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Review

Advancement in Nanobioremediation: Mechanistic insights, environmental applications, challenges and future directions

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Nanomaterials have emerged as promising tools in the field of bioremediation, offering innovative solutions for addressing environmental pollution and contamination. Recently, there have been notable findings about the ability of various nanomaterials to combat microbes and adsorb a range of biological and chemical pollutants from contaminated habitat. Additionally, advancements in creating versatile nanocomposites are opening doors for their use in designing more effective remediation approaches. This review paper explores the diverse applications of nanomaterials in bioremediation, highlighting their unique properties and potential to enhance the efficiency of traditional remediation techniques. The present review also discuss the various nanomaterials used, their mechanisms of action, and their advantages and limitations. Additionally, the environmental and safety considerations associated with nanomaterial applications are also examined. Besides, challenges including nanoparticles stability, ecotoxicological concerns and scalability issues are addressed alongside potential mitigation strategies. This comprehensive review provides insights into the current state of research in the field and suggests future directions for the development and deployment of nanomaterials in bioremediation.

Keywords : Ecotoxicology, environmental pollution, nanobioremediation, nanomaterials,

INTRODUCTION

The rapid growth of industries during the 19th and 20th centuries brought a lot of economic and technological advancements. However, this growth also led to the release of harmful materials into the environment without proper care (Singh *et al.* 2013). The industrial development increases the levels of organic and inorganic pollutants including trace metals like mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn), copper (Cu), nickel (Ni) etc. within proximate terrestrial and aquatic ecosystems causing serious threats to entire environments including living beings (Shahi *et al.* 2021).

Perturbations in the physicochemical attributes of aqueous ecosystems can precipitate the re-mobilization of these heavy metals, propelling their re-emergence into the aquatic milieu. Such phenomena can stimulate the secondary contamination events (Chen *et al.* 2017; Yi *et al.* 2011). It has been reported that various inorganic and organic pollutants and their derivatives are ubiquitously present contaminants on Earth. Specially, polycyclic aromatic hydrocarbons (PAHs), heavy metals, halogenated phenols and others originating from natural as well as anthropogenic activities, have been identified as carcinogenic, mutagenic, and teratogenic agents (Chakravarty *et al.* 2022; Shahi *et al.* 2021). Additionally, fly ash deriving from industrial sectors serves as a predominant source of environmental pollution in proximity to these facilities (Shahi *et al.* 2021).

The contamination of soil, water, and air by various pollutants, including heavy metals, organic compounds, and emerging contaminants, has necessitated the development of advanced techniques capable of restoring environmental quality. Traditional bioremediation approaches, such as phytoremediation, microbial remediation, and chemical treatment, have been indispensable tools in this endeavor (Chakravarty and Deka, 2021; Chakraborty *et al.* 2018).

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However, they often face challenges related to efficiency, selectivity, environmental safety, cost affectivity and time required for significant remediation (Chakravarty *et al.* 2023; Kumar *et al.* 2011). Besides, as contaminants continue to threaten terrestrial and aquatic ecosystems, the need for innovative and efficient remediation methods becomes increasingly imperative.

Nanotechnology, the use of matter at the nanoscale, has emerged as a transformative field with profound implications for various scientific and technological domains. In recent years, the intersection of nanomaterials and environmental science has garnered considerable attention, particularly in the context of bioremediation—a critical approach for mitigating the detrimental impacts of pollutants on ecosystems (Hidangmayum *et al.* 2023). The integration of nanomaterials into bioremediation strategies has opened new avenues for enhanced pollutant removal, offering unprecedented opportunities for addressing environmental challenges (Mandeep and Shukla, 2020). Nanomaterials, characterized by their unique physicochemical properties at the nanoscale, exhibit exceptional reactivity, large surface area-to-volume ratios, and versatile functionalities (Sharma *et al.* 2015). These features make them promising candidates for applications in bioremediation, where the goal is to accelerate the degradation or sequestration of pollutants through biological processes (Chakravarty *et al.* 2023).

This comprehensive review seeks to explore and analyze the diverse applications of nanomaterials in bioremediation strategies, encompassing various environmental matrices and pollutants. By delving into the synergistic interactions between nanomaterials and biological systems, this review aims to provide insights into the mechanisms underlying their effectiveness in pollutant removal. Additionally, it will critically examine the challenges and considerations associated with the utilization of nanomaterials in bioremediation, including potential environmental and health implications.

