Pol. J. Environ. Stud. Vol. XX, No. X (XXXX), 1-23

DOI: *10.15244/pjoes/214923* ONLINE PUBLICATION DATE: 2026-03-02

Review

Integrated Approaches for Heavy Metal Pollution Management: Mechanisms and Synergistic Remediation Strategies

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Received: 27 July 2025
Accepted: 30 November 2025

Abstract

Heavy metal pollution is a significant threat to global environmental governance, endangering both ecosystems and human health. Current technologies, though partially effective, are often limited by applicability, cost, and stability in complex scenarios. This review explores multi-technology collaborative remediation approaches, emphasizing synergies in mechanisms, governance phases, environmental adaptability, and spatiotemporal dimensions. These coupled methods enhance treatment efficacy and reduce environmental risks. The review also categorically evaluates various remediation technologies, discussing their strengths and weaknesses, and suggests improvements. These insights offer strategic guidance for managing complex pollution systems through optimized technology combinations.

Keywords: heavy metal pollution, environmental governance, multi-technology synergy, mechanism complementary synergy, spatiotemporal dimension synergy

Introduction

Heavy metal pollution has become a significant challenge to global environmental governance. Industrialization, urbanization, and intensified agricultural activities have accelerated the release of heavy metals (e.g., Cd, Pb, Hg, Cr) into soil and water systems, with industrial emissions in developing countries increasing by 5-8% annually [1]. Pollutants enter the environment through pathways such as industrial wastewater discharge, as shown in Fig. 1, mine tailings leakage, and e-waste disposal, contributing to 20% of global lead contamination [2]. The United Nations Environment Programme (UNEP) highlights substantial economic losses from heavy metal pollution, while the World Health Organization (WHO) identifies it as a major environmental health risk due to its association with renal, neurological, and developmental disorders [3]. Heavy metals are highly toxic, resistant to degradation, and bioaccumulative, with Cd causing kidney damage and Hg associated with neurotoxicity even at low concentrations [4]. Climate change further complicates remediation efforts by increasing heavy metal mobility and bioavailability. Developing countries

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face disproportionate impacts due to weak regulations and limited access to control technologies, underscoring the urgency of sustainable remediation strategies.

Current technologies for heavy metal pollution treatment are primarily categorized into physicochemical methods and bioremediation. Physicochemical methods, such as adsorption, chemical precipitation, electrochemical methods (e.g., electrodeposition), and membrane enrichment, are widely used in industrial wastewater treatment and soil remediation due to their high efficiency and broad applicability [5]. For example, adsorption technologies using biochar, sodium alginate-based hydrogels, and mineral-based adsorbents offer advantages such as ease of operation and high adsorption capacity [6]. However, these methods have limitations: chemical precipitation generates substantial heavy metal-laden sludge, necessitating further treatment to prevent secondary pollution [7]; electrochemical methods exhibit low current efficiency for low-concentration wastewater and face challenges related to electrode material durability and cost [8]; membrane enrichment technology is hindered by membrane fouling and high energy consumption [9]. Bioremediation technologies, such as phytoaccumulation and biomineralization, are environmentally friendly but face challenges, including extended remediation cycles, limited adaptability to complex pollution, and sensitivity to environmental conditions [10]. Consequently, existing technologies require optimization in terms of applicability, economic feasibility, and long-term stability in complex pollution systems.

Despite some success in addressing heavy metal pollution, existing technologies are limited in practical applications, and no single technology can fully meet treatment requirements under complex environmental conditions [11]. This requires combining the advantages of different technologies to deal with complex pollution systems. However, many current studies simply categorize remediation technologies as physical, chemical, and biological and do not classify them from the perspective of remediation mechanisms. Consequently, this study aims to synthesize and summarize heavy metal pollution control technologies from the perspective of mechanisms of action and analyze the synergistic remediation through complementary mechanisms, governance stages, environmental adaptation, and spatiotemporal dimensions. This approach provides ideas for future single-technology combinations to manage complex pollution systems [12].

Results and Discussion

Remediation Mechanisms

Adsorption Mechanism

Force adsorption is driven by weak intermolecular forces, primarily van der Waals forces, and is considered non-specific [13]. It relies on intermolecular attractions, such as electrostatic and dispersion forces, without forming or breaking chemical bonds. Due to the weak forces involved, the adsorption strength is low, with a heat of adsorption typically ranging from 20 to 40 kJ/mol. This results in rapid adsorption and desorption rates [14]. Additionally, force adsorption minimally affects the chemical properties of the adsorbent, and the process is reversible, allowing the adsorbent to re-enter the solution or gas phase

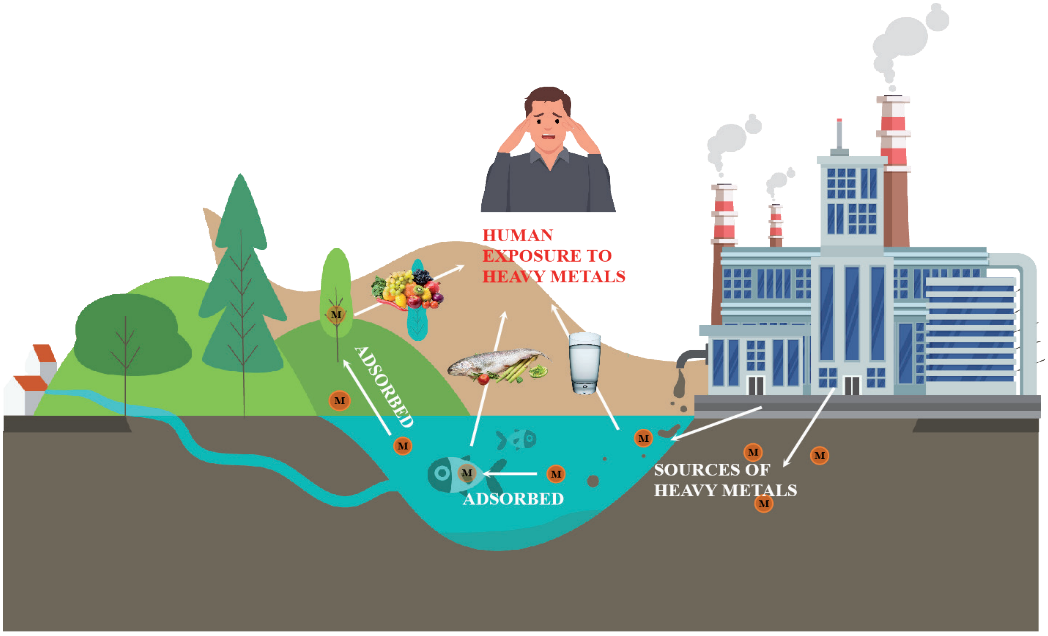

Fig. 1. Environmental pollution diagram of heavy metals.

under changing external conditions like temperature or pressure [15, 16]. Porous materials, such as activated carbon and zeolites, enhance physical adsorption due to their large specific surface areas and pore structures, which provide more adsorption sites.

Ion exchange is based on the substitution of equivalent ions, involving interactions between charged groups on the stationary phase and oppositely charged ions in the solution [17]. This process follows the principle of equivalent exchange, maintaining charge balance in the system. For example, during cation exchange, a negatively charged site on the stationary phase is displaced by a cation.

Ligand complexation involves forming stable complexes between functional groups on the adsorbent surface and heavy metal ions through coordination bonds. This mechanism is critical for heavy metal ion removal and is key in designing effective adsorbents. For instance, common ligands like amino ($-NH_2$) and carboxyl ($-COOH$) groups can form stable complexes with metal ions (e.g., Cu^{2+} and Zn^{2+}) via lone-pair electrons [18]. Similarly, chitosan derivatives with amino and hydroxyl groups can adsorb heavy metals through coordination. Chemical modification, such as introducing amino and carboxyl groups, can significantly enhance the adsorption performance of adsorbents for heavy metal ions [19].

Solidification Mechanism

Solidification and stabilization technology, encompassing chemical precipitation and biomineralization, is a crucial method for remediating heavy metal pollution. Chemical precipitation involves adding specific chemicals to transform dissolved heavy metal ions into insoluble solids (e.g., sulfides, hydroxides, and carbonates), effectively separating pollutants from water [20]. This process relies on chemical reactions between metal ions and precipitants, forming low-solubility products that efficiently remove heavy metals under optimal pH conditions [14].

In contrast, biomineralization leverages microbial or enzyme-induced mineral precipitation to immobilize free heavy metal ions into stable solid-phase minerals, thereby reducing their mobility and toxicity. For example, in microbial-induced carbonate precipitation (MICP), urease catalyzes the decomposition of urea to produce carbonate ions. These ions then combine with calcium to form calcium carbonate, which co-precipitates or adsorbs heavy metals like lead and cadmium [21].

