biomagnification, biostimulation, etc. as well as monitoring the level of toxicity of nanomaterials to the soil microorganisms is pivotal for effective remediation. A brief review is presented on the soil pollution and the various pollutants that contribute to it via different ways which are followed by the understanding of the nanoparticles (NPs) for contaminated sites, which includes field application and the challenges faced subject to their usage during field application. The effects of NPs on microorganisms, that is, the positive (biostimulant) or the negative (biocide) effects, are also discussed. Finally, the concept of nanoremediation and nanobioremediation (NBR) is proposed, which aims towards collaborating clean-up technologies for efficient and constructive decontamination. The principles are supported with examples and case studies on various nanoparticles like nZVI and graphene oxide nanoparticles and then using the process of photoinduced precipitation for the same. Nevertheless, the anticipation of integrating nanotechnology and bioremediation for the purpose of soil remediation is much more systematic and sustainable.

2 Soil Pollution and Soil Pollutants

Soil contamination is originated by the presence of perilous compounds in the soil. These are heavy metals, a common class of pollutants that are naturally present in the soil but are not very often at toxic levels. The main sources of such heavy metals are landfills of industrial waste, e.g. paint remnants, electrical generated wastes, weedicides, herbicides, chemical fertilizers, municipal or industrial sludge, etc. Heavy metals are non-degradable and persist in the environment. Mercury and selenium are the only exceptions since they can be volatilized by microorganisms. The remedial cure can be performed in situ or ex situ. The ideal procedure to handle the problem is to prevent contamination by heavy metals or by immobilization (Ma et al. 1993). The sorption-desorption reactions with other constituents of soil govern the activity of heavy metals in soil (Singh et al. 2001). Therefore, to manipulate the heavy metal bioavailability and the impediment of their diffusion in soil, amendment agents have been used. The processes involved are adsorption to mineral surfaces, ion exchange methods, surface precipitation, and stable complex formation with organic ligands (Kumpiene et al. 2008).

There are two kinds of amendment agents, i.e. mobilizing and immobilizing agents. The mobilizing agents increase mobility and bioavailability and enhance the phytoextraction process, while immobilizing amendment agents minimize the same, and they also reduce biomagnification risk, i.e. phytostabilization (Robinson et al. 2009).

In the past few years, heavy metal immobilization in the soil and groundwater via nanoscale particles has drawn immense interest. There are two requirements that are requisite while applying amendment agents as nanoparticles, i.e. conveyance of the tangibles to the contaminated zones and that the nanoparticles must remain confined in that very domain of application after removal of external injection pressure (An and Zhao 2012). However, there is a loss in defining properties like high reactivity and specific surface area of nanoparticles due to their tendency to agglomerate into micro- to millimetre scale. Therefore, organic polymers like starch and carboxymethyl cellulose (CMC) are attached to the nanoparticles as stabilizers overcome these problems and prevent agglomeration (He and Zhao 2005, 2007).

Arsenate, a soil and water pollutant was immobilized by the effective enhanced sorption of the starch-stabilized magnetite nanoparticles. The results of this investigation also resulted in the reduction of the toxicity characteristic leaching procedure (TCLP) leachability of As (V) (Liang and Zhao 2014). Phosphate compounds are effective agents for the immobilization of lead (Pb) in in situ heavy metal immobilization, where implementation of phosphate to the soil is in soluble (phosphoric acid) or solid (synthetic apatite) forms (Yang et al. 2001). A new type of apatite nanoparticle along with CMC, i.e. stabilizing agent, was synthesized to elevate the phosphate dispersion rate. The hydroxyl and carboxyl groups are integral in inhibiting further aggregation of nanoparticles (Liu and Zhao 2013). nZVIs are widely used for on-site bioremediation of heavy metals thus altering their redox state in soil.

The capacity of the ZVI nanoparticles to aggregate rapidly results in the loss of reactivity which is the major limitation of ZVI formed by conventional methods. This loss of reactivity was because the agglomerated ZVI particles attain a size in the micron scale, which shows low mobility in soils, therefore making them unsuitable for in situ treatments. This problem can be overcome by the particle stabilizing strategies with coatings or capping the nanoparticles with stabilizers like organic coating stabilizers such as cetylpyridinium chloride (Chen et al. 2004), starch (Reyhanitabar et al. 2012), sodium CMC (He and Zhao 2007), and polyvinylpyrrolidone (PVP) (Fang et al. 2011a).

The chemical reagents used during the conventional preparation such as ferrous sulphate are expensive (Fang et al. 2011b). So, to lower the cost of removal of chromium (VI), CMC-stabilized nZVI was eminently formulated from waste liquor obtained by steel pickling which reduced the 100% TCLP leachability of Cr (VI) (Wang et al. 2014c). Although soluble and solid phosphates have been reported highly effective for in situ stabilization of heavy metals at laboratory scale. On the contrary their addition to the subterrain is constricted by cost as well as the secondary contamination of groundwater by eutrophication due to the addition of increased levels (e.g. 3% of PO_3^{-4} dosage) of phosphoric acid or salts (Park et al. 2011).

3 Nanoparticles and Their Interactions

Before studying the detailed description of nanoparticles' interaction with the soil pollutants, let's first understand nanoparticles and their types. Nanoparticles are small particles that range from 1 to 100 nanometres in size (Timoshenko et al. 2021; Kumari et al. 2022; Rajput et al. 2021b). Nanoparticles exhibit different types of physical and chemical properties, and these properties, in turn, affect their association with the soil pollutants or their bulk counterparts.

Another property is solvent affinity; the nanoparticles have high solvent affinity and can be a part of the suspensions due to this very property. The interaction is significantly strong in that it overcomes density differences, unlike other materials. The following are more details given on the types of nanoparticles, their characteristics, and their functions.

4 Natural Nanoparticles

The natural nanoparticles as the name suggests are already present or occur naturally in the environment. They participate in the essential ecological processes due to their nature and surface properties, which range from cycling elements, through various processes like transporting chemical and biological contaminants, sorbing, regulating water storage, and serving as an organic carbon and plant nutrient source. Nanoparticles and nanostructures are present in all living organisms like insects, birds, plants, animals, and humans including microorganisms, i.e. bacteria, algae, and viruses.

4.1 Nanoparticles in Microorganisms

The naturally occurring nanomaterials are substances and/or by-products produced in bodies of some microorganisms like bacteria, viruses, fungi, algae, cyanobacteria, and yeast (Table 13.1).

Table 13.1 Naturally occurring nanoparticles of natural products (Griffin et al. 2018)

Organism	Examples of the organisms producing nanoparticles
Bacteria	*Lactobacillus* sp. *Shewanella* sp.
	Staphylococcus aureus
Cyanobacteria	*Synechocystis* sp.
	Limnothrix sp.
	Anabaena sp.
Fungi	*Aspergillus terreus*
	Verticillium sp.
	Fusarium oxysporum
Algae	*Coelastrum* sp.
	Botryococcus sp.
	Chlamydomonas sp.
Yeast	*Saccharomyces cerevisiae*
	Saccharomyces boulardii
	Hansenula anomala

4.2 Nanoparticles in Plants

The profound functions of plant parts especially leaves, having nanostructures are used for insect sliding (Gorb et al. 2005), mechanical stability (Bargel et al. 2006), absorption as well as reflection of visible and ultraviolet radiations (Pfündel et al. 2008). Self-cleaning and super-wettability create super hydrophobicity in lotus leaves which is the most common nanostructure property. These properties are useful in various applications, e.g. sewage water treatment plants, wettability switchers, actuators, and transparent coatings of electrodes.

4.3 Nanoparticles in Insects

The membranes of insect wings are composed of crystalline chitin polymer that provides membrane support. These building materials form a complicated vein system that imparts exceptional stability to the structure of the wings. These insect wing surfaces portray a wide range of micro and nanoscale properties of these highly ordered structures which protects them against pollutants and wetting.