TYPES OF NANOMATERIALS IN BIOREMEDIATION

Nanomaterials employed in bioremediation are available in a variety of forms, each offering unique advantages and mechanisms of action. This section explores the diverse categories of nanomaterials commonly used in bioremediation, with a focus on their distinct properties and applications.

Nanoparticles

Nanoparticles, characterized by their nanoscale dimensions, have garnered significant attention for their versatility in bioremediation. There are various types of nanoparticles used in the remediation study which include:

Metal and Metal Oxide Nanoparticles

Nanoparticles such as zero-valent iron (nZVI), titanium dioxide (TiO_2), and iron oxide nanoparticles have been extensively used in adsorbing heavy metals (Sudarsan *et al.* 2016). These materials exhibit high surface area and reactivity, making them effective in sequestering and immobilizing contaminants (Chakravarty *et al.* 2023).

Quantum Dots

Semiconductor nanoparticles known as quantum dots are valuable in tracking and monitoring bioremediation processes due to their unique optical properties (Patra, 2022). Quantum dots enable real-time visualization of contaminant removal.

Magnetic Nanoparticles

Magnetic nanoparticles like magnetite (Fe_3O_4) and maghemite (ã-Fe_2O_3) are employed in magnetic separation techniques to efficiently remove pollutants from water and soil (Singh *et al.* 2021).

Nanocomposites

Nanocomposites are hybrid materials that merge the characteristics of nanomaterials with the functionality of other materials (Okpala, 2013). This combination enhances adsorption, sequestration, and catalysis. Notable nanocomposites include:

Polymer Nanocomposites

Nanoparticles embedded within polymer matrices can increase the surface area available for adsorption, enhancing their ability to remove various contaminants from water (Shin *et al.* 2008).

Biopolymer-Based Nanocomposites

Biopolymers like chitosan and cellulose, when combined with nanoparticles, demonstrate superior sorption capacities and selectivity for specific contaminants (Doyo *et al.* 2023).

Carbon-Based Nanomaterials

Carbon-based nanomaterials have emerged as versatile candidates for bioremediation (Del Prado-Audelo *et al.* 2023). The distinguished carbon-based nanomaterials have been discussed below-

Graphene

With its high surface area and electrical conductivity, graphene is used for adsorption and electron transfer processes. It can enhance microbial activities and the removal of various contaminants from water and soil (Malik *et al.* 2022).

Carbon Nanotubes

Carbon nanotubes (CNTs) including Multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) are employed for adsorption, catalysis, and as carriers for remediation agents (Rizwan *et al.* 2014). Their tubular structures offer ideal environments for adsorption and transport (Santucci *et al.* 2003).

Nanodiamonds

Nanodiamonds, with their sp3 hybridized carbon lattice, serve as effective adsorbents for organic compounds, heavy metals, and radionuclides (Duan *et al.* 2019).

Other Nanomaterials

Beyond these categories, various other nanomaterials contribute to bioremediation which includes:

Dendrimers

Dendritic nanomaterials with highly branched structures have been used for sequestration of heavy metals and organic pollutants (Khin *et al.* 2012).

Zeolites

Nanostructured zeolites, known for their high surface area and cation exchange capacity, find applications in ion exchange and adsorption processes (Chen *et al.* 2018).

Nanostructured Materials

Materials such as mesoporous silica nanoparticles and clay minerals provide porous matrices for the encapsulation and controlled release of remediation agents (Li *et al.* 2019).

These diverse types of nanomaterials are chosen based on their specific properties and suitability for the targeted contaminants and environmental matrices. Understanding the characteristics of these nanomaterials is crucial for tailoring bioremediation strategies to meet the unique challenges of different contamination scenarios.

MECHANISMS OF NANOMATERIALS IN BIOREMEDIATION

Adsorption

Nanobioremediation, a promising approach for environmental cleanup, involves the synergistic action of nanoparticles and microorganisms to mitigate contaminants. Nanoparticles, serving as Nano-Bioremediation Agents (NBA), owing to their high surface area and tailored surface functionalities, exhibit exceptional adsorption capacities (Sharma *et al.* 2015). They can physically trap contaminants through adsorption, forming strong bonds with target molecules. For instance, metal and metal oxide nanoparticles are known to adsorb heavy metals effectively (Sudarsan *et al.* 2016). Quantum dots have also been used to adsorb organic compounds due to their unique surface chemistry (Patra, 2022). This mechanism allows nanomaterials to immobilize contaminants and prevent their migration.

