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Green technologies for mine wastewater treatment: Biosynthesized nanoparticles and enzyme-based catalysis

Kipkorir Yano Yator [1] and Abass Aliu [2,*]

[1] *Michigan Technological University, U.S.A.*
[2] *University of Development Studies, Ghana.*

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Abstract

The application of biogenic metallic nanoparticles in catalytic wastewater treatment has gained significant attention as an eco-friendly alternative to traditional physical and chemical methods of water treatment. Their advantages, including low production costs, environmental friendliness, and ease of operation, have earned them a place among essential materials for sustainable remediation technologies. This has led to an increasing number of studies exploring nanotech-based catalytic processes to address wastewater pollution issues more effectively. Mining wastewaters, particularly acid mine drainage (AMD), pose a persistent environmental challenge due to their high acidity, elevated heavy-metal concentration, and complex geochemistry. Traditional physicochemical treatment methods often produce secondary pollutants, require high energy inputs, and generate large volumes of sludge. This review examines recent advancements in green biotechnology-based remediation approaches that utilize biosynthesized nanoparticles derived and enzyme-based catalysis for treating mine wastewater. this research paper evaluates the potential of biogenic metal and metal-oxide nanoparticles, produced through microbial or plant-mediated methods, to perform multifunctional remediation via adsorption, redox reactions, and in some cases, photocatalysis. it also explore the role of enzymes, particularly oxidoreductases, and their synthetic mimics, known as nanozymes, in detoxification through catalytic actions under mild, eco-friendly conditions. An analysis of recent literature highlights emerging themes, limitations, and translational challenges, such as nanoparticle stability, ecological risks, enzyme robustness in mining environments, and scale-up barriers. the paper proposes future research directions, integrating hybrid bio-nano systems, performing field-scale pilot testing, conducting life-cycle assessments, and developing novel acid-tolerant biocatalytic systems. This review emphasizes that green biocatalytic strategies hold the potential to transform wastewater management sustainably, but significant work is required to bridge the gap from promising laboratory-scale systems to field applications.

Keywords: Acid Mine Drainage; Mine Wastewater; Biosynthesized Nanoparticles; Nanozyme; Enzyme Catalysis; Bioremediation; And Heavy Metal Remediation

1. Introduction

Mining operations are a necessity for global economic development, providing metals that are essential for infrastructure, energy, and technology [1] . However, they often generate a large amount of wastewater laden with heavy metals such as lead, zinc, copper, arsenic, sulphates, and acidity, mainly in the form of acid mine drainage (AMD) [2]. AMD occurs when sulphide minerals such as pyrite are oxidized by water and air, resulting in the formation of sulphuric acid and the mobilization of metal ions. These acidic and metal-rich effluents produced can wipe out aquatic ecosystems, pollute underground water, and pose a serious health risk through bioaccumulation of toxic metals. Traditional remediation methods, such as chemical precipitation, lime neutralization, coagulation, ion exchange, reverse

* Corresponding author: Abass Aliu

osmosis, and constructed wetlands, are widely used [3]. These methods, however, have limitations, such as high chemical demand, generation of sludge in large quantities, secondary pollution, disposal, and costs of disposal and regeneration [4]. Their performance might be reduced under low-pH, high-metal, and high-ionic-strength conditions typical of mine effluents [5].

Biosynthesized nanoparticles have emerged as promising alternatives due to their energy-efficient synthesis, low cost, and algal extracts, which act as natural reducing and stabilizing agents [6]. The biogenic nanoparticles have unique surface chemistries and bio-organic capping layers that enhance catalytic, adsorptive, and redox capabilities. BNPs such as iron oxide, silver, gold, titanium dioxide, and zinc oxide have demonstrated strong potential for the degradation of organic pollutants, oxidation of cyanides, detoxifying arsenic intermediates, and adsorption of heavy metals usually present in mine wastewater. Their stability under extreme pH, high ionic strength, and high temperatures makes them more suitable for AMD applications, although dedicated studies in real mine wastewater remain limited. The argument supporting this includes biological processes capable of producing nanomaterials at room temperature and pressure without harsh reagents, enzymes catalyzing redox reactions with high specificity and minimal waste, and the combination of biological structures in hybrid systems with nanomaterials [7].

