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Bimetallic Nanoparticles for Heavy Metal Remediation: Recent Advances in Synthesis, Mechanistic Insights, and Environmental Applications

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Abstract

Bimetallic nanoparticles (BNPs) have attracted considerable attention as effective materials for removing heavy metals from contaminated water because of their enhanced catalytic, adsorptive, and reductive capabilities. This review presents a comprehensive evaluation of recent progress in BNP synthesis, removal mechanisms, environmental applications, and current limitations in heavy metal remediation. The cooperative interactions between two metallic components within BNPs generate synergistic effects that often lead to superior performance compared with monometallic nanoparticles. Recent literature highlights important developments in synthesis strategies, persistent challenges related to scalability, and promising directions for future research.

Keywords: Bimetallic nanoparticles, Heavy metals, Environmental applications, Nanoparticles, Metal pollution

1. Introduction

Heavy metal pollution remains a major global environmental concern because metals such as lead (Pb), chromium (Cr), cadmium (Cd), mercury (Hg), and arsenic (As) are highly persistent, toxic, and capable of accumulating in living organisms. These contaminants commonly enter aquatic environments through a wide range of industrial activities, including mining operations, electroplating, metal processing, pigment manufacturing, and battery production (Sharma *et al.*, 2023). Because heavy metals are not biodegradable and can progressively accumulate in biological tissues, prolonged exposure can lead to serious health effects, including cancer, neurological damage, immune dysfunction, endocrine disruption, and developmental disorders (Abbas *et al.*, 2024). Traditional treatment approaches for removing heavy metals, such as chemical precipitation, ion exchange, activated carbon adsorption, and membrane-based filtration, are frequently constrained by several practical drawbacks. These include limited efficiency at trace concentrations, high chemical demand, elevated operating expenses, and the generation of secondary hazardous sludge (Nasrollahzadeh *et al.*, 2023). As a result, considerable research attention has shifted toward the development of advanced materials that can remove different metal species simultaneously, particularly in complex wastewater environments. Nanotechnology has introduced new possibilities for water purification because nanomaterials possess large specific surface areas, high reactivity, adjustable electronic properties, and strong catalytic performance. Within this class of materials, bimetallic nanoparticles (BNPs), which consist of two distinct metallic elements, have gained increasing interest as advanced candidates for heavy metal remediation. Their improved performance is mainly associated with synergistic interactions between the paired metals, where interfacial electron transfer enhances adsorption capacity, promotes catalytic reduction, and improves stability relative to single-metal nanoparticles (Alvarez *et al.*, 2023; Wang *et al.*, 2024). BNPs can be designed in different architectures, including alloyed particles, core-shell structures, Janus-type nanoparticles, and heterodimeric systems. Such structural arrangements influence surface energy, electron distribution, and Fermi-level alignment, thereby affecting both metal-ion binding strength and catalytic activity. For instance, Fe-Cu nanoparticles have been reported to show strong catalytic reduction performance toward Cr (VI),

whereas Au–Pd and Ag–Ni systems demonstrate high affinity for soft metal ions such as Hg (II) and Pb (II) through metallophilic interactions (Li *et al.*, 2023; Mukherjee *et al.*, 2024). More recent studies have increasingly emphasised sustainable preparation routes, such as biologically mediated reduction, plant-extract-assisted synthesis, and natural deep eutectic solvent (NADES)-based methods, to obtain BNPs with lower environmental impact (Zhang *et al.*, 2024). In parallel, hybrid nanocomposites, including BNP-loaded biochar, BNP graphene oxide (GO), and BNP–metal-organic framework (MOF) materials, have shown enhanced stability, recyclability, and selectivity under realistic wastewater conditions. **Table 1** summarises representative heavy metals, their major industrial sources, toxicity limits, and related health effects, based on recent publications from 2022 to 2024.

Table 1. Major Heavy Metals, Industrial Sources, WHO Limits, and Health Impacts

Heavy Metal	Main Industrial Sources	WHO Limit (µg/L)	Key Health Effects	Reference
Lead (Pb)	Battery production, smelting, and paint industries	10 µg/L	Neurotoxicity, cognitive decline	(Abbas <i>et al.</i> , 2024)
Chromium (Cr(VI))	Electroplating, tanning, and metal finishing	50 µg/L	Carcinogenic, mutagenic	(Mukherjee <i>et al.</i> , 2024)
Mercury (Hg)	Chlor-alkali, mining, electronics	6 µg/L	Neurotoxicity, bioaccumulation	(Sharma <i>et al.</i> , 2023)
Cadmium (Cd)	Electroplating, pigments, fertilisers	3 µg/L	Renal dysfunction, bone damage	(Nasrollahzadeh <i>et al.</i> , 2023)
Arsenic (As)	Mining, pesticide manufacturing, and metal refineries	10 µg/L	Skin lesions, carcinogenicity	(Wang <i>et al.</i> , 2024)

Considering the shortcomings of conventional treatment methods and the growing worldwide burden of heavy metal contamination, BNPs represent a highly promising basis for integrated water purification technologies. Their multiple removal pathways, including adsorption, catalytic reduction, coprecipitation, and surface-driven complexation reactions, allow them to eliminate both positively charged metal ions and anionic metal species with high efficiency. The following sections discuss BNP synthesis approaches, mechanistic pathways of metal removal, applications for key heavy metals, existing challenges, and future research directions.