Reduction Mechanism

Reduction technology is vital for remediating heavy metal pollution, with chemical reduction and electrodeposition being two key methods. Chemical reduction involves adding a reducing agent to transform heavy metal ions from a high to a low oxidation state. For example, highly toxic Cr(VI) is reduced to low-toxic Cr(III), forming insoluble $Cr(OH)_3$ precipitates, thereby decreasing its mobility and bioavailability in soil. Electrodeposition, based on electrochemical principles, directly reduces heavy metal ions (e.g., Cu^{2+} and Pb^{2+}) in solution to metallic monomers through cathodic reduction, depositing them on the cathode surface [22]. For instance, Cu^{2+} is reduced to Cu^0 by accepting electrons from the cathode. This method outperforms traditional flocculation and flotation techniques, offering high selectivity and recovery rates of up to 99%. By optimizing electrode materials (e.g., bimetallic alloys) and operating parameters, electrodeposition technology reduces energy consumption and metal residues, enhancing environmental sustainability [23].

Enrichment Mechanism

Membrane enrichment leverages the selective permeability of materials, such as polyamide composite membranes, to retain heavy metal ions through physical sieving, charge repulsion, and chemical adsorption. The retention efficiency for different ions is determined by the membrane's pore size distribution and surface charge [24]. For example, ultrafiltration membranes remove colloidal heavy metal complexes via nanoscale pores, while electrodialysis, an electrically driven process, enhances ion migration using ion-exchange membranes under an electric field [25]. Plants remediate heavy metals through bioaccumulation and translocation. Non-hyperaccumulators release root exudates (e.g., organic acids) to modify rhizosphere pH and redox potential, thereby increasing metal bioavailability [26]. In contrast, hyperaccumulators, such as Centipedegrass, use specific transporters to sequester metals like arsenic in vacuoles. Rhizospheric microbes further activate metals by secreting chelators. Chemical enhancers, such as EDTA, improve metal solubility but pose risks of secondary pollution; thus, biodegradable alternatives are preferred [27].

Advantages and Disadvantages of Single Technology Remediation

Adsorption Technology

Adsorption technology encompasses biocarbon adsorption, sodium alginate-based hydrogel adsorption, mineral-based adsorption, and microbial adsorption, each with distinct characteristics (Fig. 2).

Biochar adsorption addresses heavy metal pollution through multi-mechanism interactions between biochar's physicochemical properties and heavy metal ions. Its porous structure and large specific surface area (100-1000 m^2/g) provide ample adsorption sites [14]. Surface functional groups (e.g., carboxyl, hydroxyl, phenolic) facilitate adsorption via complexation, ion exchange, and electrostatic attraction [9]. For instance, magnetically modified biochar achieved a 47.90 mg/g adsorption capacity for Cd^{2+} through inner surface complexation and co-precipitation [28]. Biochar's benefits include lower production costs compared to activated carbon, with raw materials sourced from agricultural waste (e.g., straw, poultry manure) or municipal sludge, promoting waste-to-resource conversion [29]. Its alkaline nature (pH 8-10) neutralizes acidic soils, and its porous structure supports microbial habitats, aiding ecological restoration [30]. However, challenges persist. Raw material heterogeneity and pyrolysis variations affect product performance. For example, wood biochar has a specific surface area two to three times greater than straw biochar, and pyrolysis temperatures above 600°C can degrade functional groups [31, 32]. Additionally, heavy metal desorption is a concern in acidic ($pH<4$) or high-salinity environments, potentially causing secondary pollution.

Sodium alginate-based hydrogels adsorb heavy metals through their unique chemical structure and physical crosslinking properties [33]. Sodium alginate, a natural polysaccharide composed of β-D-mannuronic acid (M) and α-L-guluronic acid (G) units, binds heavy metal cations (e.g., Pb^{2+}, Cu^{2+}, Cd^{2+}) via its carboxylic acid groups (-COO-) to form stable complexes [34]. The "Egg-box" structure formed by calcium ion crosslinking captures heavy metals through G unit alignment, while the porous network enhances adsorption kinetics [35]. Functional modifications further improve selective adsorption. For example, hydrazide groups form chelating bonds, and dopamine grafts increase affinity through π-π interactions and hydrogen bonding. Fibrous alginate hydrogel (AFH) demonstrated a 434.89 mg/g adsorption capacity for Pb^{2+}, with Langmuir isotherm modeling indicating monolayer chemisorption [36]. Composite hydrogels (e.g., chitosan/bentonite) combine electrostatic and physical retention mechanisms, enhancing co-adsorption efficiency for multiple heavy metals [37]. These hydrogels exhibit multidimensional performance. Smart functionalized hydrogel (FSAH) achieved saturated adsorption capacities of 157.1 mg/g for Cu^{2+} and 371.4 mg/g for Pb^{2+}, surpassing commercial resins [36]. Their biocompatibility and environmental friendliness make them suitable for ecologically sensitive areas. For example, Pb^{2+} removal remained at 93.15% and Cu^{2+} at 55.18% after five cycles without secondary pollution [36]. pH-responsive characteristics enable selective desorption, facilitating targeted recycling [38]. Despite these advantages, challenges remain. Physically crosslinked networks risk destabilization under low pH or high ionic strength conditions, reducing adsorption capacity [39]. In polymetallic systems, competitive adsorption can mask active sites, with Pb^{2+} selectively occupying more sites due to its higher electronegativity (2.33 V) compared to Cd^{2+} (1.69 V) [40]. Additionally, adsorbed hydrogel regeneration exhibits irreversible decay due to active group oxidation and network structure collapse [41].

Mineral-based adsorbents address heavy metal pollution through ion exchange, surface complexation, and electrostatic interactions. Layered silicate clay minerals (e.g., montmorillonite, kaolinite) capture heavy metals via interlayer cation exchange [5]. Magnetic composites (e.g., superparamagnetic pozzolanic nanocomposites) enhance adsorption capacity and facilitate magnetic recovery [42]. Chemical modifications, such as acid activation, increase surface active sites, as seen with treated kaolinite clay showing stronger affinity for Cd^{2+} and Pb^{2+} [43]. Adsorption properties are closely linked to surface charge, pore structure, and functional groups. Mineral-based adsorbents offer ecological safety and economic viability. Derived from natural minerals (e.g., clay, diatomaceous earth), they can be efficiently modified for adsorption [44]. Their biocompatibility minimizes secondary pollution risks. In engineering applications, Fe_3O_4-pozzolan composites are suitable for large-scale wastewater treatment due to magnetic enrichment technology [45]. However, challenges include structural collapse and active site loss in clay minerals after multiple cycles, low permeability in dynamic systems leading to clogging, and particle agglomeration reducing specific surface area [42, 45].

Microbial adsorption relies on the physicochemical binding and biotransformation of heavy metals by microbial cells and metabolites. Functional groups on cell walls (e.g., carboxyl, amino, phosphate, hydroxyl) adsorb heavy metals via ion exchange, surface complexation, or electrostatic interactions [46]. For example, the peptidoglycan layer of Gram-positive bacteria and fungal chitin efficiently bind cations like Cd^{2+} and Pb^{2+}. Extracellular polymers (EPS) further enhance adsorption through chelation. Agrobacterium tumefaciens F2 EPS achieved a 94.67 mg/g adsorption capacity for Pb^{2+} [47]. Microbial adsorption offers significant environmental and economic advantages. Microbial biomass is widely available, with industrial and agricultural wastes serving as low-cost adsorbents [48]. This technology excels at removing low concentrations of heavy metals (<100 mg/L) without secondary pollution risks. For example, *Bacillus* achieved a 98% Zn^{2+} adsorption rate at pH 5 [49]. Microbial communities can resist ionic interference through interspecies collaboration, enhancing adsorption efficiency in complex substrates [50]. Despite laboratory progress, industrial application faces challenges. Complex wastewater components (e.g., organic matter, competing ions) can inhibit adsorption efficiency. For example, Cl^- reduced *Escherichia coli*'s Hg^{2+} adsorption capacity by 10% [51]. Additionally, microbial adsorbents lack sufficient mechanical strength and hydraulic stability, with immobilized materials (e.g., calcium alginate microspheres) losing biomass (20%) in continuous flow reactors, causing treatment efficiency fluctuations [52].

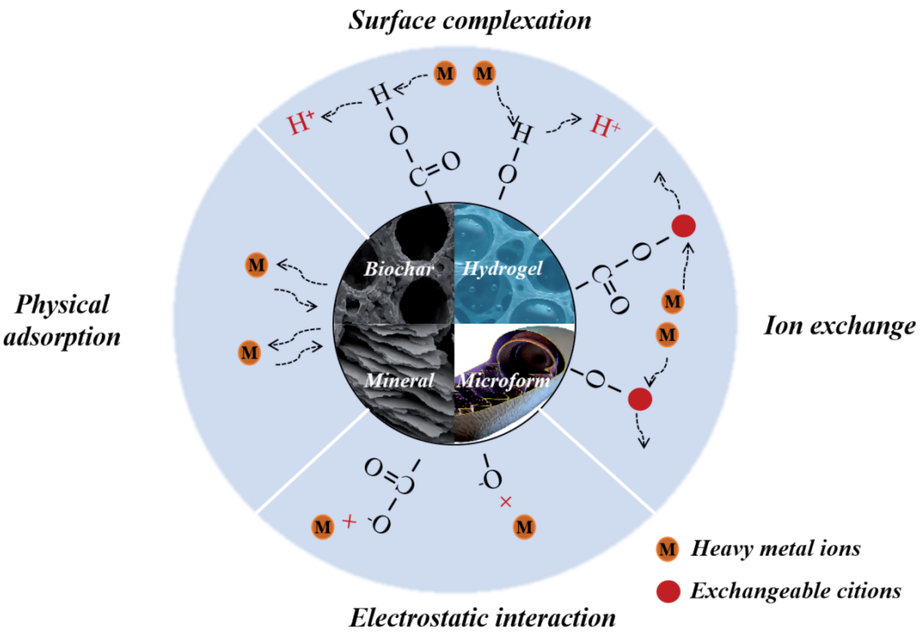

Fig. 2. Diagram of the mechanism of adsorption technology for heavy metal pollution.