Enzyme-based catalysis represents another emerging biotechnological alternative for mine wastewater treatment. Enzymes such as laccases, peroxidases, reductases, and oxidoreductases can selectively transform cyanides, phenols, thiocyanates, sulphur compounds, and certain metal complexes at mild conditions, generating minimal secondary waste [8, 9]. However, enzymes are sensitive to pH, high metal concentrations, and temperature changes typical of AMD, with heavy metals often inhibiting or denaturing catalytic sites [10]. Most enzyme-based research is also focused on generic industrial wastewater rather than mining-specific effluents.

Despite reviews on nanomaterials for wastewater treatment and on bio-nanocomposites for heavy metal remediation, only a few have explicitly focused on mine wastewater and examined the intersection of biosynthesized nanoparticles and enzyme/nanozyme catalysis in mining [4]. Many biological methods used for heavy metal remediation, such as microbial reductases, oxidoreductases, or immobilized enzyme systems, are studied in generic wastewater but not specifically assessed for AMD or mining discharge waters [11].

Therefore, this review aims to give an overview of recent advancements in green biocatalytic approaches, focusing on biosynthesized nanoparticles and enzyme-based catalysts for the treatment of mine wastewater. It assesses their operation, performance, drawbacks, and potential for field translation, and we propose future research directions to accelerate the adoption process.

2. Comparative Evaluation of BNPs and Enzyme-Based Catalysis

Biosynthesized nanoparticles (BNPs) and enzyme-based catalytic systems illustrate the two major green technologies for remediating mine wastewater. Both methods provide green solutions to conventional physicochemical treatments, but they differ in synthesis origin, catalytic behaviour, stability, environmental tolerance, scalability, and pollutant specificity. BNPs, obtained from plants, microbes, and algal extracts, show broad-spectrum activity and stability under harsh conditions, while enzyme-based catalysts offer high specificity and biodegradation, yet require a more controlled environment. A comparative evaluation of both BNPs and enzyme-based catalysis is shown in Table 1.

Table 1 A comparative evaluation of both BNPs and enzyme-based catalysis

Biosynthesized nanoparticles (BNPs)	**Enzyme-Based Catalysis**
It functions through various methods such as adsorption, redox reactions, catalytic oxidation/reduction, and radical-mediated degradation.	Catalyze precise biochemical reactions without toxic intermediates, and follow the enzyme-substrate pathways.
Stable under extreme pH, temperature, and high metal concentration typical of mine wastewater.	Sensitive to extreme pH and temperature conditions.
It is produced using plant, bacterial, fungal, or algal extracts that can reduce and adsorb metal ions.	It is derived from purified biological macromolecules (laccases, peroxidases, oxidoreductases)

3. Emerging Trends and Hybrid Green Technologies

In surveying literature, four major interrelated themes were identified:

- The production of metal and metal-oxide nanoparticles through biosynthesis for adsorption and transformation
- Catalytic remediation through enzymes and nanozymes
- Hybrid bio-nano systems that combine both methods;
- Challenges, risks, and scale-up

3.1. Biosynthesized Nanoparticles for Heavy-Metal Capture and Transformation

A biological system consisting of microorganisms (bacteria, fungi) and plants for the production of metallic or metal-oxide nanoparticles (NPs) that have excellent environmental compatibility and high reactivity has been a leading trend in recent years [12]. These biogenic NPs are produced under mild conditions, frequently employing the reducing power of biological molecules (proteins, metabolites, phytochemicals), and show surface chemistries suitable for remediation [12-14]. Compelling research conducted by Ishfaq et al [15] demonstrated the synthesis of manganese oxide (MnO) nanoparticles using microbial or plant material as a wastewater treatment method. The biosynthesised MnO NPs revealed a strong capacity for chemical oxygen demand (COD) removal, as well as for phosphate and sulphate, with removal efficiencies around 79%, 64%, and 64.5%, respectively as illustrated in Figure 1 [15]. When treated water was used to grow wheat seedlings, oxidative stress effects in the plants were reduced, implying that the NPs not only removed contaminants but also produced water of relatively lower toxicity [16]. There has been an increasing attention on embedding biogenic nanoparticles in more complex matrices to recover, reuse, and stabilize their structure [17]. Figure 1 shows Removal efficiencies of MnO nanoparticles