4.4 Nanoparticles in Animals and Birds

Animals like spiders and geckos, for example, can attach to the walls and walk against gravity on ceilings and vertical walls. This is possible because of the patterned structure present in these animals that efficiently interact with the substrate.

This is also possible due to the nanosized hairlike structures in their feet which increases the total surface area that enables them to walk on wet surfaces and against gravity as a result of strong surface adhesion mediated by the van der Waals forces of interaction (Moret 2006). Mollusc shells consist of a nanocomposite called nacre. Nacre is a hierarchical nanocomposite which is designed calcium carbonate aragonite platelets of sub-micrometre and micrometre sized which are in turn separated by a bio macromolecular glue. Nacre design is such that it incorporates traits like strength, enhanced stiffness, resistance, and toughness. The $CaCO_3$ form a thin and strong shell as the amorphous mineral transformed by lectin proteins into ordered crystals forms the $CaCO_3$ nanoparticles (Freeman et al. 2010).

4.5 Nanoparticles in Humans

The human body consists of nanostructures like proteins, enzymes, bones, antibodies, and DNA. The functioning of the human body without nanostructures is impossible. There are certain examples of nanostructures which play a crucial role in some of the most important cycles of human body and generally in its functioning as well. Their DNA has a size range of 2.2–2.6 nm, glucose is 1 nm, and haemoglobin is 6.5 nm (Papazoglou and Parthasarathy 2007); proteins ranges from 3 to 6 nm (Milo and Phillips 2015), etc.

4.6 Clay Minerals

Clay minerals are natural nanoparticles comprising of layer silicates, involving three weathering processes, namely, transformation, inheritance, and neoformation by abiotic pathway. The transformation is a process involving the alteration of the interlayer region, while the overall structure remains intact; inheritance as the name suggests the birth of the layers from parent rocks and clay materials, and lastly neoformation is a process of weathering that involves crystallization or precipitation from a solution or gel precursor. Wilson (1999) studied that micaceous nanoscale minerals in the soil are mostly acquired from the parent rock, for example, soil smectites are formed by transformation, inheritance, and neoformation, while kaolinite is a product of neoformation. One of the important functions of bacteria is forming mineral nanoparticles, comprising layer silicates. Bacteria have negatively charged cell walls and a large surface area to volume ratio, which is well suited for mediating mineral formation as they can oxidize and reduce metals and also cause precipitation (Bargar et al. 2008).

4.7 Short-Range-Order Minerals

The principal nanoscale materials in volcanic soil minerals are allophane, imogolite, ferrihydrite, and Al- and Fe-humic complexes. These minerals are formed by rapid volcanic ash weathering, and they are present in abundance in the volcanic soil. Imogolite has fixed chemical composition. Unlike imogolite, allophane does not have the same as the Al/Si ratio may vary.

Ferrihydrite through a solid-state reaction forms hematite, followed by goethite produced via dissolution and precipitation. Ferrihydrite has nanosize (2–5 nm) which is the principal constituent of the juvenile volcanic soils (Schwertmann 2008). The allophanic andisols accumulate organic matter particularly humic substances. The strong association of allophane with humic substances is the reason for its stability in volcanic soils.

Allophane shows a powerful tendency for sorbing phosphate and arsenate, which offers possible evolution of an eco-friendly process of secluding arsenic from potable water and phosphorus in the outflow, for the remediation of arsenic-contaminated soils (Violante and Pigna 2002; Arai et al. 2005; Yuan and Wu 2007). Non-allophanic andisols accumulate aluminium and iron humic complexes which are present in minimal quantity than aluminium complexes as iron forms iron oxides, hydroxides, and oxyhydroxides (Dahlgren et al. 2004).

4.8 Metal Oxides, Hydroxides, and Oxyhydroxides

Soils consist of various oxides, hydroxides, and oxyhydroxides[(hydr) oxide] of Al, Fe, and Mn, which are formed through microbial pathways or by weathering of primary and secondary silicate minerals. Gibbsite [γ-Al(OH)$_3$] is the most widespread aluminium (hydr)oxide, and its production includes the liberation of aluminium from primary alumina silicate minerals, subsequently by hydrolysis and precipitation, whereas the desilication of kaolinite leads to gibbsite formation in many highly weathered tropical soils. Fe (hydr)oxides present in almost all types of soils; some are dynamically coloured, for example, goethite which imparts yellowish-brown colour; during the presence of red hematite, this colour is concealed. Goethite and hematite are the most common species in soil as they are thermodynamically stable, followed by magnetite, maghemite, and ferrihydrite. Soil aggregate stabilization and clay flocculation are encouraged by these nanomaterials which are integral for the adsorption and retention of nutrient anions, for example, phosphate by electrostatic interactions and ligand exchange (McBride 1994; Schwertmann 2008).

Birnessite and vernadite, Mn (III, IV)- (hydr)oxides, occur as poorly crystalline nanoparticles, and they form coverings on mineral surfaces in alliance with iron (hydr)oxides and constituents of soil. Humics are chemically recalcitrant due to their structural complexity; therefore the macromolecular humics are replaced by relatively low molecular weight molecules that are bound by weak dispersive forces and are capable of forming micelles in solution (Sutton and Sposito 2005).

The sorption of Cu and Cd is enhanced by humic acid and allophane complexes (Yuan et al. 2002). In most of the study, it is found that various factors and variables like ionic strength, pH, and contaminant loading influence the contaminant-nanoparticle interaction (Chorover et al. 2007). The sorption of metalloids, organic contaminants, and heavy metals by soil nanomaterials depends on contact time. The rate of sorption is biphasic that occurs in two phases, the initial phase which is rapid that occurs in a few milliseconds while the slow phase takes days due to diffusion, precipitation, and structural rearrangement (Sparks 2018). The bioavailability of contaminants decreases with contact time ("ageing") as a result of the above-mentioned phases (Chorover et al. 2007). The intrinsic complexity of physiochemical processes of the soil urges a broad, multidisciplinary application along with high-resolution modern instrumental techniques for a better understanding of sorption phenomena and nanoparticle interactions. The question that arises here is that if there are so many nanoparticles already present in the environment, then what is the requirement of artificially synthesizing nanoparticles? The answer to this question is given in the next section, that is, synthesized nanoparticles.

5 Synthesized Nanoparticles

The anthropogenic pollution of the lithosphere and hydrosphere due to past and present activities has been one of the biggest concerns for human health and sustainable development all over the world. The day-to-day industrial activities involving production of harmful substances along with abandoned contaminated plants and sites are a potent source of pollution. Therefore, a thorough cleaning of the effluents produced by these industries is crucially required followed by remediation of polluted soil and water. The nanosized zero-valent iron (nZVI) is a potent nanomaterial arising in the field of remediation due to lower expected impact on the environment and its high reactivity with the contaminants. The usefulness of nZVI in processes of removing contamination from soil and water along with modification of material properties for fulfilling specific requirements of application is still being taken up under extensive research. The aim is the removal of contaminants from the soil with various processes like the catalytic activity, efficiently by nZVI and eliminating any harmful effect further on soil biota and plants.

nZVI, nanosized zero-valent iron, is a nanoparticle with various distinct features as compared to iron. nZVI is a key synthetic nanomaterial used for environmental remediation due to good adsorption capacity, its higher reactivity, and lower cost (Machado and Pacheco 2016; Liu and Hong 2017; Phenrat and Lowry 2019; Yan et al. 2013). nZVI has a strong reducing power and reacts with numerous organic and inorganic compounds, consisting of heavy metal ions, halogenated hydrocarbons, antibiotics, organic dyes, etc. They readily react with water and oxygen and also have a high tendency of agglomeration due to such reasons; nanoparticles are usually supported or capped as shown in Fig. 13.1. The nZVI is a core shell nanoparticle which is either capped or supported by inorganic or organic materials like pumice to reduce the immediate reactivity of nZVI with water and oxygen. The support and capping also slows down rapid agglomeration and increases transport properties as well as stability. Capping and support agents increase the stability and properties for transport while reducing reactivity up to some extent, during reaction. The nZVI has high reactivity and strong reducing power towards inorganic (like ammonium ions, heavy metal ions, Cr(VI), etc.) and organic compounds (like polychlorinated biphenyls, fuels, PAH, etc.).The photosensitive core shell nanoparticle adsorbs the contaminants from water and soil after the removal of protective layer by irradiated UV light, which is known as photoinduced precipitation.