Solidification Technology

Solidification technology, particularly chemical precipitation and biomineralization (Fig. 3), holds significant potential for remediating heavy metal pollution. Chemical precipitation transforms dissolved heavy metal ions into insoluble solids (e.g., sulfides, hydroxides, carbonates) by adding specific chemicals, facilitating physical separation of pollutants [53]. This process relies on chemical reactions between heavy metal ions and precipitants, forming low-solubility products [54]. For example, sodium sulfide (Na_2S) precipitates cadmium and lead as CdS ($K_{sp} = 1.26\times10^{-9}$) and PbS ($K_{sp}\approx1\times10^{-7}$), respectively, under optimized conditions [55]. pH is a critical parameter, with optimal ranges varying by metal and precipitant. In hydroxide precipitation, metals like copper and zinc form stable hydroxides (e.g., $Cu(OH)_2$, $K_{sp} = 2.2\times10^{-20}$; $Zn(OH)_2$, $K_{sp} = 3\times10^{-17}$) within pH 8-10, though excessive alkalinity can cause re-solubilization [56]. Electrolyte concentration and co-existing ions also affect precipitation efficiency. Sulfate ions can reduce solubility through the common-ion effect, while chloride ions may inhibit precipitation by forming soluble complexes (e.g., $CuCl_2^+$, $PbCl_4^{2-}$) [57].

Chemical precipitation is a key industrial wastewater treatment method due to its simplicity, cost-effectiveness, and scalability. It achieves heavy metal removal rates exceeding 90% in a single treatment, making it suitable for high-concentration pollutant systems [7]. For example, sodium sulfide precipitation removes over 90% of cadmium in electroplating wastewater, while calcium hydroxide precipitation is similarly effective for lead [58]. Economic analyses show that chemical precipitation's unit treatment cost is significantly lower than electrodialysis and ion exchange, enhancing its industrial applicability. Moreover, it supports circular economy principles by repurposing precipitation products. Recovered metal sulfides can serve as metallurgical raw materials, and phosphate precipitates can be converted into slow-release fertilizers, offering dual environmental and economic benefits [59]. In multi-technology scenarios, chemical precipitation is often used as a pretreatment step to reduce the load on subsequent processes, mitigating membrane fouling risks in downstream enrichment stages.

Despite its widespread use, chemical precipitation faces several challenges. Sludge generation and disposal are significant issues; each ton of treated wastewater produces 5-20 kg of sludge with 80% water content, containing unreacted agents and heavy metals requiring additional stabilization or thermal treatment [11]. Excessive chemical use can cause secondary pollution, such as toxic H_2S gas release from sodium sulfide overdose or eutrophication from phosphate precipitants [60]. Wastewater complexity further challenges efficiency. Organic ligands (e.g., EDTA) and competing cations (e.g., Ca^{2+}) can reduce precipitation efficiency through complexation or ion competition [61]. For instance, the high stability constant of Cu-EDTA complexes ($\log K>18$) results in <40% removal efficiency with traditional methods [62]. Achieving selectivity in multi-metal systems is also problematic, often necessitating hybrid approaches like ion exchange or flotation [63].

Biomineralization addresses heavy metal contamination through microbial or enzyme-induced mineral precipitation, transforming free heavy metal ions into stable solid-phase minerals to reduce their mobility and toxicity [64]. Microorganisms, such as sulfur-oxidizing bacteria (e.g., *Acidithiobacillus ferrooxidans*) and iron-reducing bacteria, facilitate heavy metal binding to carbonate, phosphate, or sulfide, forming mineral precipitates by modifying local pH or redox potential [65]. For example, in microbial-induced carbonate precipitation (MICP), urease catalyzes urea breakdown to release CO_3^{2-}, which combines with Ca^{2+} to form $CaCO_3$, immobilizing ions like Pb^{2+} and Cd^{2+} through coprecipitation or adsorption [66]. Certain microorganisms can also secrete phosphatases to hydrolyze organic phosphorus, releasing PO_4^{3-} to form stable phosphate minerals (e.g., $Pb_5(PO_4)_3OH$) with heavy metals, exhibiting solubility products as low as 10^{-76}, significantly more stable than carbonates (e.g., $PbCO_3$ with a solubility product of 10^{-13}) [67]. Biomineralization can also complete crystallization through amorphous precursor phases (e.g., liquid nanoparticles), a non-classical nucleation pathway that encapsulates heavy metals more effectively [21]. For example, *Bacillus subtilis* synthesizes micro and nanoscale $CaCO_3$ with a flower-like or reticulated structure, achieving adsorption capacities of 112 mg/g for Cd^{2+} and 294 mg/g for Pb^{2+} [68].

Compared to conventional physicochemical methods, biomineralization offers significant advantages in terms of environmental sustainability and eco-friendliness. It operates without high-temperature or high-pressure conditions, using only 10-20% of the energy required for chemical precipitation and preventing secondary pollution [21]. Microorganisms can address multiple heavy metal pollutants simultaneously. For instance, Microbially Induced Calcite Precipitation (MICP) can remove over 90% of Cu^{2+}, Zn^{2+}, and Pb^{2+} from wastewater under optimal conditions [69]. The resultant mineral phase (e.g., $(Cu, Zn)_5(CO_3)_2(OH)_6$) remains stable over extended periods [70]. Biomineralized materials also enhance soil microbial diversity, facilitating ecological recovery [71]. This technology is adaptable to various media, including water, soil, and solid wastes. For example, combining mineralizing bacteria with biochar increases As(III) immobilization efficiency due to biochar's pore structure (2-50 nm), which provides nucleation sites for mineral deposition [72]. Extremophilic microorganisms, such as *Chlamydomonas radiodurans*, can sustain mineralization activity in extreme environments (e.g., pH 1.5 or salinity 15%), offering potential for treating acidic mine wastewater [73].

Reduction Technology

Chemical reduction converts metal ions from a high-valence state to a lower-valence state using reducing agents, crucial for addressing heavy-metal contamination (Fig. 4). For example, highly toxic Cr(VI) can be reduced to less toxic Cr(III) using $FeSO_4$ or Na_2SO_3, forming insoluble $Cr(OH)_3$ precipitates that reduce Cr's mobility and bioavailability in soil [74, 75]. This method is highly efficient and broadly applicable, significantly decreasing heavy metal activity within hours to days, faster than physical adsorption or phytoremediation. Zero-valent iron nanoparticles, with their large surface area and high reactivity, are effective for rapid Cr(VI) remediation in groundwater [76]. Optimizing reductant ratios, such as Fe^0 combined with biochar, can address composite pollution (e.g., Pb and Cd) with minimal impact on soil microbial communities [77].

However, chemical reduction faces several challenges. Reducing agents' insufficient selectivity can cause side reactions. For instance, in acidic soils, excess zero-valent iron (Fe^0) may oxidize to Fe^{2+}, triggering the Fenton reaction and generating hydroxyl radicals that can damage organic matter [78]. Environmental fluctuations, such as freeze-thaw cycles, can alter soil pore structure and promote the reoxidation of $Cr(OH)_3$, affecting the long-term stability of reduction products [79]. Residual chemical reagents can cause secondary pollution; for example, excessive sulfide reductants can lead to soil acidification or H_2S release [80]. In multi-metal systems, varying reduction potentials complicate simultaneous treatment, necessitating multifunctional composite reductants. Economically, the high cost of preparing highly active materials (e.g., nano zero-valent iron) and the substantial volume of sludge generated (up to 20% of the treatment volume) pose significant challenges [81-83].

