

Review Article

Nanomaterials for Sustainable Soil Remediation and Contaminant Immobilization

Abstract

Soil contamination poses a significant threat to the environment and human health, necessitating effective and sustainable remediation strategies. Nanomaterials have emerged as promising agents for soil remediation due to their unique properties, such as high surface area, reactivity, and adsorption capacity. This review explores the application of various nanomaterials, including iron-based nanoparticles, carbon nanotubes, graphene, and metal oxide nanoparticles, in the remediation of contaminated soils. The mechanisms of contaminant immobilization, such as adsorption, reduction, and degradation, are discussed in detail. The article also highlights the potential environmental risks associated with the use of nanomaterials and the need for responsible application and monitoring. Furthermore, the review examines the integration of nanomaterials with other remediation techniques, such as bioremediation and phytoremediation, to enhance the overall efficiency and sustainability of the remediation process. The challenges and future perspectives in the field of nanomaterial-based soil remediation are also addressed. This comprehensive review provides valuable insights into the application of nanomaterials for sustainable soil remediation and contaminant immobilization, emphasizing the need for further research to optimize their performance and minimize potential risks.

Keywords: Nanomaterials, Soil remediation, Contaminant immobilization, Sustainable remediation, Environmental nanotechnology

1. Introduction

Soil contamination has become a global concern due to the increasing anthropogenic activities, such as industrial processes, agricultural practices, and improper waste disposal [1]. The presence of contaminants in soil, including heavy metals, organic pollutants, and pesticides, poses significant risks to the environment and human health; Secondary pollution refers to the unintended consequences or byproducts of remediation processes that can lead to further environmental contamination. For example, when contaminated soil is excavated and transported to landfills, there is a risk of the contaminants leaching into groundwater or being released into the air during transportation. Similarly, chemical treatments used to remediate soil can sometimes introduce new pollutants or mobilize existing contaminants, leading to their spread to previously uncontaminated

areas. These secondary pollution issues highlight the need for careful consideration and planning when implementing soil remediation strategies to ensure that the remediation process itself does not exacerbate environmental problems. [2]. Conventional soil remediation techniques, such as excavation and landfilling, are often costly, time-consuming, and may lead to secondary pollution [3]. Therefore, there is an urgent need for sustainable and efficient remediation strategies to address soil contamination.

Nanotechnology has emerged as a promising approach for soil remediation, offering unique advantages over traditional methods [4]. Nanomaterials, defined as materials with at least one dimension in the nanoscale range (1-100 nm), exhibit extraordinary properties, such as high surface area, reactivity, and adsorption capacity [5]. These properties make nanomaterials excellent candidates for the immobilization and degradation of contaminants in soil [6].

Nanotechnology, particularly the use of nanomaterials, is considered a sustainable approach for soil remediation due to several factors:

1. **High efficiency:** The unique properties of nanomaterials, such as high surface area and reactivity, enable them to effectively adsorb, immobilize, or degrade contaminants in soil more efficiently than conventional methods. This means that a smaller amount of nanomaterials can treat a larger volume of contaminated soil, reducing the overall environmental footprint of the remediation process.
2. **In-situ application:** Nanomaterials can be applied directly to the contaminated soil, allowing for in-situ remediation. This eliminates the need for excavation and transportation of contaminated soil, which are energy-intensive processes that can lead to secondary pollution. In-situ remediation using nanomaterials minimizes the disturbance to the environment and reduces greenhouse gas emissions associated with soil transportation.
3. **Reduced use of chemicals:** Nanomaterials can often achieve soil remediation without the need for large quantities of chemicals, which are commonly used in traditional remediation methods. By minimizing the use of chemicals, nanotechnology reduces the risk of introducing new pollutants into the environment and helps maintain soil quality.
4. **Potential for regeneration and reuse:** Some nanomaterials, such as those based on magnetic properties, can be easily separated from the soil after remediation. This allows for the regeneration and reuse of the nanomaterials, further enhancing the sustainability of the approach by minimizing waste generation and conserving resources.

2. Types of Nanomaterials for Soil Remediation

2.1. Iron-based Nanoparticles

Iron-based nanoparticles, particularly zero-valent iron (nZVI), have gained significant attention in soil remediation due to their high reactivity and adsorption capacity [7]. nZVI particles can effectively reduce and immobilize a wide range of contaminants, including chlorinated organic compounds, heavy metals, and radionuclides [8]. The small size and high surface area of nZVI particles enhance their reactivity and mobility in soil, allowing for in situ remediation [9].

Table 1. Properties and applications of iron-based nanoparticles in soil remediation

Nanoparticle	Size (nm)	Surface Area (m ² /g)	Contaminants Targeted
nZVI	10-100	20-40	Chlorinated organics
FeO	20-50	50-100	Heavy metals
Fe/Pd	10-30	30-60	PCBs, TCE

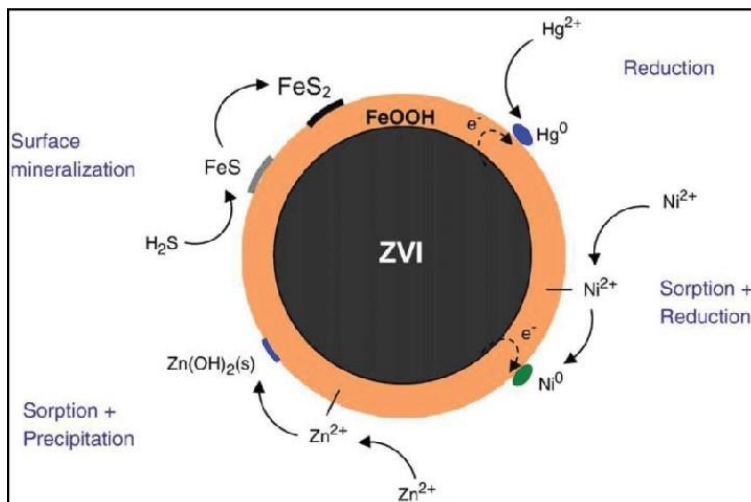


Figure 1. Schematic representation of the remediation mechanism of nZVI particles in contaminated soil.

