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REVIEW ARTICLE

Remediation of contaminated soils by biotechnology with nanomaterials: bio-behavior, applications, and perspectives

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ABSTRACT
Soil contamination caused by heavy metals and organic pollutants has drawn world-wide concern. Biotechnology has been applied for many years to the decontamination of soils polluted with organic and inorganic contaminants, and novel nanomaterials (NMs) has attracted much concern due to their high capacity for the removal/stabilization/degradation of pollutants. Recently, developing advanced biotechnology with NMs for the remediation of contaminated soils has become a hot research topic. Some researchers found that bioremediation efficiency of contaminated soils was enhanced by the addition of NMs, while others demonstrated that the toxicity of NMs to the organism negatively influenced the repair capacity of polluted soils. This paper reviews the application of biotechnology and NMs in soil remediation, and further provides a critical view of the effects of NMs on the phytoremediation and micro-remediation of contaminated soils. This review also discusses the future research needs for the combined application of biotechnology and NMs in soil remediation.

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Introduction

Soils have been suffered from large numbers of different classes and types of contaminants. Some pollutants persist for a long time and remain in soils for decades, thus disturbing the ecological balance of soil ecosystems and posing a potential threat to human health [1]. Main soil contaminants include organic pollutants such as: chlorinated solvents, polycyclic aromatic hydrocarbons (PAHs), organophosphorus pesticides, and inorganic pollutants, particularly heavy metals [2,3]. Biotechnology, such as phytoremediation or micro-remediation, has been developed as an efficient technology for contaminant removal, stabilization or degradation. The above two biotechnologies share environment-friendly and cost-effective advantages over most conventional chemical and physical remediation strategies. Over the years, extensive research has certified the effectiveness of biotechnology for the remediation of soils contaminated with organic and inorganic pollutants [4–6].

Significant research efforts have been made towards developing novel materials (e.g. graphene-based materials, bio-sorbent, and nanoparticles) for soil cleanup [7–10]. Nanomaterials (NMs) are usually defined as the particles with sizes of 100 nm or less in at least one dimension [11]. The possession of unique sizes between individual molecules and their corresponding bulk form resulted in unusual physicochemical properties. Nowadays, using NMs for the treatment of different kinds of environmental pollutants has proven to be feasible [12–15]. For instance, nanoscale zero valent iron (nZVI) with 1 or 10 g kg^{-1} was used to degrade dichlorodiphenyltrichloroethane (DDT), and the results showed that the addition of nZVI led to about 50% degradation of DDT in the spiked soil [16]. Li et al. [17] investigated the mobility of naphthalene, fluorene, phenanthrene, and pyrene in the presence of NMs in soil. The results of this study suggested that carbon NMs showed potential capacity in the immobilization of pollutants by their low mobility and strong PAHs sorption properties. Shipley et al. [18] found that magnetite and hematite NMs could be used for the removal of metals such as As, Cr, Cd, Mn, and Pb from the polluted soils. In addition, NMs-decorated composites also exhibit highly efficient performance for the decontamination of environmental pollutants [19–21]. More recently, the synergistic use of NMs and biotechnology,

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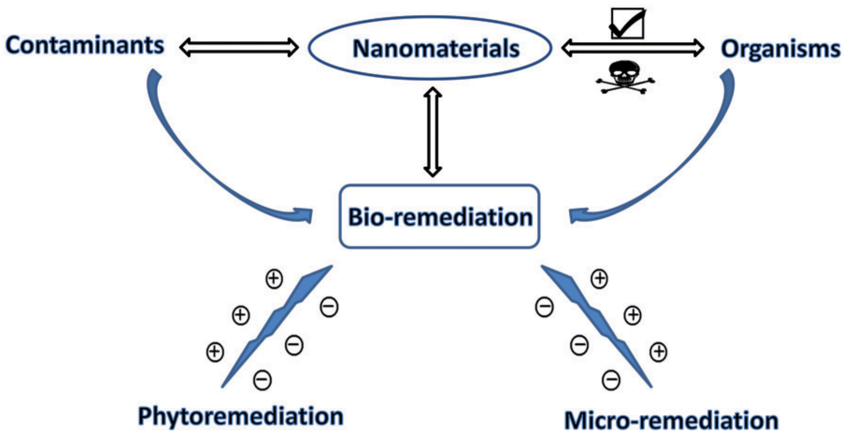

Figure 1. Applications of nanomaterials in the bioremediation of soil contaminants.

to solve environment problems, has opened new pathways for pollutant removal from soils. First, the interaction between NMs and contaminants might provide favorable conditions for soil remediation by biotechnology. For instance, the introduction of graphene oxide (GO) nanoparticles and fullerene nanoparticles enhanced the transport of pollutants in saturated soils, which might improve the removal efficiency of contaminants by plants or microorganisms [22,23]. Besides, it is also worth noticing that the unique properties of NMs allow them to interact with biological systems both positively and negatively. As discussed by Ditta and Arshad [24], NMs could not only be used as sources of micro- and macro-nutrients but also the nutrients' carriers, thus promoting plant growth and improving crop productivity. Conversely, extensive ongoing research proposed that NMs exposures at concentrations higher than 100 ppm are toxic to plants [25]. Meanwhile, recent reports also showed the positive or toxic effects with regard to the influence of NMs on microorganisms [26–28]. The interactions between NMs and organisms will inevitably affect the bioremediation efficiency of the contaminated soils. According to Torre-Roche et al. [29], the application of fullerene nanoparticles increased plant uptake of organic chlorine contaminants from soil. On the other hand, the toxicity of NMs to microorganisms inhibited the microbial degradation rate of organic pollutants in soil [30].

