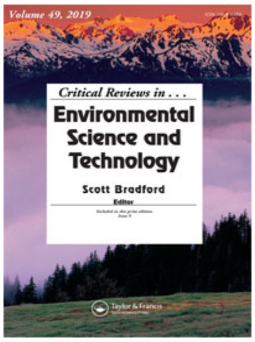

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Using nanomaterials to facilitate the phytoremediation of contaminated soil

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ABSTRACT

Soil pollution has been an environmental problem drawing worldwide attention. Phytoremediation is a good and highly accepted method for treating contaminated soil. Numerous studies have been performed to enhance the phytoremediation efficiency by various approaches. The development of nanotechnology provides an effective alternative method. This article reviews recent advances in using nanomaterials to facilitate the phytoremediation of contaminated soil. Nanomaterials can function in the phytoremediation system through directly removing pollutants, promoting plant growth, and increasing pollutant phytoavailability. Phytoextraction is the most effective and recognized phytoremediation strategy for remedying contaminated soil. Nanoscale zero-valent iron is the most studied nanomaterials for facilitating the phytoremediation due to its successful engineering applications in treating contaminated soil and groundwater. Fullerene nanoparticles can increase the phytoavailability of pollutant. In general, using nanomaterials to facilitate the phytoremediation of contaminated soil can be an effective strategy, but it is still in the phase of exploration and attempt. The experience from more application cases is required and the long-term performance of nanomaterials in phytoremediation systems needs further research.

KEYWORDS

Nanomaterial; phytoavailability; phytoremediation; phytotoxicity; plant growth; soil contamination

1. Introduction

Soil is very precious to humans. It performs many important functions including life support, food production, carbon storage, water purification, and biodiversity conservation (Blum, 2005; Amundson et al., 2015). Sustainable development of human society requires safe and healthy soil. However, our soil is under serious threat. Over the past decades, increasing accumulation of toxic metals/metalloids and persistent organic pollutants in

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soil has been found due to rapid industrialization and various human activities (e.g., industrial waste discharge, sewage irrigation, and improper use of chemical pesticides and fertilizers). These substances are harmful to human health and ecological safety (Cachada, Pato, Rocha-Santos, Ferreira da Silva, & Duarte, 2012; Li, Ma, van der Kuijp, Yuan, & Huang, 2014). Therefore, the remediation of contaminated soil is necessary.

Many technologies have been developed to abate soil pollution (Chen et al., 2015; Song, Zeng, Gong, Liang, et al., 2017). Phytoremediation is a popular bioremediation method. Compared with some other methods, phytoremediation is of low cost, simple operation, esthetic appearance, wide adaptability, little destruction to the soil structure, and high public acceptance (Macek, Macková, & Káš, 2000; Glick, 2003; Gong, Huang, Liu, Zeng, et al., 2018). Since 1980s, phytoremediation has been greatly developed and widely used in field studies at sites contaminated with heavy metals, radionuclides, crude oil, pesticides, explosives, and chlorinated solvents (Sharma & Pandey, 2014; Dubchak & Bondar, 2019). Successful field cases of phytoremediation have been extensively documented worldwide and the global phytoremediation market is broad (Gerhardt, Gerwing, & Greenberg, 2017; Thijs, Sillen, Weyens, & Vangronsveld, 2017). In China, widespread use of phytoremediation began in 1990s. This green technology has been applied to the remediation of arable land contaminated with heavy metals, metalloids, and pesticides (Tang, 2007; Tang & Mo, 2007). For example, many phytoremediation projects that use *Pteris vittata* for arsenic extraction from contaminated soil have been successfully implemented in Hunan, Yunnan, Henan, Hebei, Guangxi, and Beijing in China (Chen, Lei, Wan, Yang, & Zhou, 2018). However, phytoremediation usually needs long time (several years), and its application is limited by weather conditions, soil quality, and pollutant phytotoxicity. In order to improve the phytoremediation efficiency, many strategies are employed, such as agronomic management, treatment with chemical additives, inoculation of rhizospheric microorganisms, and use of genetic engineering (Gerhardt et al., 2017). Development of nanotechnology brings new inspiration and ideas to the phytoremediation of contaminated soil. (Gong, Huang, Liu, Peng, et al., 2018). Many studies have reported the benefits of using nanomaterials in plant systems. Ghormade, Deshpande, and Paknikar (2011) studied the applications of nanomaterials in plant protection and nutrition, and reported that nanomaterials could help with the delivery of pesticides and fertilizers, the detection of plant disease and pollutants, and the protection of soil structure. In a review of nanomaterials in plant protection and fertilization, it was introduced that 40% of all contributions deal with carbon-based nanomaterials including carbon nanotubes, liposomes, and organic polymers, followed by titanium dioxide, silver, silica, and alumina nanomaterials (Gogos, Knauer,

& Bucheli, 2012). Over the past decade, many nano-enabled patents and products have been developed to control plant disease and increase crop yield, such as nanopesticides, nanofertilizers, and nanosensors (Servin et al., 2015). Recently, some studies that aim at using nanomaterials to improve the phytoremediation efficiency have been conducted. This article reviews recent advances in using nanomaterials to facilitate the phytoremediation of contaminated soil. The review mainly focuses on how the applied nanomaterials function in the phytoremediation. Interactions between pollutants and plants in the presence of nanomaterials are analyzed. Additionally, the challenges of using nanomaterials in phytoremediation are discussed for identifying future research needs.

2. Phytoremediation of contaminated soil

Phytoremediation uses plants to remove, degrade, or contain pollutants in environmental media (water, air, sediment, and soil). Phytoremediation technologies used for soil pollution include phytovolatilization, phytoextraction, phytodegradation, phytostabilization, and rhizodegradation (Figure 1).

Phytovolatilization (Figure 1A) is the absorption and transpiration of pollutants by plants. After being absorbed by plants, some pollutants can be transformed into volatile forms or degraded into volatile products. These volatile substances are then transported to leaves and transpired. Arsenic and mercury are commonly studied in phytovolatilization because these inorganic pollutants have volatile forms and can be biologically transformed into gaseous species by plants (Sakakibara, Watanabe, Inoue, Sano, & Kaise, 2010). Some volatile organic compounds (e.g., trichloroethylene)

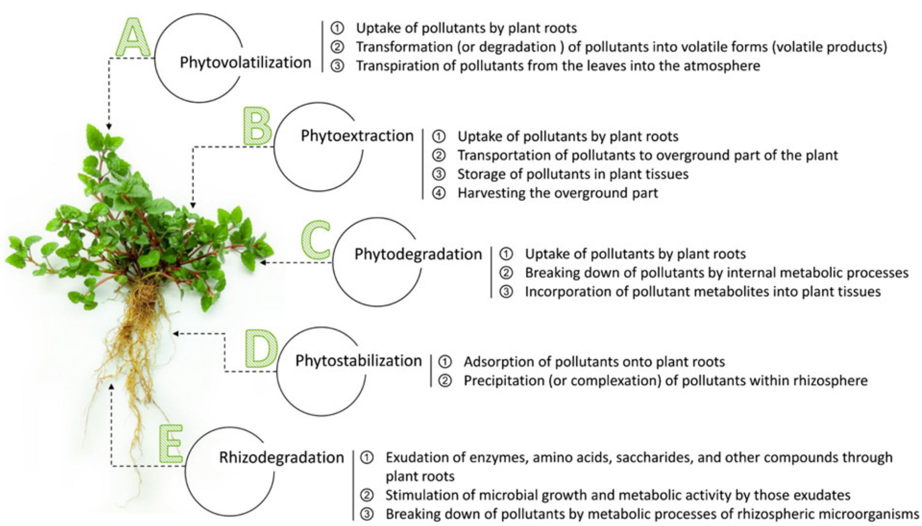

Figure 1. Phytoremediation technologies for abating soil pollution.