2.2. Carbon-based Nanomaterials

Carbon-based nanomaterials, such as carbon nanotubes (CNTs) and graphene, have gained attention for their exceptional adsorption capacity and high surface area [10]. CNTs possess a hollow tubular structure with a large specific surface area, making them effective adsorbents for various contaminants, including organic pollutants and heavy metals [11]. Graphene, a two-dimensional carbon nanomaterial, exhibits excellent adsorption properties due to its large surface area and π - π interactions with aromatic contaminants [12].

Table 2. Adsorption capacities of carbon-based nanomaterials for various contaminants

Nanomaterial Contaminant Adsorption Capacity (mg/g)

CNTs	Lead (Pb)	100-200
CNTs	Phenanthrene	50-100
Graphene	Cadmium (Cd)	200-300
Graphene	Naphthalene	80-120

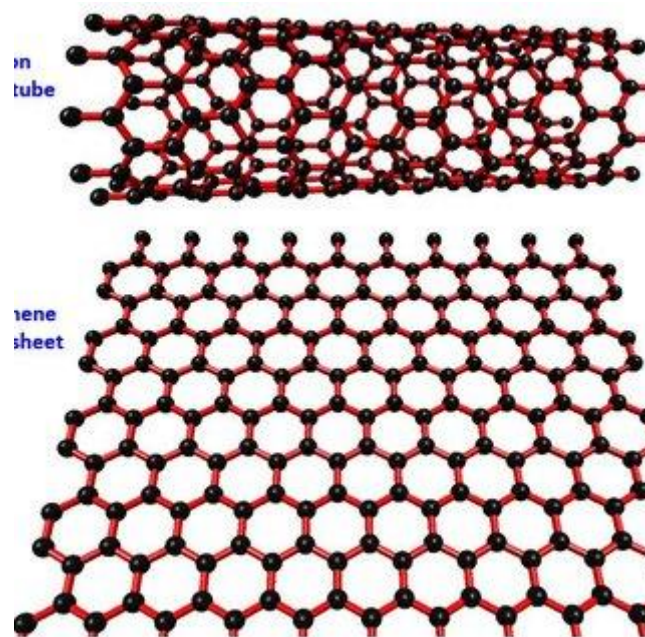


Figure 2. TEM images of (a) carbon nanotubes and (b) graphene nanosheets.

2.3. Metal Oxide Nanoparticles

Metal oxide nanoparticles, such as titanium dioxide (TiO₂), zinc oxide (ZnO), and manganese oxide (MnO), have been investigated for their potential in soil remediation [13]. These nanoparticles exhibit photocatalytic properties, enabling the degradation of organic contaminants upon exposure to light [14]. Additionally, metal oxide nanoparticles can adsorb and immobilize heavy metals through surface complexation and ion exchange mechanisms [15].

Table 3. Photocatalytic degradation efficiencies of metal oxide nanoparticles for organic contaminants

Nanoparticle	Contaminant	Degradation Efficiency (%)
TiO	Methylene blue	80-90
ZnO	Rhodamine B	70-80
MnO	Phenol	60-70

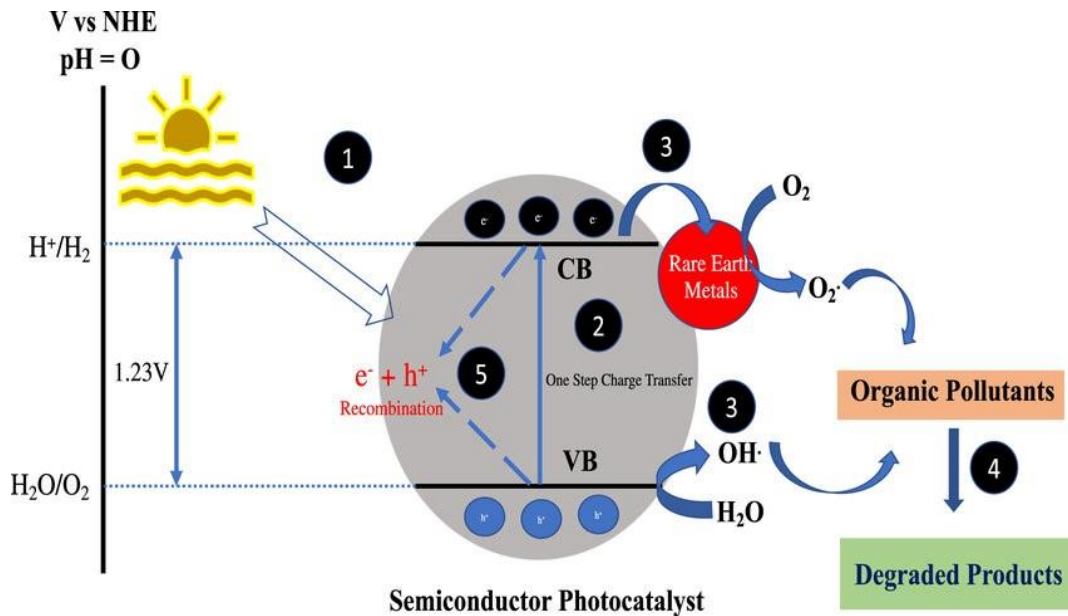


Figure 3. Schematic representation of the photocatalytic degradation mechanism of organic contaminants by metal oxide nanoparticles.

3. Synthesis and Characterization of Nanomaterials

3.1. Synthesis Methods

Various synthesis methods have been employed to produce nanomaterials for soil remediation, including chemical reduction, sol-gel, hydrothermal, and green synthesis [16]. Chemical reduction is a common method for synthesizing metal nanoparticles, such as nZVI, where a reducing agent is used to convert metal ions into their elemental form [17]. Sol-gel and hydrothermal methods are widely used for the synthesis of metal oxide nanoparticles, allowing for the control of particle size and morphology [18]. Green synthesis methods, which utilize plant extracts or microorganisms as reducing and stabilizing agents, have gained attention due to their eco-friendly nature and cost-effectiveness [19].

The cost-effectiveness of green synthesis methods for producing nanomaterials is indeed a significant factor that contributes to their sustainability and potential for widespread use in soil remediation applications.

