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Nanoparticles in Soil Remediation: Challenges and Opportunities

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ABSTRACT: Nanoremediation emerges as a promising technology for mitigating soil contamination, encompassing various nanotechnology applications, including chemical degradation, Fenton-type oxidation, photocatalytic degradation, immobilization, and integration with bioremediation techniques like phytoremediation. In addressing soil pollution, the most extensively researched nanomaterials (NMs) are based on carbon, metal and metal oxide, nZVI, and other nanocomposites. Nevertheless, limitations accompany the use of NMs in soil remediation. To assess whether nanotechnology applications outweigh environmental threats, it is crucial to investigate potential effects of NMs on terrestrial vegetation, soil organisms, and human well-being. The impacts of NMs on ecology and the soil environment must be taken into consideration when formulating remediation strategies. Future directions for applied and fundamental studies could include developing multifaceted nanocomposites, integrating them with technologies like bioremediation. Additionally, exploring real-time control and monitoring of NMs and their efficacy in removing pollutants is worth consideration. Pursuing these avenues is vital for advancing the field of soil remediation and comprehending the impact of nanotechnology on the environment.

KEYWORDS: Soil remediation; nanotechnologies; heavy metals; nanomaterials

1. Introduction

The paramount challenge confronting humanity today is environmental degradation. Ongoing research into breakthrough technology remains pivotal for reducing toxins in the air, water, and soil [1]. A myriad of pollutants, encompassing heavy metals, pesticides, herbicides, fertilizers, and various organic compounds (such as volatile organic compounds, chlorinated organic compounds, organophosphorus compounds, and polycyclic aromatic hydrocarbons), as well as oil spills and poisonous gases, necessitate immediate attention [2]. Diverse materials can be employed to remediate the environment, offering a range of techniques to address this urgent issue. Among various remediation methods, current endeavors to enhance the identification and purification of contaminants primarily rely on nanotechnologies [3]. This innovative approach holds the potential to advance new environmental clean-up technologies.

Nanotechnology has garnered increased interest in recent decades due to the distinctive material characteristics at the nanoscale. Involving the study and manipulation of matter at the nanoscale, typically ranging from 1 to 100 nanometers, nanotechnology exhibits unique characteristics, including small particle size and high surface area, enabling a broad range of potential applications. Nanoscale materials, possessing higher surface-to-volume ratios, are more effective and reactive than their larger counterparts. These nanomaterials (NMs) can feature specialized surface chemistry, facilitating the attachment of functional groups to target specific molecules and contaminants, thereby enhancing remediation efficiency [4]. Additional characteristics, such as size, shape, chemical composition, and porosity, contribute to the improved performance of NMs in pollutant remediation. The versatility of surface modification chemistry and the ability to adjust the physical properties of nanoparticles offer significant advantages over conventional techniques, allowing the blending of multiple materials to form hybrids or composites that are more effective, stable, and selective [5].

Nanotechnology finds widespread use in pollution remediation across air, water, and soil [1]. NMs, including organic nanoparticles (NP), inorganic NP, and polymer-based NP, are commonly employed in pollution mitigation measures such as filtration, chemical reaction, photocatalysis, adsorption, and absorption. Studies have indicated that incorporating nanotechnology into disinfection processes successfully controls bacterial activities, thereby mitigating their environmental impacts [6,7]. Researchers such as Alizadeh Fard et al. [8], Bessa da Silva et al. [9], and Gu et al. [10] have explored the effectiveness of using titanium dioxide NP for polycyclic aromatic hydrocarbons (PAHs), nutrient remediation to prevent eutrophication, and the degradation of phenanthrene via photocatalysis in soil, respectively. Another study focused on using titanium oxide and silver-doped titanium oxide to degrade organic composites in wastewater [11]. Polymer-based NP have been investigated for treating soil contaminated with PAHs [12], and iron oxide NP coated with polyvinylpyrrolidone (PVP) have been studied to enhance the bioremediation of metals [13].

2. Pollutants

2.1. Inorganic pollutants.

Inorganic contaminants encompass inorganic salts, radioactive elements, and heavy metals. Unlike organic contaminants, heavy metals present in the soil cannot undergo biodegradation. Instead, they will either persist in the ground or migrate towards aquifers [14]. Heavy metals are elements with atomic numbers greater than 20, and due to their indestructible and hazardous effects on living organisms, elevated concentrations can pose environmental hazards. These metals have the potential to bioaccumulate, posing a threat to human health when entering the food chain. Anthropogenic sources, prevalent in both urban and rural areas, release metals into the environment, primarily absorbed by the soil. Table 1 illustrates the origins and impacts of various heavy metals.