Besides, this process is facilitated by the interaction with microorganisms, either indigenous or intentionally introduced, which enhances the overall remediation efficacy (Hidangmayum *et al.* 2023). The contaminants, ranging from heavy metals to organic pollutants, bind to these nanoparticles, and subsequent microbial activities contribute to their transformation and eventual detoxification (Chakravarty *et al.* 2023). While the specifics of nanobioremediation mechanisms can vary based on nanoparticle composition and microbial involvement (Aboutaleb *et al.* 2021), the approach holds promise for addressing diverse environmental pollution challenges. It is essential to consider the specific characteristics of nanoparticles and their interplay with microbial communities for optimal remediation outcomes.

Enhancement of Microbial Activity and Catalysis

Nanobioremediation, an innovative approach to environmental cleanup, integrates nanomaterials with biological agents to enhance pollutant degradation processes. The catalytic mechanism involving nanoparticle-driven microbial interactions and electron transfer, present a promising avenue for efficient environmental remediation by augmenting the efficiency of microbial degradation mechanisms, as supported by recent research in the field (Yogalakshmi *et al.* 2020). Nanoparticles provide high surface area-to-volume ratio, for microbial attachment, facilitating the formation of biofilms (Ouyang *et al.* 2020). This enhances the contact between microorganisms and contaminants, promoting effective degradation (Bhatt *et al.* 2023). Besides this, nanoparticles often possess reactive sites or functional groups on their surfaces (Rizwan *et al.* 2014). These sites can interact with pollutants, promoting their binding and subsequent degradation by microbial enzymes. Nanoparticles can also act as electron shuttles, facilitating electron transfer between microorganisms and pollutants (Kumari and Singh, 2016). These facilitate redox reactions and enhance the microbial metabolic pathways involved in the degradation of recalcitrant compounds such as chlorinated solvents (Li and Zhang, 2006). Nanoparticles such as zero-valent iron (nZVI) as well as carbon-based nanomaterials like graphene and carbon nanotubes, due to their high conductivity, have been shown to act as electron mediators and enhance the efficiency of microbial degradation of organic compounds (Sudarsan *et al.* 2016; Rizwan *et al.* 2014). Again, nanoparticles, due to their small size, have a high surface area-to-volume ratio and this increased surface area provides more sites for microbial activity, promoting enzymatic reactions involved in the breakdown of pollutants (Chakravarty *et al.* 2023). The different phenomena occur due the interactions of nanomaterials, microorganisms and contaminants during nanobioremediation approaches have been presented in Fig.1.

Moreover, nanoparticles can encapsulate or bind with contaminants, making them more bioavailable to microbial cells (Nandini *et al.* 2023). This increased bioavailability ensures that pollutants are more efficiently metabolized by the microbial consortia present in the environment (Sharma *et al.* 2009).Nanoparticles can also protect microbial cells from harsh environmental conditions or toxic intermediates generated during biodegradation. They can act as carriers for nutrients or essential co-factors, ensuring sustained microbial activity over prolonged periods (do Espirito Santo Pereira *et al.* 2021).Further, some nanomaterials possess catalytic properties, making them adept at facilitating chemical reactions that lead to the degradation of pollutants. For example, zero-valent iron nanoparticles (nZVI) are renowned for their ability to reduce chlorinated compounds through reductive dechlorination (Bruton *et al.* 2015). These nanoparticles act as electron donors, thereby promoting the breakdown of toxic substances. Similarly, silver nanoparticles have been employed in catalytic processes for the degradation of textile dyes and organic pollutants (Wang *et al.* 2019). Again, some nanoparticles exhibit photocatalytic properties also when exposed to light. This can generate reactive oxygen species (ROS) that aid in the degradation of pollutants and enhance microbial remediation processes (Sultana *et al.* 2020).