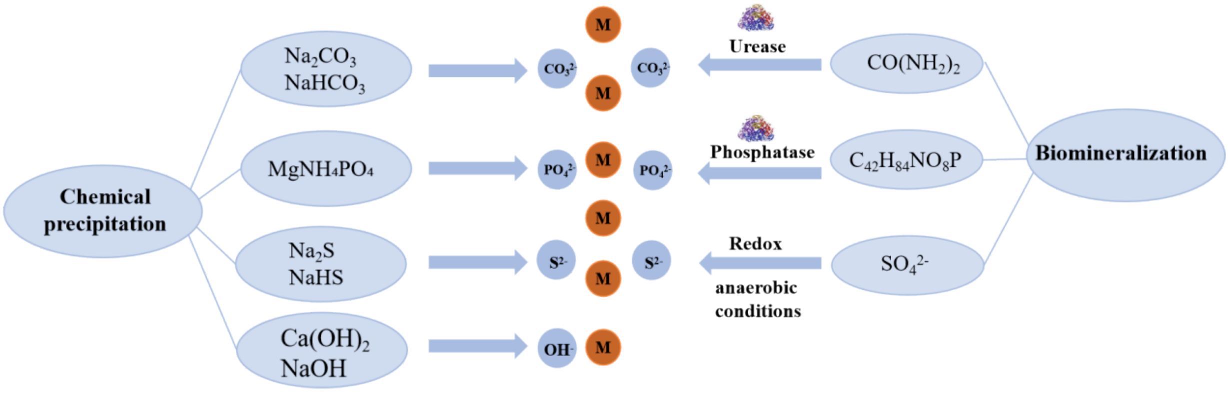

Fig. 3. Diagram of the mechanism of stabilization technology for heavy metal pollution.

Electrodeposition (ED) is a metal recovery technology based on electrochemical principles, reducing heavy metal ions (e.g., Cu^{2+}, Pb^{2+}) to metallic monomers via cathodic reduction reactions, enabling efficient resource recovery [14]. The core mechanism involves cathodic reduction within an electrolytic cell, where metal cations (M^{n+}) migrate to the cathode surface, accept electrons, and deposit as metal atoms (M^0) [84]. For example, the reduction of Cu^{2+} follows the reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu^0$$

(standard electrode potential is approximately +0.34V vs. SHE)

Compared to traditional methods like flocculation and flotation, ED offers distinct advantages for heavy metal removal and resource utilization. It is highly selective, enabling efficient recovery of specific ions (e.g., Cu, Ag, Pb) with recovery rates up to 90% under optimized conditions [14]. For example, in copper-containing wastewater treatment, ED combined with pulsed current technology enhances deposition efficiency by 17.4% compared to steady-state methods, due to improved mass transfer and reduced polarization [85]. This technology (electrocoagulation, EC) enhances efficiency while minimizing energy consumption. Furthermore, it reduces metal residues compared to conventional EC by optimizing electrode materials and operational parameters, thereby improving environmental sustainability [86]. Coupling EC with electroflotation (EF) or electrooxidation (EO) enhances treatment efficiency through synergistic effects, such as simultaneous Cr(VI) reduction and Cr(0) deposition in chromium-containing wastewater.

Despite its advantages, electrodeposition faces several technical challenges in large-scale implementation. The primary issue is the limitation of current efficiency (CE) [87]. In wastewater with low concentrations or complex components, the mass transfer resistance of metal ions increases, resulting in intensified cathodic side reactions such as hydrogen evolution, which can significantly reduce CE [88]. For instance, in wastewater containing chelating agents like EDTA, stable complexes formed between heavy metal ions and chelating agents hinder electrodeposition kinetics, necessitating pretreatment methods like persulfate-based oxidation to decompose the complexes [89]. Additionally, the durability and cost of electrode materials pose economic constraints. Conventional metal electrodes (e.g., stainless steel, titanium) are prone to passivation or corrosion, while precious metal-coated electrodes (e.g., platinum, iridium) are expensive [22]. Dendrite growth is another critical challenge. During the deposition of metals like lead and zinc, uneven nucleation can result in dendrite formation, diminishing deposit quality and potentially causing electrode short circuits [90]. Studies indicate that introducing pulsed currents or modulating the electrolyte flow field can alleviate dendrite issues, though their reliability in industrial applications requires further verification [91].

Enrichment Technology

Membrane enrichment technology addresses heavy metal contamination by leveraging the selective permeability of membrane materials [25]. This technology employs multiple mechanisms, including physical sieving, charge rejection (Donnan effect), and chemical adsorption, to efficiently retain heavy metal ions (Fig. 5). The retention efficiency is determined by the pore size distribution and surface charge of membranes, such as polyamide (PA) thin-film composite

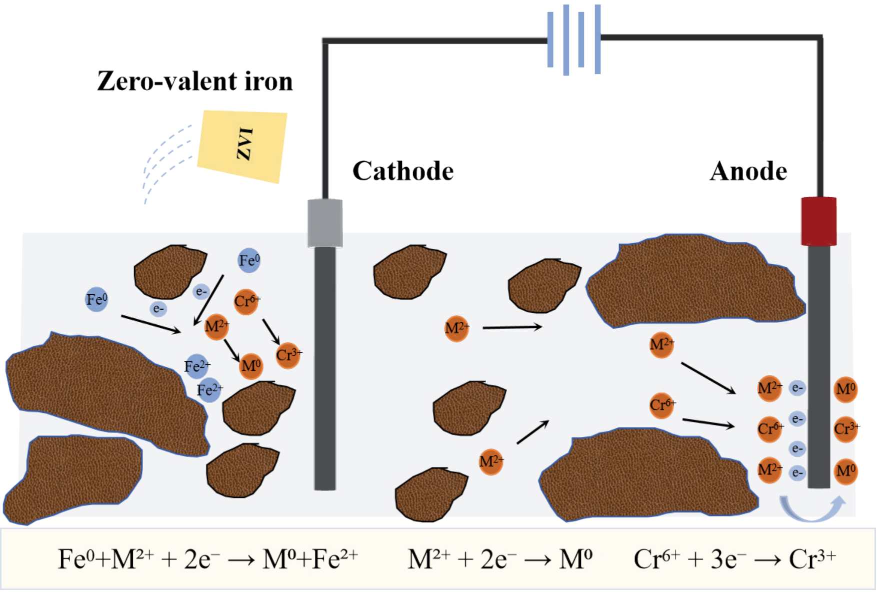

Fig. 4. Diagram of the mechanism of reduction technology for heavy metal pollution.

(TFC) membranes [92]. For example, ultrafiltration (UF) membranes filter colloidal heavy metal complexes through nanoscale pores (2-50 nm), while nanofiltration (NF) and reverse osmosis (RO) membranes retain dissolved ions using a dense separating layer and the Donnan effect [93]. Electrically driven processes, like electrodialysis, enhance ion migration using cation and anion exchange membranes under an electric field [94]. Recent advancements, such as graphene oxide (GO) and polyethylenimine (PEI)-modified membranes, improve enrichment performance by enhancing hydrophilicity and chemical coordination. Techniques like surface grafting of amphiphilic polymers or incorporating nanomaterials (e.g., TiO_2) further boost membrane hydrophilicity, antifouling properties, and heavy metal adsorption capacity [95]. Coupling processes, such as micelle-enhanced ultrafiltration (MEUF), extend retention capabilities for low-concentration ions by using surfactants (e.g., SDS) to form micelles that encapsulate metal ions.

Membrane enrichment offers significant advantages in heavy metal pollution control. It achieves high enrichment efficiency and selectivity, with electrodialysis reaching 97% removal rates for Cu^{2+} and RO exceeding 95% retention for various heavy metals [94]. The technology operates without chemical additives, avoiding secondary pollution and aligning with green chemistry principles [96]. Modular membrane systems enable compact integration and automated control, making them suitable for high-salinity or complex wastewater treatment [97]. From a resource recovery perspective, membrane technology combined with chelating agents (e.g., EDTA) can concentrate heavy metals for reuse, achieving over 80% nickel ion concentration in electroplating wastewater [98]. These environmental and efficiency synergies position membrane enrichment as a leading technology for heavy metal pollution control.

However, membrane contamination is a primary challenge. The coexistence of heavy metal ions and organic matter on the membrane surface forms a dense contamination layer, leading to flux attenuation and reduced lifespan. This necessitates frequent chemical cleaning with agents like sodium hypochlorite and citric acid [99]. Strong oxidizing agents accelerate hydrolysis and aging of polymer membranes (e.g., polyethersulfone), causing pore expansion and mechanical strength decline, especially when metal ions (e.g., Cu^{2+}) coexist with chlorine. High operating pressures significantly increase energy consumption, particularly in RO processes treating high-concentration heavy metal wastewater [100]. Traditional membranes lack sufficient selectivity for low-concentration ions (e.g., As^{3+}), while novel two-dimensional materials (e.g., MOF-based membranes) offer high permeability and selectivity but face challenges in scale-up preparation and stability [101]. Integrating membrane processes with other technologies (e.g., bioreactors) is complex, making it difficult to synergistically regulate membrane performance and biological activity under dynamic conditions [94].

Phytoaccumulation leverages plants' ability to bioconcentrate and translocate heavy metals [102]. Hyperaccumulating plants release organic acids, phenolic compounds, and other metabolites through their roots, modifying rhizosphere soil pH and redox potential to enhance heavy metal bioavailability (Fig. 5). For example, Centipedegrass (*Pteris vittata*) transports arsenic via specific transporters, storing it in vesicular compartments. Rhizosphere microbes can activate heavy metals (e.g., reducing Cr(VI) to Cr(III)) and alleviate toxicity by secreting siderophores and organic acids [103]. Chemical enhancement strategies using chelating agents like EDTA and citric acid form stable complexes with heavy metals, increasing solubility and phytoaccumulation efficiency [104]. These mechanisms enable targeted heavy metal migration from soil to plants, with hyperaccumulators achieving enrichment coefficients over 1,000 times higher than ordinary plants.