Currently, considerable effort has been conducted to investigate a combined soil remediation technique using biotechnology and NMs to deal with different kinds of soil pollutions. For example, nano-titanium dioxide ($nTiO_2$) has been applied to remove Cd from the polluted soils in combined with phytoremediation [31]; the synergistic use of nanoparticles and microorganisms to remediate petroleum hydrocarbon contaminated soils has been investigated [32]. However, there are no consistent conclusions about whether the combined technique is beneficial to improve contaminant removal efficiency, and to date, the overall review of the combined application of NMs and bioremediation techniques for soil remediation has not been reported as is known. With this in mind, this review attempts to present a summary of the bio-behavior, applications, and perspectives of NMs in the remediation of contaminated soil using biotechnology. The present review aims to: (1) describe the positive and toxic effects of NMs on plants and microorganisms; (2) discuss the effects of NMs on the phytoremediation and micro-remediation of contaminated soils; (3) enumerate future research needs for the combined remediation techniques of NMs and biotechnology (Figure 1).

Phytoremediation affected by NMs

Delivery of NMs into plants

The uptake, delivery, and accumulation of NMs in plants have been confirmed by many researchers [33–35]. Plants provide a potential route for environmental NMs into organisms which might promote the bioaccumulation of NMs into the food chain. For the above-ground parts, NMs exposure in the air can be directly attached to the plants. Nevertheless, the interactions between water-soluble/soil-associated NMs and plants often take place in plant roots. A study specifically designed to demonstrate the entrance route of NMs into plant roots was conducted by using a confocal laser-scanning microscope. The images obtained showed that the uptake of nanocrystals into *Phalaenopsis* and *Arabidopsis* roots appeared from velamen radicum, then to the passage cells of exodermises, followed in the parenchyma, and finally the vascular tissues as time goes by Hischemöller et al. [36]. In addition, the absorbed NMs can be transferred into certain plant organs. Lin et al. [37] conducted research to investigate the uptake and translocation of carbon NMs into plants and they found that fullerene nanoparticles could be transferred from the leaves and stems to the roots of rice plants. The roots possess a larger opportunity to contact studies with NMs and plant transpiration plays the driving force for NMs transport and the upward translocation of NMs from plant roots to the above-ground parts. It has been found that multi-walled carbon nanotubes (MWCNTs) were able to penetrate to the roots and then transport the leaves and shoots of lettuce and red spinach [38]. Otherwise, translocations of nanoscale copper and cerium oxide nanoparticles in the plants have also been observed [39,40].

Various studies are now paying attention to the influence factors that limiting the delivery of NMs into plants [41,42]. The uptake and transportation of NMs are dependent on plant species, the size, charge, shape and chemical composition of NMs themselves, and the environment conditions. For instance, *Typha latifolia* and *Populous deltoids* × *Populous nigra* were used to evaluate the accumulation and phytotoxicity of nZVI in the plants [43]. Scanning electron microscope images and energy dispersive X-ray analysis confirmed that nZVI coated on the *Typha* root surface aggregates. The penetration and internalization of nZVI in plant cells was only observed in *Populous deltoids* × *Populous nigra*, which further demonstrated that the uptake and translocation of NMs in the plants was plant species-dependent. Larue et al. [44] investigated the impact of the diameter of NMs on the accumulation and translocation of $nTiO_2$ in wheat. Results showed that $nTiO_2$ nanoparticles with a diameter below 140 nm could be taken up by the roots of wheat without dissolution or crystal phase modification. Only if the $nTiO_2$ nanoparticles with a diameter below 36 nm could be translocated from plants roots to the aerial parts. Moreover, a study conducted by Barrios et al. [45] investigated the effects of cerium oxide NMs ($nCeO_2$) on *Solanum lycopersicum* L. plants. The results showed that the citric acid coated $nCeO_2$ reduced its uptake by plant roots, but neither the coated nor uncoated NMs affected the translocation of $nCeO_2$ to the above-ground tissues of the test plants. In addition, the positive, neutral and negative charged gold NMs (nano-Au) were used to explore the uptake of NMs into *Oryza sativa* L. It turned out that the uptake and translocation of nano-Au in the plants depended on the surface charge of the NMs. The positive nano-Au was most efficiently taken up by plant roots, and the negative nano-Au was preferential in the translocation of NMs from the roots to the above-ground parts [46].

Interaction of NMs with plants

The increasing application of NMs in all walks of life inevitably incurred interactions between NMs and plants. A growing number of researchers have paid their attention to this issue [47]. However, there was no consistent conclusion to the response of plants to different kinds of NMs. The contradictory results mainly consisted of two parts: the phytotoxicity and the positive effects. Otherwise, some studies also found the inconsequential effects of NMs on plants. For instance, a study conducted with six different kinds of plants indicated that the effects of carbon nanotubes (CNTs) on root growth of cabbage and carrots were negligible either with functionalized or non-functionalized CNTs [48]. The different responses of plants to NMs will certainly affect combined remediation technique efficiency of NMs and phytoremediation in soil remediation. In this part, we briefly discuss the phototoxicity and the positive effects of NMs on plants, respectively.