Combining nanoparticles with specific microbial strains can create synergistic effects. For instance, nanoparticles can enhance the metabolic pathways of microbes, leading to the simultaneous degradation of multiple pollutants or the breakdown of complex chemical structures

Selective Sorption and Ion Exchange

Selective sorption and ion exchange are pivotal mechanisms employed in nanobioremediation for the efficient removal of contaminants from polluted environments. In selective sorption, nanobiomaterials such as nanoparticles, nanotubes or other nanostructures derived from biological sources like bacteria, fungi, or plants exhibit specific functional groups that facilitate the preferential adsorption of contaminants based on their chemical nature (Mohmood *et al.* 2013). The sorption occurs due to various interactions such as electrostatic attraction, hydrogen bonding, and van der Waals forces (Saxena *et al.* 2020). The selectivity arises from the specific functional groups present on the nanobiomaterials' surface, which can bind particular contaminants based on their chemical nature (Mohmood *et al.* 2013).

Conversely, ion exchange involves the replacement of ions adsorbed onto the nanobiomaterials' surface with ions present in the surrounding solution, particularly effective for removing heavy metals and ionic pollutants (Gupta *et al.* 2021). The nanobiomaterials possess charged sites that attract and exchange ions with the solution (Gupta *et al.* 2021). For instance, negatively charged nanobiomaterials can exchange cations (positively charged ions) present in the solution. It has been reported that nanomaterials like dendrimers possess cation exchange capacity, which enables them to remove heavy metals and organic pollutants selectively (Khin et al. 2012). These mechanisms capitalize on nanobiomaterials' unique properties, including high surface area and functional group availability, thereby enhancing remediation efficiency while maintaining environmental sustainability and leveraging biological entities' renewable nature (Mohmood *et al.* 2013; Khin *et al.* 2012).

Complexation and Encapsulation

Complexation and encapsulation are fundamental mechanisms utilized in nano-bioremediation for the effective treatment of environmental contaminants. Complexation involves the formation of stable complexes between nanobiomaterials and contaminants, typically through coordination interactions, hydrogen bonding or electrostatic interactions (Trujilo-Reyes *et al.* 2014). These complexes facilitate the sequestration and immobilization of pollutants, particularly heavy metals and organic compounds, rendering them less bioavailable and toxic (Wang *et al.* 2022). On the other hand, encapsulation entails the confinement of contaminants within the interior or matrix of nanobiomaterials, such as nanoparticles or vesicles derived from biological entities (Cvancarová *et al.* 2020). This mechanism provides a protective barrier that prevents the leaching or release of contaminants into the surrounding environment, thereby mitigating potential ecological risks. It was reported that the polymer nanocomposites and biopolymer-based nanomaterials are known for their capacity to encapsulate pollutants and deliver controlled release of remediation agents (Kolya and Kang, 2023). These materials are particularly useful in delivering treatment agents to the target site. Together, complexation and encapsulation mechanisms leverage the unique physicochemical properties of nanobiomaterials to enhance remediation efficiency and minimize environmental impact. The Mechanism of actions of nanobioremediation of environmental contaminants have been depicted via (Fig. 2 and Fig. 3).

AVANTAGES OF NANOBIOREMEDIATION

The advantages outlined in this comprehensive review underscore the transformative potential of nanomaterials in bioremediation. Nanomaterials exhibit unique physicochemical properties that enable superior remediation efficiency. Their high surface area, reactivity, and specific interactions with contaminants result in enhanced pollutant removal compared to traditional remediation methods (Sharma *et al.* 2015). Nanomaterials can promote synergistic interactions with indigenous microbial communities, enhancing microbial activity and promoting pollutant degradation (Chakravarty *et al.* 2023). This collaboration between nanomaterials and microorganisms results in a more efficient and sustainable bioremediation process. Moreover, the high reactivity and catalytic properties of nanomaterials contribute to accelerate pollutant degradation (Sudarsan *et al.* 2016). Nano - materials, when designed and applied appropriately, can also minimize the generation of secondary pollutants during the remediation process (Thirunavukkarasu *et al.* 2020). This is crucial for ensuring that the cleanup efforts do not inadvertently introduce new environmental challenges. Besides, the ability to tailor nanomaterials for specific contaminants allows for a targeted approach in environmental cleanup. Customization of nanomaterials ensures optimal affinity and selectivity, addressing the diverse range of pollutants found in contaminated sites (Theron *et al.* 2008). As a whole, from their tailored design for targeted pollutant removal to their adaptability and scalability, nanomaterials contribute significantly to advancing sustainable and effective solutions for environmental cleanup challenges.

