STEM ESSENTIALS

Synthesis and Application of Eco-Friendly Nanomaterials for Heavy Metal Remediation in Wastewater

[a]Afolabi, P. O.

[a] Department of Vocational and Technology Studies, Enugu State University of Science and Technology, Enugu, Nigeria.

Corresponding Author: obarifomi@gmail.com

Abstract

Heavy metal contamination in wastewater has become a pressing global issue, posing serious risks to environmental and public health. Traditional remediation technologies, while effective to an extent, often suffer from limitations such as high cost, low selectivity, and secondary pollution. In recent years, the development and application of eco-friendly nanomaterials have emerged as promising alternatives due to their high surface area, unique physicochemical properties, and sustainable synthesis pathways. This review explores the synthesis, characterization, and practical application of green nanomaterials for the remediation of heavy metals in wastewater. It evaluates current advancements, discusses mechanisms of metal removal, and identifies the challenges and future directions in this rapidly evolving field.

KEYWORDS: Heavy Metals, Remediation, Nanomaterials, Wastewater, Pollution

Introduction

The proliferation of industrial activities and urbanization over the last few decades has led to an exponential increase in the release of hazardous substances into the environment. Among these pollutants, heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg), arsenic (As), and nickel (Ni) are of particular concern due to their toxicity, persistence, and tendency to bioaccumulate (Fu & Wang, 2011). These metals are introduced into aquatic systems through various anthropogenic sources, including electroplating industries, battery manufacturing, mining operations, smelting, pesticide usage, and the improper disposal of industrial and municipal waste (Ali et al., 2013).

Unlike organic pollutants that can undergo microbial or chemical degradation, heavy metals do not degrade and can persist in the environment for centuries. This non-biodegradable nature, combined with their ability to interfere with biological systems at even trace concentrations, renders them particularly dangerous (Fu & Wang, 2011). For instance, lead can cause neurodevelopmental disorders in children, while cadmium exposure is linked to kidney dysfunction and skeletal damage. Arsenic is a well-documented carcinogen, and mercury has severe neurological impacts.

The presence of these metals in wastewater not only threatens public health but also compromises aquatic ecosystems. Aquatic flora and fauna are highly susceptible to metal toxicity, which can disrupt reproductive systems, enzyme activity, and cellular function. Furthermore, the contamination of groundwater and surface water by heavy metals can severely limit the availability of clean water, an already scarce resource in many parts of the world.

Conventional technologies employed for heavy metal removal include chemical precipitation, ion exchange, reverse osmosis, membrane filtration, coagulation-flocculation, and electrochemical treatments (Zhao et al., 2016). While these methods can be effective, they are often associated with several limitations. High operational and maintenance costs, energy-intensive processes, and the generation of secondary pollutants (such as toxic sludge) are common drawbacks (Ali & Gupta, 2007). Moreover, these techniques often struggle to remove metals at very low concentrations, which is critical given the toxicological significance of trace-level contamination.

In response to these limitations, nanotechnology has emerged as a powerful tool for water purification. Nanomaterials, by virtue of their extremely small size (typically 1-100 nanometers) and large surface area-to-volume ratios, offer unique physicochemical properties that enhance the adsorption, reduction, and removal of contaminants. Their ability to interact with metal ions at the molecular or atomic level results in improved efficiency and selectivity in remediation processes.

Eco-friendly or green nanomaterials take this a step further by emphasizing sustainability in both synthesis and application. Unlike conventional nanomaterials, which may require toxic chemicals and high-energy processes, green nanomaterials are synthesized using environmentally benign methods. These methods typically involve biological entities such as plants, fungi, bacteria, or biopolymers, which act as reducing and capping agents. The resulting nanomaterials not only retain their functional efficacy but also reduce environmental and health risks associated with their production and use. The appeal of green nanomaterials extends beyond their environmental compatibility (Ahmed et al., 2016). They offer the potential for cost-effective production, especially when agricultural waste or renewable biomass is utilized as raw material. Additionally, the biological synthesis pathways can be easily scaled and adapted to different contexts, making them accessible for use in resource-limited settings (Iravani, 2011).