Various studies are now ascertaining the nanotoxicity of different NMs on plant growth and development [49–51]. Seed germination inhibition and plant growth suppression are the most directly or obvious symptoms to nanotoxicity. As reported by Lin et al. [52], seed germination rate of corn and ryegrass was reduced by treatment of nano-zinc and nano-zinc-oxide, and the root elongation of corn was decreased by 35% with the application of nano-Al_2O_3. The ions release from NMs, the surfactant of functional NMs and the toxic chemicals used during NMs preparation account for the NMs induced phytotoxicity. For example, *Cucurbita pepo* was chosen to investigate the phytotoxicity of NMs to plants. The germination rate and plant biomass of this plant were reduced significantly due to the increased release of Ag ion and the amended surfactant sodium dodecyl sulfate from NMs [53]. Moreover, NMs induced the physical or chemical toxicity effects that are involved with the disturbances of plant physiological and metabolic processes. For instance, C70 and MWCNT, at high concentrations, turned to impede plant development by interfering water and nutrients uptake through the blockage of vessels, intercellular spaces, and plasmodesmata [37]. Graphene showed adverse effects on tomato, red spinach, and lettuce in terms of plant growth inhibition and aggravated oxidative stress [54]. Similarly, a cellular-level study using *Oryza sativa* L. cell was carried out to study the influence of NMs on plant oxidative stress. Authors certified that the interaction of MWCNT with cell wall might activate the enzymes that were the response for reactive oxygen species (ROS) generation, thus resulting in the reduced cell viability of *Oryza sativa* L. cells [55]. What is noteworthy is that the phytotoxicity of NMs is not only from the dissolution of chemicals of the NMs, but also from their specific physical and chemical properties of nano-size particles themselves. For example, *ryegrass* exposed to ZnO nanoparticles and Zn^{2+} ions presented different toxicity symptoms. The reporters ascertained that dissolution of bulk ions from NMs only partly accounted for the nanotoxicity, while the severely damages to epidermal, endodermal and vascular cells, induced directly by ZnO nanoparticles, played more important roles in the charge of plant growth retardation [56].

As mentioned earlier, some kinds of plants showed positive responses upon the exposure of NMs. The effects of CNTs on rice germination and growth were studied to understand the potential environmental influences of NMs. CNTs promoted the water uptake of rice seeds and increased the seeds' germination rate. A boost to seedling growth was also observed by the treatment of CNTs with well-developed shoot and root systems in rice seedlings [57]. In addition, single-wall carbon nanotubes (SWCNTs) were found to promote plant photosynthetic activity through increasing electron transport rates and enhancing chloroplast solar energy utilization [58]. Moreover, some other researchers even focused on the positive effects of NMs in plants at the cellular and genetic levels. For instance, Lahiani et al. [59] investigated the interaction of carbon nanohorns with plants using tobacco cells. Results demonstrated that single-walled carbon nanohorns could be taken up by plant cells and the nanohorns were favorable for tobacco cell growth. In addition, it was also confirmed that the expression of some genes related to plant stress response were able to be modulated by the introduction of this nanohorns. Moreover, Khodakovskaya et al. [60] introduced a spectroscopic laser-based technique using Raman, photothermal, and photoacoustic methods in order to detect NMs in tomato seedlings. The results showed that absorbed MWCNT in plant seedlings changed total genes expression of tomato cells, especially the genes related to stress regulation.

Phytoremediation of contaminated soils influenced by NMs

There are various remediation technologies for soil remediation [61]. However, most remediation techniques merely transform soil pollutants into their less toxic forms or just stabilize contaminants in the soil matrix, and they actually could not remove the toxic substances from soil thoroughly. By comparison, phytoremediation is a plant-based acceptable alternative technique for soil remediation, which could remove the extract, degrade, sequester, and stabilize a wide range of soil pollutants. As it is driven by solar energy and unlikely to cause secondary pollution, phytoremediation has been considered as a promising, cost-effective, and environment-friendly technology [62]. The efficiency of phytoremediation strongly depends on the uptake ability of plants and the bioavailability of pollutants. However, the biological availability of some existed hazardous chemicals and the accumulation capacity of certain plants are limited. To solve these problems, significant progresses in improving phytoremediation capability have been made in the last few years [63], among which the combined remediation strategy using phytoremediation and NMs is an emerging technology. Due to the different responses of plants to NMs and the various impact of NMs on soil pollutants, the synergistic and antagonistic effects of the combined remediation techniques have been revealed in the decontamination of polluted soils. The effects of NMs on the phytoremediation of organic pollutants and heavy metals contaminated soils were presented in the next section, respectively (Table 1).

The effects of different types or contents of NMs on the phytoremediation of soils, contaminated with a wide variety of organic pollutants, are varied. MWCNTs and fullerene were used to investigate NMs impact on pesticides accumulation in *Cucurbita pepo*, *Zea mays*, *Solanum lycopersicum*, and *Glycine max* with the concentration ranging from 500 to 5000 mg kg^{-1} [29]. Fullerene exposure showed beneficial effects on the remediation of organic contaminated soil with a 34.9% increase of chlordane accumulation in *Solanum lycopersicum*, while the uptake of DDx (dichloro-diphenyl-tricgloroethane and its metabolites) was suppressed. As to MWCNTs exposure, the accumulation of DDx and chlordane were decreased for all the test plant species. Torre-Roche et al. [64] also conducted a study to investigate the effects of fullerene on the uptake of dichlorodiphenyldichloroethylene (DDE) in plants. For zucchini, DDE content of roots, shoots, and the whole plants increased by 30.5, 29, and 30.4%, respectively, upon exposure to fullerene NMs. When a different crop species, tomato (*Solanum lycopersicum* L.), was tested by the same NMs, the promoting impact of DDE uptake was more pronounced with 64.5 and 62.1% increase of the contaminant levels in the roots and the whole plants, respectively. One of the possible mechanisms of the increased uptake of soil contaminants is presented by the co-uptake between NMs and the contaminants. Once small-sized nanoparticles were absorbed by plants, the adhered or associated pollutants could be absorbed by plant species simultaneously. Second, the

Table 1. Phytoremediation of contaminated soils influenced by NMs.