Environmental and Safety Considerations

The incorporation of nanotechnology appears to have had a revolutionary effect on various disciplines including pollution remediation. However, it is imperative to scrutinize the environmental and safety dimensions associated with the implementation of nanotechnology in bioremediation processes. Nanomaterials exhibit unique properties that can significantly impact ecosystems, necessitating a thorough assessment of their environmental implications (Lead *et al.* 2018). Potential risks such as bioaccumulation and toxicity must be carefully evaluated to ensure the responsible application of these materials. Moreover, the synthesis, handling, and disposal of nano materials demand meticulous attention to safety protocols. Researchers need to adopt stringent measures to minimize occupational hazards and prevent unintended environmental releases during both laboratory and field applications. Emphasizing safe practices in the entire life cycle of nano materials is vital for protecting not only human health but also the broader ecological balance. Striking a balance between harnessing the benefits of nano materials in bioremediation and mitigating potential adverse effects underscores the need for a holistic approach that considers both environmental conservation and safety imperatives. This dual perspective ensures that the promising advancements in bioremediation do not compromise the well- being of ecosystems or human populations.

LIMITATION AND FUTURE DIRECTIONS

Future research should focus on the development of multifunctional nanomaterials that can address multiple contaminants simultaneously. Integrating various functionalities, such as catalysis, adsorption, and microbial support, within a single nanomaterial could enhance its efficiency and versatility in tackling complex pollution scenarios. However, customizing nanomaterials to target multiple pollutants is crucial for optimizing bioremediation processes as the potential ecotoxicological impacts of nanomaterials on non-target organisms remain a significant concern. Studies indicate that certain nanoparticles may pose risks to aquatic and terrestrial organisms, necessitating comprehensive toxicological assessments to ensure the safety of bioremediation strategies. In this regards, researchers should explore the design and synthesis of nanomaterials with enhanced affinity for multiple contaminants, allowing for more efficient and sustainable remediation strategies. Besides, understanding the long-term environmental fate of nanomaterials and their potential ecological impacts is essential. Future studies should emphasize comprehensive toxicological assessments and fate analyses to ensure the safe and sustainable application of nanomaterials in bioremediation practices. Again, scaling up laboratory-based successes to field applications remains a significant challenge. Research efforts should be directed toward developing scalable and cost-effective production methods for nanomaterials and assessing their performance under realistic environmental conditions to bridge the gap between laboratory studies and practical field applications. It was established that the exploring synergistic interactions between nanomaterials and indigenous microbial communities could enhance the overall efficiency of bioremediation processes. Future research should focus on elucidating the mechanisms of nanomaterial-microbe interactions and optimizing conditions to promote a harmonious relationship for improved pollutant degradation. In addition, the high cost associated with nanomaterial synthesis and application may limit widespread adoption. Hence, establishing clear regulatory frameworks for the synthesis and use of nanomaterials in bioremediation is found to be imperative. To overcome these limitations, future directions should include the development of standardized testing protocols, risk assessments, and guidelines to ensure the responsible and ethical application of nanomaterials in environmental cleanup.

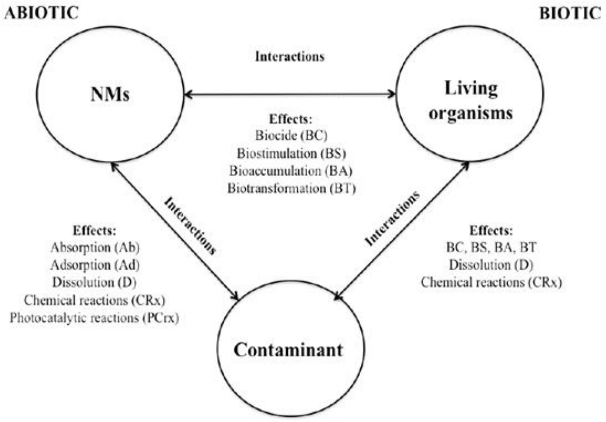

Fig. 1: Occurrence of different phenomena during interactions of nanomaterials, microbes and pollutants in nanobioremediation approach (Adopted from Vázquez-Núñez *et al.* 2020)