The two main drawbacks for catalytic application concerned nZVI are its susceptibility to aggregation and easy passivation on its surface when it comes in contact with air or an aqueous environment. The oxidation of nZVI can be avoided by encapsulating the nanoparticle in the suitable solid matrix avoiding hindrance of the access to catalytic sites. For example, nZVI/reduced graphene oxide (rGO) composite protects the nanoparticle from oxidation and also provided charge transfer to substrate (Goswami et al. 2020). Another example of the same involves the reduction of p-nitrophenol to p-aminophenol using $NaBH_4$, while the reaction is catalysed by nZVI (Bae et al. 2016). The application of nZVI/$NaBH_4$ system for reduction is highly beneficial as sodium borohydride disintegrates nZVI nanoparticles as a result of chemical etching which forms small particles that gives protection

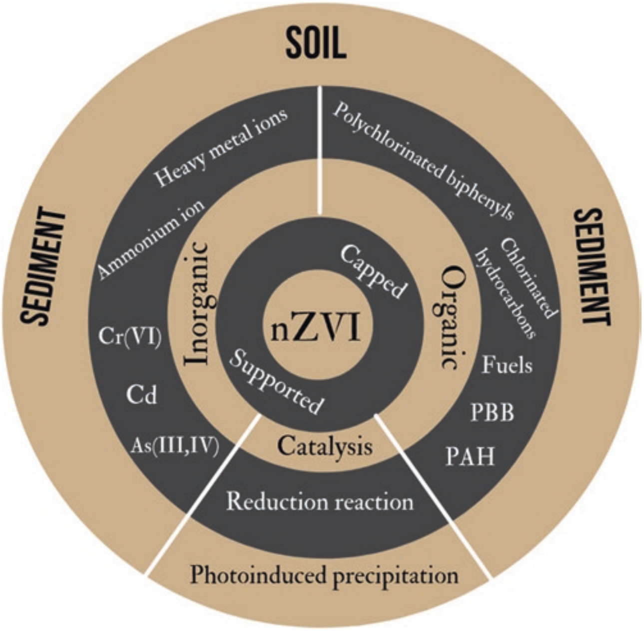

Fig. 13.1 Application of nZVI for environmental remediation

from oxidation and increasing surface area for p-nitrophenol reduction. The nZVI catalyst can be easily recycled and reused and proves to be a sustainable option.

Polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), and carboxymethyl cellulose (CMC) are capping materials that have stabilized nZVI by reducing $FeCl_3$ with hydrazine (Parimala and Santhanalakshmi 2014).

The field application in soil remediation is much more challenging as the nZVI is transported to the contaminants in sufficient concentrations. There are mainly two possibilities in field applications, creation of reactive zones with relatively mobile NPs and that the reactive nanoparticle migrates to contaminated zones. The soil and water pollutants are closely linked with respect to contamination

6 Other Categories of Nanomaterials

(i) *Organic-based nanomaterials*: Organic-based nanomaterials (NMs) are organic matter nanomaterials which are transformed into desired structures like liposomes, micelles, and dendrimers by self-assembly and noncovalent (weak) interactions.

(ii) *Inorganic-based nanomaterials*: These inorganic nanomaterials include metal and metal oxide nanoparticles and nanostructured materials (NSMs). These inorganic-based nanomaterials can be amalgamated into metals such as Ag or Au nanoparticles, metal oxides such as ZnO and TiO_2 NPs, and semiconductors such as ceramics and silicon.

(iii) *Carbon-based nanomaterials*: These NMs contain carbon and are found in morphologies such as ellipsoids or spheres. Graphene (Gr), fullerenes (C60), carbon nanotubes (CNTs), carbon black, carbon nanofibres, etc. are included in this category. These carbon-based fabrications are produced by various methods like laser ablation, chemical vapour deposition (CVD), and arc discharge (Kumar and Kumbhat 2016).

(iv) *Composite-based nanomaterials*: Composite nanomaterials are multiphase NPs and NSMs that are one or more than one phase on the nanosized dimension that combine NPs with other NPs or NPs with bulk-type materials (e.g. hybrid nanofibres) or complex structures, such as a metalorganic framework. The composites are made of combinations of inorganic or organic components, carbon-based, or metal-based NMs embedded in any form of metal, ceramic, or polymer bulk materials at the molecular level to acquire new properties.

7 Nanoremediation and Nanobioremediation

Bioremediation by definition is a process of rejuvenating and cleaning contaminated soil and water. Bioremediation utilizes microbes or microorganisms for that matter which consume the contaminants for making the environment contaminant-free.

The process of nanoremediation is somewhat similar, but, in this process, nanoparticles are used for the process of cleansing. This is one of the widely used applications that is being studied and researched. Phytoremediation coupled with nanotechnology advances the remediation process when the plant fulfills certain parameters like higher biomass, well-developed root system etc. (Ranjan et al. 2021). The nanoparticles are both naturally occurring (natural composites, volcanic ash, clay minerals, etc.) and man-made (e.g. nZVI, Fe_2O_3, Al_2O_3, etc.) which are employed for the remediation. Nanotechnology is potentially beneficial to the environment and is a much more sustainable technology than other techniques. The changes in the environment can be determined via remediation of contaminated molecules and certain chemicals acting as sensors (Neufeld et al. 2006).

Some organic compounds like polychlorinated biphenyls (PCB) and polychlorinated hydrocarbons (PCH)are broken down by nanoparticles. Carbon nanotubes strongly adsorb dioxins compared to conventionally activated carbon. Hydroxyapatite rehabilitates the polluted soils by decreasing bioavailability of heavy metals, copper and zinc, in the soil. The various mechanisms involved in the synthesis of nanoparticles by microorganisms include alteration of solubility, lack of specific metal transport system, toxicity through reduction or oxidation, biosorption, precipitation of metals, efflux system, bioaccumulation, etc. (Fan et al. 2013; Husseiny et al. 2007).

The microbiological reaction rates increase with nanoparticle catalysts present in the cells which stimulate the microbial activity (Shan et al. 2005). A good example describing this is fungi as they have many enzymes in their cells and are easy to handle and they excellently synthesize metal and metal sulphide nanoparticles (Hulkoti and Taranath 2014). It is observed that great number of proteins result in a high productivity of the nanoparticles (Husseiny et al. 2007).

Nanoparticles have various advantages, but their negative impact on the environment is the one to be concerned and cautious about as there is a possibility of release of dangerous compounds as time advances. For example, nanofibres and nanotubes can inhibit cell wall synthesis. These molecules are bactericidal. Much research is being conducted to eliminate any such harmful effects and also for better understanding the transport of nanoparticles and their sustainability and toxicological effects on diverse biological systems, including humans (Zhang et al. 2011; Cameotra and Dhanjal 2010). The Table 13.2 below consists of certain examples of nanoparticles and their effective nanoremediation of the contaminants from the soil.

7.1 Principles of Nanobioremediation

The toxic chemical compounds like polychlorinated biphenyls released every year amount to around ten million tonnes which is a massive amount, and after their release, they may also convert into more reactive forms like polychlorinated dibenzofurans or polychlorinated dibenzo-p-dioxins; those are by-products of chlorine-mediated chemical processes.