Two primary contributors to the occurrence of heavy metals are natural processes and human activities. Anthropogenic sources, such as paints, electroplating, semiconductors, batteries, smelting, sewage, mining, herbicides, pesticides, fertilizers, and aerosols [20], contribute significantly to heavy metal presence in nature. In natural processes, weathering and pedogenesis are the primary mechanisms responsible for heavy metal generation. Chemical weathering can dissolve mineral ores like cerussite, galena, arsenopyrite, and cassiterite, releasing heavy metals from their structures [21].

Table 1. Sources and impacts of heavy metals.

Heavy Metals	Sources	Impacts	References
As	Paint, cosmetics, herbicides, fungicides, antispasmodics, caustics, antipyretics, and insecticides.	Changes in adult neurogenesis, hippocampal function, glutamatergic, cholinergic, and monoaminergic signalling, glucocorticoid and hypothalamus-pituitary-adrenal (HPA) pathway signalling, along with an increase in Alzheimer's-associated diseases.	[15]
Cd	Agricultural and industrial sources	Cancer, osteoporosis, liver and kidney diseases, and mitochondria damage.	[16]
Cr	Chemical manufacturing, industrial evaporative cooling tower, combustion of coal and oil	Death, genotoxic effects, neurological impacts, immunological and lymphoreticular effects, systemic effects, and reproductive effects.	[16]
Ni	Productions of nickel alloys, volcanic emissions, coal combustion, waste incineration	Asthma, carcinogenic risk, conjunctivitis, contact dermatitis, dermal effect, inflammatory reactions,	[17]
Pb	Melting ores, pesticides, fertilizer, gasoline addictive, urban soil waste	Myelin loss, neuron reduction, impaired reproductive system, high blood pressure, heart disease, and nephropathy.	[18]
Zn	Construction, apparatus housings, HVAC conduits, galvanizing iron and steel	Oxidative stress, immunological responses, cell cycle progression, homeostasis, DNA replication, DNA damage repair, and apoptosis.	[19]

The primary factor influencing the mobility and availability of heavy metals in soil is their chemical composition. Typically, the pH levels constitute the most critical chemical property of the soil, determining the mobility of heavy metals and exerting a significant influence on metal speciation at the soil-solution interface. Under alkaline conditions, all heavy metals exhibit minimal mobility and higher sorption in the soil [22]. In an alkaline environment, functional groups in organic matter can separate, enhancing the bioavailability of heavy metals associated with organic matter. This, in turn, affects the amount of metal in the soil that can be absorbed by food chains [23]. Orhue and Frank [24] asserted that organic matter in the soil acts as a constraint on the mobility and transport of heavy metals. However, studies have also demonstrated that soil containing organic matter promotes the mobility and movement of heavy metals [25]. The mobility of heavy metals is also influenced by ionic strength, redox reactions, temperature, and the nature of the soil [26,27].

In addition to technological and financial constraints, decontamination is a complex undertaking. Heavy metals can only be chemically transformed into an insoluble state; they cannot be chemically broken down [28]. Recent material evaluations of heavy metals have highlighted their bioavailability and mobility in soil, solid, and aquatic environments. Effective and commercially viable solutions must be implemented promptly to mitigate the toxic implications of heavy metals on human health and the environment.

2.2. Persistent organic pollutants.

Persistent Organic Pollutants, or POPs, are highly detrimental compounds resistant to degradation. Examples of POPs include polychlorinated dibenzo-p-dioxins, dibenzofurans, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons (PAHs). Despite their harmful nature, significant volumes of PAHs are released into the environment, primarily originating from industrial activities [29]. These environmental contaminants, including PAHs, have adverse effects on soil quality. PAHs, classified as organic compounds with a benzene ring core, are toxic, mutagenic, and carcinogenic to plants, animals, and humans [30]. The absorption of PAHs by plants contributes to the pollution of the food chain, while the downward migration of these contaminants may lead to groundwater contamination, posing severe risks to the environment and human health [31].

Anthropogenic and natural activities contribute to PAH contamination, such as crude oil spillage or leakage [32], thermal power generation plants [33], incomplete combustion [34], forest fires, and volcanic activities [35]. Additionally, the wear of tires and vehicle emissions serve as sources of PAHs in urban areas [36]. The vapor and particle phases of PAHs released into the atmosphere can spread and deposit on the soil. Due to their high octanol-air fraction coefficient, PAHs firmly adsorb to soil organic carbon and are challenging to disperse, making soil a significant sink for PAHs [35].