1. **Lower production costs:** Green synthesis methods often utilize readily available, inexpensive, and renewable resources, such as plant extracts or microorganisms, as reducing and stabilizing agents. This reduces the overall cost of nanomaterial production compared to traditional chemical synthesis methods that require expensive reagents and equipment. The lower production costs make nanomaterials more accessible and economically viable for large-scale soil remediation projects.
2. **Reduced environmental impact:** By using natural and renewable resources, green synthesis methods minimize the environmental footprint associated with nanomaterial production. This is in contrast to chemical synthesis methods that may rely on toxic chemicals and generate hazardous waste. The eco-friendly nature of green synthesis aligns with the principles of sustainability, as it reduces the negative environmental impact of nanomaterial production.
3. **Potential for local production:** The availability of natural resources for green synthesis, such as plant extracts, may enable the local production of nanomaterials near the contaminated sites. This decentralized production approach reduces transportation costs and emissions, further enhancing the sustainability of the remediation process. Local production also promotes community involvement and empowerment, as it creates opportunities for local stakeholders to participate in the remediation efforts.

Increased adoption and implementation: The cost-effectiveness and eco-friendliness of green-synthesized nanomaterials can lead to increased adoption and implementation of nanotechnology-based soil remediation solutions. As the economic barrier is lowered and the environmental benefits are demonstrated, more stakeholders, including governments, industries, and communities, may be willing to invest in and deploy these sustainable remediation strategies.

3.2. Characterization Techniques

Characterization of nanomaterials is crucial to understand their properties and performance in soil remediation. Various techniques are employed to characterize nanomaterials, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Brunauer-Emmett-Teller (BET) surface area analysis [20]. TEM and SEM provide information on the size, shape, and morphology of nanoparticles, while XRD is used to determine the crystalline structure and phase composition [21]. FTIR helps identify functional groups present on the surface of nanomaterials, and BET analysis measures the specific surface area and pore size distribution [22].

Table 4. Characterization techniques for nanomaterials used in soil remediation

Technique	Information Provided

TEM	Size, shape, morphology
SEM	Surface morphology
XRD	Crystalline structure, phases
FTIR	Functional groups
BET	Surface area, pore size

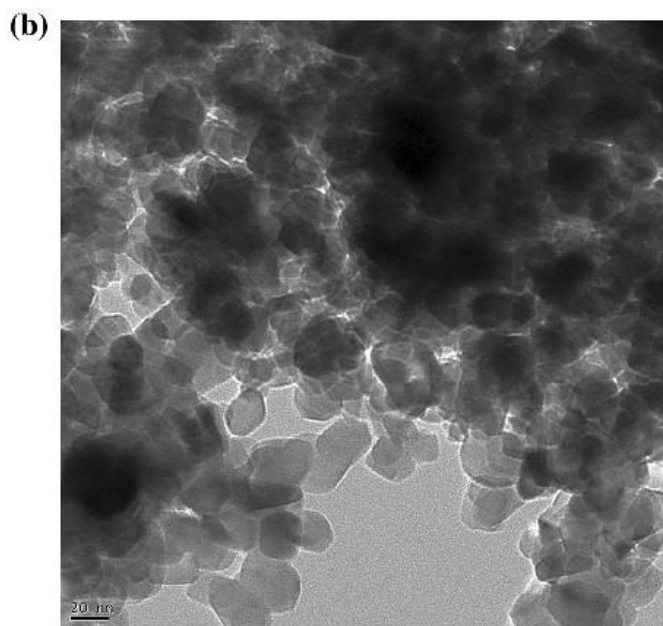
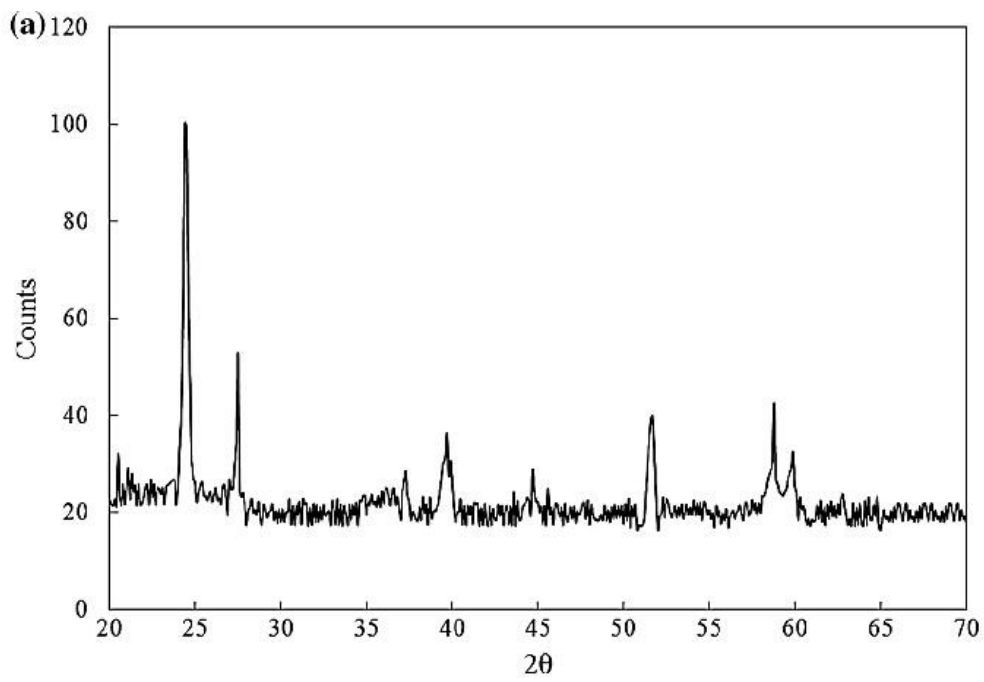


Figure 4. (a) TEM image of nZVI particles and (b) XRD pattern of TiO nanoparticles.

4. Mechanisms of Contaminant Immobilization

4.1. Adsorption

Adsorption is a key mechanism by which nanomaterials immobilize contaminants in soil [23]. The high surface area and reactive sites of nanomaterials enable them to adsorb contaminants through various interactions, such as electrostatic attraction, surface complexation, and π - π interactions [24]. The adsorption capacity of nanomaterials depends on factors such as pH, temperature, and the presence of competing ions [25]. Adsorption isotherms, such as Langmuir and Freundlich models, are used to describe the adsorption behavior and determine the maximum adsorption capacity of nanomaterials [26].

