Review on Application of Nanomaterials in Soil Remediation

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Abstract. As to the hot research aspect of soil remediation, this review elaborated the progress in the application of nanomaterials in heavy metals and organics-contaminated soil remediation, and discussed the ecological safety of nanomaterials usage as well. The mechanism of nanomaterial-based soil remediation mainly includes adsorption, complexation, transformation, etc. The activities of nanomaterials could be enhanced by modification methods. Iron based nanoparticles such as zero-valent iron (nZVI), iron oxide and iron sulphide showed promising application prospect but also possible toxicity to soil ecosystem. However, biologically synthesized nanomaterials are more effective and safer, which has been demonstrated in many studies. Therefore, bio-nanomaterials which can not only meet the requirements of soil recovery, but also contribute to soil fertility is urgently needed.

1. Introduction
Different from air pollution and water pollution, soil pollution has the characteristics of concealment and lag, but its harm to the ecological environment and human health can not be ignored. Therefore, the prevention and control of contaminated soil is of great importance to the national economy and people's livelihood. According to the results of the national soil pollution survey in 2014, the situation of soil pollution in China is not optimistic, among which heavy metal pollution is the most serious (82.8% of all the excess points), showing an increasing trend from northwest to southeast [1]. In addition, due to the long-term overuse of pesticides and fertilizers, the problem of soil organic pollution is becoming increasingly severe [2,3]. For example, in an area of northwest China [4], industrial wastewater irrigation causes heavy metal and fluoride pollution in the soil, indirectly causing human health risks. The findings of such studies are varied, and the same problem is also faced abroad [5,6]. In recent years, the state has issued a series of policies, laws and regulations. The promulgation and implementation of the Action Plan for Soil Pollution Prevention and Control and the Soil Pollution Control Act have pushed soil pollution control work to a new historical height. Therefore, the pollution control of heavy metals and organic matters in construction land and agricultural land has become the key work of soil pollution control in China.

Compared with developed countries such as Europe and America, China's soil pollution remediation started late. In 2007, BCEG Environmental Remediation Co., Ltd and BBMG Corporation cooperation was regarded as the beginning of the development of soil remediation industry in China. At present, driven by policy and market, China's soil remediation industry is developing rapidly [7]. Based on the initial methods of soil replacement and covering, more advanced technologies emerge [8].

According to the disposal site, soil remediation technology includes in-situ and ex-situ remediations. According to the principle of soil remediation, soil remediation technology includes physical, chemical, biological and combination methods. Among them, physical methods mainly include vapor extraction [9], thermal desorption [10], etc., mainly targeting volatile organic pollutants such as benzene series, polycyclic aromatic hydrocarbons, polychlorinated biphenyls and dioxins.
Chemical methods mainly include leaching [11], oxidation-reduction [12], etc. Biological methods include phytoremediation [13] and microbial remediation [14]. Among these methods, chemical leaching technology is widely used because of its short repair cycle and low technology difficulty, but the more green and environmentally friendly leaching agent [11] still needs to be broken through.

In addition, the remediation method of transferring heavy metal pollutants from soil to plant body by planting plants is more economical and feasible. For example, crops such as rape and pteris vittata have higher capacity to accumulate heavy metals than other crops, but their heavy metal absorption capacity is still limited. Therefore, in recent years, it has been studied to improve the ability of crops to absorb heavy metals through genetic engineering [13]. In other ways, biochar is a kind of aromatic porous structure material obtained by pyrolysis of biomass under anoxic or anaerobic conditions. It has adsorption effect on heavy metals and organic pollutants in the soil, and can improve soil fertility to a certain extent [15]. In addition, combined application of biomass charcoal with microorganisms could achieve better processing effect [16]. To improve the effect of soil remediation, it is also common to use combination methods, such as the combination of chemical oxidation method and biological method [17].

The above traditional technologies can meet most of the needs of soil remediation [18], but social development has higher expectations for soil remediation.

It is well known that nanomaterials have been widely used in many industries because of their unique physical and chemical properties, such as large surface areas and high surface reactivity. The application of nanomaterials in soil remediation has been promising in recent years [19,20]. Common nanomaterials used in soil remediation include metal-based nanomaterials and carbon-based nanomaterials. The former, such as nano-zero-valent iron, iron oxide, iron sulfide. The latter include graphene and carbon nanotubes. Although these nanomaterials have shown promising application prospects in soil remediation, their potential impact on soil ecology and even human health through the food chain is still controversial [21,22].