PAHs in soil undergo bioaccumulation, volatilization, and degradation. The concern over the absorption of PAHs by organisms is heightened by their accumulation in the food chain due to their adverse characteristics. Numerous studies indicate the presence of PAHs in plants [33,38,39] and animals [40-43]. PAHs with lower molecular weights are predominantly volatilized into the atmosphere due to high liquid solubility and low vapor pressure in the liquid phase. In soil and aquatic environments, PAHs undergo chemical oxidation degradation [37].

3. Applications

3.1. Immobilization.

Immobilization also known as the adsorption process is widely used in most remediation applications to remove pollutants, attributing to its ecologically friendly, cost-effective, and most importantly, excellent efficiency [44]. Various NPs additives have been used extensively to immobilise both inorganic and organic contaminants within the soil. These include carbon-based NMs (carbon nanotubes, fullerenes, graphene), metal oxide NMs (Ag, TiO_2, mixed oxide materials), and nanocomposites. While carbon-based nanoparticles adsorb organic pollutants through molecular bonding, metal oxide nanoparticles and other nanocomposites immobilize organic molecules and heavy metals through surface complexation [45]. Due to their high adsorption capabilities and surface hydrophobicity, carbon-based NPs are frequently utilized as adsorbents for removing organic pollutants in water and soils [46]. Carbon nanotubes particularly, are becoming more prevalent in soil remediation applications due to their high affinity for organic molecules, which frequently outweighs that of soil particles [47].

The iron (III) oxide (Fe_3O_4) NPs have been thoroughly investigated and have great potential to absorb different contaminants from the soil environment. Sebastian et al. [48] have reported that heavy metals like Cd and As can be effectively absorbed and immobilised by Fe_3O_4. However, in the absence of surface modification with stabilising agents like starch or carboxymethyl cellulose, Fe_3O_4 particles tend to agglomerate and trapped among soil particles [49]. Overall, this application aligns with Sustainable Development Goal 15: Life on Land, which emphasizes the need to protect, restore, and promote sustainable use of terrestrial ecosystems, including addressing land degradation and combating desertification. The understanding and management of heavy metals in soil contribute to the broader goal of ensuring the health and sustainability of land-based ecosystems.

3.2. Photocatalytic degradation.

Photocatalytic degradation process involves the use of nano-photocatalysts exposed to sunshine as well as UV radiation. It has been widely used to break down organic pollutants. Ex-situ methods typically involve washing contaminants from the soil using nonpolar solvents, followed by treating the leached water with photocatalysts to eliminate harmful substances [50]. Introducing NMs into photocatalysis enhances the efficacy of the conventional photocatalysis process, by which the time-consuming of the conventional photocatalysis process is solved [51]. This context is in line with SDG 6: Clean Water and Sanitation in terms of environmental sustainability and water resource management. An in-situ approach, on the other hand, entails directly introducing nano-photocatalysts into the polluted soils and irradiating them with sunlight. But it has severe limitations because of the weak light penetration into the soil and requires constant land plowing [10,52].

Generally, soil characteristics, pH levels and organic matter content are the factors that impact the effectiveness of photocatalysis. According to Wang et al. [53], these variables significantly influence the generation of hydroxyl radicals (OH·) by nanomaterials, along with the competing sorption of pollutants over particles of soil.

3.3. Fenton-like reaction.

Fenton reagents, which include hydrogen peroxide and ferrous iron are often used to treat organic wastewater. These reagents achieve decontamination by oxidizing organic molecules with OH· produced from H_2O_2. In this process, ferrous ions function as catalysts [54]. The investigations using Fenton reagents in soil have been conducted more often recently [55]. For subsurface Fenton-like oxidation processes, a variety of materials have been used as catalysts and the most well-known and extensively researched are the iron NMs; Fe_3O_4 and iron-containing nanocomposites [56]. Due to its abundance in the environment, affordability, ease of synthesis, possibility for reuse, and eco-friendly properties in the soil matrix, iron oxide, and in particular Fe_3O_4, is outstanding for in-situ remediation of polluted soil [56].

Fe_3O_4-catalyzed Fenton-like reactions, for example, have demonstrated the capability to remediate soils polluted with PAHs without producing hazardous byproducts and requiring pH adjustment [55]. In the PAHs degradation, the efficiency of Fenton-like reactions is directly related to the concentration of PAHs and the components of organic matter and minerals present in the soil matrix. Installing a pretreatment phase containing availability-enhancement compounds, such as cyclodextrin, ethanol, or nitrilotriacetic acid, can effectively increase treatment efficiency. However, Fenton-like reactions with Fe_3O_4 as the catalyst could have a sluggish reaction rate. To ensure an even dispersion of solid catalysts inside the soil and enhance the overall efficiency of degradation, it is necessary to supplement this method with other technologies, such as sonication. The sonication can aid in catalyst surface cleaning, ensuring the catalysts sustain their high reactivity and efficiency throughout the processes [54].