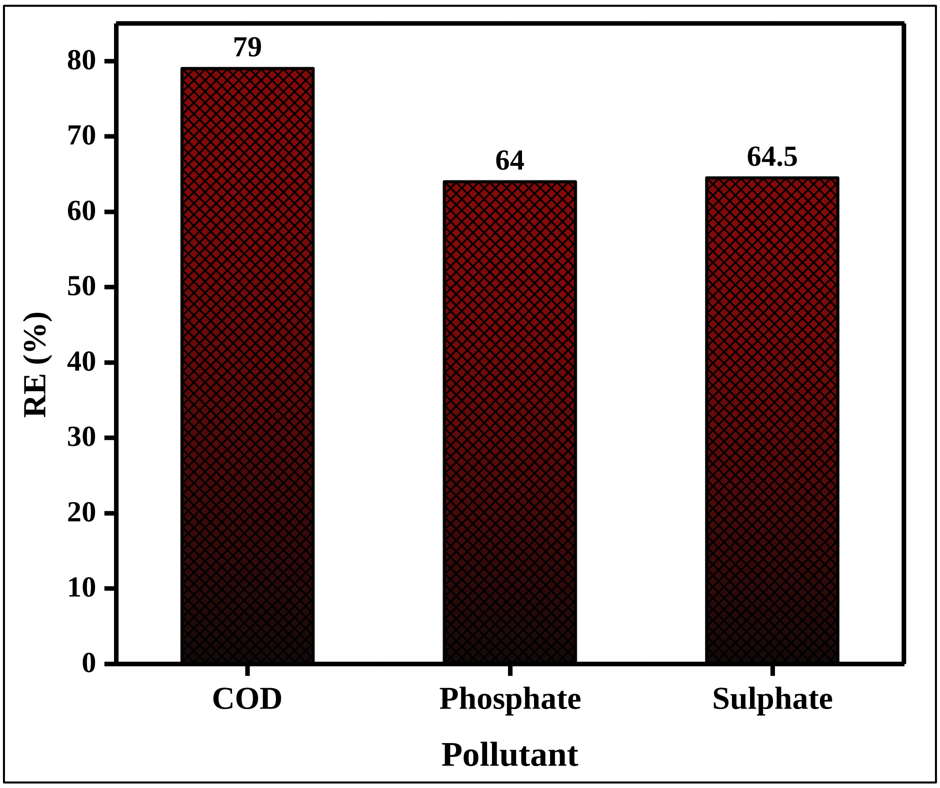

Figure 1 Removal efficiencies of MnO nanoparticles

A systematic review published by RSC Environmental Science: Nano (2024) investigated immobilization ways of biogenic metal nanoparticles on sustainable supports such as biofilms, biomass, and polymers. The review pointed out that immobilization significantly improved operational stability up to 65 %, enhanced reusability over five to seven treatment cycles, and reduced NPs leaching by 40% compared to free NPs, making them more effective in wastewater treatment uses [17, 18]. Concurrently, more general reviews on green nano-adsorbents emphasize that plants and microbial agents can produce nanoparticles with inherent capping and stabilization, enhancing the adsorption process and reducing aggregation [6, 19]. In a 2024 issue of Current Pollution Reports, Bakhtiari et al (2024) [20] published a detailed review on green nano adsorbents for heavy metals removal. They reported that antioxidants in plant extracts perform a two-function as reducing agents and stabilizers, improving colloidal stability by 50-70%, and increasing adsorption capacity for heavy metals (e.g., Pb^{2+}, Cd^{2+}, Cr^{6+}) by 30-55%, compared to non-capped nanoparticles.