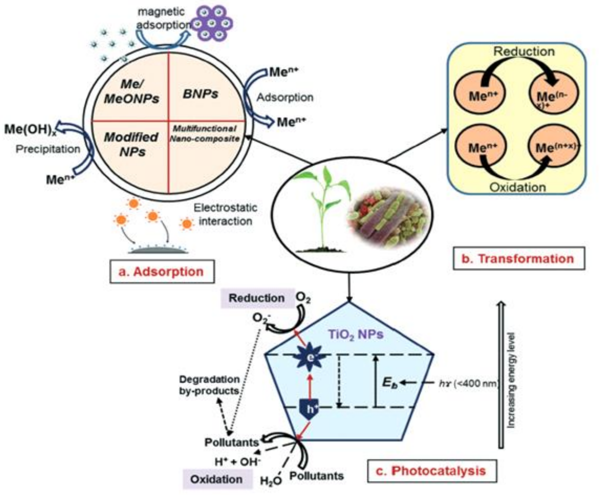

Fig. 2: Mechanistic insights of remediation of inorganic and organic contaminants via green nanomaterials (Adopted from Das *et al.* 2018)

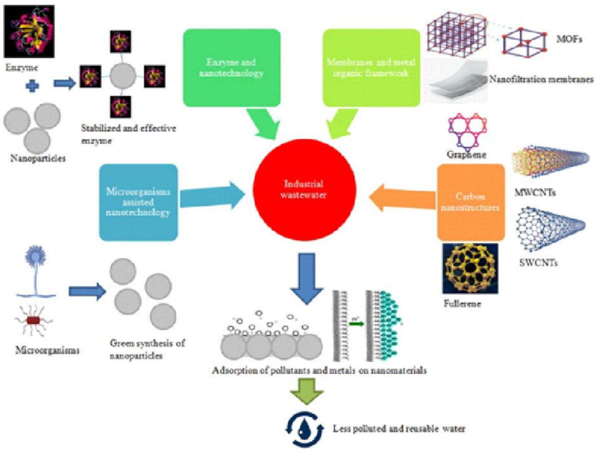

Fig.3: Application of nanobioremediation approaches in wastewater treatment. SWCNTs- Single-walled carbon nanotubes, MWCNTs- multi-walled carbon nanotubes, MOFs- Metal organic frameworks (Adopted from Mandeep and Shukla, 2020)

CONCLUSION

This inclusive review has provided an in-depth exploration of the diverse applications of nanomaterials in the field of bioremediation. The amalgamation of nanotechnology with bioremediation strategies has exhibited significant promise in addressing the ever-growing challenges posed by environmental pollution. The versatility of nanomaterials, ranging from engineered nanoparticles to nanocomposites, opens new avenues for innovative and efficient remediation approaches. Besides, the multifaceted roles played by nanomaterials, including catalysis, adsorption, and microbial support, underscore their potential as powerful tools for targeted pollutant removal. The ability to tailor nanomaterials for specific contaminants enhances the precision and efficacy of bioremediation processes, providing a tailored approach to environmental cleanup. Moreover, the integration of nanomaterials with indigenous microbial communities offers synergistic benefits, amplifying the overall remediation efficiency. However, as it navigate the promising landscape of nanomaterial applications in bioremediation, it is essential to acknowledge and address the challenges that lie ahead. Concerns surrounding the stability, reactivity, and unintended ecotoxicological effects of nanomaterials underscore the need for continued research and risk assessment. Bridging the gap between laboratory success and field applications, along with the development of standardized protocols and regulatory frameworks, is crucial for the responsible deployment of nanomaterials in environmental remediation.

Moreover, the ethical and social dimensions of nanomaterial use cannot be overlooked. Public perception, acceptance, and understanding of the ethical implications associated with the deployment of nanomaterials in bioremediation are integral to the success and sustainable integration of these technologies. As we move forward, collaborative efforts between researchers, policymakers, industry stake-holders, and the public will play a pivotal role in shaping the future of nanomaterial applications in bioremediation. The synthesis of scientific advancements, technological innovations, and ethical considerations will contribute to the development of robust and sustainable solutions for mitigating environmental pollution. In essence, the amalgamation of nanomaterials with bioremediation strategies represents a frontier where scientific ingenuity meets environmental stewardship. By addressing the challenges highlighted in this review and fostering a multidisciplinary approach, we pave the way for a future where nanomaterials contribute significantly to the restoration and preservation of our precious ecosystems.

DECLARATION

Conflict of Interest. Authors declare no conflict of interest.

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