The application of Fenton reagents, encompassing hydrogen peroxide and ferrous iron, in the treatment of organic wastewater and soil remediation aligns with several Sustainable Development Goals (SDGs). Primarily, it contributes to SDG 6: Clean Water and Sanitation by addressing the decontamination of organic wastewater. Moreover, the efficiency of Fenton-like reactions in degrading pollutants in soil ties into the broader goals of SDG 15: Life on Land.

3.4. Chemical Reaction.

Reduction processes on NMs zero-valent iron (nZVI) have proven the accomplishment in mitigating organic compounds and heavy metals, particularly Cr (VI) in polluted soil [57]. nZVI, as an effective reduction agent, converts Cr (VI) into Cr (III) and produces complex precipitates like ferrous chromite ($FeCr_2O_4$) [58]. Furthermore, by combining nZVI with compost or biochar can enhance the removal rate of Cr (VI) and reaction activity of nZVI, ascribing to inhibiting particle aggregation, which increasing iron particle dispersion and reduction of soil mixture mobility [59].

Additionally, it was found that CMC-stabilized nZVI reduced the leachability and bioavailability of Cr in soil environments through the conversion of the bulk of exchangeable Cr into states linked to carbonate and Fe-Mn oxide [60]. By adding stabilized nZVI, organic contaminants (tetrabromobisphenol A, trichloroethylene) and pesticides (2,4-dichlorophenoxyacetic acid, dichlorodiphenyltrichloroethane) have been successfully eliminated from soils [61]. According to Zhang et al. [62], one of the factors affecting stabilized nZVI is the amount of soil organic matter, suggesting that the removal rate of organic contaminants increases as the concentration of soil organic matter decreases. Besides, the soil pH levels and the nZVI characteristics, including its reactivity, size of particle, and suspension stability, are essential variables that can affect the efficacy of nZVI. This approach has aligned with SDG 15, which referring to Life on Land.

3.5. Combined Techniques.

The establishment and production of multifunctional NMs may target several and mixed pollutants at once. These technologies show enhanced selectivity for contaminants amongst complicated matrix components, is a breakthrough in environmental remediation. The interactive activity of these NMs in degradation processes and adsorption, concentrating and exposing pollutants to a higher concentrated reactant, thereby increasing the removal efficacy. Furthermore, it has been suggested that novel nanocomposites can enhance removal stability under complex environmental circumstances and achieve the one-step removal of both organic and inorganic contaminants [63].

4. Pros and Cons of Nanotechnology

The increasing number of NMs were intentionally released into the environment due to the growing usage of soil remediation, which might pose unexpected dangers to human health, the ecosystem, and the soil environment, regardless of their effects on soil remediation.

4.1. Advantages.

Under specific conditions, nanomaterials (NMs) can optimize the efficient utilization of nutrients and pesticides, stimulate seed germination and plant growth, and mitigate adverse effects on farmland [64]. Various types of NMs, such as those based on metals, metal oxides, cellulose, and carbon, have been demonstrated to enhance crop yields. This achievement is attributed to their role as carriers or platforms for delivering nutrients effectively through seeds, roots, and leaves [65]. Elmer and White [66] investigated the impact of soil amendments using metal oxide-based NMs on tomato and eggplant development. Intriguingly, even in the presence of harmful pathogens, the regular application of copper oxide to leaves promoted plant development and yields. In other studies, cowpeas exposed to copper nanoparticles demonstrated improved bioavailability and absorption of copper nutrients, subsequently enhancing the activity of enzymes in both root and leaf tissues [67].

On the other hand, the integration of nanotechnology with plants has enhanced the efficiency of soil contaminant removal. Pesticide-contaminated soil, for instance, has been remediated by combining nanoscale zero-valent iron (nZVI) with specific plants, achieving pesticide elimination rates that may exceed 80% within the first week of treatment [68]. Additionally, the buildup of cadmium in the roots and buds of plants correlates with the concentration of titanium dioxide nanoparticles (TiO_2 NPs) in the soil. Furthermore, increasing the growth rates and photosynthetic activity of plants has been shown to reduce the toxicity of cadmium in soil using TiO2 NPs [69].