Table 13.2 Nanoremediation of contaminants in soil

Nanoparticle	Contaminant	Remark	References
Fe/Ni bimetallic nanoparticles	Tetracycline (TC)	The ageing of Fe/Ni nanoparticles resulted in a decrease in the removal of TC. The ageing products responsible were found to be magnetite and maghemite	Dong et al. (2018)
Fe/Pd bimetallic nanoparticles	Polychlorinated biphenyls (PCB)	After a span of 14 days, a 20% decrease in PCB was seen from the soil	Fan et al. (2013)
nZVI	Cu, Pb, Sb	The soil washing efficiency was increased by the nanoparticle as well as portraying selective removal for Cu, Pb, and Sb	Boente et al. (2018)
Reduced graphene oxide silver nanoparticles (rGO-Ag)	Phenol, bisphenol A, and atrazine	The photocatalytic degradation results in the decrease of these compounds. Significant decline in contaminants is seen promoting oxidative degradation especially when carried under visible light	Bhunia and Jana (2014)
Palladium nanoparticles	Pentachlorobiphenyl	These nanoparticles coupled with supercritical fluid CO_2successfully remove all PCBs from the soil at all temperature ranges and 200 atm	Wang and Chiu (2009)
Manganese oxide nanoparticles	17β-oestradiol	88% of oestrogens were removed from the soil. Increased concentration of nanoparticles elevated the oestrogen degradation along with the decreased injection velocity	Han et al. (2017)

The complications that have arisen for the successful implementation of remediation technologies are due to certain factors like the high chemical and physical variability and cytotoxicity of these chemical compounds, as well as multiple interactions with abiotic and biotic environmental factors (Jeon et al. 2016; Zhu et al. 2017; Hurtado et al. 2017). The final use of nanoparticles and nanomaterials with biotechnologies propose an alteration in remedial abilities, thus increasing the speed of degradation (Kang 2014; Fulekar and Pathak 2017). The major characteristics of these technologies are that they are cost-effective and highly efficient and have a wide range of applications.

Over the years the biological processes are integrated with nanoparticles and nanomaterials to accelerate the toxic compound removal from the environment. Factors like nanotoxicity, the size of the particle, etc. affect the living organism and their entire process. It was reported by Tan et al. (2018) that there are a variety of factors influencing this interaction between the biota, microorganisms, and the nanomaterial like pH, temperature, size, and shape of the nanomaterial, their coating, media, nature of the contaminant and the nanomaterial, etc.

Wang et al. (2014) proved the stability of Au NPs in the buffer and MilliQ water; however, the stability was lost at different pH 4, 7, 8, and 10. Tang et al. (2016) also demonstrated that the thermal stability of Cu nanoparticles was influenced by different synthetic methods. Once the biota and NPs interact, events like adsorption, absorption, dissolution, and photocatalytic reactions might happen, which may further participate in the degradation of contaminants.

7.2 Bioremediation Based on Nanotechnology

Bioremediation based on nanotechnology can be simply described as the pairing of a nanoparticle with a bioagent for the purpose of effective remediation. Kim et al. (2013) studied the effect of polybrominated diphenyl ethers' (PBDEs) degradation by this method using nZVI-*Sphingomonas* sp. through the process of reductive debromination which leads to biological oxidation. This hybrid method causes remediation of heavily polluted sites especially with highly halogenated environmental pollutants. A two-step method involving biosurfactant-enhanced soil washing technology after dechlorination by nZVI removed polychlorinated biphenyls (PCB) from contaminated soil. nZVI enhanced efficiency of soil washing by reducing the interfacial tension between two phases, the oil and soil, and about 90% of PCB was removed by nZVI, and the nanoparticle-bioagent combination had the remediation efficiency of 78–99% with rapid reaction time (Jing et al. 2018). Table 13.3 contains similar examples of nanobioremediation of environmental contaminants and the process by which they are remediated.

8 Examples and Case Studies

nZVI

Soil remediation is a much more challenging task due to matrix complexity. The reagents required for soil remediation are much more than what is required for wastewater purification. Singhal et al. (2012) experimented on malathion decomposition in the soil in vitro. They added Malathion, a widely used insecticide, to the soil which was dried followed by crushing and sieving it. The nZVI, that is, the zero-valent iron nanoparticle, was added along with the dry soil, and it was observed that Malathion degraded effectively to the harmless O-dimethyl phosphorodithioic compound, but the degradation decreased with increase in the size of the nanoparticle.

Similarly, Quinn et al. (2005) included nZVI emulsified with vegetable oil for soil remediation of the soil having contamination with trichloroethane (TCE). Degradation of TCE in significant quantities was studied, but the usefulness of the process of nanoremediation was repressed, because nanoparticles weren't uniformly administered in the target treatment area, as they migrated above the target treatment depth rather than far from points of injection. There was a significant reduction of the TCE concentration in the soil and groundwater, but in turn increased the concentrations of intermediate dechlorination products, namely, cis-dichloroethene

Table 13.3 Nanobioremediation of environmental contaminants

Nanoparticle	Bioagent	Contaminant	Remark	References
nZVI-C-A beads	*Bacillus subtilis*, *E. coli*, and *Acinetobacter junii*	Cr (VI)	About 92% of Cr (VI) was removed showing enhanced removal by the combined technology where calcium alginate beads were entrapped in nZVI	Ravikumar et al. (2016)
nZVI	*Dehalococcoides* spp.	TCE	The dechlorinating bacteria were deactivated by nZVI which after a lag phase could remove TCE while producing by-product ethene. nZVI also stimulated the metabolic activity of methanogens	Xiu et al. (2010)
nZVI	*Paracoccus* sp. *strain YF1*	Nitrate	The higher the concentration, the more reduction in denitrification rate, while lower the conc. Of nZVI; there is enhanced denitrification along with slight microbial toxicity	Liu et al. (2014)
Pd/nFe	*Laccase derived from Trametes versicolor*	Triclosan	Triclosan was remediated by Fe nanoparticles, while laccase derived from *Trametes versicolor* degraded and converted the by-products into nontoxic compounds	Bokare et al. (2010)

(continued)

Table 13.3 (continued)

Nanoparticle	Bioagent	Contaminant	Remark	References
Pd/nFe	*Sphingomonas wittichii RW1 (DSM 6014)*	2,3,7,8-Tetrachlorodibenzop-dioxin (2,3,7,8-TeCDD)	The highly toxic dioxin, recalcitrant in nature, was degrades by the sequential usage of nanoparticles and the bioagent, sequentially	Bokare et al. (2012)
Pd/nFe	*Burkholderia xenovorans* LB400	Polychlorinated biphenyl (PCB) Aroclor 1248	Pd/nFe nanoparticles efficiently dechlorinated the various chlorinated biphenyls into biodegradable followed by degradation by *Burkholderia xenovorans* bioagent	Le et al. (2015)

and vinyl chloride, which were detected in the groundwater. It was studied that the TCE concentration decreased by the nZVI emulsified treatment due to the TCE sequestration into the oil and TCE abiotic degradation in alliance with nZVI. Hence, TCE concentrations were lowered by emulsified nZVI more efficiently than by nZVI alone (Hara et al. 2006).

Similarly, arsenic was successfully immobilized by commercial nZVI as iron oxides adsorbed the arsenate onto their surface covered by the shell. The electrical conductivity or pH of the soil was unaltered due to this application, additionally iron availability increased, and a remarkable reduction in phytotoxicity was witnessed (Baragaño et al. 2020a, b).

Graphene Oxide

According to a study conducted by Baragaño et al. (2020a, b), graphene which is a carbon derivative in the form of nanoparticles is especially effective in the remediation and recovery of soils polluted with arsenic. The study also showed promise in other heavy metal pollutants. Arsenic, which enters the environment from smelting, fossil fuel consumption, and pesticides, was the chief focus of the study. There is a risk of biomagnification through trophic levels which causes immediate negative effects. The currently used approaches exhibit a variety of issues such as slow speed, extensive technology involvement, or simply being an energy negative process. Another condition that is to be kept in mind while designing remedial processes is to ensure that the products formed from the process should not be harmful; otherwise it becomes futile.