While most of this work has been significantly advanced in model wastewater systems, the mining context is characterized by a range of challenges, such as low pH, high ionic strength, competing ions, and extreme redox conditions, which are often less regenerated in laboratory studies. The multifunctionality and versatility of biosynthesized NPs' properties (adsorption, redox transformation, and antimicrobial activity) indicate that they have the potential to be designed specifically to tackle the complex geochemistry of AMD and other mine effluents.

3.2. Enzyme Catalysis and Nanozymes for Detoxification

Biosynthesized NPs focus on removal, while enzymatic catalysis provides a complementary alternative, transforming pollutants instead of sequestering them [21, 22]. Enzymes, particularly oxidoreductases such as peroxidases, catalases, superoxide dismutases, and laccases, display high specificity and control over redox reactions under mild conditions. However, their direct application in AMD remains relatively underexplored [23, 24]. Recent advances in environmental biotechnology have greatly expanded our understanding of nanozymes, which are nanomaterials designed to mimic enzymatic activity [25, 26]. A recent bibliometric review by [27] highlighted the environmental applications of oxidoreductase-like nanozymes and noted their increasing use in pollutant degradation, heavy metal detoxification, and sensing. These nanozymes mainly consist of metal oxides such as iron, cerium, carbon-based materials, or hybrids, and can imitate the activities of catalase, peroxidase, and superoxide dismutase.

A notable example is cerium oxide (CeO_2) nanoparticles, which have been shown to possess catalase- and peroxidase-like activities. CeO_2 NPs, coated with polystyrene and functionalized with polymers such as poly (ethylene glycol) (PEG) anchored through phosphonic acids, have demonstrated enhanced oxidoreductase-mimicking activity [28, 29]. These engineered nanozymes are likely very useful in environments with reactive oxygen species or redox-sensitive pollutants, as they maintain their redox activity even in complex media. Figure 2 shows the nanozyme catalytic activity of CeO_2. In the broader field of bioremediation of emerging contaminants, enzymes have been employed for wastewater micropollutant biodegradation [30]. A review paper by Bittencourt et al. [30] provides an overview of how immobilization, synthetic biology, and nanozymes collectively form robust, efficient biocatalytic systems. Additionally, a review published in the Journal of Environmental Chemical Engineering in 2021 emphasizes the importance of enzyme immobilization and genetic engineering methods to improve enzyme stability and activity in real-world wastewater applications. Translating these advancements to the mining context suggests promising opportunities, such as nanozymes capable of oxidizing sulphide species, catalyzing dismutation of reactive oxygen species, or selectively reducing toxic metal ions [31, 32]. However, questions regarding their stability in low pH, high metal environments, immobilization, reuse, and recovery in large-scale industrial systems remain. Figure 2 illustrates the role of a CeO_2 nanozyme in catalyzing pollutant transformation through redox reactions involving O_2 and H_2O.