In this paper, the application of nanomaterials in soil pollution remediation and the research progress in the toxicology of nanomaterials are reviewed. Future more green, efficient and safe remediation technology of nanomaterials is prospected.

2. Application of Nano Materials in Heavy Metal Contaminated Soil Remediation

In recent years, more and more attention has been paid to the application of nano materials in soil remediation. In the remediation of heavy metal contaminated soil, iron-based nanomaterials are a research hotspot. Nano zero valent iron (nZVI) is widely used because of its excellent specific surface area and high reduction performance. Its first case for soil remediation is to use it as a filling material for permeable reaction wall in groundwater remediation. In practical application, nZVI with different modification and particle size are often used according to the properties of pollutants and soil. At the same time, in order to avoid agglomeration and other phenomena in the use of nano materials, modified nanomaterials are often used. Compared with traditional soil remediation technology, it is more economical and feasible. Maria Chrysochoou et al. [23] reported that the initial concentration of 0.1mg/L of Cr$^{6+}$ in polluted soil can be reduced to 25μg/L by injecting nZVI carried with green tea extract. In the application of nZVI with diatomite as carrier [24], the concentration of free cadmium (Cd) decreased by 30% in both acid and alkaline soils. For lead ions (Pb$^{2+}$) in acid soil, the removal capacity is 64%. In alkaline condition, As(V) is also fixed because of the complexation on the surface of nanomaterials. Cao et al. [25] accelerated the removal of Cd, Pb and Zn from the soil by adding nanometer zero-valent iron to the soil leaching.

In addition to zero-valent iron nanoparticles, iron sulfide nanoparticles are also widely used in soil remediation. Especially, their potential application in in-situ soil remediation. Liu et al. [26] found that compared with limestone alone, limestone loaded iron sulfide nanoparticles produced by iron sulfur reduction bacteria can increase the adsorption capacity of As(V) from 6.64μg/g to 187μg/g. In another study [27], the adsorption capacity of carboxymethyl cellulose modified iron sulfide nanoparticles (CMC-FeS NPs) on Cr$^{6+}$ in groundwater was as high as 1046.1mg/g, and the column experiment results showed that the material could reduce the concentration of Cr$^{6+}$ in polluted soil from 4.58mg/L.
to 46.8-80.7μg/L. In addition, Lin et al. [28] synthesized bio-based iron oxide nanoparticles, which have significant effects on the treatment of cadmium contaminated soil.

It should be noted that there are various mechanisms of action of iron-based nanomaterials on heavy metals in soil, including adsorption, complexation and transformation. Also, to avoid secondary contamination, gravity or magnetic forces are often used to separate iron-based soil remediation agents from the soil.

3. Application of Nano Materials in Organic Contaminated Soil Remediation

The main organic pollutants in soil are organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs) and other persistent organic pollutants (POPs). These substances can be enriched in plants and agricultural products, and therefore transmitted to human body through food chain, endangering human health. Helena I. Gomes et al. [29] used nZVI combined with electric remediation technology to remove 83% of PCBs in alkaline soil, but the effect was slightly worse in acid soil. Chen et al. [30] used nZVI and persulfate to degrade p-nitrochlorobenzene in soil. The results show that the removal rate of pollutants can reach 94.1% by adding nZVI and persulfate two hours later.

Although many experiments have confirmed that nZVI have good effect on soil remediation, most of current nZVI soil remediation materials are synthesized by chemical method, and the residue of which often has a toxic effect on organisms. Therefore, in recent years, there have also been studies on the synthesis of nZVI soil remediation materials by biological methods, which have achieved good results. S. Machado et al. [31] obtained green nZVI by using plant extracts instead of sodium borohydride, and proved that the purification rate of ibuprofen contaminated soil was over 95%, which is far better than that of nZVI synthesized by traditional chemical methods. It can be seen that nanoparticles modified by biological method are not only more environmentally friendly, but also show positive synergistic effect. Similarly, Ritu Singh et al. [32] synthesized bio-based Pd/Fe₀ nanomaterials using bacteria, and found that the removal rate of organochlorine pesticides (γ-HCH) in soil was 1.7-2.1 times higher than that of merely Pd/Fe₀. Wang et al. [33] took the lead in synthesizing g-C₃N₄-carried ferrosferric oxide (Fe₃O₄) nanoparticles by coprecipitation method, and applied it to the remediation of phenanthrene contaminated soil. Under natural photocatalysis, the nano-particles showed good photocatalytic oxidation performance of pollutants, which had no negative effect on the growth of lettuce. Luo et al. [34] also used mesoporous Fe₃O₄/ carboxyl-rich carbon nanomaterials to remediate phenanthrene contaminated soil, which also achieved good results and showed no biological toxicity to lettuce growth. As soil remediation is inevitably accompanied by groundwater remediation, Fatemeh Gholami et al. [35] injected calcium peroxide (CaO₂) nanoparticles into the permeation reaction wall for the removal of phenanthrene in groundwater. When the CaO₂ concentration is 400mg/L, the removal ability is the best. Under appropriate pH condition, the nanoparticles can be used stably for 70 days.