Arsenic is a highly dangerous contaminant, toxic to nearly all forms of life. It is also carcinogenic, with reported effects on the lungs, skin, bladder, and other organs (Gopalakrishnan et al. 2015; Wu et al. 2008). It shows acute toxicity in both plants and animals. The central axiom of detoxification and neutralization of this pollutant in the environment is either neutralization or immobilization. Simply put, either the pollutant is made harmless by certain treatments or simply removed from the immediate environment. Using an integrated approach, combining methods such as bionano remediation shows much more promising results than individual methods. In this particular case, the particles exhibit high reactivity and specific surface area which allows for the present metal to form complexes. This reduces toxicity, altering the mobility of the ion itself. This result shows some variation depending on the nature of the metal ion.

In the study, both zero-valent iron (nZVI) nanoparticles and graphene oxide (nGOx) nanoparticles were assessed. The former is widely known and applied but less is known about graphene. The results were compared and assessed using various microscopic techniques (atomic force microscopy), X-ray techniques, and dynamic light scattering. When tested, it was observed that using graphene gave significantly better results than nZVIs in various tests with heavy metals in samples such as copper, iron, magnesium, arsenic, and others. This has many implications, starting from opening the gateways to testing out graphene nanoparticles for other pollutants. It also reinforces the paradigm that this is a diverse avenue where so far, only hit and trial can tell us what pollutant can be handled best by what nanotechnology.

Photoinduced Precipitation

The adsorption on nanoparticles is a widely used technology for removal of hydrophobic contaminants from water and soil. The amphiphilic deblock copolymers are used to form photosensitive core-shell nanoparticles, and the irradiation with the UV light removes the protective layer which is responsible for colloidal stability which rapidly gets converted into aggregates. Decreasing the particle size led to enhanced interactions, which was suggested by the aqueous phase separation measuring the partitioning between the nanoparticles and the aqueous phase. Some preliminary in vivo experiments suggested that the treatment with photocleavable nanoparticles reduces teratogenicity significantly of triclosan, bisphenol A, and 17α-ethinyl oestradiol without producing toxic by-products.

The polychlorinated biphenyls, pesticides, and exposure to certain other kinds of chemicals associated with increased disposition led to certain endocrine disorders, cancer, infertility, diabetes, etc. The meticulous influence of these chemicals and agents in the ubiquity of these ailments is still unknown, but it is always recommended and tried to reduce the presence of these substances as much as possible. Sustainable practices will only ensure the safety of the environment and health. Therefore, keeping the soil and water contaminant free is extremely integral. The fast and effective methods offered by nanotechnology provide the appropriate solution to this problem of clean-up. The methods like sequestration and reactive remediation present viable alternatives which are lesser energy intensive. The percolation of the colloidal solutions of amphiphilic nanoparticles through the sediment is also the preferred method of soil remediation, although the most advanced remediation technology is the nanoparticle zero-valent iron or magnesium which we have already discussed in the section above. The nZVI injected in the soil remediates it by reducing the water-metal interface. The two concerns that are being worked on regarding nanoparticles are their persistence and prevalence in the soil and the formation of secondary toxic products. The photoinduced precipitation by nanoparticles for extraction of pollutants from the soil is an effective method that has been proposed and proved.

The paramagnetic iron oxide and titanium oxide core-shell nanoparticles have been proposed for separation. The titanium oxide shell acts as a photocatalyst which degrades organic pollutants, while the iron oxide allows magnetic separation from the dispersion. The biodegradable, photo-responsive core-shell nanoparticles are developed with a combination of several design principles to bind and extract the contaminants from the contaminated soil. The hydrophobic core acts as a “trap” for the hydrophobic molecules, while the hydrophilic structures stabilize the system. The nanoparticles shed their stabilizing layer in ultraviolet irradiation which results in the loss of their colloidal stability and leads to the formation of macroscopic aggregates. The aggregates contain pollutants and can easily be separated by methods like decantation, sedimentation, centrifugation, etc. The use of ultraviolet light helps in disrupting the colloidal stability, that is, it helps in exploiting its stability and large surface area for handling the bulkier material (Brandl et al. 2015).

9 Future Prospects

The applications mentioned above for environmental biotechnology, specifically soil, are some of the best methods for remediation. In addition to these applications, innovations have emerged for other fields involving nanotechnology, like clinical nanotechnology, agricultural nanotechnology, biomaterial energy production, etc. The incorporation of nanobioremediation has provided a new edge for better agriculture as well as improving the health of the soil to uphold more minerals for better flourishment. The distinct nano-based products such as nano-insecticides, nano-pesticides and nano-herbicides can jointly help in management of insects, pests and weeds which are of paramount concern to farmers (Rajput et al. 2021a). A balanced environment makes it feasible for the microorganism and the plants to dwell. These nanoparticles introduced must be biodegradable in nature or must have least to zero participation in producing toxic by-products. The biosystem is enhanced by classic and next-generation biotechnological modifications such as gene editing, protein engineering, or mutagenesis which makes the synthesis of cellulose-based nanomaterials more comprehensible.

The latest research in the field of RNA-based fungicides showcase their feasibility over traditional biochemical fungicides. The RNA-based fertilizers are foliar sprayed on plant parts or fruits which silences the fungal pathogen. The use of nanomaterials such as graphene, gold particles, photonic crystals, etc. as biosensors has now become a major aspect in the field of diagnostics. The biological component in biosensors responsible for recognition incudes enzymes, nanoparticles, microorganism, receptors, antibodies, etc. These biosensors exhibit enhanced selectivity and sensitivity when modified with biorecognition layers using nanomaterials, providing appropriately accurate diagnostics results. The concept of biosensors in healthcare and clinical monitoring has been incorporated with various substances like temporary tattoos, patches, and many more, among others (Kim et al. 2019). However, the workers employed in treacherous environments performing tasks in potentially toxic, radioactive, or enclosed areas can be protected with the advancements in real-time surveillant bio-nano technologies. These innovations can somewhat change the outlook of the healthcare sector starting right the step of timely diagnosis. Nanotechnology is mostly a cost-effective and environmentally friendly alternative, exhibiting efficient results and promising a sustainable future.

10 Conclusion

Nanotechnology is a massive and upcoming field. The advantages listed by the methodologies are alone sufficient to tell their success. The nanoparticles utilized in the remediation of soil have opened new doors to combat soil pollution. Intertwined with soil pollution is water pollution which also is being worked on at a great speed. Natural nanoparticles contribute a lot towards keeping equilibrium in the environment as a whole. But the advancements in the technologies have increased the level of toxicity which cannot be combatted by natural nanoparticles alone. Iron based, titanium based, iron and palladium based nanoparticles, etc. are the advancements required for an efficient remediation. This chapter thus involves the various prospects of such integration and combination of processes along with bioremediation. The nZVI and graphene oxides are some of the most commonly used effective and efficient methods that fulfil the requirement of remediation sustainably. These advances are one of the many successful methods for creating a sustainable environment without hindering the health of the entire ecosystem as whole.