This review aims to provide a comprehensive examination of the current state of research on eco-friendly nanomaterials for heavy metal remediation in wastewater. The subsequent sections will delve into the various methods of green synthesis, the critical properties and characterization techniques of nanomaterials, the mechanisms by which they remove heavy metals, and real-world applications. The study will also address the environmental and economic aspects of deploying these materials and highlight the challenges and future directions in this field. By compiling and synthesizing recent advancements, this article seeks to inform researchers, practitioners, and policymakers about the potential of green nanotechnology to address one of the most pressing environmental challenges of our time—ensuring clean and safe water through sustainable means.

Green Synthesis of Nanomaterials

Green synthesis refers to the development of nanomaterials using environmentally benign methods that avoid the use of toxic chemicals and high-energy inputs. These methods leverage biological systems such as plant extracts, microorganisms (bacteria, fungi, algae), and biopolymers as reducing, capping, and stabilizing agents in nanoparticle formation (Ahmed et al., 2016). The move toward green synthesis is driven not only by environmental concerns but also by the need for scalable, cost-effective, and safe production technologies that can be adapted for use in various industrial and environmental applications.

One of the most widely explored green synthesis routes involves the use of plant extracts. Plants contain a variety of phytochemicals, such as polyphenols, flavonoids, terpenoids, and alkaloids, which can act as both reducing and stabilizing agents. For example, neem (Azadirachta indica) leaves have been used to synthesize silver and gold nanoparticles due to their high antioxidant content. The plant-mediated synthesis is typically carried out at room temperature, with water as the solvent, making it one of the most sustainable methods (Iravani, 2011).

Microbial synthesis employs bacteria, fungi, and algae to produce nanoparticles either intracellularly or extracellularly. Fungi like Aspergillus niger and bacteria such as Bacillus subtilis have been shown to synthesize metal nanoparticles with controlled shapes and sizes. These microorganisms have enzymatic systems that facilitate the reduction of metal ions into nanoparticles. While microbial synthesis can be more time-consuming compared to plant-based methods, it often results in nanoparticles with high stability and monodispersity (Iravani, 2011).

Algae-based synthesis is an emerging area of interest due to the rich bioactive compound profile of marine and freshwater algae. Algae such as Spirulina and Sargassum have been utilized to synthesize zinc oxide and silver nanoparticles. These organisms are highly efficient in metal uptake and transformation, making them suitable for large-scale production (Iravani, 2011).

Biopolymers such as chitosan, starch, and cellulose derivatives are also gaining traction as green templates for nanoparticle synthesis. These natural polymers can form complexes with metal ions and assist in their reduction and stabilization. For instance, chitosan—a derivative of chitin—has been used to synthesize iron oxide and gold nanoparticles, offering advantages like biocompatibility and biodegradability.

The advantages of green synthesis are manifold. Firstly, it eliminates the need for hazardous reducing agents like sodium borohydride or hydrazine, thereby reducing the potential for environmental contamination. Secondly, the biologically derived capping agents impart biocompatibility, which is crucial for applications in water treatment where contact with living organisms is inevitable. Thirdly, the cost-effectiveness and scalability of these methods make them suitable for deployment in developing countries where traditional nanomaterial synthesis might not be feasible.

Despite these benefits, challenges remain. Reproducibility and consistency in nanoparticle size, shape, and functionality can vary due to the complex nature of biological extracts. Moreover, the exact mechanisms of nanoparticle formation in green synthesis are not fully understood, necessitating further research. The optimization of synthesis parameters such as pH, temperature, concentration, and reaction time is also critical to achieving desirable material properties.

Recent studies have demonstrated the successful application of green nanomaterials in the removal of heavy metals from aqueous solutions. For example, green-synthesized iron oxide nanoparticles using Moringa oleifera extract have shown high efficiency in removing arsenic and lead. Similarly, silver nanoparticles synthesized from green tea extract have been effective in mercury adsorption.

Characterization and Properties of Green Nanomaterials

The characterization of green nanomaterials is vital for understanding their structure-function relationships and potential performance in environmental remediation, particularly in heavy metal removal from wastewater. Comprehensive characterization provides insights into the morphology, size, crystallinity, surface chemistry, functional groups, and reactivity of nanomaterials. This section outlines the fundamental techniques used for characterization and discusses the implications of these properties on the nanomaterials' functionality and environmental compatibility.