can be removed through volatilizing from leaves and stems or from soil induced by plant root activities (Doucette et al., 2013; Limmer & Burken, 2016). Phytoextraction (Figure 1B) is the accumulation of pollutants in the overground part of plant. It is a translocation process of pollutants, and the pollutants do not undergo transformation but are stored in plant shoots after being taken in by the roots. Through harvesting the overground part, these accumulated pollutants are removed from the site and can be further treated or recycled. Phytoextraction is the most effective and recognized phytoremediation strategy for abating soil pollution (Figure 2). This strategy is usually conducted with hyperaccumulators that can accumulate specific pollutant to a level that is 100 times greater than that for most plants (Reeves et al., 2018). Indian mustard and sunflower are widely used plant species for phytoextraction. They attract researchers because of large biomass, rapid growth, and excellent accumulation capacity for various pollutants (Shaheen & Rinklebe, 2015). Phytodegradation (Figure 1C) is the breakdown of organic pollutants by metabolic processes in plant tissues. Organic pollutants can be taken in by the plant roots. Through the internal metabolic processes, the pollutants are broken down into simple molecules that can be incorporated into the plant tissues. Plants can catalyze the degradation of organic pollutants by generating various enzymes with specific functions, such as nitroreductase, peroxidases, and dehalogenase (Lee, 2013). Specific degradation pathways in various plant species are different and have not been fully understood. Phytostabilization (Figure 1D) is the in-situ immobilization of pollutants by plant roots. This process takes place in rhizosphere, but not in the plant body. Through adsorption onto plant roots and precipitation (or complexation) within rhizosphere, pollutant

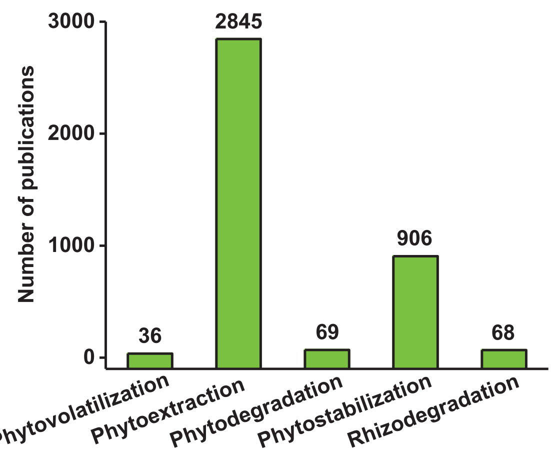

Figure 2. Number of publications on various types of phytoremediation technologies in the last decade. The data were extracted from Web of Science in August 2018 by searching publications containing "phytovolatilization", "phytoextraction", "phytodegradation", "phytostabilization", or "rhizodegradation" in the topic.

mobility can be reduced, thereby decreasing the possibility of entering ground water or food chain. Phytostabilization is effective for treating toxic metals (Jadia & Fulekar, 2009). However, pollutants are not actually removed from the soil by phytostabilization, which is the major disadvantage of this technique. Rhizodegradation (Figure 1E) is the breakdown of organic pollutants within rhizosphere by rhizospheric microorganisms. It is a plant-assisted process. The microorganisms play a dominant role in degrading the pollutants by their metabolic processes. The plant roots loosen the soil, provide attachment surface for microbial growth, and exude enzymes, amino acids, saccharides, and other compounds that can stimulate the microbial metabolic activity. Since the interaction of roots and rhizospheric microorganisms is vital to the success of rhizodegradation, some grasses that have extensive root systems are usually used, such as ryegrass and tall fescue (Lin, Lerch, Kremer, & Garrett, 2011).

Although phytoremediation has many advantages in treating contaminated soil, the final remediation efficiency is usually limited by plant species, pollutant bioavailability, soil characteristics, and weather. The primary disadvantage of phytoremediation is the long remediation time and it is only effective seasonally. Considering the limiting factors and disadvantages of phytoremediation, strategies are needed to facilitate it for practical applications.

3. Applications of nanomaterials in the phytoremediation of contaminated soil

With the development of nanotechnology, nanomaterials for environmental remediation and pollution abatement are drawing increasing attention of environmental researchers. Nanomaterials are a kind of material with nanoscale size (1–100 nm) in at least one dimension (Tang et al., 2014). Among the nanomaterials, carbon-based nanomaterials and metal-based nanomaterials are widely studied (Gong et al., 2009; Chen et al., 2017). Many field applications of engineered nanomaterials for the remediation of soil and groundwater have been successfully carried out in Europe and USA (Mueller & Nowack, 2010). Recently, some studies reported the applications of nanomaterials in the phytoremediation of contaminated soil. It is promising to incorporating nanomaterials into conventional phytoremediation systems.

3.1. Removing pollutants by phytoremediation assisted with nanomaterials

Some examples of phytoremediation assisted with nanomaterials are displayed in Table 1. Most of these studies were conducted for the removal of

Table 1. Some recent examples of phytoremediation assisted with nanomaterials.

Pollutants	Plant species	Nanomaterials	Roles of nanomaterials	Main results	Reference
Trinitrotoluene	Panicum (*Panicum maximum* Jacq.)	nZVI	Direct trinitrotoluene removal by nZVI particles	Zero-valent iron nanoparticles enhanced the removal efficiency of trinitrotoluene from 85.7%#[a] to 100%# after 120 days.	Jiamjitrpanich et al. (2012)
Endosulfan	Chittaratha (*Alpinia calcarata* Roscoe), Tulsi (*Ocimum sanctum* L.), and lemongrass [*Cymbopogon citratus* (DC.) Stapf.]	nZVI	Direct endosulfan removal by nZVI particles	With nZVI, removal rates of endosulfan from the soil were increased from 81.2% to 100%, from 20.76% to 76.28%, and from 65.08% to 86.16% for *A. calcarata*, *O. sanctum*, and *C. citratus*, respectively.	Pillai and Kottekottil (2016)
Trichloroethylene	Eastern cottonwood (*Populus deltoides* Bartr.)	Fullerene nanoparticles	Increasing phytoavailability of trichloroethylene as carriers	The trichloroethylene uptake increased by 26% and 82% with 2 and 15 mg/L of fullerene nanoparticles, respectively.	Ma and Wang (2010)
Pb	Ryegrass (*Lolium perenne* L.)	Nano-hydroxyapatite and nano-carbon black	Direct Pb stabilization by the nanomaterials, thus alleviating phytotoxicity and promoting plant growth	After 12 month, removal rates of Pb from the soil were increased from 31.76% to 46.55% and 45.53%# with nano-hydroxyapatite and nano-carbon black, respectively.	Liang et al. (2017)
Cr	Pea (*Pisum sativum* L.)	Silicon nanoparticles	Promoting plant growth in the tolerance to Cr(VI) stress through alleviating phytotoxicity	With silicon nanoparticles, accumulation concentrations of Cr in the root and shoot decreased from 1472.6 to 516.6 mg/kg DW[b], and from 62.5 to 35.2 mg/kg DW, respectively.	Tripathi et al. (2015)
Pb	Ryegrass (*Lolium perenne* L.)	Nano-hydroxyapatite	Direct Pb stabilization by nano-hydroxyapatite, and promoting plant growth through increasing phosphorus concentration in soil	With nano-hydroxyapatite, content of Pb in the root and shoot decreased by 2.86-21.1% and 13.19-20.3%, respectively.	Ding et al. (2017)
As	(*Isatis cappadocica* Desv.)	Salicylic acid nanoparticles	Increasing the absorption and utilization rate of nutrients for plant growth	With salicylic acid nanoparticles, maximum accumulation concentrations of As in the shoot and root reached 705 and 1188 mg/kg DW, respectively.	Souri et al. (2017)
Cd		TiO_2 nanoparticles			