References

B. An, D. Zhao, Immobilization of As (III) in soil and groundwater using a new class of polysaccharide stabilized Fe–Mn oxide nanoparticles. J. Hazard. Mater. **211**, 332–341 (2012)

Y. Arai, D.L. Sparks, J.A. Davis, Arsenate adsorption mechanisms at the allophane− water interface. Environ. Sci. Technol. **39**(8), 2537–2544 (2005)

S. Bae, S. Gim, H. Kim, K. Hanna, Effect of NaBH4 on properties of nanoscale zero-valent iron and its catalytic activity for reduction of p-nitrophenol. Appl. Catal. B Environ. **182**, 541–549 (2016)

D. Baragaño, J. Alonso, J.R. Gallego, M.C. Lobo, M. Gil-Díaz, Zero valent iron and goethite nanoparticles as new promising remediation techniques for As-polluted soils. Chemosphere **238**, 124624 (2020a)

D. Baragaño, R. Forján, L. Welte, J.L.R. Gallego, Nanoremediation of As and metals polluted soils by means of graphene oxide nanoparticles. Sci. Rep. **10**(1), 1–10 (2020b)

J.R. Bargar, R. Bernier-Latmani, D.E. Giammar, B.M. Tebo, Biogenic uraninite nanoparticles and their importance for uranium remediation. Elements **4**(6), 407–412 (2008)

H. Bargel, K. Koch, Z. Cerman, C. Neinhuis, Evans review no. 3: Structure–function relationships of the plant cuticle and cuticular waxes—A smart material? Funct. Plant Biol. **33**(10), 893–910 (2006)

S. Bayen, O. Wurl, S. Karuppiah, N. Sivasothi, H.K. Lee, J.P. Obbard, Persistent organic pollutants in mangrove food webs in Singapore. Chemosphere **61**(3), 303–313 (2005)

S.K. Bhunia, N.R. Jana, Reduced graphene oxide-silver nanoparticle composite as visible light photocatalyst for degradation of colorless endocrine disruptors. ACS Appl. Mater. Interfaces **6**(22), 20085–20092 (2014)

C. Boente, C. Sierra, D. Martínez-Blanco, J.M. Menéndez-Aguado, J.R. Gallego, Nanoscale zero-valent iron-assisted soil washing for the removal of potentially toxic elements. J. Hazard. Mater. **350**, 55–65 (2018)

V. Bokare, K. Murugesan, Y.M. Kim, J.R. Jeon, E.J. Kim, Y.S. Chang, Degradation of triclosan by an integrated nano-bio redox process. Bioresour. Technol. **101**(16), 6354–6360 (2010)

V. Bokare, K. Murugesan, J.H. Kim, E.J. Kim, Y.S. Chang, Integrated hybrid treatment for the remediation of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin. Sci. Total Environ. **435**, 563–566 (2012)

F. Brandl, N. Bertrand, E.M. Lima, R. Langer, Nanoparticles with photoinduced precipitation for the extraction of pollutants from water and soil. Nat. Commun. **6**(1), 1–10 (2015)

S.S. Cameotra, S. Dhanjal, Environmental nanotechnology: Nanoparticles for bioremediation of toxic pollutants, in *Bioremediation Technology*, (Springer, Dordrecht, 2010), pp. 348–374

V.A. Chaplygin, T.M. Minkina, S.S. Mandzhieva, O.G. Nazarenko, I.V. Zimulina, T.V. Bauer, Y.A. Litvinov, V. Rajput, Heavy metals in agricultural crops of Rostov region through the example of soft wheat (Triticum aestivum), in *IOP Conference Series: Earth and Environmental Science*, vol. 624, (2021), p. 012204. https://doi.org/10.1088/1755-1315/624/1/012204

S.S. Chen, H.D. Hsu, C.W. Li, A new method to produce nanoscale iron for nitrate removal. J. Nanopart. Res. **6**(6), 639–647 (2004)

J. Chorover, R. Kretzschmar, F. Garcia-Pichel, D.L. Sparks, Soil biogeochemical processes within the critical zone. Elements **3**(5), 321–326 (2007)

R.A. Dahlgren, M. Saigusa, F.C. Ugolini, The nature, properties and management of volcanic soils. Adv. Agron. **82**(3), 113–182 (2004)

H. Dong, Z. Jiang, J. Deng, C. Zhang, Y. Cheng, K. Hou, L. Zhang, L. Tang, G. Zeng, Physicochemical transformation of Fe/Ni bimetallic nanoparticles during aging in simulated groundwater and the consequent effect on contaminant removal. Water Res. **129**, 51–57 (2018)

G. Fan, L. Cang, W. Qin, C. Zhou, H.I. Gomes, D. Zhou, Surfactants-enhanced electrokinetic transport of xanthan gum stabilized nanoPd/Fe for the remediation of PCBs contaminated soils. Sep. Purif. Technol. **114**, 64–72 (2013)

Z. Fang, X. Qiu, J. Chen, X. Qiu, Debromination of polybrominated diphenyl ethers by Ni/Fe bimetallic nanoparticles: Influencing factors, kinetics, and mechanism. J. Hazard. Mater. **185**(2–3), 958–969 (2011a)

Z. Fang, X. Qiu, J. Chen, X. Qiu, Degradation of the polybrominated diphenyl ethers by nanoscale zero-valent metallic particles prepared from steel pickling waste liquor. Desalination **267**(1), 34–41 (2011b)

C.L. Freeman, J.H. Harding, D. Quigley, P.M. Rodger, Structural control of crystal nuclei by an eggshell protein. Angew. Chem. Int. Edit. **49**(30), 5135–5137 (2010)

M.H. Fulekar, B. Pathak, *Environmental Nanotechnology* (CRC Press, 2017), eBook ISBN: 9781315157214

A. Gopalakrishnan, R. Krishnan, S. Thangavel, G. Venugopal, S.J. Kim, Removal of heavy metal ions from pharma-effluents using graphene-oxide nanosorbents and study of their adsorption kinetics. J. Ind. Eng. Chem. **30**, 14–19 (2015)

E. Gorb, K. Haas, A. Henrich, S. Enders, N. Barbakadze, S. Gorb, Composite structure of the crystalline epicuticular wax layer of the slippery zone in the pitchers of the carnivorous plant Nepenthes alata and its effect on insect attachment. J. Exp. Biol. **208**(24), 4651–4662 (2005)

A. Goswami, R.G. Kadam, J. Tuček, Z. Sofer, D. Bouša, R.S. Varma, M.B. Gawande, R. Zbořil, Fe (0)-embedded thermally reduced graphene oxide as efficient nanocatalyst for reduction of nitro compounds to amines. Chem. Eng. J. **382**, 122469 (2020)

S. Griffin, M.I. Masood, M.J. Nasim, M. Sarfraz, A.P. Ebokaiwe, K.H. Schäfer, C.M. Keck, C. Jacob, Natural nanoparticles: A particular matter inspired by nature. Antioxidants **7**(1), 3 (2018)

B. Han, M. Zhang, D. Zhao, In-situ degradation of soil-sorbed 17β-estradiol using carboxymethyl cellulose stabilized manganese oxide nanoparticles: Column studies. Environ. Pollut. **223**, 238–246 (2017)

S.O. Hara, T. Krug, J. Quinn, C. Clausen, C. Geiger, Field and laboratory evaluation of the treatment of DNAPL source zones using emulsified zero-valent iron. Remed. J. J. Environ. Cleanup Costs Technol. Techniq. **16**(2), 35–56 (2006)

F. He, D. Zhao, Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. Environ. Sci. Technol. **39**(9), 3314–3320 (2005)

F. He, D. Zhao, Manipulating the size and dispersibility of zerovalent iron nanoparticles by use of carboxymethyl cellulose stabilizers. Environ. Sci. Technol. **41**(17), 6216–6221 (2007)

M. Houde, D.C. Muir, K.A. Kidd, S. Guildford, K. Drouillard, M.S. Evans, X. Wang, D.M. Whittle, D. Haffner, H. Kling, Influence of lake characteristics on the biomagnification of persistent organic pollutants in lake trout food webs. Environ. Toxicol. Chem. Int. J. **27**(10), 2169–2178 (2008)

N.I. Hulkoti, T.C. Taranath, Biosynthesis of nanoparticles using microbes—A review. Colloids Surf. B: Biointerfaces **121**, 474–483 (2014)