Phytoaccumulation offers ecological and economic benefits. It mitigates soil structure damage and secondary pollution risks while achieving carbon fixation through photosynthesis, improving soil health and carbon sequestration [105]. Economically, phytoremediation costs approximately one-fifth to one-third of traditional thermal desorption (e.g., \$0.25M/ha vs. \$1M/ha). Biomass can be pyrolyzed to recover valuable metals like palladium. Deep-rooted plants, such as hybrid poplars (*Populus deltoides*), can remediate contamination exceeding 60 cm in depth, crucial for sites like mine tailings. Integrating microbial-plant systems further enhances efficacy. For example, inoculating arsenic-tolerant *Pseudomonas putida* significantly increases arsenic accumulation in Indian mustard (*Brassica juncea*) while restoring rhizosphere microbial functions [106]. Halophytic plants like *Suaeda salsa* exhibit dual remediation potential in coastal salinized soils, accumulating cadmium and regulating sodium ion balance via salt gland secretion [107].

Despite these advantages, large-scale implementation of phytoaccumulation faces challenges. Low biomass yield of hyperaccumulators extends remediation periods to 5-10 years [108]. For example, *Thlaspi caerulescens* extracts 3.7 kg Zn/ha annually in calcareous soils and up to 20 kg Zn/ha in acidic soils, insufficient for highly contaminated sites [109]. Antagonistic effects under compound pollution conditions significantly diminish remediation efficiency. For instance, plant uptake of cadmium (Cd) decreases in the presence of lead (Pb), likely due to competition for binding sites on transport proteins [110]. Root depth limitations restrict many hyperaccumulators to the 0-30 cm surface layer, necessitating complementary techniques like electrokinetic remediation for deeper contamination [111]. Environmental risks associated with synthetic chelators (e.g., EDTA) include prolonged half-lives and potential groundwater pollution due to heavy metal

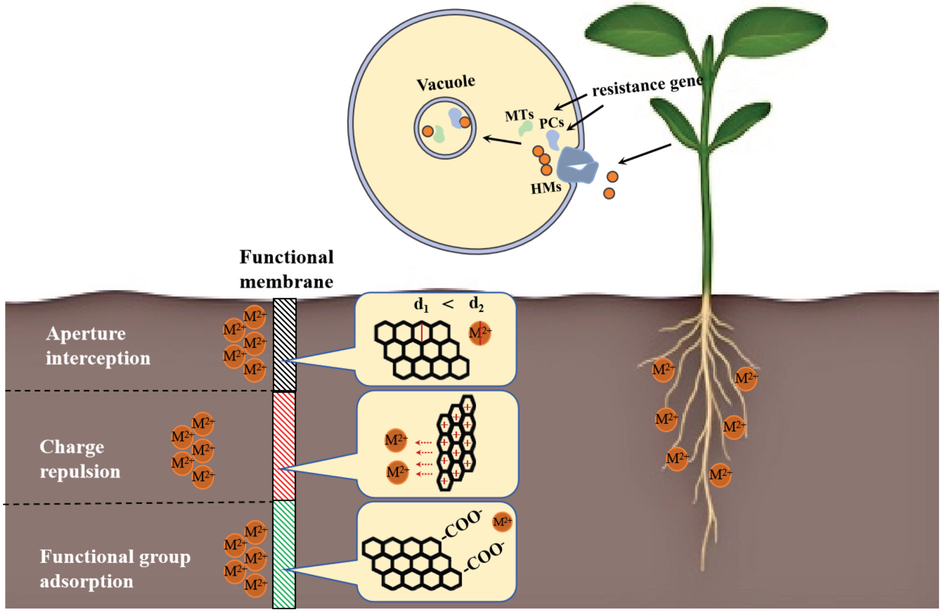

Fig. 5. Diagram of the mechanism of enrichment technology for heavy metal pollution.

migration [112]. Additionally, the limited geographical adaptability of hyperaccumulators, such as *Alyssum murale*, which experiences reduced biomass in temperate regions compared to its native Mediterranean climate, restricts widespread application [113].

The Research Directions of Single Technology Remediation

Although each technology has certain defects, many scientists are working hard to find solutions. There are still many directions worth studying in the future, as shown in Table 1.

Adsorption Technology

Biochar adsorption technology is excellent and economical, but the heterogeneity of the raw materials and variations in the pyrolysis process lead to fluctuations in the product properties. In addition, the possibility of heavy metal desorption is a major problem. To address the current multiple bottlenecks, future research should prioritize innovations in material modification and process optimization. Chemical modifications, such as nitrogen doping and metal oxide loading, can enhance the performance of biochar. The development of porous composite materials is another critical area of focus [114]. The specific surface area of KOH-activated biochar is 2000-2200 m^2/g, and its microporous-mesoporous hierarchical structure increases the diffusion rate of heavy metals by 2-3 times [115]. Regarding the production process, microwave-assisted pyrolysis reduces energy consumption and shortens the treatment time, while ball milling technology enhances the density of adsorption sites by 5-7 times through nanosizing [114, 116].

Despite the significant advantages of sodium alginate adsorption technology, it still faces the risk of structural instability within a physically crosslinked network in practical applications. Conventional Ca^{2+} cross-linking systems tend to dissolve and disintegrate the cross-linking network under low pH or high ionic strength conditions, resulting in a significant decrease in adsorption capacity. The development of bifunctional crosslinking systems is crucial for future research, such as integrating the Diels-Alder click reaction with ionic crosslinking, which can simultaneously enhance mechanical strength and pH stability [117].

Mineral-based adsorbents provide a combination of ecological safety and economic viability for environmental management, but structural collapse of clay minerals and loss of active sites after multiple cycles in practical engineering applications greatly reduce adsorption efficiency. Future research should prioritize the multidimensional optimization of materials, processes, and systems to enhance the efficiency and sustainability of water pollution treatment methods. Regarding material design, the development of a composite system comprising biochar, clay, and magnetic nanoparticles can concurrently improve the adsorption performance and recovery efficiency [118]. This composite material integrates the high specific surface area and abundant functional groups of biochar, the ion-exchange capacity of clay, and the facile enrichment properties of magnetic nanoparticles, which is anticipated to achieve effective removal of multiple pollutants [119]. In terms of process innovation, there is an urgent need to investigate more environmentally friendly and cost-effective preparation techniques such as biotemplate synthesis. This method utilizes natural biological structures as templates to prepare adsorbent materials with unique morphology and properties [120]. In addition, while developing new adsorbent materials, it is also crucial to optimize regeneration techniques, as efficient regeneration methods can extend the life of the material and reduce disposal costs. At the system integration level, adsorption technology can be synergized with microbial remediation to build a joint treatment system. For example, in permeable reactive wall (PRB) technology, the combination of mineral adsorption and biodegradation can achieve more comprehensive and long-lasting pollutant removal [45]. This multidimensional optimization strategy not only enhances the effectiveness of water pollution treatment but also promotes the sustainable development of related technologies.

Microbial adsorption technology is environmentally friendly, but still faces challenges in industrial applications, where complex constituents (e.g., organics and competing ions) in the actual wastewater can inhibit adsorption efficiency. Future research should address the limitations of molecular mechanisms, process optimization, and system integration. Mechanistic studies should utilize multi-omics approaches (e.g., metagenomics and metaproteomics) to analyze microbial-metal networks, such as CRISPR-edited *Pseudomonas putida*, which enhances Cd^{2+} adsorption capacity to 150 mg/g [121]. Process development requires multifunctional bioreactors, such as MABR systems, which integrate microbial adsorption with membrane enrichment to achieve efficient heavy metal removal and water purification. Resource recovery should prioritize selective technologies, such as magnetically modified *Aspergillus niger* spores for rare-earth enrichment under magnetic fields [122].

Solidification Technology

Chemical precipitation technology is easy to operate and highly efficient, but the large amount of sludge generated after treatment poses disposal difficulties, and overdosing of chemicals can easily cause secondary pollution. Future research should prioritize two areas: technology integration and material innovation. In technology integration, synergistic mechanisms of chemical precipitation and bioremediation are critical. For instance, microbial-induced precipitation (MICP) combined with chemical agents achieves simultaneous metal immobilization and soil structure enhancement, with experiments showing a 40% reduction in permeability for lead-contaminated soil [71]. Electrochemical-assisted precipitation, which regulates pH and redox potential via electric fields, demonstrates advantages in low-concentration pollutant remediation (e.g., >95% removal at <10 ppm) [63]. For material innovation, nanoscale precipitants like functionalized sulfur copolymers exhibit a cadmium adsorption capacity of 450 mg/g due to their high surface area and selective sites [123]. These materials can be integrated with multi-fluid bed systems, where real-time sensor feedback optimizes pH and dosage, enhancing solid-liquid separation.