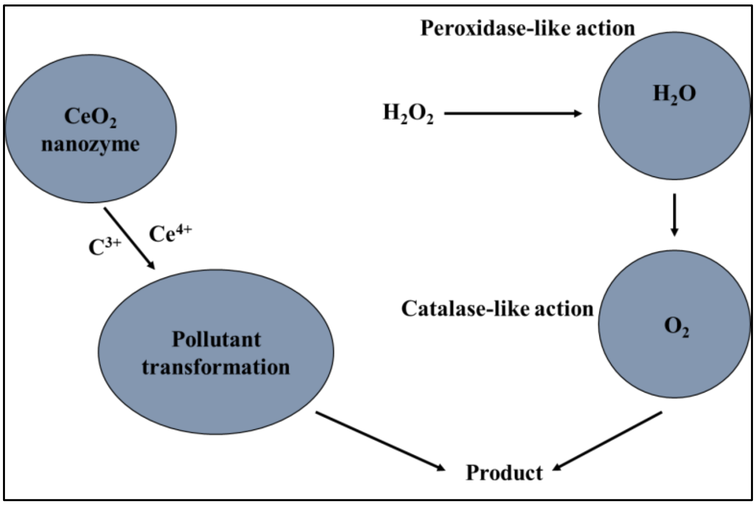

Figure 2 CeO_2 nanozyme catalytic activity

3.3. Hybrid Bio-Nano Composites for Integrated Remediation

Recognizing the combined strength of biosynthesized NPs and catalytically active enzymes or nanozymes, recent studies are increasingly focused on hybrid bio-nano composites (Figure 3) [33]. These structures integrate biological materials such as microbial biomass, fungal filaments, and plant biomolecules with nanoparticulate catalysts, using both adsorption and transformation. A recent article published in Frontiers in Nanotechnology talked about the application of fungal biomass-metal nanocomposites as highly effective biosorbents. The metal-oxide nanoparticles are thoroughly dispersed within the fungal matrix, which not only stabilizes them for repeated use but also facilitates their separation. At the same time, the embedded nanoparticles provide reactive sites for metal binding and transformation [34]. The writers, however, point out that despite these composites performing brilliantly in lab-scale adsorption tests, very few studies cover real wastewater (particularly mining effluent) or long-term reuse under environmental conditions. Another frontier is enzyme-nanoparticle hybrid systems, in which the enzymes are trapped on or in the biogenic NP structures [35]. Such systems have the potential to conduct a series of reactions: for instance, first, metal ions are adsorbed (through the NP), then they are enzymatically transformed (through enzyme or nanozyme), effectively detoxifying while concentrating contaminants [25]. While specific applications in mine wastewater are still limited in published literature, the conceptual groundwork is strong, and such multifunctional systems could solve the issues of many limitations of other methods [25]. Figure 3 shows Hybrid Bio-Nano composite