Plants	NMs	Pollutants	Effects	References
Cucurbita pepo, *Zea mays*, *Solanum lycopersicum*, and *Glycine max*	MWCNT and C60	Chlordane and DDx	MWCNT decreased chlordane and DDx accumulation in all the plants; C60 increased chlordane accumulation in *Solanum lycopersicum* and *Glycine max,* and suppressed DDx uptake in *Zea mays* and *Solanum lycopersicum*.	[29]
Cucurbita pepo L., *Glycine max* L., and *Solanum lycopersicum* L.	C60	DDE	C60 increased the root and total plant DDE content in all the plants; C60 increased shoot DDE content of *Cucurbita pepo* L. by 29%, reduced shoot DDE content of *Glycine max* L. by 48%.	[64]
Chlorella vulgaris	CNT	Diuron	CNT increased diuron bioavailability, stronger diuron toxic effect on the photosynthetic activity of *Chlorella vulgaris*.	[67]
Chinese cabbage	Ni/Fe bimetallic nanoparticles	PBDEs	Ni/Fe nanoparticles promoted PBDEs translocation from soils into plants, and decreased PBDEs phytotoxicity with the increased germination rate, plant biomass, and shoot and root lengths.	[65]
Zea mays, *Cucumis sativus*, *Glycine max*, *Brassica oleracea*, and *Daucus carota*	Al_2O_3 nanoparticles	Phenanthrene	Phen successfully loaded on Al_2O_3 nanoparticles; Loaded Phen nanoparticles reduced root elongation inhibition in the plants.	[66]
Wheat	GO	As	GO enhanced As uptake, and amplified As phytotoxicity in wheat by decrease plant biomass and root numbers and increase the oxidative stress.	[68]
Barley	nZVI	As	nZVI reduced As availability and decreased As uptake in barley; nZVI increased plant growth rate and the biomass of plants.	[69]
Soybean	TiO_2 NMs	Cd	TiO_2 NMs increased plant Cd uptake, decreased Cd stress in the plants.	[31]
Wheat	Citrate-coated magnetite nanoparticles	Cd and Cr	Citrate-coated magnetite nanoparticles reduced metal phytoavailability, and alleviated the individual and mixed toxicity of Cd and Cr in the plant.	[71]
Chlamydomonas reinhardtii	TiO_2 NMs	Cd	TiO_2 NMs reduced free Cd ion contents, lowered Cd bioavailability, mitigated Cd-induced growth inhibition.	[70]
Pisum sativum	Silicon NMs	Cr	Silicon NMs improved plant growth, protein, nitrogen, carotenoids and chlorophyl contents, and antioxidative enzymes activities; Silicon NMs decreased Cr accumulation and ROS production in the plants.	[72]
Microcystis aeruginosa	GO	Cd	GO enhanced Cd toxicity with increased ROS production and MDA contents, changed photosynthetic parameters, suppressed plant growth in the plants.	[73]
Rape and Chinese cabbage	CMC-stabilized nZVI	Cr	CMC-stabilized nZVI reduced Cr leachability, bioaccumulation and bioavailability; and suppressed Cr uptake in rape and Chinese cabbage by 61 and 36%.	[74]

phytotoxicity of NMs might damage plant membrane and cell walls, resulting in the loss of membrane integrity and cell function, subsequently facilitating the entrance of contaminants from soils into plants. In addition to considering the impact of pollutant accumulation, mediated plant toxicity by NMs, under contaminated conditions, also deserves attention. For instance, Wu et al. [65] used Ni/Fe bimetallic NMs combined with phytoremediation to remediate polybrominated diphenyl ethers (PBDEs) contaminated soils. Results showed that the phytotoxicity in Ni/Fe NMs and PBDEs treated plants were decreased compared with the plants in the treatment of individual NMs or contaminants in which the increased germination rate and the improved plant biomass were detected, indicating that the combined remediation technique could reduce the toxicities of soil contaminants and NMs in the plants simultaneously. Moreover, Yang et al. [66] investigated the impact of phenanthrene loaded Al_2O_3 NMs on the root elongation of the five plant species. They found that phenanthrene could be immobilized onto the surface of Al_2O_3 NMs, and plants root elongation inhibition was significantly reduced by exposure to 10, 100, or 432.4% phenanthrene-loaded nanoparticles compared to the root treated only with Al_2O_3 nanoparticles. The authors ascribed the mitigation of root growth inhibition to the disappearance of free hydroxyl groups in NMs loading by phenanthrene. The experiment also demonstrated that the combined use of NMs and phytoremediation not only could stabilize pollutants in the environment, but also could alleviate the toxicity of NMs in the plants. In contrast, the aggravated toxicities of NMs to plants in the phytoremediation process also have been notified. For example, Schwab et al. [67] demonstrated that the toxic effects of diuron in *Chlorella vulgaris* were equal to, or stronger in, the exposure of CNTs.