	Soybean [*Glycine max* (L.) Merr.]		Enhancing the sprouting, development and photosynthetic rates of plants	The Cd uptake increased from 128.5 to 507.6 μg per plant with increasing concentration of TiO_2 nanoparticles from 100 to 300 mg/kg.	Singh and Lee (2016)
Pb	Ryegrass (*Lolium perenne* L.)	nZVI	Promoting plant growth at low nZVI concentration	Maximum accumulation concentrations of Pb in the root and shoot reached 1175.4 μg per pot with 100 mg/kg nZVI.	Huang et al. (2018)
As, Cd, Pb, and Zn	Sunflower (*Helianthus annuus* L.) and ryegrass (*Lolium perenne* L.)	nZVI	Direct pollutant stabilization by nZVI particles	After using nZVI for phytostabilization, the concentrations of As, Cd, Pb and Zn in roots and shoots decreased by 50–60% compared to the control sample.	Vítková et al. (2018)
Cd	Ramie [*Boehmeria nivea* (L.) Gaudich]	nZVI	Promoting plant growth at low nZVI concentration	With nZVI, concentrations of Cd in the leaves, stems, and roots increased by 31-73%, 29-52%, and 16-50%, respectively.	Gong et al. (2017)
Cd and Pb	Rye (*Secale montanum* Guss.)	Nano-silica	Increasing phytoavailability of Pb, and promoting plant growth	Maximum accumulation concentrations of Pb (533.6 mg/kg DW) and Cd (208.6 mg/kg DW) in the roots were achieved with nano-silica.	Moameri and Abbasi Khalaki (2017)
Cd and Pb	White popinac [*Leucaena leucocephala* (Lam.) de Wit]	ZnO nanoparticles	Promoting plant growth via alleviating phytotoxicity	With ZnO nanoparticles, accumulation of Cd and Pb in the plant increased from 1253.1 to 1863.5 mg/kg DW and 1026.8 to 1343.4 mg/kg DW, respectively.	Venkatachalam, Jayaraj, et al. (2017)
Pb	Ryegrass (*Lolium perenne* L.)	Nano-hydroxyapatite	Direct Pb stabilization by nano-hydroxyapatite, and enhancing plant growth	After 6 weeks, removal efficiency of Pb by the plant was increased from 11.67%# to 21.97%# with nano-hydroxyapatite under a Pb stress of 800 mg/kg.	Jin et al. (2016)
Cd, Pb and Ni	Maize (*Zea mays* L.)	Silver nanoparticles	Enhancing root area and root length	With silver nanoparticles, accumulation concentrations of Cd, Pb, and Ni in the shoot increased from 0.65# to 0.73# mg/kg DW, from 129.1# to 232.7# mg/kg DW, and from 0# to 12.4# mg/kg DW, respectively.	Khan and Bano (2016)

[a]The datum with # was read from the figure of the reference.
[b]mg/kg DW: milligram for per kilogram of the plant in dry weight.

heavy metals. Nanoscale zero-valent iron (nZVI) is most used for facilitating phytoremediation. More details are introduced as follows.

3.1.1. Nanomaterial-facilitated phytoremediation for removal of heavy metals

Heavy metal pollution in soil is a serious problem worldwide and poses a significant threat to food safety and human health. Phytoremediation is widely used for in-situ remediation of soil contaminated with heavy metals (Liang et al., 2017). It has been reported that the phytoremediation of soil contaminated with cadmium, chromium, lead, nickel, and zinc could be enhanced by applying nanomaterials (Tripathi, Singh, Prasad, Chauhan, & Dubey, 2015; Khan & Bano, 2016; Singh & Lee, 2016; Liang, Jin, et al., 2017; Vítková, Puschenreiter, & Komárek, 2018). Lead and cadmium are the most studied heavy metals since the two metals are the most common in contaminated sites.

Lead is a common industrial metal that is widely used in storage batteries, gasoline additives, ammunition, and solder, but it is also a well-known soil contaminant bringing great health risks (Yu, Zhang, Shukla, Shukla, & Dorris, 2001). Phytoextraction is the most recognized phytoremediation technique used to remove lead from contaminated soil (Ali, Khan, & Sajad, 2013). In experimental research, ryegrass (*Lolium perenne* L.) is typically used for phytoextraction of Pb from contaminated soil due to its relatively rapid growth, high tolerance to Pb, and low cost. Using nanomaterials has been reported effective in promoting Pb phytoextraction efficiency by ryegrass. For example, Liang et al. (2017) studied the effects of applying nano-hydroxyapatite on the Pb phytoextraction by ryegrass, and determined the remediation efficiency after 1, 1.5, 2, 3, and 12 months. The experimental results showed that the addition of 0.2% (w/w) nano-hydroxyapatite significantly increased the accumulation of Pb in the overground part of plant after 1.5 months. In the control group with only ryegrass, the removal rates of Pb in the soil ranged from 16.74% to 31.76%. With the assistance of nano-hydroxyapatite, ryegrass removed over 30% of Pb in the soil after one month. The removal rate reached 44.39% after three months, and such a treatment time was considered most effective compared with a removal rate of 46.55% after 12 months. In a study by Huang et al. (2018), nZVI particles of various concentrations (0, 100, 200, 500, 1000, and 2000 mg/kg) were added to assist Pb phytoextraction by ryegrass. After a treatment of 45 days, the authors observed that low concentrations of nZVI (100, 200, and 500 mg/kg) could enhance the Pb accumulation in ryegrass. The maximum accumulation of Pb was 1175.40 μg per pot and obtained with nZVI particles of 100 mg/kg. However, the nZVI particles of high concentrations (1000 and 2000 mg/kg) caused severe oxidative stress in the plant, thus decreasing the Pb accumulation.

Cadmium is a toxic metal commonly released into the soil from various industrial processes and products such as mining, smelting, electroplating, storage batteries, color pigments, and phosphate fertilizers (Godt et al., 2006; Mahabadi, Hajabbasi, Khademi, & Kazemian, 2007). Using hyperaccumulators to extract Cd from contaminated soil is the main phytoremediation strategy, but available Cd hyperaccumulator species are limited in amount and capacity (Kirkham, 2006). Some nanomaterials have been demonstrated to enhance the phytoextraction of Cd in soil. Singh and Lee (2016) reported the positive effect of TiO_2 nanoparticles on Cd accumulation in soybean plants. The authors added TiO_2 nanoparticles of 100, 200, and 300 mg/kg to the soil, and analyzed the accumulation and distribution of Cd in plants on the 60^{th} day after sowing. With the assistance of TiO_2 nanoparticles, the Cd accumulation in the shoots increased by about 1.9, 2.1, and 2.6 times, while the Cd accumulation in the roots increased by 2.5, 2.6, and 3.3 times, respectively. The maximum accumulation of Cd reached 1534.7 mg/g with TiO_2 nanoparticles of 300 mg/kg. In a study of Cd phytoextraction by ramie, it was reported that applying nZVI particles could improve the phytoremediation efficiency (Gong et al., 2017). In this study, the authors added starch-stabilized nZVI particles of 100, 500, and 1000 mg/kg to the contaminated sediment before planting the ramie seedlings. The experimental results showed that the addition of nZVI particles increased the Cd accumulation in the roots, stems, and leaves by 16–50%, 29–52%, and 31–73%, respectively.