1.1 Rationale, novelty, and scope of this review

Conventional precipitation, coagulation, ion exchange, membrane separation, and activated-carbon adsorption remains essential treatment options, but their performance can decline at trace concentrations or in high-salinity and multi-solute matrices. These processes may also require substantial chemical or energy input, transfer contaminants to a sludge or concentrate, suffer membrane fouling or resin exhaustion, and incur additional costs for residual management. Nanoparticles do not remove these engineering constraints automatically; however, their high

density of accessible sites and tunable interfacial chemistry can integrate capture and transformation within one material. The central advantage of a bimetallic nanoparticle over its monometallic counterpart is not simply the presence of a second metal. Alloying, galvanic coupling, lattice strain, ligand effects, and core-shell or Janus architectures can redistribute surface electron density, expose new interfacial sites, accelerate electron transfer, protect a reactive metal from passivation, and improve magnetic recovery or contaminant selectivity. The benefit is therefore composition- and architecture-dependent and must be demonstrated against the corresponding monometallic controls under matched conditions. Unlike earlier reviews that treat nanoadsorbents broadly or focus on a single metal pair or contaminant, this review links six elements in one critical framework: synthesis variables; composition and architecture; physicochemical characterisation; removal mechanism; performance in complex water matrices; and safety, regeneration, and life-cycle considerations. The scope covers Fe-, Pd-, Ag-, Cu-, and Ni-containing bimetallic systems used for Pb, Cr, Hg, Cd, and as remediation, with particular emphasis on evidence reported from 2022 to 2025. Cross-study capacity and efficiency values are compared cautiously because pH, dose, initial concentration, contact time, competing ions, and analytical definitions are not standardised.

2. Synthesis of Bimetallic Nanoparticles

The route selected for producing bimetallic nanoparticles (BNPs) has a strong influence on their structural features, surface chemistry, catalytic behaviour, stability, and interaction with heavy metal ions. Synthesis conditions determine key characteristics such as particle dimensions, surface charge, crystallinity, metal distribution within the alloy or heterostructure, surface functional groups, and electron-transfer efficiency, all of which govern adsorption and catalytic reduction performance. In recent years, especially from 2022 to 2024, notable advances have been reported in both conventional and sustainable preparation strategies, including chemical reduction, biological routes, coprecipitation, sol-gel processing, electrochemical methods, laser ablation, and seed-mediated or core-shell fabrication. Because each technique presents specific strengths and limitations, careful selection of the synthesis pathway is essential for tailoring BNPs with optimal performance in wastewater remediation. Figure 1 presents a schematic representation of the principal architectural forms of bimetallic nanoparticles.

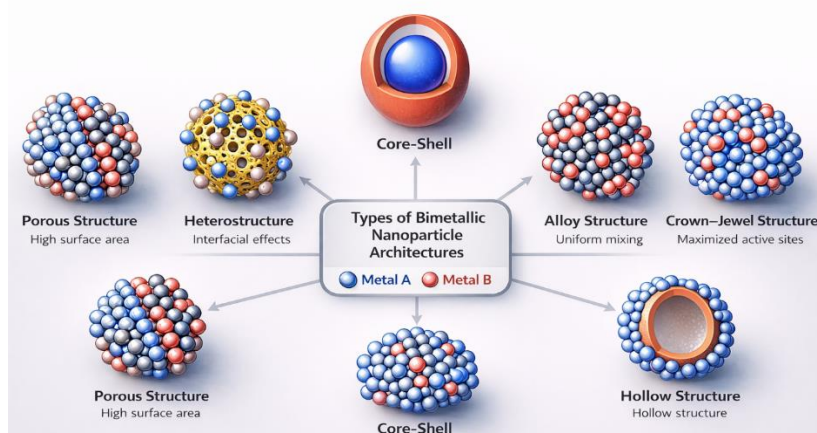


Figure 1. Schematic illustration of the main architectures of bimetallic nanoparticles, including core-shell, alloy, porous, heterostructure, crown-jewel, and hollow structures.