It is worth noting that metal accumulation or toxicity in plants was differentially influenced by various NMs. GO is reported to enhance the uptake of As, a widespread toxic pollutants, in wheat, which was conducive to removal of heavy metals from the environment. The authors attributed the increased accumulation of heavy metals to three possible ways associated with NMs: (i) enhanced permeability of the cell wall, (ii) co-transportation of NMs and heavy metals, and (iii) regulated transporter gene expression, such as As-uptake relevant phosphate transporters gene. Meanwhile, exposure to GO was found to amplify the toxicity of As in the plants. Compared to the application of NMs or heavy metals alone, GO combined with As treatment, significantly reduced the biomass and root numbers of plants, and increased the oxidative stresses in wheat seedlings. The adverse effects were thought to be involved in the inhibited carbohydrates and fatty acid metabolism, enhance secondary and amino acid metabolism, disrupt the urea cycle and the transformation of As(V) to As(III) [68]. The above results indicated that we should balance the increased metal uptake or bioaccumulation against the phytotoxicity of NMs in plants when choosing to use the combination remediation technique of NMs and phytoremediation. Conversely, Gil-Díaz et al. [69] investigated the influence of nZVI treatment on soil recovery of As-polluted soils. The authors found that the application of 10% nZVI significantly reduced the uptake of As in plant shoots and roots, and increased the height and dry weight of barley plants under metal stress. In addition, TiO_2 NMs also were proved to have the capacity to increase metal uptake and to ameliorate metal toxicity in the plants simultaneously. The application of TiO_2 NMs promoted Cd bioaccumulation from the contaminated soils and it restricted Cd toxicity by increasing photosynthesis rate and promoting plant growth in soybean plants [31]. As reported by Yang et al. [70], TiO_2 NMs also could mitigate the growth inhibition of *Chlamydomonas reinhardtii* under Cd stress. It has also been reported that the uptake of magnetite NMs by wheat plants considerately alleviated the toxicity of Cd(II) and Cr(VI) in the plants [71]. In addition, Tripathi et al. [72] investigated the effects of silicon NMs on the Cr phytotoxicity of *Pisum sativum* (L.) seedlings. Results showed that silicon NMs protected plant seedlings against Cr toxicity by reducing Cr accumulation and ROS generation, and increasing antioxidant enzyme activities and mineral nutrients uptake in the plants. The positive effects on plant growth and the ameliorated toxicity effects of NMs are beneficial to the phytoremediation of heavy metals contaminated soils in terms of the enhanced total amounts of metal accumulation and long-term remediation efficiency. However, the antagonistic effects of NMs on plant tolerance to heavy metal stress have been observed, which are adverse to the phytoremediation of contaminated soils. For instance, the combined effects of GO and Cd on plants were studied. The results showed that GO, at low content, enhanced Cd toxicity in *Microcystis aeruginosa* through stimulating ROS generation, negatively influencing photosynthesis, and suppressing plant growth [73]. Likewise, suppression in seed germination, reduced biomass production, yellowing of plant leaves were more obvious in rape and Chinese cabbage cultivated in Cr contaminated soils with the addition of sodium carboxymethyl cellulose (CMC) stabilized nZVI [74]. The aggravated metal toxicities by NMs could be attributed mainly to two points: (i) the nanotoxicity to the plants by NMs themselves, and (ii) the interaction of NMs and metals thus amplifying the toxic effects of metals.

Taking into account present studies, the impact of NMs on the phytoremediation of contaminated soils were NMs categories, plant species, and pollutant types dependent. To date, the combined application of phytoremediation and NMs sheds new light on the remediation of soil pollution. NMs themselves could serve as contaminant carriers that increase the mobilization of the toxic materials or enhance the bioavailability of some hazardous substances, thus promoting the uptake of pollutants by plants. Moreover, it has been reported that exposure of NMs to plants regulated the expression of genes associated with metal stress, water homeostasis, oxidative stress, cell division, photosynthetic pathways, and cell wall formation [75–77], which might be beneficial to the phytoremediation of contaminated soils. However, the amplified phytotoxicity of the contaminants by the addition of NMs has also been certified. Therefore, further investigations should be conducted in order to understand the different effects of NMs on plants under certain contaminated conditions before using the combined technique of phytoremediation and NMs to remove pollutants from the contaminated soil.

Micro-remediation impacted by nanoparticles

Microorganisms associated with applied nanoparticles

Microorganisms are essential components of ecological systems. The wide usage of NMs has led to high likelihood that these substances will inevitably release into soils and interact with soil microorganisms. The effects of NMs on microorganisms will certainly influence the micro-remediation of the contaminated soils. Based on this, the effects of the most commonly used two kinds of NMs, carbon-related NMs (CNMs) and metal NMs (MNMs), on the microorganisms will discussed before using the combined remediation technique of micro-remediation and NMs to deal with soil pollution problems.

Because of the extensive utilization of CNMs, many studies investigated the impact of NMs on microorganisms have focused on CNMs. However, the overall impact of CNMs on soil microorganisms did not reveal a specific consistent pattern. Some studies reported the inconsequential effects of NMs on microorganisms. For example, Tong et al. [78] studied the influence of fullerene on soil microorganism activities. The findings of the study indicated that fullerene had limited effects on soil microbial community function and structure. Microbial biomass in soils amended with GO up to 1 mg g^{-1} was not significantly different from that in control soils during a 59-days soil incubation period [79]. Moreover, the positive biological effects of NMs on microorganisms have been observed. A study conducted by Wang et al. [80], using GO to investigate the effects of NMs on microorganisms, found that the usage of GO at doses of 0.1 g L^{-1} enhanced the activity of anammox bacteria. Ruiz et al. [81] found that the bacteria grew 2 and 3 times better on the filters coated with 25 and 75 μg mL^{-1} GO than on filters without GO. However, extensive studies revealed the negative effects of CNMs on microorganism, especially at high concentrations. For instance, Johansen et al. [82] observed a decreased number of fast-growing bacteria in soil exposure to fullerene. High concentrations of SWCNTs dramatically reduced the microbial biomass carbon and nitrogen levels in soils with the addition of powder or suspended forms of NMs [83]. In addition, absorption of nutrients on the surface of NMs could create a shortage of the required nutrients in the microorganisms, and thus shortage might negatively affect the growth of microorganisms. Furthermore, the toxicity effects of SWCNTs on soil microorganisms were found to be associated with the NMs-regulated carbon and phosphorus biogeochemical cycles [84].