In addition to iron-based nanomaterials, multi-walled carbon nanotubes (MWCNTs) are also used in the remediation of phenanthrene contaminated soil. Song et al. [36] found that MWCNTs could remove phenanthrene and heavy metals from the soil by adsorption, thus reducing the biological toxicity caused by pollutants.

4. Biological Toxicity of Nanomaterials

The research progress in recent years shows that nanomaterials have a good application prospect in soil remediation, which can not only be used for in-situ soil remediation, reducing the interference to the soil environment, but also effectively avoid high energy consumption of traditional soil pollution control equipment. However, the impact of nanomaterials on soil ecological environment and soil biology remains to be clarified, especially those prepared by chemical method. K. V. G. Ravikumar et al. [21] compared the remediation capability and biological toxicity of nZVI to Cr⁶⁺ contaminated soil, which were synthesized by chemical and biological method respectively. The experimental results demonstrate that these two kinds of nZVIs have the same capability to remove Cr⁶⁺, but the nanoparticles synthesized by biological method have less damage to bacteria cell activity and cell membrane. M. Bhuvaneshwari et al. [37] also verified the toxicity of the above two nanoparticles. The
results showed that nZVIs synthesized by chemical method had more significant toxicity to Daphnia. Though microbial experiment, Deepak Kumar et al. [38] found that nZVI have certain toxicity to artemia salina. The order of toxicity is: nZVI (chemical synthesis) > nZVI (biological synthesis) > Fe²⁺.

In addition to nZVI, the toxicity of iron oxide nanoparticles, another widely used iron-based nanomaterial, has also been investigated. Zhu et al. [39] used early life stage zebrafish to evaluate the effect of iron oxide nanoparticles on embryonic development, and found that when the concentration of nanoparticles was greater than 10mg/L, different degrees of damage could be caused to embryonic development, such as death, incubation delay and malformation. In view of iron oxide nanoparticles, Ahamed M A A et al. [40] found that iron oxide nanoparticles can cause oxidative stress response of human epithelial cells (A431) and lung epithelial cells (A549).

In addition to iron-based nanomaterials, there are also studies on the biological toxicity of carbon-based nanomaterials such as nanotubes. Rosadele Cicchetti et al. [41] found through human oral cytotoxicity tests that the single-walled carbon nanotubes they used had genotoxicity and can seriously affect cell proliferation and even cause cell death when the nanotubes concentration was high. Jia et al. [22] studied the toxicity of multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs) and fullerenes, and found that the order of toxicity was SWCNTs > MWCNTs > fullerenes.

Many biological toxicity experiments had showed that it is necessary to understand the adverse effects of nanoparticles on ecological environment although they have good soil remediation ability. Furthermore, when choosing nanomaterials as soil remediation agents, it is crucial to use environmentally friendly nanomaterials to effectively management environment and avoid secondary pollution.

5. Summary and Outlook
Soil quality is related to national economy and people's livelihood, and soil pollution prevention is imperative. At the same time, soil pollution remediation is a large-scale systematic project and no single technique can be applied to all soil types. It not only needs to consider the removal of pollutants, but also needs to consider the long-term impact of pollution remediation process on environment, especially on farmland soil, which is closely related to human food safety. Therefore, when choosing nanomaterials as remediation agents for soil and even groundwater, appropriate synthesis methods and control means should be selected to ensure their good activity and stability, as well as their low toxicity and environmental friendliness. For example, biological materials can be used as carriers of nanomaterials, or nanomaterials can be synthesized in vivo by organisms such as bacteria. Furthermore, innovative remediation materials that are low-cost, environment-friendly, and can simultaneously increase soil fertility and improve soil quality, will be of great promise in the future.

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