C. Hurtado, Y.N. Montano-Chávez, C. Domínguez, J.M. Bayona, Degradation of emerging organic contaminants in an agricultural soil: Decoupling biotic and abiotic processes. Water Air Soil Pollut. **228**(7), 1–8 (2017)

M.I. Husseiny, M. Abd El-Aziz, Y. Badr, M.A. Mahmoud, Biosynthesis of gold nanoparticles using Pseudomonas aeruginosa. Spectrochim. Acta A Mol. Biomol. Spectrosc. **67**(3–4), 1003–1006 (2007)

J.R. Jeon, K. Murugesan, P. Baldrian, S. Schmidt, Y.S. Chang, Aerobic bacterial catabolism of persistent organic pollutants—Potential impact of biotic and abiotic interaction. Curr. Opin. Biotechnol. **38**, 71–78 (2016)

R. Jing, S. Fusi, B.V. Kjellerup, Remediation of polychlorinated biphenyls (PCBs) in contaminated soils and sediment: State of knowledge and perspectives. Front. Environ. Sci. **6**, 79 (2018)

J.W. Kang, Removing environmental organic pollutants with bioremediation and phytoremediation. Biotechnol. Lett. **36**(6), 1129–1139 (2014)

B.C. Kelly, M.G. Ikonomou, J.D. Blair, A.E. Morin, F.A. Gobas, Food web–specific biomagnification of persistent organic pollutants. Science **317**(5835), 236–239 (2007)

M. Khajeh, S. Laurent, K. Dastafkan, Nanoadsorbents: Classification, preparation, and applications (with emphasis on aqueous media). Chem. Rev. **113**(10), 7728–7768 (2013)

S.A. Kim, S. Kamala-Kannan, K.J. Lee, Y.J. Park, P.J. Shea, W.H. Lee, H.M. Kim, B.T. Oh, Removal of Pb (II) from aqueous solution by a zeolite–nanoscale zero-valent iron composite. Chem. Eng. J. **217**, 54–60 (2013)

J. Kim, A.S. Campbell, B.E.F. de Ávila, J. Wang, Wearable biosensors for healthcare monitoring. Nat. Biotechnol. **37**(4), 389–406 (2019)

N. Kumar, S. Kumbhat, Carbon-based nanomaterials, in *Essentials in Nanoscience and Nanotechnology*, (2016), pp. 189–236, Print ISBN:9781119096115, Online ISBN:9781119096122, DOI:10.1002/9781119096122, John Wiley & Sons, Inc

B. Kumar, D.P. Mukherjee, S. Kumar, M. Mishra, D. Prakash, S.K. Singh, C.S. Sharma, Bioaccumulation of heavy metals in muscle tissue of fishes from selected aquaculture ponds in East Kolkata wetlands. Ann. Biol. Res. **2**(5), 125–134 (2011)

A. Kumari, P. Kumari, V.D. Rajput, S.N. Sushkova, and T. Minkina, Metal (loid) nanosorbents in restoration of polluted soils: Geochemical, ecotoxicological, and remediation perspectives. Environmental Geochemistry and Health, **44**(1), pp.235–246 (2022)

N. Kumar, S. Kumbhat, Carbon-based nanomaterials, in Essentials in Nanoscience and Nanotechnology, (2016), pp. 189–236, Print ISBN:9781119096115, Online ISBN: 9781119096122, DOI:10.1002/9781119096122

J. Kumpiene, A. Lagerkvist, C. Maurice, Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments–a review. Waste Manag. **28**(1), 215–225 (2008)

T.T. Le, K.H. Nguyen, J.R. Jeon, A.J. Francis, Y.S. Chang, Nano/bio treatment of polychlorinated biphenyls with evaluation of comparative toxicity. J. Hazard. Mater. **287**, 335–341 (2015)

Q. Liang, D. Zhao, Immobilization of arsenate in a sandy loam soil using starch-stabilized magnetite nanoparticles. J. Hazard. Mater. **271**, 16–23 (2014)

P. Liu, Y. Hong, Magnetic nanomaterials for water remediation, in *Magnetic Nanomaterials: Fundamentals, Synthesis and Applications*, (2017), pp. 515–546, online ISBN: 978-3-527-80326-2, print ISBN: 978-3-527-34134-4, Wiley

R. Liu, D. Zhao, Synthesis and characterization of a new class of stabilized apatite nanoparticles and applying the particles to in situ Pb immobilization in a fire-range soil. Chemosphere **91**(5), 594–601 (2013)

Y. Liu, S. Li, Z. Chen, M. Megharaj, R. Naidu, Influence of zero-valent iron nanoparticles on nitrate removal by Paracoccus sp. Chemosphere **108**, 426–432 (2014)

Q.Y. Ma, S.J. Traina, T.J. Logan, J.A. Ryan, In situ lead immobilization by apatite. Environ. Sci. Technol. **27**(9), 1803–1810 (1993)

S. Machado, J.G. Pacheco, Nanoremediation with zero-valent iron nanoparticles, in *From Soil Remediation*, ed. by J. T. Albergaria, H. P. A. Nouws, 1st edn., (2016), pp. 108–120, ISBN: 9781498743624, CRC Press

M.B. McBride, *Environmental Chemistry of Soils* (Oxford Press, New York, 1994)

A. Medvedeva, O. Buryukova, A. Kucherenko, Y. Ilchenko, V. Chaplygin, V.D. Rajput, R. Kizilkaya, Content of heavy metals in Haplic Chernozem under conditions of agrogenesis. E3S Web Conf., 169, pp. 01024. Available at: https://doi.org/10.1051/e3sconf/202016901024 (2020)

R. Milo, R. Phillips, *Cell Biology by the Numbers* (Garland Science, 2015)

R. Moret, *Nanomonde: des nanosciences aux nanotechnologies* (CNRS Éditions, 2006), ISBN: 13 978-2-271-06468-4

J.D. Neufeld, W.W. Mohn, V. De Lorenzo, Composition of microbial communities in hexachlorocyclohexane (HCH) contaminated soils from Spain revealed with a habitat-specific microarray. Environ. Microbiol. **8**(1), 126–140 (2006)

E.S. Papazoglou, A. Parthasarathy, Bionanotechnology. Synth. Lect. Biomed. Eng. **2**(1), 1–139 (2007)

L. Parimala, J. Santhanalakshmi, Studies on the iron nanoparticles catalyzed reduction of substituted aromatic ketones to alcohols. J. Nanopart. **2014** (2014), pp 1–10

J.H. Park, N. Bolan, M. Megharaj, R. Naidu, Comparative value of phosphate sources on the immobilization of lead, and leaching of lead and phosphorus in lead contaminated soils. Sci. Total Environ. **409**(4), 853–860 (2011)

E.E. Pfündel, G. Agati, Z.G. Cerovic, Optical properties of plant surfaces, in *Biology of the Plant Cuticle*, vol. 3, (2008), pp. 216–239, ISBN: 9781405171571, John Wiley & Sons

T. Phenrat, G.V. Lowry, Nanoscale zerovalent iron particles for environmental restoration, in *From Fundamental Science to Field Scale Engineering Applications*, (2019), ISBN print: 978-3-319-95338-0, ISBN: 978-3-319-95340-3 (eBook), Springer International Publishing AG, part of Springer Nature

J. Quinn, C. Geiger, C. Clausen, K. Brooks, C. Coon, S. O'Hara, T. Krug, D. Major, W.S. Yoon, A. Gavaskar, T. Holdsworth, Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron. Environ. Sci. Technol. **39**(5), 1309–1318 (2005)

V. Rajput, T. Minkina, A. Kumari, S. Shende, A. Ranjan, M. Faizan, A. Barakvov, A. Gromovik, N. Gorbunova, P. Rajput, A. Singh, I. Khabirov, O. Nazarenko, S. Sushkova, R. Kizilkaya, A review on nanobioremediation approaches for restoration of contaminated soil. Eurasian J. Soil Sci. (EJSS), xx–xx (2021a). https://doi.org/10.18393/ejss.990605

V.D. Rajput, A. Singh, T.M. Minkina, S.S. Shende, P. Kumar, K.K. Verma, T. Bauer, O. Gorobtsova, S. Deneva, A. Sindireva, Potential applications of nanobiotechnology in plant nutrition and protection for sustainable agriculture, in *Nanotechnology in Plant Growth Promotion and Protection: Recent Advances and Impacts*, (2021b), pp. 79–92, print ISBN:9781119745853, online ISBN:9781119745884, DOI:10.1002/9781119745884, John Wiley & Sons Ltd.