4.2. Reduction

Reduction is another important mechanism for contaminant immobilization, particularly for heavy metals and chlorinated organic compounds [27]. Nanomaterials with reducing properties, such as nZVI, can donate electrons to contaminants, converting them into less toxic or insoluble forms [28]. The reduction process can lead to the precipitation of heavy metals as insoluble hydroxides or sulfides, rendering them immobile in soil [29]. In the case of chlorinated organic compounds, the reduction mechanism involves the breaking of carbon-chlorine bonds, resulting in the formation of less toxic byproducts [30].

4.3. Degradation

Nanomaterials can also facilitate the degradation of organic contaminants in soil through photocatalytic and oxidative processes [31]. Metal oxide nanoparticles, such as TiO and ZnO, possess photocatalytic properties, generating reactive oxygen species (ROS) upon exposure to light [32]. These ROS, including hydroxyl radicals and superoxide anions, can oxidize and degrade organic contaminants into less harmful compounds [33]. The efficiency of photocatalytic degradation depends on factors such as the intensity and wavelength of light, the concentration of nanoparticles, and the nature of the contaminants [34].

Table 5. Mechanisms of contaminant immobilization by nanomaterials

Mechanism	Description	Nanomaterials Involved
Adsorption	Binding of contaminants to surface	CNTs, graphene, nZVI
Reduction	Conversion to less toxic forms	nZVI, bimetallic NPs
Degradation	Breakdown of organic contaminants	TiO, ZnO

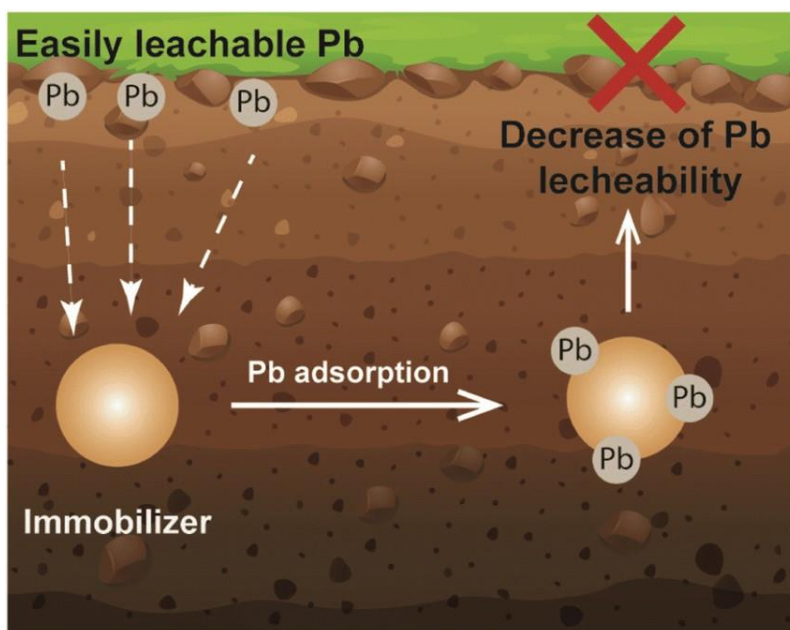


Figure 5. Schematic representation of the adsorption, reduction, and degradation mechanisms of contaminant immobilization by nanomaterials.

5. Environmental Risks and Responsible Application

While nanomaterials offer promising solutions for soil remediation, their potential environmental risks cannot be overlooked [35]. The release of nanomaterials into the environment may lead to unintended consequences, such as toxicity to non-target organisms and the potential for bioaccumulation [36]. Therefore, responsible application and monitoring of nanomaterials in soil remediation are crucial to minimize potential risks [37].

To ensure the safe and responsible use of nanomaterials, several strategies can be employed. Firstly, the selection of nanomaterials should be based on their environmental compatibility and biodegradability [38]. Biodegradable nanomaterials, such as those derived from natural polymers or green synthesized nanoparticles, can minimize the long-term environmental impact [39]. Secondly, the application of nanomaterials should be optimized to minimize their release into the environment, such as using stabilized nanoparticles or incorporating them into support materials [40].

Furthermore, comprehensive risk assessment and monitoring protocols should be established to evaluate the fate, transport, and potential toxicity of nanomaterials in soil [41]. This includes studying the interactions of nanomaterials with soil components, such as organic matter and clay minerals, and assessing their impact on soil microbial communities [42]. Long-term monitoring of remediated sites is essential to ensure the stability and effectiveness of the applied nanomaterials [43].

The cost-effectiveness of green synthesis methods for producing nanomaterials is indeed a significant factor that contributes to their sustainability and potential for widespread use in soil remediation applications.

1. **Lower production costs:** Green synthesis methods often utilize readily available, inexpensive, and renewable resources, such as plant extracts or microorganisms, as reducing and stabilizing agents. This reduces the overall cost of nanomaterial production compared to traditional chemical synthesis methods that require expensive reagents and equipment. The lower production costs make nanomaterials more accessible and economically viable for large-scale soil remediation projects.
2. **Reduced environmental impact:** By using natural and renewable resources, green synthesis methods minimize the environmental footprint associated with nanomaterial production. This is in contrast to chemical synthesis methods that may rely on toxic chemicals and generate hazardous waste. The eco-friendly nature of green synthesis aligns with the principles of sustainability, as it reduces the negative environmental impact of nanomaterial production.
3. **Potential for local production:** The availability of natural resources for green synthesis, such as plant extracts, may enable the local production of nanomaterials near the contaminated sites. This decentralized production approach reduces transportation costs and emissions, further enhancing the sustainability of the remediation process. Local production also promotes community involvement and empowerment, as it creates opportunities for local stakeholders to participate in the remediation efforts.
4. **Increased adoption and implementation:** The cost-effectiveness and eco-friendliness of green-synthesized nanomaterials can lead to increased adoption and implementation of nanotechnology-based soil remediation solutions. As the economic barrier is lowered and the environmental benefits are demonstrated, more stakeholders, including governments, industries, and communities, may be willing to invest in and deploy these sustainable remediation strategies.