Morphological and Structural Characterization

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) are widely used to visualize the shape, size, and surface morphology of nanomaterials. Green-synthesized nanoparticles typically exhibit diverse morphologies—spherical, rod-like, or sheet-like—depending on the biomaterials used during synthesis. For instance, nanoparticles synthesized using neem extract tend to form spherical aggregates, whereas those derived from tea polyphenols might exhibit plate-like morphologies.

Atomic Force Microscopy (AFM) is also employed to map surface topographies and assess the three-dimensional structure of nanoparticles, especially for biopolymer-encapsulated nanostructures. AFM data help confirm the dispersion and agglomeration tendencies of nanoparticles, which are crucial for understanding their interaction with metal ions in solution.

Size Distribution and Surface Area

Dynamic Light Scattering (DLS) is commonly used to determine the hydrodynamic size distribution of nanoparticles in colloidal suspensions. Smaller particle sizes are generally associated with larger surface-to-volume ratios, which enhance metal adsorption capacities. However, high surface energy in small particles may also lead to aggregation, reducing their effectiveness.

Brunauer–Emmett–Teller (BET) surface area analysis provides quantitative data on surface area and porosity. Green nanomaterials with high BET surface areas tend to exhibit improved heavy metal adsorption capacities due to the abundance of accessible binding sites. For example, biochar-supported iron nanoparticles often demonstrate superior surface areas (200–500 m^2/g), making them highly effective for adsorption processes.

Crystallinity and Phase Composition

X-ray Diffraction (XRD) analysis is used to identify the crystalline phases present in the nanomaterials and to estimate their average crystallite size using the Scherrer equation. Crystalline structure significantly influences the stability and reactivity of the nanomaterials. For instance, crystalline iron oxide nanoparticles typically offer better magnetic properties and greater stability compared to amorphous forms, which is advantageous in magnetic separation techniques.

Selected Area Electron Diffraction (SAED), when combined with TEM, can provide further insights into crystallographic orientations, helping distinguish between polycrystalline and monocrystalline structures, which influence the material's interaction with heavy metals.

Functional Group Analysis

Fourier Transform Infrared Spectroscopy (FTIR) is employed to identify functional groups and chemical bonds present on the nanoparticle surface. Green nanomaterials often contain hydroxyl, carboxyl, amine, and phenolic groups derived from the natural capping agents used during synthesis. These functional groups play a critical role in metal ion binding through mechanisms such as complexation and ion exchange.

For example, FTIR analysis of green-synthesized ZnO nanoparticles from aloe vera extract has shown strong peaks associated with C=O and O–H stretching vibrations, which are active sites for metal adsorption. This confirms the role of plant phytochemicals in functionalizing the nanoparticle surface.

Surface Charge and Stability

Zeta potential measurements assess the surface charge and colloidal stability of nanoparticles in aqueous solutions. Nanoparticles with high absolute zeta potential values (±30 mV or more) tend to remain stable and dispersed, minimizing agglomeration. This enhances their availability for interaction with metal ions. Additionally, the surface charge influences the electrostatic attraction between the nanomaterials and metal cations or anions. In green nanomaterials, zeta potential can be manipulated by adjusting the pH or through surface functionalization with natural stabilizers such as chitosan or starch, thereby tuning the adsorption behavior under various environmental conditions.

Optical and Electronic Properties

UV-Vis spectroscopy provides information on the optical properties and electronic transitions of nanoparticles. A characteristic surface plasmon resonance (SPR) peak, particularly for metal nanoparticles like silver or gold, confirms nanoparticle formation and can indicate particle size and shape. Moreover, optical band gap analysis through UV-Vis absorption helps understand the photocatalytic potential of semiconducting green nanomaterials such as TiO_2 or ZnO.

Photoluminescence (PL) spectroscopy further aids in understanding defect states and electronic properties, which are crucial for redox reactions during heavy metal transformation or photocatalytic degradation.