A. Ranjan, V.D. Rajput, T. Minkina, *Nanotechnology in Sustainable Agriculture, Soil Chemistry and Remediation of Polluted Soil* (2021), pp. 173–196. https://doi.org/10.18485/green_economy_4ir.2021.ch7

K.V.G. Ravikumar, D. Kumar, G. Kumar, P. Mrudula, C. Natarajan, A. Mukherjee, Enhanced Cr (VI) removal by nanozerovalent iron-immobilized alginate beads in the presence of a biofilm in a continuous-flow reactor. Ind. Eng. Chem. Res. **55**(20), 5973–5982 (2016)

A. Reyhanitabar, L. Alidokht, A.R. Khataee, S. Oustan, Application of stabilized Fe^0 nanoparticles for remediation of Cr (VI)-spiked soil. Eur. J. Soil Sci. **63**(5), 724–732 (2012)

B.H. Robinson, G. Bañuelos, H.M. Conesa, M.W. Evangelou, R. Schulin, The phytomanagement of trace elements in soil. Crit. Rev. Plant Sci. **28**(4), 240–266 (2009)

U. Schwertmann, Iron oxides, in *Encyclopedia of Soil Science*, ed. by W. Chesworth, (Springer, Dordrecht, 2008), pp. 363–369

G. Shan, J. Xing, H. Zhang, H. Liu, Biodesulfurization of dibenzothiophene by microbial cells coated with magnetite nanoparticles. Appl. Environ. Microbiol. **71**(8), 4497–4502 (2005)

S.P. Singh, L.Q. Ma, W.G. Harris, Heavy metal interactions with phosphatic clay: Sorption and desorption behavior. J. Environ. Qual. **30**(6), 1961–1968 (2001)

R.K. Singhal, B. Gangadhar, H. Basu, V. Manisha, G.R.K. Naidu, A.V.R. Reddy, Remediation of malathion contaminated soil using zero valent iron nano-particles. Am. J. Anal. Chem. **2012** (2012), pp 76–82

A.I. Smical, V. Hotea, V. Oros, J. Juhasz, E. Pop, Studies on transfer and bioaccumulation of heavy metals from soil into lettuce. Environ. Eng. Manag. J. **7**(5), 609–615 (2008)

D.L. Sparks, Kinetics and mechanisms of chemical reactions at the soil mineral/water interface, in *Soil Physical Chemistry*, (CRC Press, 2018), pp. 135–192, ISBN:9781351415781

R. Sutton, G. Sposito, Molecular structure in soil humic substances: The new view. Environ. Sci. Technol. **39**(23), 9009–9015 (2005)

W. Tan, J.R. Peralta-Videa, J.L. Gardea-Torresdey, Interaction of titanium dioxide nanoparticles with soil components and plants: Current knowledge and future research needs–a critical review. Environ. Sci. Nano **5**(2), 257–278 (2018)

H. Tang, X. Chen, Y. Niu, X. Luo, Z. Wang, M. Chen, G. Shi, Thermal stability characteristics of in situ nano-particles formed in metal melt. Mater. Lett. **162**, 261–264 (2016)

A. Timoshenko, S. Kolesnikov, V.D. Rajput, T. Minkina, Chapter 14 – Effects of zinc-oxide nanoparticles on soil microbial community and their functionality, in *Zinc-Based Nanostructures for Environmental and Agricultural Applications*, ed. by K. A. Abd-Elsalam, (Elsevier, 2021), pp. 267–284,Paperback ISBN: 9780128228364,eBook ISBN: 9780128236567, Elsevier

A. Violante, M. Pigna, Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil Sci. Soc. Am. J. **66**(6), 1788–1796 (2002)

J.S. Wang, K. Chiu, Destruction of pentachlorobiphenyl in soil by supercritical CO2 extraction coupled with polymer-stabilized palladium nanoparticles. Chemosphere **75**(5), 629–633 (2009)

A. Wang, H.P. Ng, Y. Xu, Y. Li, Y. Zheng, J. Yu, F. Han, F. Peng, L. Fu, Gold nanoparticles: Synthesis, stability test, and application for the rice growth. J. Nanomater. **2014** (2014), pp 1-6

Y. Wang, Z. Fang, B. Liang, E.P. Tsang, Remediation of hexavalent chromium contaminated soil by stabilized nanoscale zero-valent iron prepared from steel pickling waste liquor. Chem. Eng. J. **247**, 283–290 (2014c)

M.J. Wilson, The origin and formation of clay minerals in soils: Past, present and future perspectives. Clay Miner. **34**(1), 7–25 (1999)

Y. Wu, X. Ma, M. Feng, M. Liu, Behavior of chromium and arsenic on activated carbon. J. Hazard. Mater. **159**(2–3), 380–384 (2008)

Z.M. Xiu, Z.H. Jin, T.L. Li, S. Mahendra, G.V. Lowry, P.J. Alvarez, Effects of nano-scale zero-valent iron particles on a mixed culture dechlorinating trichloroethylene. Bioresour. Technol. **101**(4), 1141–1146 (2010)

W. Yan, H.L. Lien, B.E. Koel, W.X. Zhang, Iron nanoparticles for environmental clean-up: Recent developments and future outlook. Environ. Sci.: Processes Impacts **15**(1), 63–77 (2013)

J. Yang, D.E. Mosby, S.W. Casteel, R.W. Blanchar, Lead immobilization using phosphoric acid in a smelter-contaminated urban soil. Environ. Sci. Technol. **35**(17), 3553–3559 (2001)

C.K. Yap, A.R. Azmizan, M.S. Hanif, Biomonitoring of trace metals (Fe, Cu, and Ni) in the mangrove area of peninsular Malaysia using different soft tissues of flat tree oyster Isognomonalatus. Water Air Soil Pollut. **218**(1), 19–36 (2011)

G. Yuan, L. Wu, Allophane nanoclay for the removal of phosphorus in water and wastewater. Sci. Technol. Adv. Mater. **8**(1–2), 60 (2007)

G. Yuan, H.J. Percival, B.K.G. Theng, R.L. Parfitt, Sorption of copper and cadmium by allophane-humic complexes, in *Developments in Soil Science*, vol. 28, (Elsevier, 2002), pp. 37–47, ISBN: 444-51038-9

Y.X. Zhang, J. Zheng, G. Gao, Y.F. Kong, X. Zhi, K. Wang, X.Q. Zhang, D.X. Cui, Biosynthesis of gold nanoparticles using chloroplasts. Int. J. Nanomedicine **6**, 2899 (2011)

X. Zhu, B. Chen, L. Zhu, B. Xing, Effects and mechanisms of biochar-microbe interactions in soil improvement and pollution remediation: A review. Environ. Pollut. **227**, 98–115 (2017)

Vishnu D., Rajput Abhishek, Singh Tatiana, Minkina Sapna, Rawat Saglara, Mandzhieva Svetlana, Sushkova Victoria, Shuvaeva Olga, Nazarenko Priyadarshani, Rajput Komariah Krishan K., Verma Awani Kumar, Singh Mahesh, Rao Sudhir K., Upadhyay (2021) Nano-Enabled Products: Challenges and Opportunities for Sustainable Agriculture. Plants 10(12) 2727-10.3390/plants10122727