6. Integration with Other Remediation Techniques

The integration of nanomaterials with other remediation techniques can enhance the overall efficiency and sustainability of the remediation process [44]. Nanomaterials can be combined with bioremediation, phytoremediation, and chemical oxidation to achieve synergistic effects and overcome the limitations of individual methods [45].

6.1. Nanomaterials and Bioremediation

Bioremediation involves the use of microorganisms to degrade or transform contaminants in soil [46]. The integration of nanomaterials with bioremediation can enhance the bioavailability of contaminants, provide additional electron acceptors or donors, and improve the survival and activity of the degrading microorganisms [47]. For example, nZVI particles can stimulate the growth of anaerobic bacteria by acting as an electron donor, promoting the reductive dechlorination of chlorinated organic compounds [48].

6.2. Nanomaterials and Phytoremediation

Phytoremediation employs plants to extract, accumulate, or degrade contaminants in soil [49]. Nanomaterials can be used to enhance the phytoremediation process by improving the uptake and translocation of contaminants in plants [50]. Metal oxide nanoparticles, such as TiO and ZnO, can be applied to the soil or foliar surfaces of plants to facilitate the photocatalytic degradation of organic contaminants [51]. Additionally, nanomaterials can be used to improve the stress tolerance and growth of plants in contaminated soils [52].

6.3. Nanomaterials and Chemical Oxidation

Chemical oxidation involves the use of strong oxidizing agents, such as hydrogen peroxide or persulfate, to degrade organic contaminants in soil [53]. Nanomaterials can act as catalysts to enhance the efficiency of chemical oxidation processes [54]. For instance, iron oxide nanoparticles can activate persulfate to generate sulfate radicals, which are powerful oxidizing agents capable of degrading a wide range of organic contaminants [55].

7. Challenges and Future Perspectives

Despite the promising potential of nanomaterials in soil remediation, several challenges need to be addressed to ensure their widespread application and commercialization [56]. One of the main challenges is the scalability and cost-effectiveness of nanomaterial production and application [57]. The development of low-cost and environmentally friendly synthesis methods, such as green synthesis, can help overcome this challenge [58].

Another challenge is the lack of long-term field studies to evaluate the performance and stability of nanomaterials in real-world soil conditions [59]. Most studies have been conducted at the laboratory scale, and the transfer of these results to field applications requires further investigation [60]. Long-term monitoring and risk assessment of nanomaterial-treated soils are necessary to ensure their safety and effectiveness [61].

Future research should focus on the development of novel nanomaterials with enhanced specificity, selectivity, and stability for targeted contaminants [62]. The functionalization of nanomaterials with specific ligands or biomolecules can improve their adsorption capacity and selectivity towards specific contaminants [63]. Additionally, the development of multifunctional nanomaterials that combine adsorption, reduction, and degradation properties can provide a more comprehensive remediation approach [64].

The integration of nanomaterials with advanced technologies, such as sensors and remote monitoring systems, can enable real-time monitoring and optimization of the remediation process [65]. Nanosensors can be deployed in soil to detect and quantify contaminants, providing valuable information for site assessment and remediation planning [66]. Remote monitoring systems can help track the fate and transport of nanomaterials in soil, ensuring their effective distribution and minimizing potential risks [67].

8. Conclusion

Nanomaterials have emerged as promising agents for sustainable soil remediation and contaminant immobilization. Their unique properties, such as high surface area, reactivity, and adsorption capacity, make them effective in adsorbing, reducing, and degrading a wide range of contaminants. Iron-based nanoparticles, carbon-based nanomaterials and metal oxide nanoparticles have shown great potential in immobilizing various soil contaminants through mechanisms such as adsorption, reduction, and degradation. The integration of nanomaterials with other remediation techniques, like bioremediation and phytoremediation, offers synergistic benefits and improved overall efficiency.

Disclaimer (Artificial intelligence)

Option 1:

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

Option 2:

Author(s) hereby declare that generative AI technologies such as Large Language Models, etc. have been used during the writing or editing of manuscripts. This explanation will include the name, version, model, and source of the generative AI technology and as well as all input prompts provided to the generative AI technology

Details of the AI usage are given below:

1.

2.

3.

References

1. Adeleye, A. S., Conway, J. R., Garner, K., Huang, Y., Su, Y., & Keller, A. A. (2016). Engineered nanomaterials for water treatment and remediation: Costs, benefits, and applicability. *Chemical Engineering Journal*, 286, 640-662. <https://doi.org/10.1016/j.cej.2015.10.105>
2. Cai, X., Qiu, R., & Chen, B. (2020). Application of nanomaterials in the remediation of contaminated soils. *Environmental Science and Pollution Research*, 27(20), 24585-24611. <https://doi.org/10.1007/s11356-020-08722-3>
3. Gong, X., Huang, D., Liu, Y., Zeng, G., Wang, R., Wei, J., Huang, C., Xu, P., Wan, J., & Zhang, C. (2018). Pyrolysis and reutilization of plant residues after phytoremediation of heavy metals contaminated sediments: For heavy metals stabilization and dye adsorption. *Bioresource Technology*, 253, 64-71. <https://doi.org/10.1016/j.biortech.2018.01.018>
4. Huang, D., Qin, X., Peng, Z., Liu, Y., Gong, X., Zeng, G., Huang, C., Cheng, M., Xue, W., Wang, X., & Hu, Z. (2018). Nanoscale zero-valent iron assisted phytoremediation of Pb in sediment: Impacts on metal accumulation and antioxidative system of *Lolium perenne*. *Ecotoxicology and Environmental Safety*, 153, 229-237. <https://doi.org/10.1016/j.ecoenv.2018.01.060>
5. Karn, B., Kuiken, T., & Otto, M. (2009). Nanotechnology and in situ remediation: A review of the benefits and potential risks. *Environmental Health Perspectives*, 117(12), 1813-1831. <https://doi.org/10.1289/ehp.0900793>
6. Li, X. Q., Elliott, D. W., & Zhang, W. X. (2006). Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. *Critical Reviews in Solid State and Materials Sciences*, 31(4), 111-122. <https://doi.org/10.1080/10408430601057611>
7. Zhao, X., Liu, W., Cai, Z., Han, B., Qian, T., & Zhao, D. (2016). An overview of preparation and applications of stabilized zero-valent iron nanoparticles for soil and groundwater remediation. *Water Research*, 100, 245-266. <https://doi.org/10.1016/j.watres.2016.05.019>
8. Araújo, R., Castro, A. C. M., Fiúza, A., & Vila, M. C. (2015). The use of nanoparticles in soil and water remediation processes. *Materials Today: Proceedings*, 2(1), 315-320. <https://doi.org/10.1016/j.matpr.2015.04.055>
9. Bardos, P., Bone, B., Daly, P., Elliott, D., Jones, S., Lowry, G., & Merly, C. (2015). A risk/benefit appraisal for the application of nano-scale zero valent iron (nZVI) for the remediation of contaminated sites. *Environmental Science and Pollution Research*, 22(24), 19325-19335. <https://doi.org/10.1007/s11356-015-4249-5>