3.1.2. Nanomaterial-facilitated phytoremediation for removal of arsenic

Arsenic is a metalloid widely found in the environment. Due to the high toxicity and carcinogenicity of arsenic, a growing concern has been raised about the soil arsenic contamination resulting from the widespread use of arsenic-containing pesticides, herbicides, phosphate fertilizers, and wood preservatives, as well as related industrial activities (Singh, Singh, Parihar, Singh, & Prasad, 2015). Phytoextraction and phytostabilization are two main phytoremediation strategies used to abate soil arsenic contamination. Plants can absorb arsenic via three separate systems: active uptake by the symplast; passive uptake by the apoplast; and direct transcellular transport from the environment to the plant vascular system (Vithanage, Dabrowska, Mukherjee, Sandhi, & Bhattacharya, 2012). Thus, phytoextraction has been preferentially used as an effective remediation method for soil arsenic contamination (Lei, Wan, Guo, Yang, & Chen, 2018). Souri, Karimi, Sarmadi, and Rostami (2017) reported that using salicylic acid nanoparticles could improve the arsenic phytoextraction by *Isatis cappadocica*. The authors incorporated salicylic acid nanoparticles into the arsenic phytoextraction system based on the consideration that salicylic acid plays important roles in plant growth and arsenic tolerance. In their experiments, the plant seedlings were pretreated with 250 μM of salicylic acid nanoparticles for 10 days before the arsenic phytoextraction. With the assistance of salicylic acid nanoparticles, not only the plant growth but also the phytoremediation efficiency increased markedly. Maximum arsenic accumulation in the shoot and root reached 705 and 1188 mg/kg, respectively. Recent study by Vítková et al. (2018) demonstrated that applying nZVI particles had a positive effect on the arsenic stabilization in sunflower rhizosphere. In this study, nZVI particles of 1% (w/w) were added to the contaminated soil before the sunflowers were planted. After the growth period of five weeks, the arsenic concentrations in soil pore water decreased by over 80% compared to the control (from 5.55 to 0.95 mg/L), and the arsenic accumulation in the plant roots and shoots decreased by 47% and 24%, respectively. These results increased the application potential of using nZVI particles in phytostabilization systems.

3.1.3. Nanomaterial-facilitated phytoremediation for removal of organic pollutants

Organic pollutants are widespread in soil and mainly emitted from anthropogenic sources. Organochlorine pesticides, polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, polychlorinated biphenyls, phenols, and their derivatives are common organic pollutants in soil, and it is crucial to remove these pollutants due to their toxicity, persistence, and bioaccumulation (Jones & de Voogt, 1999). Phytoremediation has been an effective approach for remedying soil contaminated with organic pollutants, especially pesticides, polycyclic aromatic hydrocarbons, petroleum, and explosives (Kang, 2014). It has been observed that applying nanomaterials enhanced the phytoremediation of soil contaminated with trichloroethylene, endosulfan, and trinitrotoluene (Ma & Wang, 2010; Jiamjitrpanich, Parkpian, Polprasert, & Kosanlavit, 2012; Pillai & Kottekottil, 2016). Ma and Wang (2010) reported that fullerene nanoparticles could increase the uptake of trichloroethylene by eastern cottonwood in the phytoremediation system. The uptake of trichloroethylene increased by 26% and 82% after applying fullerene nanoparticles of 2 and 15 mg/L, respectively. Simultaneously, the addition of fullerene nanoparticles did not cause any acute toxicity to the plants. In the study of removing trinitrotoluene from contaminated soil by *Panicum maximum*, Jiamjitrpanich et al. (2012) added nZVI particles of various concentrations (100, 500, and 1000 mg/kg) to the soil and determined the residual trinitrotoluene concentrations in soil during a remediation period of 120 days. The results indicated that applying nZVI particles could effectively improve the phytoremediation efficiency. In their experiments, the best removal performance was observed with a trinitrotoluene-nZVI ratio of 1/10, and the phytoremediation process could be finished within 60 days when the initial trinitrotoluene concentration was 100 mg/kg. Pillai and Kottekottil (2016) used nZVI particles to assist the phytoremediation of soil contaminated with endosulfan. The experiments were conducted with three plant species, *Alpinia calcarata*, *Ocimum sanctum*, and *Cymbopogon citratus*, in the presence or absence of nZVI particles. With the assistance of nZVI particles, the removal rates of endosulfan from soil were increased from 81.2% to 100%, from 20.76% to 76.28%, and from 65.08% to 86.16% for *A. calcarata*, *O. sanctum*, and *C. citratus*, respectively.

3.2. Roles of nanomaterials in phytoremediation

The system of nanomaterial-assisted phytoremediation consists of three primary parts: plants, pollutants, and nanomaterials. On the one hand, nanomaterials can improve phytoremediation by directly acting on the pollutants and plants. On the other hand, the applied nanomaterials may be involved in the interactions between the pollutants and plants, indirectly affecting the final remediation efficiency. Based on this, the following section discusses how the applied nanomaterials function in the phytoremediation from three aspects: direct pollutant removal by nanomaterials, promoting plant growth, and increasing phytoavailability of pollutants. A schematic diagram is presented in Figure 3.

3.2.1. Direct pollutant removal by nanomaterials

Many nanomaterials are able to remove pollutants directly from the soil in phytoremediation system, which reduces the burden of removing pollutants by plants. Nanomaterials can function through adsorption or redox reactions for direct pollutant removal (Mueller & Nowack, 2010). For example, pollutants can be immobilized through adsorption by carbon nanotubes. This is similar to phytostabilization. It has been demonstrated that carbon nanotubes have excellent adsorption capacity towards various pollutants, especially some hydrophobic organic pollutants (Song, Zeng, Gong, Zhang, et al., 2017; Kang et al., 2018). Carbon nanotubes may stabilize organic pollutants through the interactions of electrostatic attraction, hydrophobic interaction, and π-π bonding, while the interactions between carbon nanotubes and heavy metals involve complexation, electrostatic attraction, physical adsorption, and surface precipitation (Song et al., 2018). Multiple interactions may coexist in the adsorption process, which makes the combination of carbon nanotubes and pollutants relatively stable. As for removing pollutants through redox reactions, nZVI is the most studied. Generally, nZVI can be used as an electron donor for reductive degradation

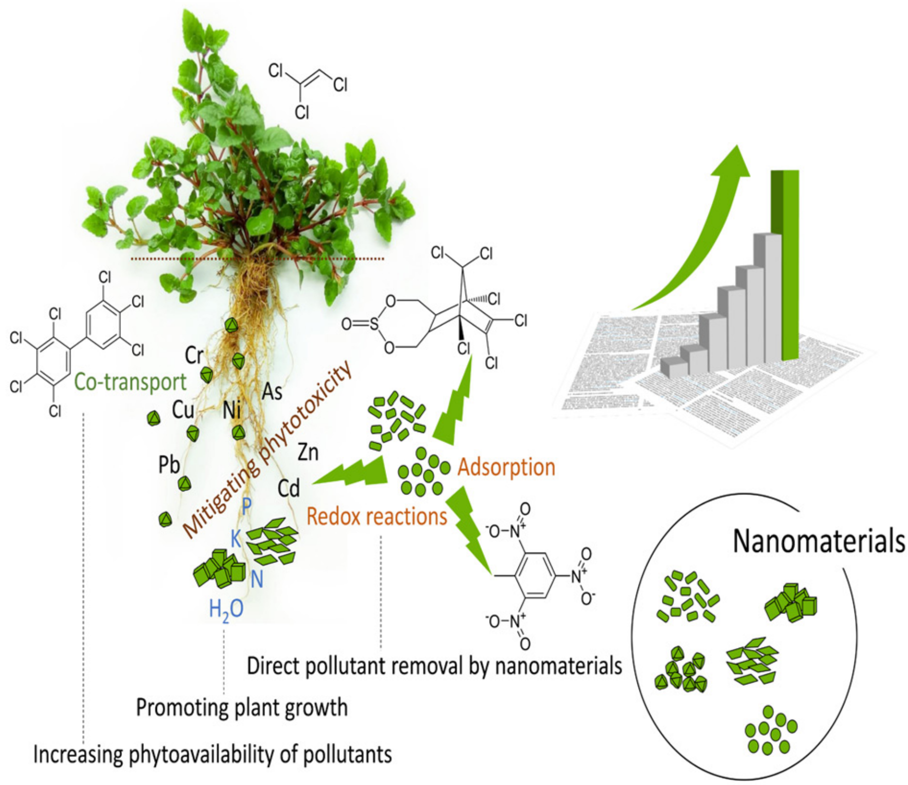

Figure 3. Roles of nanomaterials in facilitating phytoremediation of contaminated soil.