Moreover, several studies also have certified the impact of NMs on microorganisms exposed to MNMs. Dehner et al. [85] demonstrated that ferrihydrite nanoparticles could be used as the bacterial iron sources by *Pseudomonas aeruginosa*, thus promoting microorganism growth. Similarly, the application of nZVI stimulated the growth of Gram-positive bacteria in the soil. The authors ascribed the promotion to the positive correlation between the number of bacteria and the concentration of Fe after the introduction of nZVI [86]. Furthermore, certain studies indicated that apart from the positive effects, the potential undesirable changes of MNMs on microorganisms also need to be noted. A study conducted by Brayner et al. [87] investigated the toxicological impacts of ZnO NMs on *Escherichia coli* Bacteria, and it was noticed that the contact of NMs with bacteria caused Gram-negative triple membrane disorganization and increased membrane permeability of the bacteria. The antibacterial activity of nano-sized silicon dioxide ($nSiO_2$), $nTiO_2$, and nZnO have also been investigated. Growth inhibition of Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli* were observed with the application of the above three NMs. The exhibited antibacterial property of NMs was presumably due to their role in the promotion of ROS generation [88]. Another investigation showed that exposure to CuO and TiO_2 nanoparticles resulted in a decline of soil microbial biomass as indicated by the decreased microbial biomass carbon content and the reduced total phospholipid fatty acid concentration. The authors also found that the adverse effects of CuO nanoparticles were more obvious than that of TiO_2 nanoparticles [89]. However, current researches have not reached consistent conclusions as to the interactions of NMs and microorganisms. Further studies are needed to better illuminate these interactions.

Micro-remediation of contaminated soils affected by NMs

Bioremediation using microorganisms has emerged as a potentially useful alternative technology for the clean-up of contaminated sites [90,91]. Particular attention has been paid to exploring the microorganisms which have the potential ability to restore soil contaminated with heavy metals and organic pollutants. The mechanisms for heavy metal micro-remediation mainly include: metal-binding, extracellular chemical precipitation, valence transformation, volatilization, and so forth [92,93]. A study conducted by Hao et al. [94] found that metal binding of Au^{3+}, Cd^{2+}, CrO_4^{2-}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pd^{2+}, and Zn^{2+} to microbial cells occurred, and the binding reduced the mobility and toxicity of these metals. Besides, Polti et al. [95] studied the bioremediation of Cr(VI) contaminated soils by microorganisms. They found that *Streptomyces* sp. MC1 was able to reduce Cr(VI) to Cr(III) in soil samples, and the latter form is more stable and less toxic than the former form. For metals with volatile states such as Hg, metal volatilization by microorganisms is feasible [96]. As for organic pollutants, they could be degraded by a number of microorganisms or their enzymes. Some specific organic contaminates could be utilized as the sources of carbon, nitrogen, and energy by microorganisms, and, thereby decontaminating the pollutants from soil. For instance, four microorganisms, *Pseudomonas putida* 4CD1, *Pseudomonas nitroreducens* 4CD2, *Rhodotorula glutinis* 4CD4, and *Pseudomonas putida* 4CD3, were isolated from soil planting rice, bamboo or pine in order to remediate the contaminated soil. All the isolated microorganisms degraded *p*-coumaric acid, *p*-hydroxybenzoic acid, ferulic acid, and *p*-hydroxybenzaldehyde effectively by using these phenols as a carbon source [97]. Besides, *Pseudomonas stutzeri* OX1 was found to be capable for tetrachloroethylene degradation. Researchers ascribed this degradation to the expression of toluene-o-xylene monooxygenase induced by *Pseudomonas stutzeri* OX1 since this enzyme led to the aerobic degradation of pollutants in the microorganisms [98].

The potential impact of NMs on microorganisms will affect the micro-remediation efficiency in the remediation of polluted soil (Table 2). A study conducted by Shrestha et al. [99] used MWCNTs to evaluate the impact of NMs on soil microbial community structure and function. Pyrosequencing results confirmed that the application of 10 g kg^{-1} MWCNTs increased the abundance of some bacterial genera like *Cellulomonas*, *Pseudomonas*, *Nocardioides*, and *Rhodococcus* that are considered as potential degraders of recalcitrant pollutants. This study also certified that NMs were capable of creating a shift in soil microbial community composition to microbial species with more tolerant or stronger degradation ability, which were beneficial to the micro-remediation of the contaminated soils. Similarly, the degradation of 2,4-dichlorophenoxyacetic acid in soils by the combined use of Fe_3O_4 nanoparticles in conjunction with soil microorganisms was investigated. Addition of Fe_3O_4 nanoparticles not only simply degraded 2,4-dichlorophenoxyacetic acid but also increased microbial population and enzyme activities (such as amylase, urease, catalase, and acid phosphatase) in the soil, thus leading to higher degradation efficiency of this organic contaminant than the treatment with microorganisms alone [100]. Moreover, Ye et al. [101] studied the impact of iron-based NMs on the biodegradation of phenol by microorganisms. Results showed that the biodegradation of phenol by *Bacillus fusiformis* was accelerated in the presence of nZVI and Ni/Fe NMs. However, the negative impacts of NMs on microorganisms associated with micro-remediation will also affect the fate of organic contaminants in the soil. In a study conducted by Tilston et al. [102], it was noticed that polyacrylic acid (PAA)-coated nZVI addition altered soil bacterial community composition and reduced the activity of chloroaromatic mineralizing microorganisms in aroclor-1242 contaminated soil. Similar population reduction of *Dehalococcoides* was

Table 2. Micro-remediation of contaminated soils affected by nanomaterials.