10. Caliman, F. A., Robu, B. M., Smaranda, C., Pavel, V. L., & Gavrilesco, M. (2011). Soil and groundwater cleanup: Benefits and limits of emerging technologies. *CLEAN - Soil, Air, Water*, 39(5), 414-427. <https://doi.org/10.1002/clen.201000029>
11. Chen, H., Teng, Y., Lu, S., Wang, Y., & Wang, J. (2015). Contamination features and health risk of soil heavy metals in China. *Science of The Total Environment*, 512-513, 143-153. <https://doi.org/10.1016/j.scitotenv.2015.01.025>
12. Gomes, H. I., Dias-Ferreira, C., & Ribeiro, A. B. (2012). Electrokinetic remediation of organochlorines in soil: Enhancement techniques and integration with other remediation technologies. *Chemosphere*, 87(10), 1077-1090. <https://doi.org/10.1016/j.chemosphere.2012.02.037>
13. He, F., Zhao, D., & Paul, C. (2010). Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for in situ destruction of chlorinated solvents in source zones. *Water Research*, 44(7), 2360-2370. <https://doi.org/10.1016/j.watres.2009.12.041>
14. Hou, D., Ai, C., Liang, J., Zhao, X., Li, P., Xiao, X., & Li, G. (2017). Remediation of Cd-contaminated soil by recycling of immobilized fungal biomass with nano-hydroxyapatite. *Ecotoxicology and Environmental Safety*, 139, 135-141. <https://doi.org/10.1016/j.ecoenv.2017.01.038>
15. Huang, P., Ye, Z., Xie, W., Chen, Q., Li, J., Xu, Z., & Yao, M. (2013). Rapid magnetic removal of aqueous heavy metals and their relevant mechanisms using nanoscale zero valent iron (nZVI) particles. *Water Research*, 47(12), 4050-4058. <https://doi.org/10.1016/j.watres.2013.01.054>
16. Karn, B., Kuiken, T., & Otto, M. (2009). Nanotechnology and in situ remediation: A review of the benefits and potential risks. *Environmental Health Perspectives*, 117(12), 1813-1831. <https://doi.org/10.1289/ehp.0900793>
17. Kharissova, O. V., Dias, H. V. R., Kharisov, B. I., Pérez, B. O., & Pérez, V. M. J. (2013). The greener synthesis of nanoparticles. *Trends in Biotechnology*, 31(4), 240-248. <https://doi.org/10.1016/j.tibtech.2013.01.003>
18. Kumar, S., Bhanjana, G., Sharma, A., Sidhu, M. C., & Dilbaghi, N. (2014). Synthesis, characterization and on field evaluation of pesticide loaded sodium alginate nanoparticles. *Carbohydrate Polymers*, 101, 1061-1067. <https://doi.org/10.1016/j.carbpol.2013.10.025>
19. Li, X. Q., Elliott, D. W., & Zhang, W. X. (2006). Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. *Critical Reviews in Solid State and Materials Sciences*, 31(4), 111-122. <https://doi.org/10.1080/10408430601057611>
20. Sharma, V. K., Filip, J., Zboril, R., & Varma, R. S. (2015). Natural inorganic nanoparticles - formation, fate, and toxicity in the environment. *Chemical Society Reviews*, 44(23), 8410-8423. <https://doi.org/10.1039/c5cs00236b>

21. Tian, H., Liang, Y., & Zhu, Y. (2015). Porous nano/micro-structured materials for environmental applications. *Materials Today: Proceedings*, 2(1), 409-415. <https://doi.org/10.1016/j.matpr.2015.04.066>
22. Wang, X., & Zhao, X. (2016). Synthesis, characterization and application of birnessite-type manganese oxide nanosheets for enhanced adsorption and oxidation of arsenite. *Environmental Science and Pollution Research*, 23(12), 11835-11843. <https://doi.org/10.1007/s11356-016-6376-z>
23. Zou, Y., Wang, X., Khan, A., Wang, P., Liu, Y., Alsaedi, A., Hayat, T., & Wang, X. (2016). Environmental remediation and application of nanoscale zero-valent iron and its composites for the removal of heavy metal ions: A review. *Environmental Science & Technology*, 50(14), 7290-7304. <https://doi.org/10.1021/acs.est.6b01897>
24. Araújo, R., Castro, A. C. M., Fiúza, A., & Vila, M. C. (2015). The use of nanoparticles in soil and water remediation processes. *Materials Today: Proceedings*, 2(1), 315-320. <https://doi.org/10.1016/j.matpr.2015.04.055>
25. Bardos, P., Bone, B., Daly, P., Elliott, D., Jones, S., Lowry, G., & Merly, C. (2015). A risk/benefit appraisal for the application of nano-scale zero valent iron (nZVI) for the remediation of contaminated sites. *Environmental Science and Pollution Research*, 22(24), 19325-19335. <https://doi.org/10.1007/s11356-015-4249-5>
26. Caliman, F. A., Robu, B. M., Smaranda, C., Pavel, V. L., & Gavrilescu, M. (2011). Soil and groundwater cleanup: Benefits and limits of emerging technologies. *CLEAN - Soil, Air, Water*, 39(5), 414-427. <https://doi.org/10.1002/clen.201000029>
27. Chen, H., Teng, Y., Lu, S., Wang, Y., & Wang, J. (2015). Contamination features and health risk of soil heavy metals in China. *Science of The Total Environment*, 512-513, 143-153. <https://doi.org/10.1016/j.scitotenv.2015.01.025>
28. Gomes, H. I., Dias-Ferreira, C., & Ribeiro, A. B. (2012). Electrokinetic remediation of organochlorines in soil: Enhancement techniques and integration with other remediation technologies. *Chemosphere*, 87(10), 1077-1090. <https://doi.org/10.1016/j.chemosphere.2012.02.037>
29. He, F., Zhao, D., & Paul, C. (2010). Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for in situ destruction of chlorinated solvents in source zones. *Water Research*, 44(7), 2360-2370. <https://doi.org/10.1016/j.watres.2009.12.041>
30. Hou, D., Ai, C., Liang, J., Zhao, X., Li, P., Xiao, X., & Li, G. (2017). Remediation of Cd-contaminated soil by recycling of immobilized fungal biomass with nano-hydroxyapatite. *Ecotoxicology and Environmental Safety*, 139, 135-141. <https://doi.org/10.1016/j.ecoenv.2017.01.038>