or stabilization of pollutants. Many studies used nZVI for reductive dechlorination of chlorinated organic pollutants (e.g., polychlorinated biphenyls and organochlorine pesticides) and for reductive transformation of toxic metals with high valence (e.g., Cr(VI) and U(VI)) (Di Palma, Gueye, & Petrucci, 2015; El-Temsah, Sevcu, Bobcikova, Cernik, & Joner, 2016; Huang et al., 2016). Apart from the reducing capacity, nZVI can also function through adsorbing inorganic ions and coprecipitating with them (e.g., As(III)) (Lackovic, Nikolaidis, & Dobbs, 2000; Li et al., 2018). Other nanomaterials that are widely studied for removing pollutants from the contaminated soil include iron oxide nanoparticles, iron-containing bimetallic nanoparticles, natural mineral nanoparticles, phosphate-based nanoparticles, etc (Long et al., 2011; Liu & Lal, 2012; Xu, Zeng, Huang, Feng, et al., 2012; Xu, Zeng, Huang, Lai, et al., 2012; Trujillo-Reyes, Peralta-Videa, & Gardea-Torresdey, 2014; Wan et al., 2018). Using engineered nanomaterials for remediation of contaminated soil is still a focus point of environmental research these years. Table 2 summarizes some recently reported studies about the utilization of engineered nanomaterials for the remediation of contaminated soil. It is theoretically possible for all these nanomaterials to be involved in phytoremediation.

Table 2. Some representative studies reported in 2014–2018 about the utilization of engineered nanomaterials for remediation of contaminated soil.

Nanomaterials	Pollutants	Main remediation mechanism	Reference
Nano-chlorapatite	Cd and Pb	Immobilization by precipitation as metal-phosphate compounds	Wan et al. (2018)
nZVI	Cr	Stabilization by reductive transformation of Cr(VI) into more stable and less toxic form	Wang, Fang, Kang, and Tsang (2014)
Carbon nanotubes	Organochlorine pesticides	Immobilization by adsorption for in situ remediation	Zhang, Gong, Zeng, Yang, and Zhang (2017)
Nano-hydroxyapatite	Cu and Zn	Stabilization by ion exchange, surface complexation, and precipitation as new metal phosphates	Sun, Chen, Fan, Zhou, and Wang (2018)
Nano-selenium	Hg	Immobilization of elemental mercury by forming insoluble mercuric selenide (HgSe)	Wang et al. (2017)
Ferrous phosphate nanoparticles	Cd	Stabilization by formation of cadmium phosphate through precipitation	Xu, Yan, Fan, and Fang (2016)
Ni/Fe bimetallic nanoparticles	Polybrominated diphenyl ethers	Degradation by hydrogenation debromination reaction with Ni/Fe nanoparticles	Xie, Fang, Cheng, Tsang, and Zhao (2014)
Pd/Fe bimetallic nanoparticles	Polychlorinated biphenyls (PCBs)	Degradation by hydrogenation dechlorination reaction with Pb/Fe nanoparticles	Chen et al. (2014)
Magnetite nanoparticles	As	Stabilization by adsorption and coprecipitation	Liang and Zhao (2014)
Fe-Mn binary oxide nanoparticles	Se	Immobilization by adsorptive immobilization	Xie, Liang, Qian, and Zhao (2015)
Fe/Cu bimetallic nanoparticles	Cr	Stabilization by reductive transformation of Cr(VI) with Fe/Cu nanoparticles	Zhu, Li, Ma, and Shang (2016)

Initial pollutant concentration significantly influences the phytoremediation efficiency. Plants are generally more effective in accumulating and metabolizing pollutants with relatively low concentration (Li, Zhang, Xie, Li, & Zhang, 2015). Too high concentration of pollutant, especially a level over the tolerance limit of the used plant, will have obvious phytotoxicity towards plant and result in a decrease of plant biomass and pollutant accumulation (Liu, Zhou, & Wang, 2010). Generally, a plant can only accumulate or be tolerant to a certain pollutant within a certain concentration range. Other coexisting pollutants or extremely high concentration of the targeted pollutant may cause failure of the phytoremediation. Thus, some strategies for mitigating phytotoxicity during phytoremediation are proposed (Figure 4). Nanomaterials can directly remove part of pollutants in phytoremediation systems, which reduces phytotoxicity resulted from the stress of high concentration pollutants. Chai et al. (2013) investigated the effect of carbon nanotubes on Cd accumulation in smooth cordgrass. According to their experimental results, carbon nanotubes did not cause phytotoxicity under low Cd concentration (50 mg/kg), but protected the plants from growth inhibition under high Cd concentration (200 mg/kg).

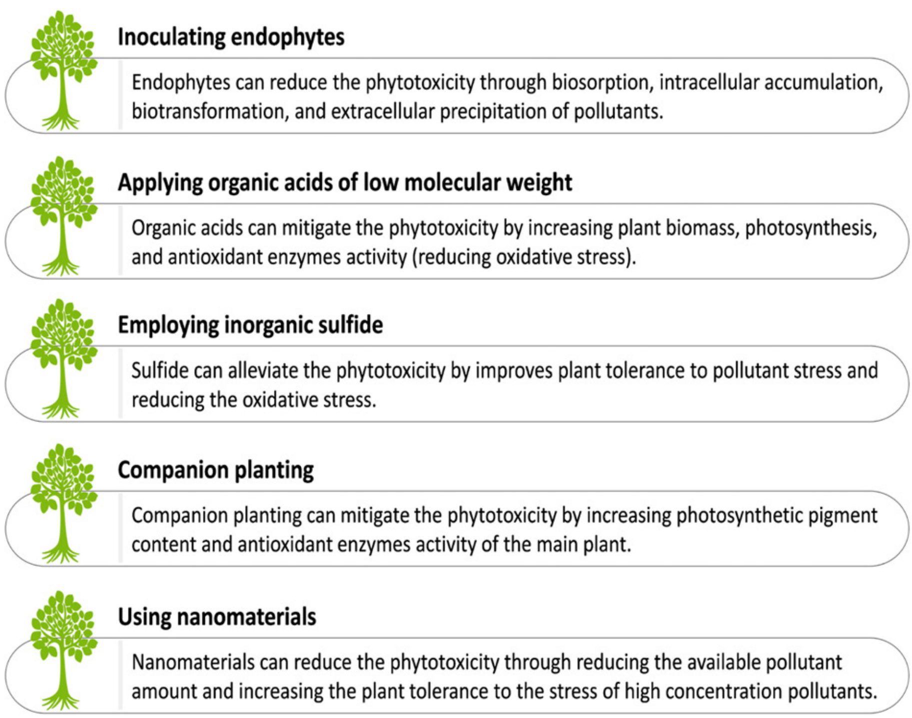

Figure 4. Some strategies for mitigating phytotoxicity during phytoremediation. Summarized from the corresponding references: inoculating endophytes (Ma, Rajkumar, Zhang, & Freitas, 2016a), applying organic acids of low molecular weight (Ehsan et al., 2014), employing inorganic sulfide (Guan, Zhang, Pan, Jin, & Lin, 2018), companion planting (Xiong et al., 2018), using nanomaterials (Chai et al., 2013; Liang et al., 2017; Praveen et al., 2018; Tripathi et al., 2015).