NMs	Pollutants	Effects	References
Fe_3O_4 nanoparticles	2,4-dichlorophenoxyacetic acid (2,4-D)	Fe_3O_4 nanoparticles combined with soil indigenous microorganisms induced higher 2,4-D degradation efficiency; Fe_3O_4 nanoparticles reduced the half-lives of 2,4-D, and it increased the soil microbial populations and enzyme activity.	[100]
nZVI and Ni/Fe nanoparticles	Phenol	nZVI and Ni/Fe nanoparticles promoted the *Bacillus fusiformis* strain growth and accelerated it biodegradation of phenol.	[101]
PAA-coated nZVI	Aroclor 1242	PAA-coated nZVI changed soil bacterial community composition, reduced chloroaromatic mineralizing microorganisms activity, and inhibited chloroaromatic biodegradation potential.	[102]
SWCNTs and MWCNTs	^{14}C-phenanthrene and ^{14}C-benzo-[a] pyrene	CNTs reduced PAH extractability and mineralization with increasing CNTs concentration; SWCNTs have greater impact on PAHs bioaccessibility than MWCNTs.	[30]
C60, MWCNTs and fullerene soot	Phenanthrene	High contents of MWCNTs and fullerene soot decreased the population of phenanthrene degrading bacteria and reduced phenanthrene catabolic activity; Low contents of NMs had no detrimental effects on pollutant degrading microorganisms.	[104]
MWCNTs	Phenanthrene	Phenanthrene was adsorbed by MWCNTs; MWCNTs decreased phenanthrene biodegradation and mineralization efficiencies.	[105]
CNTs	^{14}C-2,4-DCP	CNTs inhibited ^{14}C-2,4-DCP mineralization and degradation in soil; CNTs limited soil endogenous microorganisms activities, posed potential toxicities to the microorganisms, and reduced ^{14}C-2,4-DCP bioavailability; SWCNTs had a higher effect than MWCNTs on ^{14}C-2,4-DCP biodegradation.	[106]

observed in the presence of 0.1 g L^{-1} nZVI, which bacteria was capable of dechlorinating chlorinated organic contaminants [103]. The above adverse impact of NMs on microorganisms inhibited contaminants' biodegradation potential in the polluted soils. In addition, the impact of NMs on the micro-remediation of contaminated soils varied with NM types and concentration. It was proposed that the extractability and microbial degradation of PAHs was reduced with increasing CNT concentration. SWCNTs showed a greater impact upon PAHs mineralization and extraction compared with MWCNTs [30]. Besides, the application of fullerene and low concentrations of CNTs in the soil had no detrimental effect on microbial activity, whereas the high concentrations of MWCNTs significantly decreased the population of phenanthrene degrading bacteria and reduced the development of catabolic activity of phenanthrene in the soil [104]. When discussing bioremediation, it is worth noting that the absorbed contaminants on NMs will affect their bioavailability by microorganisms. The reduced bioavailability of pollutants negatively affected microbial remediation capacity of the contaminated soils. For example, biodegradation and mineralization of MWCNTs adsorbed phenanthrene by *Agrobacterium* were studied. The results indicated that the adsorption of pollutants by MWCNTs led to a significant decrease in the bioavailability of hydrophobic organic compounds in the environment [105]. Another study, using radioactive labeled 2,4-dichlorophenol (^{14}C-2,4-DCP) as the aim pollutant to determine the mineralization, degradation, and residue distribution of ^{14}C-2,4-DCP in the presence of SWCNTs and MWCNTs, found that SWCNTs at the concentration of 2 g kg^{-1} significantly inhibited the microbial mineralization and degradation of ^{14}C-2,4-DCP in the polluted soil. They ascribed the inhibitory effects to the reduced bioavailability of 2,4-DCP, the potential toxicities of CNTs to the microorganisms and the limited activities of the soil's endogenous microorganisms [106].

Taken together, micro-remediation of contaminated soils will be affected by NMs both positively and adversely (Figure 2). The combined remediation technique using NMs and microorganisms is currently only at its starting point – merely being employed in organic pollutant removal. In addition, studies on the application of this new technology to decontaminate metals or other inorganic pollutants contaminated soils are rare. In order to open new avenues in the combined application of NMs and micro-remediation, further studies are needed to explore the specific causes of the positive effects and to address the adverse impact of NMs in the micro-remediation of different kinds of polluted soils.

Conclusions and perspectives

Nano-remediation using NMs could be applied for the transformation and detoxification of a variety of environmental contaminants from soil. The application of NMs can improve the effectiveness of bioremediation through increasing the uptake and accumulation of pollutants in the plants as well as enhancing the degradation rate of contaminants by microorganisms. However, the negative impact of NMs on organisms will inevitably induce adverse effects on the soil bioremediation process. In order to improve the soil remediation efficiency by utilizing the combined remediation technique of NMs and biotechnology, the interactions between NMs and plants/microorganisms in contaminated soils, the likely fate of NMs themselves, and the potential impact of NMs on environmental pollutants need to be carefully taken into consideration. Further studies are still needed since the application of NMs to facilitate soil bioremediation is only starting to be realized.