31. Huang, P., Ye, Z., Xie, W., Chen, Q., Li, J., Xu, Z., & Yao, M. (2013). Rapid magnetic removal of aqueous heavy metals and their relevant mechanisms using nanoscale zero valent iron (nZVI) particles. *Water Research*, 47(12), 4050-4058. <https://doi.org/10.1016/j.watres.2013.01.054>
32. Karn, B., Kuiken, T., & Otto, M. (2009). Nanotechnology and in situ remediation: A review of the benefits and potential risks. *Environmental Health Perspectives*, 117(12), 1813-1831. <https://doi.org/10.1289/ehp.0900793>
33. Kharissova, O. V., Dias, H. V. R., Kharisov, B. I., Pérez, B. O., & Pérez, V. M. J. (2013). The greener synthesis of nanoparticles. *Trends in Biotechnology*, 31(4), 240-248. <https://doi.org/10.1016/j.tibtech.2013.01.003>
34. Kumar, S., Bhanjana, G., Sharma, A., Sidhu, M. C., & Dilbaghi, N. (2014). Synthesis, characterization and on field evaluation of pesticide loaded sodium alginate nanoparticles. *Carbohydrate Polymers*, 101, 1061-1067. <https://doi.org/10.1016/j.carbpol.2013.10.025>
35. Li, X. Q., Elliott, D. W., & Zhang, W. X. (2006). Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. *Critical Reviews in Solid State and Materials Sciences*, 31(4), 111-122. <https://doi.org/10.1080/10408430601057611>
36. Sharma, V. K., Filip, J., Zboril, R., & Varma, R. S. (2015). Natural inorganic nanoparticles - formation, fate, and toxicity in the environment. *Chemical Society Reviews*, 44(23), 8410-8423. <https://doi.org/10.1039/c5cs00236b>
37. Tian, H., Liang, Y., & Zhu, Y. (2015). Porous nano/micro-structured materials for environmental applications. *Materials Today: Proceedings*, 2(1), 409-415. <https://doi.org/10.1016/j.matpr.2015.04.066>
38. Wang, X., & Zhao, X. (2016). Synthesis, characterization and application of birnessite-type manganese oxide nanosheets for enhanced adsorption and oxidation of arsenite. *Environmental Science and Pollution Research*, 23(12), 11835-11843. <https://doi.org/10.1007/s11356-016-6376-z>
39. Adeleye, A. S., Keller, A. A., Miller, R. J., & Lenihan, H. S. (2013). Persistence of commercial nanoscaled zero-valent iron (nZVI) and by-products. *Journal of Nanoparticle Research*, 15(1), 1418. <https://doi.org/10.1007/s11051-013-1418-7>
40. Bystrzejewska-Piotrowska, G., Golimowski, J., & Urban, P. L. (2009). Nanoparticles: Their potential toxicity, waste and environmental management. *Waste Management*, 29(9), 2587-2595. <https://doi.org/10.1016/j.wasman.2009.04.001>
41. Cecchin, I., Reddy, K. R., Thomé, A., Tessaro, E. F., & Schnaid, F. (2017). Nanobioremediation: Integration of nanoparticles and bioremediation for sustainable remediation of chlorinated organic contaminants in soils. *International Biodeterioration & Biodegradation*, 119, 419-428. <https://doi.org/10.1016/j.ibiod.2016.09.027>
42. Chen, Z., Wang, Y., Xia, D., Jiang, X., Fu, D., Shen, L., Wang, H., & Li, Q. B. (2016). Enhanced bioreduction of iron and arsenic in sediment by biochar amendment influencing microbial

- community composition and dissolved organic matter content and composition. *Journal of Hazardous Materials*, 311, 20-29. <https://doi.org/10.1016/j.jhazmat.2016.02.069>
43. Crane, R. A., & Scott, T. B. (2012). Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. *Journal of Hazardous Materials*, 211-212, 112-125. <https://doi.org/10.1016/j.jhazmat.2011.11.073>
 44. El-Temsah, Y. S., & Joner, E. J. (2012). Ecotoxicological effects on earthworms of fresh and aged nano-sized zero-valent iron (nZVI) in soil. *Chemosphere*, 89(1), 76-82. <https://doi.org/10.1016/j.chemosphere.2012.04.020>
 45. Grieger, K. D., Fjordbøge, A., Hartmann, N. B., Eriksson, E., Bjerg, P. L., & Baun, A. (2010). Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: Risk mitigation or trade-off?. *Journal of Contaminant Hydrology*, 118(3-4), 165-183. <https://doi.org/10.1016/j.jconhyd.2010.07.011>
 46. Jiang, C., Xu, X., Megharaj, M., Naidu, R., & Chen, Z. (2015). Inhibition or promotion of biodegradation of nitrate by *Paracoccus* sp. in the presence of nanoscale zero-valent iron. *Science of The Total Environment*, 530-531, 241-246. <https://doi.org/10.1016/j.scitotenv.2015.05.044>
 47. Kocur, C. M., Chowdhury, A. I., Sakulchaicharoen, N., Boparai, H. K., Weber, K. P., Sharma, P., Krol, M. M., Austrins, L., Peace, C., Sleep, B. E., & O'Carroll, D. M. (2014). Characterization of nZVI mobility in a field scale test. *Environmental Science & Technology*, 48(5), 2862-2869. <https://doi.org/10.1021/es4044209>
 48. Lefevre, E., Bossa, N., Wiesner, M. R., & Gunsch, C. K. (2016). A review of the environmental implications of in situ remediation by nanoscale zero valent iron (nZVI): Behavior, transport and impacts on microbial communities. *Science of The Total Environment*, 565, 889-901. <https://doi.org/10.1016/j.scitotenv.2016.02.003>
 49. Li, H., Qiu, Y., Wang, X., Yang, J., Yu, Y., Chen, Y., & Liu, Y. (2017). Biochar supported Ni/Fe nanoparticles to remove 1,1,1-trichloroethane under various reaction conditions. *Chemosphere*, 169, 534-541. <https://doi.org/10.1016/j.chemosphere.2016.11.109>
 50. Li, S., Wang, W., Liang, F., & Zhang, W. X. (2017). Heavy metal removal using nanoscale zero-valent iron (nZVI): Theory and application. *Journal of Hazardous Materials*, 322, 163-171. <https://doi.org/10.1016/j.jhazmat.2016.01.032>
 51. Liu, Y., Phenrat, T., & Lowry, G. V. (2007). Effect of TCE concentration and dissolved groundwater solutes on NZVI-promoted TCE dechlorination and H₂ evolution. *Environmental Science & Technology*, 41(22), 7881-7887. <https://doi.org/10.1021/es0711967>
 52. Ma, X., Gurung, A., & Deng, Y. (2013). Phytotoxicity and uptake of nanoscale zero-valent iron (nZVI) by two plant species. *Science of The Total Environment*, 443, 844-849. <https://doi.org/10.1016/j.scitotenv.2012.11.073>