Through further analyzing the ion contents of potassium (K^+), sodium (Na^+), and calcium (Ca^{2+}), the authors demonstrated that carbon nanotubes could mitigate phytotoxicity of Cd by increasing K^+ and Ca^{2+} for osmotic adjustment. In the study using nano-hydroxyapatite and nano-carbon black to promote Pb phytoextraction by ryegrass, the nanomaterials alleviated the phytotoxicity of Pb in soil through adsorbing and stabilizing the pollutant (Liang et al., 2017). Though the accumulation amount of Pb in the plant roots decreased in the first month, the final phytoremediation efficiency increased after 12 months due to the reduced phytotoxicity. Additionally, the phytoremediation efficiency within a single growing season is limited, and it may take several years (even decades) to completely remove pollutants of high concentrations by plant alone. Using nanomaterials to directly remove part of pollutants can reduce the burden of removing pollutants by plants and shorten the remediation time. Jiamjitrpanich et al. (2012) used nZVI particles for enhancing the phytoremediation of trinitrotoluene-contaminated soil with panicum. In their study, the remediation experiments were conducted with or without plants, respectively. Based on the experimental results, nZVI particles can directly remove a considerable amount of trinitrotoluene. When only using the plant for remediation, it took more than 120 days to completely remove trinitrotoluene of 500 mg/kg in the soil. With the assistance of nZVI, the phytoremediation time was shortened to 90 days. Similar effects were also observed by Pillai and Kottekottil (2016). They applied nZVI particles in the phytoremediation of soil contaminated with endosulfan (an organochlorine pesticide). The used nZVI particles can directly remove 34.96% endosulfan in the soil through reductive dechlorination, which significantly enhanced the phytoremediation efficiency within a remediation period of 28 days.

3.2.2. Promoting plant growth

Plant biomass and growth rate are two important considerations in choosing plant species for phytoremediation. Many applied plants are often not satisfactory due to their low plant biomass and slow growth rate resulting from limited tolerance to pollutants and poor soil conditions for plant growth. Therefore, some strategies are used in phytoremediation processes to promote plant growth, such as inoculating plant growth promoting rhizobacteria (PGPR), applying plant growth regulators, and using transgenic plants (Ma, Rajkumar, Zhang, & Freitas, 2016b; Aderholt, Vogelien, Koether, & Greipsson, 2017; Nahar, Rahman, Nawani, Ghosh, & Mandal, 2017; Yadu et al., 2018). Research on nanomaterials and plants has shown that some nanomaterials could enhance plant growth, such as graphene quantum dots, carbon nanotubes, Ag nanoparticles, ZnO nanoparticles, nZVI particles, and upconversion nanoparticles (Table 3). The mechanisms

Table 3. Some representative studies about the effects of nanomaterials on plant growth.

Nanomaterials	Plant species	Effect	Main mechanism	Reference
Carbon-based nanomaterials				
Graphene quantum dots	Coriander (*Coriandrum sativum* L.) and garlic (*Allium sativum* L.)	Enhanced	The graphene quantum dots were served as nano-fertilizer and pesticide.	Chakravarty et al. (2015)
Carbon nanotubes	Tomato (*Solanum lycopersicum* L.)	Enhanced	The used carbon nanotubes activated the plant reproductive system, thus leading to the increase of fruit production.	Khodakovskaya et al. (2013)
Graphene	Tomato (*Solanum lycopersicum* L.)	Decreased	Graphene penetrated vacuole and deposited in root tips, which reduced the biomass production.	Zhang, Gao, Chen, and Li (2015)
Watersoluble C_{70} fullerenes	Cress [*Arabidopsis thaliana* (L.) Heynh.]	Inhibited	The nanoparticles caused auxin disruption, abnormal cell division, and microtubule disorganization, which retarded the plant growth.	Liu, Zhao, et al. (2010)
Metal-based nanomaterials				
Ag nanoparticles	Kidney bean (*Phaseolus vulgaris* L.)	Enhanced	The applied nanoparticles stimulated the plant metabolism and increased nitrogen uptake, thus facilitating the chlorophyl activity and biomass accumulation.	Das et al. (2018)
TiO_2 nanoparticles	Common duckmeat [*Spirodela polyrrhiza* (L.) Schleid.]	Decreased	The nanoparticle toxicity might inhibit the photosynthesis, protein synthesis, and nitrogen fixation.	Movafeghi et al. (2018)
ZnO nanoparticles	Cotton (*Gossypium hirsutum* L.)	Enhanced	The coated ZnO nanoparticles increased the utilization of zinc and phosphorus, and released zinc ions into cell by a slow and sustainable manner without causing phytotoxicity.	Venkatachalam, Priyanka, et al. (2017)
γ-Fe_2O_3 nanoparticles	Shaddock [*Citrus maxima* (Burm. f.) Merr.]	No significant difference	The effect on plant growth is dependent on the exposure concentration and is not obvious at the experimental concentrations.	Hu et al. (2017)
$CoFe_2O_4$ nanoparticles	Tomato (*Solanum lycopersicum* L.)	No significant difference	The nanoparticles might not pass through seed coat or root system at early germination stage.	López-Moreno et al. (2016)
Al_2O_3 nanoparticles	Wheat (*Triticum aestivum* L.)	Inhibited	The nanoparticles damaged the epidermal and cortex cells due to vacuolization and shrinkage, and the toxic effect inhibited plant growth.	Yanık and Vardar (2015)
CuO nanoparticles	Indian Mustard (*Brassica juncea* L.)	Decreased	The nanoparticle exposure enhanced lignification and subsequent rigidification of plant cells, which reduced the plant growth.	Nair and Chung (2015)

nZVI particles	Cress [*Arabidopsis thaliana* (L.) Heynh.]	Enhanced	The nanoparticles enhanced root elongation by triggering hydroxyl radical-induced cell wall loosening.	Kim et al. (2014)
Others				
Nano-hydroxyapatite	Mung bean (*Phaseolus radiatus* L.)	Inhibited	The nanostructure and local high intracellular Ca^{2+} concentration caused by hydroxyapatite nanoparticles were considered to result in cell apoptosis and plant growth inhibition.	Jiang et al. (2014)
Upconversion nanoparticles	Mung bean (*Phaseolus radiatus* L.)	Enhanced	The underlying mechanism is not clear.	Peng et al. (2012)

of these nanomaterials in promoting plant growth are different. For example, Chakravarty, Erande, and Late (2015) considered that graphene quantum dots might serve as nanofertilizer and pesticide to enhance the growth rates of *Coriandrum sativam* and *Allium sativum*, while Khodakovskaya et al. (2013) reported that carbon nanotubes could activate the plant reproductive system, thus leading to the enhancement of tomato growth.

In phytoremediation systems, nanomaterials can increase the remediation efficiency by promoting plant growth. Direct pollutant removal by nanomaterials reduces the phytotoxicity, which is beneficial to plant growth. In addition, nanomaterials may act on plants to increase the tolerance to pollutants. For reducing the phytotoxicity of Cd and Pb towards white popinac in phytoremediation, zinc oxide (ZnO) nanoparticles were used as physiological regulators of the plants by Praveen et al. (2018). It was inferred from the experimental results that ZnO nanoparticles increased the plant tolerance through regulating the genetic expression of enzymes. Similarly, Tripathi et al. (2015) reported their study on alleviating Cr(VI) phytotoxicity towards pea by using silicon nanoparticles. The applied nanoparticles promoted the plant tolerance to Cr(VI) stress, which was demonstrated by a resulting low level of reactive oxygen species and an enhancement in antioxidant activities and photosynthetic performance. Apart from alleviating pollutant phytotoxicity, nanomaterials may increase plant growth in phytoremediation systems by facilitating absorption of water and nutrients, enhancing photosynthetic rate, regulating soil microbial community, as well as alleviating abiotic stress (e.g., high salinity and drought). Ding, Li, Liu, Zuo, and Liang (2017) applied nano-hydroxyapatite to assist removal of lead by ryegrass, and the plant growth was promoted, resulting in enhanced phytoremediation efficiency. The authors explained it by the increased phosphorus concentration in soil after the addition of nano-hydroxyapatite. Souri et al. (2017) used salicylic acid nanoparticles to increase the absorption and utilization rate of nutrients, which increased the plant biomass (fresh weight) of *Isatis cappadocica* in the arsenic phytoextraction system. In a Cd phytoextraction process by soybean, TiO_2 nanoparticles were reported to be helpful in promoting plant growth by enhancing the photosynthetic rate (Singh & Lee, 2016). According to their results, Cd uptake increased with TiO_2 nanoparticles, and the authors proposed a possible mechanism that the small TiO_2 nanoparticles can enter the chloroplasts and accelerate light adaptation and electron transfer. Recent research by Timmusk, Seisenbaeva, and Behers (2018) showed that TiO_2 nanoparticles could improve the performance of PGPR. In their experiments, the rhizobacteria performed better under all abiotic stress (drought, pathogen, and salt), and resulted in an increase of the plant biomass. The experience from these cases is valuable for using nanomaterials to promote plant growth in phytoremediation systems.