Thermal and Compositional Analysis

Thermogravimetric Analysis (TGA) is used to evaluate the thermal stability and organic content of green nanomaterials. A high percentage of organic matter can indicate the presence of plant-derived capping agents or biopolymers, which may affect the degradation rate and environmental compatibility of the nanomaterials.

Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) provide compositional analysis, identifying the elemental makeup and oxidation states of nanoparticles. These techniques are critical for verifying the successful incorporation of metal or metal oxide phases and for understanding redox behavior during remediation.

Implications for Heavy Metal Remediation

The physicochemical characteristics identified through these techniques directly impact the performance of green nanomaterials in heavy metal remediation. Smaller, more stable, and functionalized nanoparticles tend to show enhanced sorption capacities and selective affinity for target metals. Crystallinity affects not only stability but also magnetic or catalytic behaviors that are useful in advanced treatment systems.

Furthermore, the integration of multi-functional properties—such as magnetic separation, photocatalytic activity, and high adsorption capacity—into a single nanomaterial platform is increasingly being achieved through hybrid nanocomposites. Characterization, therefore, not only guides material development but also supports regulatory approval by establishing environmental safety and reproducibility.

Mechanisms of Heavy Metal Removal by Eco-Friendly Nanomaterials

Eco-friendly nanomaterials remove heavy metals from wastewater through a range of physicochemical mechanisms, each influenced by the material's composition, structure, surface properties, and functional groups. The most common removal mechanisms include adsorption, ion exchange, reduction, complexation, and precipitation. These processes often work synergistically, enhancing the overall remediation efficiency.

Adsorption

Adsorption is the most dominant and widely studied mechanism in heavy metal remediation using green nanomaterials. It involves the adhesion of metal ions onto the surface of nanoparticles through physical or chemical interactions. The high surface area-to-volume ratio of nanomaterials provides abundant active sites for metal binding. For instance, bio-synthesized iron oxide nanoparticles exhibit strong adsorption affinity towards arsenic (As^{5+}) and lead (Pb^{2+}), facilitated by surface hydroxyl and carboxyl groups.

Functionalization of nanomaterials with specific ligands—such as amine, thiol, or phosphate groups—can further enhance metal selectivity. For example, chitosan-coated silver nanoparticles demonstrate improved affinity for mercury (Hg^{2+}) due to the presence of amino functional groups that coordinate with mercury ions.

Ion Exchange

Ion exchange involves the substitution of metal ions in solution with ions originally present on the surface of the nanomaterial. This mechanism is particularly effective with materials like biogenic zeolites, green-synthesized layered double hydroxides (LDHs), and functionalized biopolymers. For example, calcium ions on the surface of biopolymer-stabilized hydroxyapatite nanoparticles can be exchanged with toxic metal ions such as cadmium (Cd^{2+}) or lead (Pb^{2+}), thus facilitating their removal from wastewater.

Reduction

Some eco-friendly nanomaterials can chemically reduce toxic metal ions to less toxic or insoluble forms. Green-synthesized zero-valent iron nanoparticles (nZVI), for instance, are capable of reducing hexavalent chromium (Cr^{6+}) to the less toxic trivalent form (Cr^{3+}).

This transformation not only reduces the toxicity but also aids in the immobilization of metals through subsequent precipitation or adsorption. Biogenic compounds used in green synthesis, such as polyphenols and flavonoids, often act as reducing agents themselves, contributing to the detoxification process during nanoparticle formation. The inherent reducing capabilities of these phytochemicals enhance the nanomaterial's remediation performance post-synthesis.

Complexation and Chelation

Complexation involves the formation of stable metal-ligand complexes between heavy metal ions and functional groups on the nanomaterial surface. Biopolymer-based nanomaterials, such as those synthesized with alginate or cellulose, provide multiple coordination sites—typically hydroxyl, carboxyl, or amino groups—that strongly interact with metal ions. Chelation, a specific form of complexation, creates ring-like structures that tightly bind metal ions, making them easier to isolate and remove from aqueous systems. For example, green-synthesized ZnO nanoparticles functionalized with polyphenolic compounds have demonstrated strong complexation with copper (Cu^{2+}) and nickel (Ni^{2+}), effectively reducing their mobility and bioavailability.