4.2. Disadvantages.

NMs can be advantageous to soil organisms when present and released under certain conditions. However, when their concentration surpasses acceptable thresholds and exceeds the beneficial range, nanoparticles can become harmful to microorganisms, terrestrial plants, and the soil ecosystem. The literature has examined the detrimental effects of NMs on plants in great detail. The findings indicated that NMs inhibited several plant life stages, involving root, shoot, and seedling growth, ability to photosynthesis, reproduction, and yield attributes [70]. The absorption of NMs into plant cells is a crucial consideration of the remediation actions. Lin et al. [71] investigated the paths of carbon-based nanomaterials in plant tissues and cells. In their findings, has showed improvement with the assistance of natural organic matter. Moreover, metal and metal oxide nanomaterials can also detrimentally affect terrestrial plants. Copper NPs, for instance, have been discovered to hinder wheat roots to growth nearly 60% and accelerate lateral roots development, attributing to the introduction of oxidative stress [70]. According to Jośko et al. [72], particle size, solubility, bioaccessibility, as well as the dosage and duration of the test, along with the physicochemical properties of the plants under study, are all closely related to the harmful effects of NMs on organisms.

NMs have the potential to endanger not just terrestrial plants but also microbes and animals found in the soil. According to Asadishad et al. [73], genotoxicity on microbial cells, suppression of soil enzyme activity, and alterations in the structural composition of microbial communities are some of the possible risks that NMs pose to soil microorganisms. Ge et al. [74] reported that the detrimental impacts of titanium dioxide and zinc oxide NPs on soil microbiota indicates NMs diminished microbial abundance as well as microbial biomass. The risks to the site workers, which exposing to NMs for longer time period in a variety of exposure situations need to be seriously considered. By consumption, breathing, or contact with the skin, human exposure can have negative direct or indirect health impacts [75]. NMs can cause illnesses, cellular and genetic impacts, organ damage, or biochemical alterations once they enter the body through the blood circulation system [76].

The existing methods for swiftly identifying and tracking nanoparticles in environments exhibit deficiencies in both efficiency and accuracy. This highlights the pressing need to devise analytical tools that are both effective and capable of elucidating the mechanisms and distribution of injected nanoparticles in soil, sediments, and water, accounting for diverse environmental variables [77]. An alternative approach involves utilizing biomarkers within a biological monitoring instrument for tracking nanoparticles in environmental systems.

Additionally, a solution involves designing permeable iron barriers (PIBs) for shallow aquifers with the aim of capturing nanoscale zero-valent iron (nZVI) for post-remediation [76]. These barriers, utilizing granular iron or zero-valent metals for contaminant reduction, can be configured as single or multiple units. They can be installed permanently, semi-permanently, or as interchangeable barriers in the flow pathway of the polluted source. This allows for the reduction of contamination through both immobilization and transformation mechanisms. This process facilitates the real-time monitoring of nZVI levels post-decontamination. Nanoparticles trapped in barriers can be subsequently removed from water bodies to prevent their further spread into deeper water aquifers.

In a recent development, a geophysical method incorporating an intricate electric conductivity visualization system has been utilized to track the high-pressure injection of microscale zero-valent iron (mZVI) into groundwater [78]. Although preliminary results show promise, additional research is deemed necessary. An additional strategy for synthesizing more advanced engineered nanomaterials for environmental remediation involves utilizing advanced NMs with novel coatings or functional groups.

5. Conclusions

This overview emphasizes developments and risk assessment, providing a comprehensive evaluation of the current state of nanomaterials (NMs) in soil remediation. Applications of nanotechnology encompass various processes, including chemical degradation, Fenton-type oxidation, photocatalytic degradation, immobilization, and integration with bioremediation techniques. Carbon-based nanomaterials, metal and metal oxide-based nanomaterials, and nZVI have demonstrated high effectiveness in reducing soil contamination.

However, the use of NMs in soil comes with associated risks. To determine whether the benefits of nanotechnology applications outweigh potential environmental hazards, it is crucial to investigate their potential effects on terrestrial plants, soil organisms, and human health. The impact of NMs on the soil environment and ecosystem must be considered when selecting remediation technologies. To further advance the field of soil remediation and gain a comprehensive understanding of the effects of nanotechnology in environmental applications, future research should focus on developing multifunctional nanocomposites and integrating them with other technologies. Additionally, the implementation of real-time monitoring and control of applied NMs and their efficacy in pollutant removal is essential. These directions are critical for advancing the field of soil remediation and comprehending the implications of nanotechnology in environmental applications.

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Competing Interest

The authors declare no conflicts of interest related to this study.

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