3.2.3. Increasing phytoavailability of pollutants

Phytoavailability of pollutants is a key factor that affects phytoremediation efficiency, especially for phytoextraction. Plants only absorb pollutants in available forms. The phytoavailability of pollutants strongly depends on their chemical speciation and distribution in soil. For example, in a study about the phytoavailability of cadmium in different binding forms, it was shown that the cadmium adsorbed on gibbsite is the most available to reed compared with other oxide minerals (alumina, goethite, magnetite, and manganese oxide) in soil (Wang, Jia, Wang, Zhu, & Wu, 2009). Generally, the highest phytoavailability of metals is in exchangeable forms (dissolved in the soil solution), then in combined forms with minerals, oxides, and organic matters, and lowest in crystalline phase (Sheoran, Sheoran, & Poonia, 2016; Liang et al., 2017). Additionally, soil physicochemical properties and plant physiological characteristics also affect the phytoavailability of pollutants (Sheoran et al., 2016; Ren et al., 2018). Low phytoavailability often limits the phytoremediation process. For example, lead usually exists in insoluble forms in soil due to adsorption, complexation, and precipitation, which makes it difficult for phytoextraction (Zaier et al., 2014). Therefore, many methods have been proposed to increase pollutant phytoavailability, including agronomic management (e.g., fertilization), treatment with chemical additives (e.g., chelating agent), inoculation of rhizospheric microorganisms, and use of genetic engineering (Glick, 2010; Habiba et al., 2015; Jacobs, De Brabandere, Drouet, Sterckeman, & Noret, 2018). Increasing phytoavailability of pollutants has been proven effective in improving the phytoremediation efficiency.

Nanomaterials have two divergent influences on the phytoavailability of pollutants in soil (Table 4). On the one hand, nanomaterials can serve as a carrier of pollutants when they enter the cell, thereby increasing the bioavailability (Wild & Jones, 2009; Su et al., 2013). On the other hand, adsorption of pollutants onto nanomaterials outside organism may reduce the free pollutants, thereby decreasing the bioavailability (Glomstad et al., 2016). Based on this, two key conditions need to be met for improving the phytoavailability of pollutants with nanomaterials: (1) The used nanomaterial can combine with the pollutant (mainly through adsorption); (2) The nanomaterial is phytoavailable. The fullerene nanoparticles are widely studied nanoparticles that can increase the phytoavailability of pollutant. Ma and Wang (2010) used C_{60} fullerene nanoparticles in the phytoremediation system with eastern cottonwood for facilitating the removal of trichloroethylene from contaminated soil. Their results showed that fullerenes

Table 4. Effects of nanomaterials on the uptake and accumulation of pollutants by plants.

Pollutants	Plant species	Nanomaterials	Main effects	Reference
Dichlorodiphenyldichloroethylene (*p,p′*-DDE)	Zucchini (*Cucurbita pepo* L.), soybean [*Glycine max* (L.) Merr.], and tomato (*Solanum lycopersicum* L.)	C_{60} fullerenes	The fullerenes increased the uptake of *p,p′*-DDE by 30% to 65%.	Torre-Roche et al. (2012)
Chlordane, dichlorodiphenyltrichloroethane (DDT), and metabolites of DDT	Zucchini (*Cucurbita pepo* L.), soybean [*Glycine max* (L.) Merr.], corn (*Zea mays* L.), and tomato (*Solanum lycopersicum* L.)	Multiwalled carbon nanotubes and C_{60} fullerenes	The nanotubes decreased the accumulation of these pollutants by all the plants, while the fullerenes increased the accumulation of chlordane in tomato and soybean.	De La Torre-Roche, Hawthorne, Deng, et al. (2013)
p,p′-DDE	Zucchini (*Cucurbita pepo* L.) and soybean [*Glycine max* (L.) Merr.]	Ag nanoparticles	Ag nanoparticles deceased the uptake and accumulation of *p,p′*-DDE by both the plants.	De La Torre-Roche, Hawthorne, Musante, et al. (2013)
p,p′-DDE	Pumpkin (*Cucurbita pepo* L.)	C_{60} fullerenes	The fullerenes had little impact on *p,p′*-DDE bioaccumulation by the plant.	Kelsey and White (2013)
Cd and Pb	Fava bean (*Vicia faba* L.)	Carboxylated multi-walled carbon nanotubes	The used carbon nanotubes facilitated the enrichment of Cd and Pb in the leaves.	Wang, Liu, et al. (2014)
Chlordane and *p,p′*-DDE	Garden lettuce (*Lactuca sativa* L.)	Non/amino-functionalized multiwall carbon nanotubes	Both the carbon nanotubes decreased pesticide content in the root and shoot, and the effects caused by amino-functionalized nanotubes were modest.	Hamdi, De La Torre-Roche, Hawthorne, and White (2015)
Phenanthrene, 3-CH_3-phenanthrene, and 9-NO_2-phenanthrene	Maize (*Zea mays* L.)	Carbon nanotubes	Carbon nanotubes reduced bioaccumulation of phenanthrene in maize seedling roots and shoots, and the nanotubes were detected in plant roots.	Wang, Liu, et al. (2016)
Pb	Rice (*Oryza sativa* L.)	TiO_2 nanoparticles	TiO_2 nanoparticles reduced the bioaccumulation of Pb in rice at high exposure levels, and anatase nanoparticles did accumulate in rice roots.	Cai et al. (2017)
Carbamazepine	Collard greens (*Brassica oleracea* L.)	Multiwall carbon nanotubes	Carbon nanotubes suppressed carbamazepine accumulation, and the functionalization of carbon nanotubes enhanced carbamazepine translocation.	Deng, Eitzer, White, and Xing (2017)
Tetracycline	Rice (*Oryza sativa* L.)	TiO_2 nanoparticles	The presence of TiO_2 NPs lowered the tetracycline accumulation in rice seedlings.	Ma et al. (2017)

Pyrene and 1-methylpyrene	Maize (*Zea mays* L.)	Multiwalled carbon nanotubes	Multiwalled carbon nanotubes reduced the concentrations of pyrene and 1-methylpyrene in roots and shoots, and suppressed their translocation in plant.	Zhang, Liu, et al. (2017)
Cd	Soybean [*Glycine max* (L.) Merr.]	CeO_2 nanoparticles	CeO_2 nanoparticles significantly reduced the translocation of Cd from roots to shoots by 70%.	Rossi, Sharifan, Zhang, Schwab, and Ma (2018)
Anthracene, phenanthrene, pyrene, fluoranthene, benzo[a]pyrene, hexachlorobenzene, *p,p′*-DDE, and deca-brominated diphenyl ether	Swamp morning-glory (*Ipomoea aquatica* Forssk.), cucumber (*Cucumis sativus* L.), corn (*Zea mays* L.), spinach (*Spinacia oleracea* L.), and pumpkin (*Cucurbita moschata* Duchesne)	TiO_2, Ag, and Al_2O_3 nanoparticles, grapheme, and carbon nanotubes	All the nanomaterials increased, to different degrees, the accumulation of these pollutants by the plants.	Wu, Wang, and Zhu (2018)
Pyrene	Cucumber (*Cucumis sativus* L.)	Multiwalled carbon nanotubes	The nanotubes reduced root uptake of pyrene, but enhanced the translocation of pyrene from root to shoot.	Shen et al. (2018)
Cd, Cu, and Pb	Rice (*Oryza sativa* L.)	C_{60} fullerenes	The fullerenes could accumulate in rice panicles, and their effects on the uptake of heavy metal ions depended on rice cultivars, type of metal ions, and their concentrations in soil.	Liang, Xiao, Hu, Zhang, and Hu (2018)