Despite the significant advantages of biomineralization technology, large-scale applications still have multiple limitations. The first challenge is the sensitivity of microorganisms to high concentrations of heavy metals, which leads to a decrease in urease activity, resulting in a sudden decrease in mineralization efficiency. Second, the remediation process may produce by-product interference, which may trigger eutrophication of water bodies. Furthermore, the long-term stability of mineral products is affected significantly by environmental factors. Future research must address these current limitations by focusing on three key areas: enhancement of microbial function, process optimization, and the integration of multiple technologies. At the microbial level, genome editing technologies, such as CRISPR-Cas9, can be employed to knock out metal-sensitive genes and overexpress phosphatase genes, thereby increasing the tolerance of the strain to Pb^{2+} concentrations. CRISPR-Cas9 has been widely used to enhance microbial capabilities in bioremediation, including increasing tolerance to heavy metals and improving metabolic pathways [124]. Regarding process optimization, the development of a microfluidic reactor can facilitate precise control of the mineralization process. For instance, with a Ca^{2+}/UO_2^{2+} molar ratio of 2:1, the efficiency of uranium mineralization can be increased significantly. Microfluidic devices have shown promise in optimizing reaction conditions and improving efficiency in industrial applications [125]. The integration of multiple technologies is another crucial direction, exemplified by coupling Microbially Induced Calcite Precipitation (MICP) with electrokinetic remediation, which can enhance the Cd^{2+} migration rate and increase mineralization coverage. MICP technology has been successfully integrated with other remediation methods to improve heavy metal removal efficiency [126].

Reduction Technology

Chemical reduction techniques are effective, but when the selectivity of the reducing agent is insufficient, it may lead to side reactions, and residual chemical reagents may cause secondary pollution. Future research should prioritize advancements in material innovation, process optimization, and technology integration. Regarding the development of reductants, biogenic reductants, such as humic acid-iron nanocomposites, offer the advantage of minimizing secondary pollution owing to their environmental compatibility and slow-release characteristics. Intelligent responsive materials, such as pH-sensitive sulfides, can dynamically regulate the reduction reaction process, thereby enhancing selectivity [127]. The combined approach of chemical reduction and microbial remediation has garnered significant attention in the realm of technology integration. For instance, reductant pretreatment can convert Cr(VI) to Cr(III), which can subsequently form stable chromites through microbial mineralization [77]. In addition, the incorporation of artificial intelligence in remediation design is becoming increasingly prevalent. Models based on artificial neural networks can predict the optimal reductant dosage under varying soil conditions, thereby reducing the trial-and-error costs.

Despite the significant advantages of electrodeposition technology, the increased mass transfer resistance of metal ions results in a decreased current efficiency. Additionally, the formation of stable complexes between heavy metal ions and chelating agents can significantly inhibit the electrodeposition kinetics. Furthermore, traditional metal electrodes such as stainless steel and titanium are susceptible to passivation and corrosion. While precious metal-coated electrodes, like platinum or iridium, can enhance stability, they come at a high cost. Future research should prioritize three key areas: innovation in electrode materials, process optimization, and system integration. In the domain of electrode materials, the development of cost-effective nanocomposites with high catalytic activity, such as carbon-based materials and metal-organic frameworks (MOFs), represents a significant direction [128]. For instance, a graphene/PANI composite cathode can improve electrochemical performance in supercapacitors by enhancing its specific surface area and electrical conductivity [129]. With regard to process optimization, technologies such as Pulsed Electrodeposition (ED) and fluidized bed ED are anticipated to overcome mass transfer limitations. The former achieves this by suppressing side reactions through intermittent currents, whereas the latter employs granular electrodes to increase the interfacial reaction rate [130]. In terms of system integration, coupling electrodeposition with bioprocesses, such as microbial fuel cells or membrane-based desalination technologies, holds promise. For example, a microbial electrolysis cell (MEC) can utilize electroactive bacteria to degrade organic matter and release electrons, thereby assisting in heavy metal reduction (production), while membrane technologies enable resource recovery (recovery), forming an integrated “treatment-production-recovery” system. In summary, through multidisciplinary cross-innovation, electrodeposition technology can achieve broader applications in the fields of heavy metal pollution control and resource recovery [131].

Enrichment Technology

Membrane enrichment technology holds significant promise in heavy metal removal and resource recovery, yet faces challenges such as membrane fouling and high energy consumption [25]. In complex wastewater treatment, enhancing the long-term stability of membranes, their selectivity for low-concentration ions, anti-fouling capabilities, and enrichment efficiency remains critical [132]. Future research should prioritize advancements in material innovation, process optimization, and intelligent control. At the material level, the development of biomimetic membranes embedded with water channel proteins (e.g., aquaporins) can enhance ion selectivity and anti-fouling properties [133]. Additionally, hybridized membranes such as MXene/polymer composites have shown promise in improving mechanical stability and ion transport efficiency. In intelligent control, IoT-based real-time monitoring combined with machine learning algorithms (e.g., neural networks) optimizes cleaning cycles and transmembrane pressure, improving energy efficiency by up to 20% [134]. Through multidisciplinary innovation, membrane enrichment technology is poised to achieve efficient and sustainable solutions for heavy metal pollution.

Phytoaccumulation technology offers notable ecological and economic benefits in managing heavy metal pollution, yet its application is constrained by the low biomass of hyperaccumulating plants, antagonistic effects of compound pollution, and geographical adaptability. Future technological advancements are expected to concentrate on the development of a multidisciplinary cross-innovation system. These technologies integrate genetic engineering, microbiology, and nanotechnology to achieve synergistic effects. Gene editing technology can be employed to modify metal transporter proteins such as the PvACR3;1 gene in rice, resulting in a reduction of inorganic arsenic content by up to 46% in seeds and increased heavy metal adsorption. Microbial community engineering constructs functional bacterial colonies through synthetic biology. For instance, engineered *Pseudomonas* species (e.g., *Pseudomonas putida*) expressing metallothionein can enhance cadmium mobilization in plant rhizospheres, although further validation is required for specific strains like *Pseudomonas fluorescens* [135]. Synergistic integration of these approaches may enable comprehensive remediation of co-contaminated soils. The integration and innovation of intelligent monitoring systems is emerging. Hyperspectral remote sensing technology can monitor the metal enrichment status of hyperaccumulated plants in real time through the reflective characteristics of the 780-900 nm band. When combined with machine-learning algorithms, it can predict the progress of remediation with an accuracy of 89% [136].

The Coupled Approaches of Multi-Technology Collaborative Remediation

Addressing complex pollution scenarios using a single remediation technology is challenging due to its limited mechanisms of action and inadequate environmental adaptability [137], as shown in Table 2. It is imperative to consider four dimensions: complementary action mechanisms, pollutant migration

Table 1. The research directions of single technology remediation.

Type of technology	Research direction	Research approach
Biochar adsorption	Chemical modification	Enhancing adsorption performance with metal oxide loading
	Process optimization	Increasing adsorption sites through ball milling and nanomaterial technology
Hydrogel adsorption	Material modification	Developing a dual-function crosslinking system (Diels-Alder + ionic crosslinking) to improve mechanical strength and pH stability
Mineral-based material adsorption	Material design	Biochar-clay-magnetic nanoparticle ternary system
	Process optimization	Green synthesis via biomimetic template method
	System integration	Microbial remediation coupled with PRB technology
Microbial adsorption	Molecular mechanism analysis	CRISPR editing to enhance microbial metalloproteins
	Process optimization	MABR system coupled with membrane enrichment technology
	Resource technology	Magnetic modification of *Aspergillus niger* spores for rare-earth enrichment under a magnetic field
Chemical precipitation	Technology coupling	Combined remediation with biomineralization and chemical agents
	Technology coupling	Electrochemical regulation of pH and redox potential to aid precipitation
	Material innovation	Development of nanoscale sulfur copolymer precipitants
Microbial mineralization	Microbial function enhancement	Genetic editing to enhance heavy metal tolerance
	Process optimization	Development of microfluidic reactors for precise control of the mineralization process
	Multi-technology coupling	Biomineralization coupled with electrokinetic remediation
Chemical reduction	Material innovation	Development of humic acid–nano-iron composite materials
	Technology coupling	Chemical reduction coupled with microbial mineralization
	Intelligent optimization	Artificial neural network model to predict reductant dosage
Electrodeposition	Electrode material innovation	Development of nanocomposites with high catalytic activity and cost-effectiveness, such as graphene/polyaniline composite cathode
	Process optimization	Pulsed electrodeposition technique to suppress side reactions
	Process optimization	Fluidized bed electrodeposition technique to increase interfacial reaction rate
	System integration	Combining electrodeposition with biological processes to form microbial fuel cells
Membrane treatment technology	Material innovation	Development of MXene/polymer hybrid membranes to improve mechanical stability and ionic transport efficiency
	Material innovation	Embedding aquaporin-based biomimetic membranes to enhance permeability
	Process optimization	Coupling MFC systems to reduce membrane fouling
	Intelligent control	IoT combined with machine learning to optimize cleaning cycles
Phytoremediation	Gene editing	Genetic editing technology to modify metal transport proteins for increased adsorption efficiency
	Microbial engineering	Microbial community engineering through synthetic biology to construct functional bacterial consortia
	Intelligent monitoring	Hyperspectral remote sensing + machine learning to predict remediation progress

and transformation stages, adaptability to environmental conditions, and spatial-temporal synergism [138]. By integrating these dimensions through multidimensional technology coupling, remediation efficiency can be enhanced while providing scalable, systematic solutions for complex environmental governance [139].