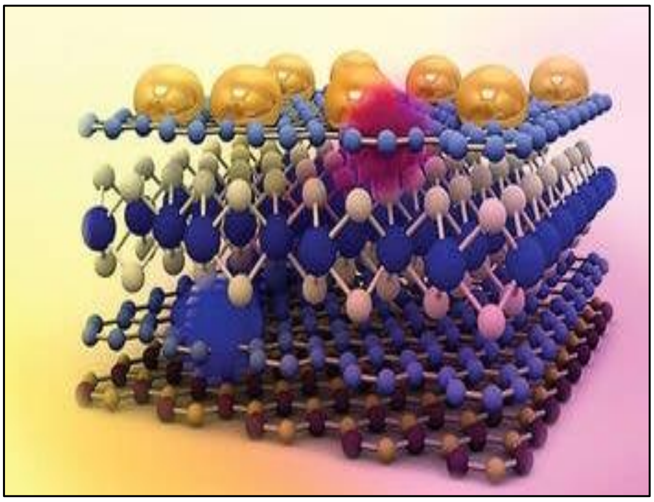

Figure 3 Hybrid Bio-Nano composite

3.4. Challenges, Risks, and Translational Barriers

Despite the potential for significant benefits, green biocatalytic approaches face major setbacks that need to be resolved for translation to mine water treatment. Ecotoxicity and the fate of nanoparticles pose unresolved risks. Biosynthesized nanoparticles may have less harmful effects than their chemically synthesized ones, but once they are released into the environment, they may aggregate, dissolve, or undergo unpredictable changes in their chemical composition, especially under extreme geochemical conditions prevalent in mining areas [19]. Although it is promising, only a few studies have conducted rigorous ecotoxicological assessments of biogenic NPs in AMD-like matrices [24]. The stability of the enzyme and nanozyme is a major barrier. The acidic pH, high ionic strength, and metal concentrations, which are characteristics of mine effluents, can cause denaturing of enzymes and deactivate nanozymes over time [26, 35]. Techniques such as immobilization, polymer coating, and making more robust catalysts are still under development, but their long-term performance in mining environments has not been adequately evaluated. Economic and life-cycle factors are also major concerns. Although biosynthesis reduces the usage of hazardous reagents, production of scaled-up biological nanoparticles, stabilizing, recovering, and regenerating them, as well as synthesizing and immobilizing nanozymes, may incur high cost. Life-cycle assessments (LCA) and techno-economic analysis (TEA) are required to evaluate and compare these green biocatalytic systems with well-established remediation methods [36, 37]. Regulatory and social issues could impede deployment. The regulations for nanoparticle discharge are being implemented slowly, and biogenic materials are the least developed in this aspect. Communities near mines might feel suspicious of unknown nanomaterials and bioengineered catalysts. Good governance, safety standards, and transparent stakeholder engagement must be maintained [38, 39]. Scale-up to pilot and field deployment remains rare. Most research remains at laboratory proof-of-concept, using spiked model solutions instead of real mine water, and only for short times. To achieve true translation, researchers must devise and evaluate hybrid reactors, immobilized systems, or packed-bed arrangements in the actual mining environment, with continuous flow, regeneration, and monitoring over an extended period [40, 41].

Future Directions and Research Gaps

Field-scale demonstration and pilot testing are urgently needed to go beyond batch laboratory studies and validate biosynthesized nanoparticles, nanozymes, and hybrid systems under actual mine wastewater conditions. This should include building pilot reactors at mining-impacted areas, evaluating long-term performance, regeneration cycles, and material losses [42]. Ecotoxicological and environmental fate studies on biogenic nanoparticles are equally important under mining geochemistry, such as their aggregation, dissolution, speciation, mobility, and bioavailability, along with toxicity assays on aquatic organisms and microbial communities. Research should also focus on the development of durable biocatalysts by identifying enzymes and nanozymes that remain active under acidic, metal-rich conditions through extremophilic enzyme screening, acid-resistant immobilization matrices, and protective nanozyme coatings [28]. Progress further relies on hybrid reactor design and system integration, where biosynthesis, adsorption, and catalysis are co-designed into systems such as NP-producing biofilm reactors, immobilized enzyme or nanozyme columns, and modular units compatible with existing mine-water treatment facilities [43]. Life-cycle assessment and techno-economic evaluation are important for the comparison of green biocatalytic strategies and conventional treatments, as well as for modelling costs of large-scale production that includes synthesis, regeneration, recovery, energy, labour, and disposal [44]. The responsible implementation will necessitate legal frameworks and involvement of stakeholders with regulators, mining companies, and local communities to determine governance models for nanomaterials usage, containment, recycling, and disposal while maintaining transparency and risk communication [39, 45]. The industry will benefit from data sharing and standardization through unified testing protocols for nanoparticle toxicity, enzyme stability, and regeneration, as well as open-access databases that record performance across various geochemical matrices to improve comparability and accelerate adoption.

4. Conclusion

Green biocatalytic methods, especially biosynthesized nanoparticles and enzyme/nanozyme-mediated catalysis, offer a promising and potentially revolutionary approach to mine water remediation. Biosynthesized nanoparticles combine environmentally friendly production with multifunctional remediation capabilities, including adsorption, redox, and antimicrobial effects, while nanozymes and immobilized enzymes enable selective and efficient catalytic conversion of contaminants under mild conditions. Hybrid systems integrating these components could lead to resource-sharing benefits and more effective utilization of technologies. However, to fully realize their potential in the mining industry, future research must move decisively toward field-scale validation, long-term stability testing, environmental risk assessment, and techno-economic analysis. Interdisciplinary collaboration among microbiology, materials science, environmental engineering, and regulatory science will be essential to design systems that are effective, safe, and socially acceptable. If green biocatalytic methods are successfully developed and implemented in mine water treatment, the industry can reduce its chemical footprint and minimize secondary pollution, fostering more sustainable water management practices in mining.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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