enhanced the trichloroethylene uptake by plant. The authors explained the experimental phenomenon by co-transporting trichloroethylene with fullerene nanoparticles. The adsorbed trichloroethylene on fullerene entered the plant along with the uptake of nanoparticles. Torre-Roche et al. (2012) demonstrated the enhancement of dichlorodiphenyldichloroethylene (*p,p*'-DDE) accumulation in zucchini, soybean, and tomato in the presence of C_{60} fullerene. The addition of fullerene increased all plant uptake of the pollutant by 30% to 65%, and the effect was especially evident in roots. Additionally, it has been demonstrated that some other nanomaterials, such as short carbon nanotubes, Fe_3O_4 nanoparticles, TiO_2 nanoparticles, silica nanoparticles, and quantum dots, could be directly taken in by plants (Wang, Lombi, Zhao, & Kopittke, 2016). This enables more nanomaterials to be used for increasing the phytoavailability of pollutants in phytoremediation systems in future research.

3.3. Phytoremediation efficiency

For evaluating phytoremediation efficiency, residual pollutant amount in soil (for phytovolatilization, phytoextraction, phytodegradation, and rhizodegradation), pollutant amount in bioavailable and high toxic forms (for phytostabilization), or pollutant accumulation in plant tissue (for phytoextraction) is often determined after remediation treatment (Liang et al., 2017). When evaluating the phytoremediation efficiency with nanomaterials, an experimental group without nanomaterials is usually used as control, so that the beneficial effects of nanomaterials on the remediation efficiency can be clearly identified. In the summarized examples of nanomaterial-facilitated phytoremediation (Table 1), the residual amount of pollutant in soil (RAS), accumulated amount of pollutant in plant tissue (AAP), bioconcentration factor (BCF), translocation factor (TF), and remediation factor (RF) are used to quantify the phytoremediation efficiency. For organic pollutants, the RAS is reliable to reflect the enhanced degradation efficiency by using nanomaterials. A typical example can be found in the article by Pillai and Kottekottil (2016). The authors conducted their experiments with three control groups: without any treatment, with addition of nZVI, and with only phytoremediation. The phytoremediation treatment assisted with nZVI was implemented in the experimental group. Both the values of RAS in the control and experimental group were measured after 0, 7, 14, 21, and 28 days. By comparing the RAS results, it is clear that the nZVI increased phytoremediation efficiency. For heavy metals or arsenic, the nanomaterial-induced changes of AAP are generally measured. The AAP is expressed as the pollutant concentration in root, shoot, or whole plant. For example, Souri et al. (2017) measured the arsenic concentration in root and shoot of *Isatis cappadocica* after the phytoremediation with salicylic acid nanoparticles, and found that the nanoparticles increased the arsenic concentration in root but showed no significant influence on the arsenic accumulation in shoot. The BCF, TF, and RF are used for evaluating phytoextraction processes. The calculation methods are as follows:

$$\mathrm{BCF} = C_{\mathrm{plant}}/C_{\mathrm{soil}}$$

$$\mathrm{TF} = C_{\mathrm{shoots}}/C_{\mathrm{roots}}$$

$$\mathrm{RF} = C_{\mathrm{plant}}/C_{\mathrm{soil}} \times W_{\mathrm{plant}}/W_{\mathrm{soil}}$$

where C_{shoots}, C_{roots}, C_{plant}, and C_{soil} are pollutant concentrations in the plant shoots, the plant roots, the harvested plant biomass, and the soil, respectively. W_{plant} is weight of the harvested plant biomass and W_{soil} is weight of the soil. The value of BCF is used to divide the plant as excluder ($\mathrm{BCF} < 1$), accumulator ($1 < \mathrm{BCF} < 10$), or hyperaccumulator ($\mathrm{BCF} > 10$) (Lam, Gálvez, Cánovas, Montofré, & Keith, 2018). The value of TF indicates the plant capacity to translocate pollutant to the harvestable part, and the RF is calculated to evaluate the phytoextraction capacity for soil remediation (Ali et al., 2013; Liang et al., 2017; Moameri & Abbasi Khalaki, 2017). Liang et al. (2017) determined the efficiency of Pb phytoextraction assisted with nano-hydroxyapatite, and found that the nanoparticles could significantly increase the BCF and TF after a treatment of 2 months. However, in the phytoremediation study by Moameri and Abbasi Khalaki (2017), the nano-silica of 500 mg/kg increased the BCF of Cd in rye but decreased the TF. The authors further calculated the RF value, and found no significant difference compared with the control due to the decrease of plant growth and biomass. This case suggests that the RF is more suitable for evaluating the phytoremediation efficiency as it involves the changes of both pollutant and plant during the phytoremediation assisted with nanomaterials.

3.4. Challenges and recommendations

Using nanomaterials to facilitate phytoremediation is an emerging idea appeared along with the development of nanotechnology and bioremediation technology. It faces many challenges in practical applications. Environmental risk of nanomaterials in the soil ecosystem is the most concerned problem. Many nanomaterials are toxic to animals, plants, and microbial communities in the soil (Maurer-Jones, Gunsolus, Murphy, & Haynes, 2013). The phytotoxicity of nanomaterials is especially concerned in phytoremediation. Therefore, on the one hand, more research on environmental risk of nanomaterials is needed to fully understand the toxicity. On the other hand, using nanomaterials in phytoremediation needs to be regulated to take maximum advantage of them but minimize their risk. Currently, using nanomaterials in phytoremediation is in the phase of exploration and attempt, though many positive results have been obtained. Experience from more application cases is required and long-term performance of the nanomaterials needs further research. Based on the currently known cases of phytoremediation assisted with nanomaterials, nZVI is mostly studied. Compared with other nanomaterials, using nZVI to facilitate the phytoremediation of contaminated soil has certain advantages. Firstly, field-scale commercial applications of nZVI have already implemented for soil remediation (Mueller & Nowack, 2010). Much successful experience can be used in the phytoremediation. Additionally, the high reactivity and controllable phytotoxicity of nZVI may ensure a successful phytoremediation (Terzi et al., 2016; Gil-Díaz & Lobo, 2018). However, in a review article by Crane and Scott, it was reported that nZVI might suffer from particle aggregation, oxidation corrosion, and interference from soil components in their applications (Crane & Scott, 2012). Thus, it is important to design the structure of nanomaterials and fully understand the reasons and conditions that cause the failure of using nanomaterials in phytoremediation. Moreover, specific responses of nanomaterials to different plant species, pollutants, soil types, and weather conditions in phytoremediation systems should be further investigated for general applicability. Other methods including agronomic management, treatment with chemical additives, inoculation of rhizospheric microorganisms, and use of genetic engineering may be incorporated into the phytoremediation assisted with nanomaterials to regulate the performance of nanomaterials and further improve the remediation efficiency.

4. Concluding remarks

Phytoremediation is a green biotechnology with many competitive advantages in treating contaminated soil, yet the long remediation time, changeable weather conditions, and phytotoxicity of high concentration pollutants limit its extensive use. Considerable effort has been made in order to increase the phytoremediation efficiency. Over the past few years, using nanomaterials in phytoremediation has shown great prospect for enhancing the remediation efficiency. This article reviews the latest research and knowledge on using nanomaterials to facilitate the phytoremediation of contaminated soil. Nanomaterials are capable of removing pollutants, promoting plant growth, and increasing pollutant phytoavailability, thus facilitating the phytoremediation of contaminated soil. Currently, using nanomaterials in phytoremediation is in the phase of exploration and attempt but provides an alternative means to enhance phytoremediation efficiency. More work is needed to be done to further confirm these findings and advance the knowledge.

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