53. Machado, S., Pacheco, J. G., Nouws, H. P. A., Albergaria, J. T., & Delerue-Matos, C. (2015). Characterization of green zero-valent iron nanoparticles produced with tree leaf extracts. *Science of The Total Environment*, 533, 76-81. <https://doi.org/10.1016/j.scitotenv.2015.06.091>
54. Machado, S., Pinto, S. L., Grosso, J. P., Nouws, H. P. A., Albergaria, J. T., & Delerue-Matos, C. (2013). Green production of zero-valent iron nanoparticles using tree leaf extracts. *Science of The Total Environment*, 445-446, 1-8. <https://doi.org/10.1016/j.scitotenv.2012.12.033>
55. Miyajima, K., & Noubactep, C. (2013). Impact of Fe⁰ amendment on methylene blue discoloration by sand columns. *Chemical Engineering Journal*, 217, 310-319. <https://doi.org/10.1016/j.cej.2012.11.128>
56. Mueller, N. C., Braun, J., Bruns, J., Černík, M., Rissing, P., Rickerby, D., & Nowack, B. (2012). Application of nanoscale zero valent iron (NZVI) for groundwater remediation in Europe. *Environmental Science and Pollution Research*, 19(2), 550-558. <https://doi.org/10.1007/s11356-011-0576-3>
57. O'Carroll, D., Sleep, B., Krol, M., Boparai, H., & Kocur, C. (2013). Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. *Advances in Water Resources*, 51, 104-122. <https://doi.org/10.1016/j.advwatres.2012.02.005>
58. Patil, S. S., Shedbalkar, U. U., Truskewycz, A., Chopade, B. A., & Ball, A. S. (2016). Nanoparticles for environmental clean-up: A review of potential risks and emerging solutions. *Environmental Technology & Innovation*, 5, 10-21. <https://doi.org/10.1016/j.eti.2015.11.001>
59. Phenrat, T., Long, T. C., Lowry, G. V., & Veronesi, B. (2009). Partial oxidation ("aging") and surface modification decrease the toxicity of nanosized zerovalent iron. *Environmental Science & Technology*, 43(1), 195-200. <https://doi.org/10.1021/es801955n>
60. Reddy, K. R. (2010). Nanotechnology for site remediation: Dehalogenation of organic pollutants in soils and groundwater by nanoscale iron particles. In *Proceedings of the 6th International Congress on Environmental Geotechnics* (pp. 1-14). https://doi.org/10.1007/978-3-642-04460-1_1
61. Reddy, K. R., Darko-Kagya, K., & Al-Hamdan, A. Z. (2011). Electrokinetic remediation of pentachlorophenol contaminated clay soil. *Water, Air, & Soil Pollution*, 221(1-4), 35-44. <https://doi.org/10.1007/s11270-011-0769-x>
62. Shi, Z., Fan, D., Johnson, R. L., Tratnyek, P. G., Nurmi, J. T., Wu, Y., & Williams, K. H. (2015). Methods for characterizing the fate and effects of nano zerovalent iron during groundwater remediation. *Journal of Contaminant Hydrology*, 181, 17-35. <https://doi.org/10.1016/j.jconhyd.2015.03.004>
63. Su, C. (2017). Environmental implications and applications of engineered nanoscale magnetite and its hybrid nanocomposites: A review of recent literature. *Journal of Hazardous Materials*, 322, 48-84. <https://doi.org/10.1016/j.jhazmat.2016.06.060>

64. Tosco, T., Petrangeli Papini, M., Cruz Viggi, C., & Sethi, R. (2014). Nanoscale zerovalent iron particles for groundwater remediation: a review. *Journal of Cleaner Production*, 77, 10-21. <https://doi.org/10.1016/j.jclepro.2013.12.026>
65. Tratnyek, P. G., & Johnson, R. L. (2006). Nanotechnologies for environmental cleanup. *Nano Today*, 1(2), 44-48. [https://doi.org/10.1016/s1748-0132\(06\)70048-2](https://doi.org/10.1016/s1748-0132(06)70048-2)
66. Wang, C. B., & Zhang, W. X. (1997). Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environmental Science & Technology*, 31(7), 2154-2156. <https://doi.org/10.1021/es970039c>
67. Wei, Y. T., Wu, S. C., Chou, C. M., Che, C. H., Tsai, S. M., & Lien, H. L. (2010). Influence of nanoscale zero-valent iron on geochemical properties of groundwater and vinyl chloride degradation: A field case study. *Water Research*, 44(1), 131-140. <https://doi.org/10.1016/j.watres.2009.09.012>

UNDER PEER REVIEW