Complementary Synergies in Mechanisms of Action

The application of a single technology for heavy metal remediation is often constrained by limited efficiency. For example, electrokinetic migration facilitates ion transport via electric fields, but its efficiency decreases in clay-rich soils due to high resistivity caused by low permeability and strong ion adsorption [140]. Conversely, chemical complexing agents (e.g., EDTA) enhance metal solubility [141]. Integrating complementary technologies can overcome these limitations. Electrokinetic remediation (EKR) combined with chemical complexation exemplifies such synergy: complexing agents form soluble metal-ligand complexes (e.g., Pb-EDTA), which migrate efficiently toward electrodes under a direct current field [142]. Additionally, polarity reversal in electrodialysis (a subcategory of EKR) directs metal accumulation in specific zones, improving recovery. Concurrently, complexing agents, such as citric acid and EDTA, form stable and soluble complexes with metal ions via functional groups (e.g., carboxylic acids), thereby inhibiting their re-adsorption or precipitation during migration. Citric acid is effective under acidic conditions (pH 4-5) by lowering soil pH and solubilizing metal ions, while EDTA performs better in neutral to alkaline environments due to its higher complexation stability with Pb^{2+} (equilibrium constant of 19.0). In lead-contaminated soil remediation, electrodialysis combined with 0.05 mol/L EDTA achieved a Pb removal rate of 82.1% by forming negatively charged Pb-EDTA complexes, which enhanced electrophoretic mobility [143, 144]. The synergistic effect of EDTA arises from its ability to competitively displace Pb^{2+} adsorbed on iron oxides and its strong negative charge, which increases the electric field's drag force [145]. However, optimizing the dosage is critical: excessive EDTA may cause groundwater contamination due to its persistence, whereas citric acid's biodegradability reduces environmental risks [146].

The integration of biosorption and chemical precipitation offers distinct advantages in wastewater treatment. Microorganisms such as cyanobacteria and fungi adsorb heavy metal ions via sulfhydryl and amino groups on their cell walls, yet their capacity is constrained by the limited active sites on the biomass surface [147]. To address residual metal ions after biosorption, sodium sulfide (Na_2S) or phosphate is introduced to convert dissolved metals into sulfide (e.g., CdS, PbS) or phosphate precipitates, achieving advanced purification. For instance, in cadmium-laden wastewater from an electroplating facility, cyanobacterial biosorption reduces Cd^{2+} concentration from 50 to 20 mg/L (60% removal). Subsequent Na_2S addition induces CdS precipitation, further lowering Cd^{2+} (<0.1 mg/L), yielding a total removal rate of 99%. This sequential approach allows biomass recovery (e.g., cadmium-rich cyanobacteria for metal recycling) while minimizing sludge generation from excessive chemical dosing. Notably, sulfide nanoparticles may pose ecological risks due to their mobility and toxicity; thus, flocculants like polyacrylamide are recommended to enhance solid-liquid enrichment and mitigate environmental hazards [148, 149].

Synergistic Mechanism of NF and Adsorption for Arsenic Removal

Nanofiltration (NF) membranes exhibit over 90% rejection for high-valence As(V) via size exclusion and charge repulsion, while the rejection of electrically neutral As(III) remains below 50% due to the absence of electrostatic interactions. To address this limitation, Fe_3O_4-modified activated carbon is coupled with NF to specifically adsorb residual As(III) in the permeate. In a smelting wastewater case, the integrated system reduced As(III) concentration from 100 μg/L to <1 μg/L, meeting the Class I Surface Water Standard. The synergy relies on material design: Fe_3O_4 enables magnetic recovery of adsorbents, while its surface hydroxyl groups enhance As(III) selectivity through coordination [150, 151]. However, membrane fouling caused by organic/inorganic deposition remains a challenge for long-term operation. To mitigate fouling, TiO_2-coated membranes with photocatalytic self-cleaning properties and in-situ adsorbent regeneration processes are proposed as engineering solutions [152].

Pollutant Transport Transformation Stage Synergies

The transport and transformation of heavy metals in environmental media exhibit distinct phase characteristics. For instance, heavy metals in soil can infiltrate groundwater through leaching processes (e.g., ion exchange induced by acid rain) or undergo redox-mediated transformations altering their toxicity [153]. Based on these migration mechanisms, designing stage-specific technological combinations enables comprehensive pollution control. In contaminated soil remediation, the synergy between pretreatment (e.g., chemical leaching) and deep treatment (e.g., immobilization) has been widely adopted. Specifically, citric acid and EDTA leaching can rapidly transfer metals from solid to liquid phases via chelation and ion exchange. However, the resultant high-concentration metal leachates require further treatment, where electrochemical regeneration achieves 97% metal recovery. After treatment with 1.0 M citric acid, the concentration of Cu^{2+} in the soil was reduced from 2500 mg/kg to 1000 mg/kg, and the Cu^{2+} concentration in the leachate reached 200 mg/L. Subsequent electrodeposition recovered Cu(II) from the leachate with a purity of 99.2%, supported by optimized organic acid systems. Following leaching, the soil was amended with lime to neutralize acidity and then planted with *Brassica juncea* for phytoremediation, further reducing Cu^{2+} to below 500 mg/kg within six months [154]. Economic analysis showed that metal recovery offset over 50% of leaching costs, while phytoremediation reduced tail-end treatment expenses. Although citric acid may disrupt soil microbial communities, organic fertilizers were applied to restore ecological function, though monitoring is required to prevent Cu remobilization [155].

In extensive areas with low contamination levels, the combined strategy of synergistic in situ passivation and targeted ex situ treatment can significantly reduce remediation costs. In situ passivators, such as biochar and hydroxyapatite, immobilize heavy metals through adsorption, co-precipitation, and surface complexation mechanisms, making them suitable for large-scale applications with low to moderate contamination [156]. Conversely, *ex situ* electrochemical technology is highly effective for rapid remediation of small, heavily contaminated hotspots. For example, in a lead-zinc mine remediation project, the leaching concentration of Pb was reduced from 15 mg/L to below 0.5 mg/L after applying 5% biochar to the topsoil (0-20 cm), demonstrating biochar's strong immobilization capacity for Pb. Simultaneously, soils with localized Pb contamination exceeding 5,000 mg/kg were treated in an electrochemical reactor, achieving an 85% Pb removal rate. This integrated approach resulted in a 60% cost reduction compared to comprehensive ex situ treatment of the entire site [150].

The long-term stability of the passivation agent was evaluated using accelerated aging experiments. Kinetic modeling indicated that the Pb fixation rate of biochar could remain above 90% for over 20 years under simulated acid rain (pH 4.0) conditions [157]. The synergy between redox modulation and adsorption/precipitation is particularly valuable for the transformation of toxic forms. Hexavalent chromium (Cr(VI)) is significantly more toxic than trivalent chromium (Cr(III)); however, Cr(III) is more readily removed by precipitation [158]. In the remediation of Cr(VI)-contaminated groundwater at an electroplating facility, a zero-valent iron (ZVI) permeable reaction wall was employed to reduce Cr(VI) to Cr(III), decreasing the effluent Cr(VI) concentration from 10 mg/L to 0.05 mg/L. Subsequent NaOH addition adjusted the pH to 8.5, facilitating $Cr(OH)_3$ precipitation and reducing the total Cr concentration to below 0.1 mg/L. The efficacy of this process depends on the maintenance of ZVI reactivity [159]. Although nano-zero-valent iron (nZVI) exhibits a rapid reaction rate, it is prone to deactivation through agglomeration. The use of a composite carrier comprising nZVI and biochar can extend the operational lifespan to over five years [160].