Co-precipitation and Surface Precipitation

Co-precipitation refers to the simultaneous precipitation of heavy metals along with other compounds, often facilitated by the nanomaterial acting as a nucleation center. In contrast, surface precipitation involves the formation of insoluble metal compounds directly on the nanoparticle surface. For instance, phosphate-functionalized nanomaterials can induce the precipitation of lead as lead phosphate, thereby immobilizing it.

Magnetic nanomaterials, such as Fe_3O_4 synthesized via green routes, can promote co-precipitation of chromium or arsenic species while offering easy post-treatment separation using an external magnetic field.

Photocatalytic Transformation

Some green nanomaterials, such as titanium dioxide (TiO_2) and zinc oxide (ZnO) synthesized using plant extracts, exhibit photocatalytic properties. Under light irradiation, these materials generate reactive oxygen species (ROS) that can oxidize or reduce heavy metals. For example, photocatalytic reduction of Cr^{6+} to Cr^{3+} has been achieved using green-synthesized TiO_2 nanoparticles derived from Moringa oleifera extract. While photocatalysis is more common in organic pollutant degradation, its role in heavy metal transformation is gaining attention, especially in hybrid systems combining nanomaterials and solar energy for sustainable remediation.

Synergistic Mechanisms and Material Optimization

In practice, multiple removal mechanisms often occur simultaneously. For instance, adsorption and reduction may both contribute to chromium removal by iron-based nanomaterials. This synergistic effect can be enhanced by engineering nanocomposites—combinations of two or more green nanomaterials with complementary properties.

The efficiency of these mechanisms is influenced by several factors, including pH, temperature, initial metal concentration, contact time, and the presence of competing ions. Optimization of these parameters is crucial for real-world applications, as it determines not only the removal efficiency but also the selectivity and reusability of the nanomaterials.

Real-World Applications and Case Studies

The real-world deployment of eco-friendly nanomaterials for heavy metal remediation has gained traction over the last decade, particularly in regions where conventional treatment technologies are either cost-prohibitive or environmentally unsustainable. This section highlights notable case studies and practical applications that demonstrate the efficacy, scalability, and economic viability of green nanomaterials in actual wastewater treatment settings.

Pilot-Scale Wastewater Treatment Using Green Iron Nanoparticles in India

In a pilot-scale project conducted in Tamil Nadu, India, biosynthesized zero-valent iron nanoparticles (nZVI) derived from banana peel extract were employed to treat electroplating wastewater containing high concentrations of hexavalent chromium (Cr^{6+}). Over a 30-day trial period, the treatment system achieved over 95% reduction in Cr^{6+} levels. The system utilized a flow-through reactor with periodic replenishment of the nanomaterials, which demonstrated excellent stability and reusability over multiple cycles. Cost analysis revealed that the green synthesis route reduced the overall expenditure by approximately 40% compared to commercially available nZVI, while minimizing secondary waste generation.

Use of Green Synthesized ZnO Nanoparticles for Industrial Effluent Treatment in China

A textile factory in Jiangsu Province integrated green-synthesized zinc oxide (ZnO) nanoparticles into their wastewater treatment plant to address contamination by heavy metals such as lead (Pb^{2+}) and cadmium (Cd^{2+}). The nanoparticles, synthesized using green tea extract, were incorporated into a membrane bioreactor (MBR) system. Field results indicated a 90–96% removal efficiency for Pb^{2+} and Cd^{2+}, with minimal membrane fouling and negligible leaching of ZnO. The plant reported an improvement in effluent quality, enabling compliance with national discharge regulations, while also reducing operational costs due to lower chemical usage and sludge production.

Biochar-Iron Composite for Groundwater Remediation in Sub-Saharan Africa

In a community-led initiative supported by NGOs in Ghana, a biochar-supported iron nanoparticle composite was used to remediate groundwater contaminated with arsenic (As^{5+}) in rural wells. The biochar, produced from coconut husks, served as a sustainable scaffold for iron nanoparticle dispersion. The installed filtration units successfully reduced arsenic concentrations from an average of 120 μg/L to below the WHO guideline of 10 μg/L. The systems were low-maintenance, required no electricity, and were regenerated using a mild acid rinse. Community feedback emphasized the technology's ease of use and significant improvement in water taste and safety.