Although significant progress has been achieved in the combined application of NMs and biotechnology for pollutant removal, the exact mechanisms have not yet been clearly elucidated. Further research is needed to clarify the mechanisms affecting the accumulation and degradation of pollutants by NMs, the interactions between NMs and the organism, their interactions with pollutants, and how the soil remediation is influenced by the combined application of NMs and biotechnology.

The use of NMs for soil remediation will inevitably lead to the release of NMs and their transformation products into the environment. The potential toxicity and pathology of NMs at the ecosystem level needs to be studied. The usage of NMs with high sorption and transportation capacities to remove pollutants from the soils may also induce groundwater pollution problems. Progress is being made in identifying the factors influencing the fate of NMs in the environment. Theoretical models are being developed to predict NMs risks based on the identified factors with semi- or non-empirical analysis [107]. Risk assessment research related to the combined application of NMs and biotechnology is still lacking. It is clear that additional models on this issue are required to further estimate NMs-induced potential risks to the plants/microorganisms/soils in the presence of contaminants.

Even if NMs are extensively used, large-scale preparation is still costly. There are only a few small scale approaches for NMs preparation, and most of the processes are cumbersome and require expensive reagents and strict preparation conditions. Since the combined

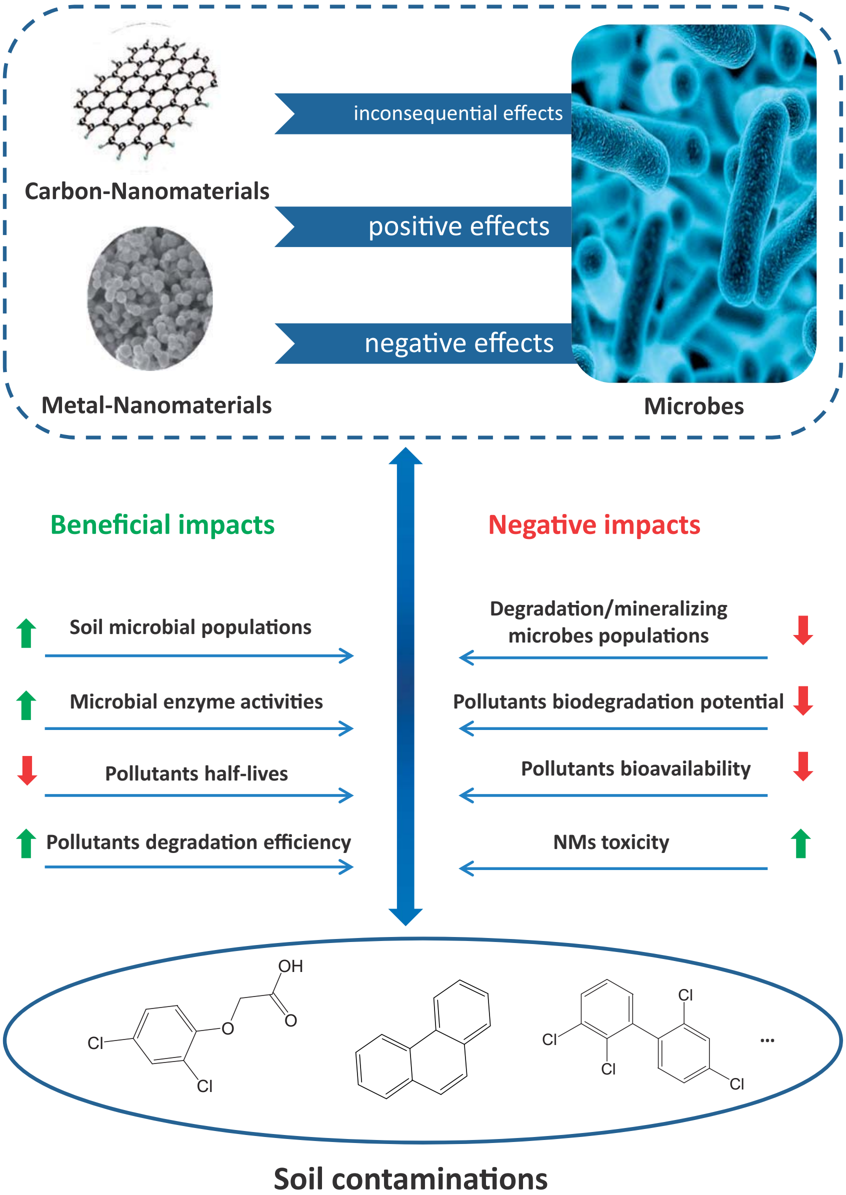

Figure 2. Beneficial and negative impacts of nanomaterials on soil micro-remediation. Green arrows indicate up-regulation. Red arrows indicate down-regulation.

use of NMs and the biotechnology for environmental remediation is quite promising, more work is needed to reduce preparation costs and to explore new preparation methods that will produce NMs with high quality and improved performance. In addition, up to now, majority studies using NMs and the biotechnology to remove pollutants from soil have been conducted only at the laboratory scale. Field applications are needed since the natural environment is quite complex and difficult to imitate. Besides, the combined pollution (e.g. heavy metals and organic pollutants) has caused significant concern. The potential application of NMs and biotechnology to remediate soils contaminated with multiple pollutants also requires further examination.

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