Synergy of Adaptation to Environmental Conditions

The spatiotemporal heterogeneity of environmental parameters such as pH, salinity, and temperature represents a significant constraint on the efficacy of remediation technologies [161]. Intelligent adaptation and dynamic regulation of environmental conditions can effectively overcome the limitations of technological applications and enhance remediation efficiency [162]. pH-gradient adaptation technology has distinct advantages in the treatment of acid mine drainage (AMD), as exemplified by the selective application of electrodialysis and lime neutralization in specific pH ranges. For instance, electrodialysis can markedly improve the migration selectivity of Cd^{2+} and Zn^{2+} in acidic environments ($pH<5$), whereas lime neutralization and precipitation achieve complete sedimentation of metal hydroxides in alkaline environments ($pH \geq 8.5$) [163]. In the context of lead-zinc mine wastewater, the pH was precisely regulated in stages: initially, the metabolism of sulfate-reducing bacteria (SRB) was activated at pH 6.0 under slightly acidic conditions, resulting in the generation of metal sulfide precipitation to remove 70% of Zn^{2+} [164]. Subsequently, the system pH was adjusted to 4.5 with supplemental sulfide addition to facilitate electrodialysis enrichment, which reduced residual Zn^{2+} from 300 mg/L to 150 mg/L [165]. Finally, lime neutralization precipitation at pH 7.5 further decreased Zn^{2+} from 150 mg/L to 30 mg/L. This multi-stage control system reduces lime consumption by 40% compared to the traditional neutralization method while simultaneously mitigating the risk of secondary pollution by H_2S gas.

Complementary technologies for salinity tolerance constitute a synergistic mechanism for the treatment of high-salinity industrial wastewater [166]. The high salt retention properties of reverse osmosis (RO) membranes, combined with the selective degradation capabilities of biological methods, form a technical coupling that addresses the issue of microbial toxicity inhibition owing to high chloride concentrations (>20000 mg/L). In a coastal electroplating park, the chloride concentration was incrementally reduced to below 2000 mg/L using RO membranes with enhanced salt rejection [167], followed by bioreduction using salt-tolerant bacterial strains of *Halomonas* spp., which reduced nickel (Ni^{2+}) concentrations from 50 mg/L to 0.1 mg/L via bioaccumulation and precipitation [166]. Macro-genomic analysis indicated that salt-tolerant bacteria maintained intracellular osmotic homeostasis through the synthesis of compatible solutes such as ectoine, and the expression levels of nickel resistance gene clusters (e.g., *ncrB* and *ncrC*) were significantly elevated compared to conventional strains [168]. The temperature synergistic regulation strategy demonstrated systematic value in restoration projects within seasonal climate zones. To address the stagnation of phytoremediation caused by low winter temperatures in northern regions, low-temperature electrochemical remediation technology was introduced to develop a trans-seasonal remediation model. In a mercury (Hg)-contaminated farmland remediation project, the soil Hg content was reduced from 50 to 30 mg/kg through electrokinetic remediation in winter, supported by renewable energy sources to minimize energy consumption [169]. Subsequently, as ground temperatures rose in spring, transgenic poplar trees expressing the mercury reductase gene (*merA*) were planted, achieving a reduction in Hg concentration to below the alert threshold of 5 mg/kg within six months via enhanced microbial and root activity [170]. This time-sequence control program considers both technical economy and engineering continuity, with the application of transgenic plants requiring a comprehensive life-cycle biosafety assessment [171].

Table 2. Basic information on the major heavy metal pollution remediation technologies.

Technology type	Heavy metal types	Pollutant medium	Purpose of remediation	Technical advantages	Technical bottlenecks
Biocarbon adsorption	Cu, Cd, As, Pb, Zn, etc.	Soil, water body, etc.	Reduce mobility	1 Economically feasible 2 Environment-friendly	1 Performance fluctuations can be caused by differences in raw materials and processes 2 There is a risk of heavy metal desorption
Sodium alginate-based hydrogel adsorption	Cu, Pb, Zn, etc.	Water body	Reduce mobility	1 High adsorption capacity 2 Environment-friendly 3 pH response selectivity	1 The structure is prone to collapse in low pH and high salinity environments 2 Multiple ions compete for adsorption 3 Regenerative performance decay
Mineral-based adsorption	Cu, Cd, Pb, etc.	Soil, water body, etc.	Reduce mobility	1 Economically feasible 2 Environment-friendly	1 After cycling, the structure collapses and the active sites decrease 2 During the synthesis of materials, particle aggregation leads to a decrease in specific surface area
Microbial adsorption	Cd, Pb, Cr(VI), Hg, Cu, Zn, etc.	Soil, water body, etc.	Reduce mobility	1 Economically feasible 2 Environment-friendly	1 Competitive ions inhibit adsorption efficiency 2 The adsorption efficiency of high-concentration pollution is insufficient
Chemical precipitation	Cd, Pb, Cu, etc.	Soil, water body, etc.	Reduce biological effectiveness	1 Easy to operate 2 Cost-effective 3 High processing efficiency	1 Easy to generate secondary pollution 2 Susceptible to complex matrix interference
Biomineralization	Pb, Cd, Cu, Zn, etc.	Soil, water body, etc.	Reduce biological effectiveness	1 Environment-friendly 2 Good biocompatibility	1 High concentrations of pollution easily inactivate microorganisms 2 The cost is high
Chemical reduction	Cr(VI), Pb, Cd, etc.	Soil, water body, etc.	Reduce biological effectiveness	1 High processing efficiency 2 Wide range of environmental applicability	1 The reducing agent easily causes secondary pollution 2 Long-term stability is susceptible to environmental fluctuations
Electrodeposition	Cu, Ag, Pb, Zn, etc.	Water body	Reduce biological effectiveness	1 High selectivity 2 Environment-friendly	1 Deposition dendrites cause the electrode to short circuit 2 The cost of the coated electrode is high, and the stainless steel electrode is easily passivated
Membrane enrichment	Cu, Ni, As, etc.	Water body	Reduce mobility	1 Selective control 2 High enrichment efficiency 3 Environment-friendly	1 The membrane is prone to blockage 2 The cost is high
Phytoaccumulation	As, Pb, Cd, etc.	Soil	Reduce mobility	1 Economically feasible 2 Environment-friendly	1 The repair cycle is long 2 Complex pollution has antagonistic effects

Synergies between Time and Space Dimensions

The spatial heterogeneity of heavy metal pollution, coupled with the urgent need for timely remediation, has led to the development of innovative applications of synergistic technologies across spatial and temporal dimensions [172]. In instances of unexpected pollution events, the integration of emergency treatments with long-term remediation strategies can effectively mitigate ecological risks. For example, in the case of arsenic contamination in a river resulting from a tailing pond dam failure, polyferric silicate (PFS) was initially employed to facilitate coagulation and precipitation, successfully reducing the dissolved arsenic concentration from 5 mg/L to 0.5 mg/L within one hour in similar coagulation processes. After emergency treatment, artificial wetlands were established in the river, and the plant *reed* was introduced, leading to a reduction in the arsenic content of the substrate through phytostabilization and microbial synergy [173]. The critical factor in the emergency phase is the selection of rapid-response chemicals; PFS offers a broader pH range (pH 4-10 in laboratory conditions) compared to traditional $FeCl_3$, which enhances its applicability in diverse water conditions, and the Fe-As flocs formed are more readily settled [174].

Spatial zoning remediation technology facilitates precise management by categorizing the degree of pollution. In the soil of an electronic waste dismantling site, Cu contamination exhibited a core-edge distribution pattern, with concentrations exceeding 1000 mg/kg in the core area and less than 500 mg/kg in the edge area [175]. Electric remediation was applied in the core area utilizing a current density of 1 A/m^2 over 30 days, achieving a copper removal rate of 70% [176]. In contrast, sunflowers (*Helianthus annuus*) were cultivated in the edge area, reducing soil Cu concentration by 150 mg/kg over six months [177]. An economic evaluation indicated that the zoning strategy reduced costs by 45% compared to whole-site electric remediation, avoiding excessive remediation in low-pollution areas [178].

Conclusions

This review examines various remediation technologies for heavy metal pollution, including adsorption, solidification/stabilization, reduction, separation, and phytoaccumulation, as well as multi-technology synergistic strategies. While individual technologies offer some value in controlling heavy metal pollution, they face significant limitations in applicability, economic feasibility, and long-term stability in complex systems. In contrast, multi-technology synergistic approaches, such as electrokinetic-microbial coupling and chelate-enhanced phytoextraction, integrate the strengths of different techniques. These integrated solutions enhance treatment efficiency, mitigate environmental risks, and address limitations like secondary contamination from EDTA leaching or high energy consumption in electrokinetic separation, offering more cost-effective and sustainable outcomes.

Future advancements in heavy metal pollution control require innovations in materials science, technological integration, and interdisciplinary collaboration. Developing novel adsorbents (e.g., hydrogels) with high efficiency, low cost, and environmental sustainability is crucial for selective metal removal. Technological integration should explore synergistic methods (e.g., electrocoagulation-adsorption hybrids) and leverage AI and big data to optimize process efficiency and decision-making. Interdisciplinary research is essential to address complex challenges by combining expertise in materials science, environmental engineering, and data analytics. For instance, integrating materials science and biotechnology can lead to the design of bioactive adsorbents, such as green-synthesized nanoparticles. Cross-disciplinary research between chemical engineering and environmental sciences can optimize pollutant conversion and resource recovery processes. Such multidisciplinary synergistic innovation not only enhances treatment efficacy but also fosters resource recycling and promotes the sustainable development of environmental treatment technologies.

Acknowledgments

The research described in this paper was financially supported by the Start-up Research Fund of Southeast University (Grant No. 4012002501). Their financial support is gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

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