Chitosan-Based Nanocomposite Beads for Municipal Wastewater in Brazil

A treatment system implemented in São Paulo utilized chitosan-based nanocomposite beads embedded with green-synthesized silver nanoparticles to treat municipal wastewater containing trace levels of mercury (Hg^{2+}) and nickel (Ni^{2+}). The beads were deployed in a fixed-bed column and operated continuously over a six-month period. Analytical monitoring confirmed over 85% average removal efficiency for both metals. Importantly, the antimicrobial properties of silver contributed to a concurrent reduction in microbial load, enhancing overall effluent quality. Environmental impact assessments confirmed low toxicity and biodegradability of the spent materials.

Solar-Driven Photocatalytic System in Egypt

Researchers at Cairo University developed a solar-assisted photocatalytic system using green-synthesized TiO_2 nanoparticles obtained from Moringa oleifera leaf extract. The system was deployed in a solar reactor to treat tannery wastewater rich in chromium and organic matter. Over 30 sunlight exposure cycles, the process achieved 88% removal of

Cr^{6+} and 72% reduction in chemical oxygen demand (COD), indicating simultaneous removal of metal and organic contaminants. This field test demonstrated the dual-functionality of photocatalytic nanomaterials and the potential for integrating renewable energy in low-cost water treatment technologies.

Key Lessons from Case Studies

These case studies collectively illustrate several important aspects of green nanomaterials in real-world applications:

- **Scalability and Cost-Effectiveness**: Many green nanomaterials can be synthesized at scale using locally available biomass and simple techniques, making them suitable for deployment in low-resource settings.
- **Selectivity and Efficiency**: Functionalized nanomaterials exhibit high specificity and efficiency toward targeted heavy metals, often outperforming conventional adsorbents.
- **Reusability and Stability**: Several systems demonstrated the ability to regenerate and reuse nanomaterials over multiple cycles without significant performance loss, reducing operational costs and waste.
- **Environmental Compatibility**: Most green nanomaterials used in these applications showed minimal ecological impact and low toxicity, satisfying critical criteria for environmental safety and sustainability.
- **Integration into Existing Infrastructure**: The adaptability of nanomaterials into various treatment configurations—such as filters, reactors, or membranes—enhances their versatility and ease of adoption.

Conclusion

Real-world applications and case studies confirm that eco-friendly nanomaterials are not only effective in laboratory conditions but also in diverse and complex field settings.

Their ability to adapt to local resource availability, comply with regulatory standards, and integrate into existing treatment frameworks underscores their potential as viable tools for global wastewater remediation. Continued efforts are needed to monitor long-term impacts, optimize synthesis routes for field use, and promote technology transfer to ensure widespread adoption in both developed and developing countries.

Conclusion

The application of eco-friendly nanomaterials in heavy metal remediation represents a transformative advancement in wastewater treatment technologies. These materials, synthesized through green pathways using plant extracts, biopolymers, and other natural resources, exhibit exceptional physicochemical properties such as high surface area, enhanced reactivity, and the presence of functional groups favorable for metal ion interaction. Detailed characterization of these nanomaterials has revealed critical insights into their structure–function relationships, enabling the development of targeted remediation strategies.

Multiple mechanisms—including adsorption, ion exchange, reduction, complexation, and photocatalysis—govern the removal of heavy metals by these green nanomaterials. These mechanisms often act synergistically, making the materials not only efficient but also selective and environmentally benign. Furthermore, the integration of these materials into hybrid systems and nanocomposites continues to improve their performance, recyclability, and scalability. Despite these advancements, challenges remain in terms of standardizing green synthesis protocols, understanding long-term environmental impacts, and scaling up for industrial application. Therefore, future research should prioritize life cycle assessments, real-world pilot studies, and regulatory harmonization to facilitate the transition from laboratory innovation to commercial deployment. Ultimately, eco-friendly nanomaterials offer a sustainable, cost-effective, and high-performance solution to one of the most pressing environmental issues of our time—heavy metal pollution in wastewater.

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