2.1 Chemical Reduction

Chemical reduction remains one of the most established approaches for fabricating BNPs because it allows effective regulation of nucleation behaviour, particle dimensions, and bimetallic composition. In this route, metal salts, commonly nitrates or chlorides, are converted into zero-valent metallic nanoparticles using strong reducing agents such as sodium borohydride (NaBH_4), hydrazine (N_2H_4), or ascorbic acid. The formation process generally involves three sequential steps: reduction of metal ions into atomic species, formation of metallic nuclei, and subsequent particle growth into alloy, core-shell, or heterostructured forms, depending largely on the relative reduction potentials of the paired metals.

Recent reports indicate that differences in reduction potential between the two metallic precursors strongly determine the final BNP structure. Metals with more positive standard reduction potentials, such as Ag^+/Ag and Au^{3+}/Au , are usually reduced first during co-reduction and therefore act as initial nucleation centers. Metals with lower reduction potentials tend to deposit later, often producing core-shell configurations (Li *et al.*, 2023). In contrast, metal pairs with comparable reduction potentials, such as Cu/Ni or Fe/Cu , typically nucleate at similar rates and form more uniform alloy nanoparticles. Because NaBH_4 promotes rapid electron transfer, it has frequently been associated with the production of well-dispersed nanoparticles with relatively narrow particle-size distributions (Wang *et al.*, 2024).

For example, Cu-Ni BNPs prepared with NaBH_4 have recently shown 99% reduction of Cr(VI) under acidic conditions, which was attributed to improved electron transport across the Cu-Ni interface (Mukherjee *et al.*, 2024). Likewise, chemically reduced Fe-Ag BNPs demonstrated high Pb(II) uptake because Ag provides strong metallophilic interaction sites, whereas Fe contributes reactive oxygen-containing surface groups (Alvarez *et al.*, 2023). Nevertheless, the use of aggressive reducing agents raises environmental concerns, encouraging current research to move toward greener chemical protocols based on milder reductants and solvent-engineering strategies.

2.2 Green Synthesis

Green synthesis has gained considerable attention as it avoids hazardous reductants and instead uses biomolecules that can function simultaneously as reducing, stabilising, and capping agents. Plant-derived extracts, microbial metabolites, polysaccharides, amino acids, and natural deep eutectic solvents (NADES) provide sustainable reaction environments for producing nanoparticles under environmentally favourable conditions. Bioactive compounds such as polyphenols, flavonoids, terpenoids, and alkaloids transfer electrons to metal ions and also bind to newly formed nanoparticle surfaces, thereby improving colloidal stability and biocompatibility (Zhang *et al.*, 2024).

One recent investigation reported that Fe-Ag BNPs produced using neem (*Azadirachta indica*) extract removed more than 98% of Pb(II) , mainly because phytochemicals increased surface defects and supplied abundant functional groups for metal binding (Sharma *et al.*, 2023). Biogenic reduction using microorganisms has also become increasingly important; bacterial species such as *Shewanella oneidensis* and fungal species such as *Aspergillus niger* have been applied to generate Fe-Ni and Ag-Ni BNPs with hollow or dendritic structures that enhance adsorption capacity (Thapa *et al.*, 2024). In addition, NADES-assisted synthesis allows better regulation of metal-ion solvation and nucleation while maintaining a biodegradable reaction medium (Abbas *et al.*, 2024). Despite its environmental benefits, green synthesis still faces limitations related to slower reaction kinetics, batch-to-batch variability, and inconsistent phytochemical composition. Even so, its low toxicity, sustainability, and ability to introduce useful surface functional groups make it a highly promising route for future BNP development.

2.3 Coprecipitation and Sol–Gel Techniques

Coprecipitation is commonly employed for preparing Fe-based BNPs because it is simple, scalable, and capable of generating relatively homogeneous mixed-metal hydroxide precursors. The process usually involves controlling the solution pH or adding alkaline agents such as NaOH or NH₄OH to induce the simultaneous precipitation of two metal ions. Subsequent drying and calcination transform these precipitates into oxide-based BNPs with notable adsorption and catalytic properties (Velasquez *et al.*, 2023).

In sol–gel synthesis, metal alkoxides undergo hydrolysis and condensation to form a gel-like network that produces porous BNPs with high surface area and controlled composition after drying and calcination. Fe–Mn BNPs obtained through this method have shown effective arsenic removal, as Fe (III) hydroxides provide strong adsorption sites while Mn (II)/Mn (IV) redox cycling promotes the conversion of As (III) into the more easily adsorbed As(V) form (Wang *et al.*, 2024). However, both coprecipitation and sol–gel methods may lead to particle agglomeration and provide limited control over precise nanoparticle morphology. Nevertheless, their low cost and operational simplicity continue to make them attractive options for large-scale BNP production.

2.4 Electrochemical Synthesis

Electrochemical synthesis provides precise control over nanoparticle size, morphology, and metal composition without the need for chemical reducing agents. In this technique, metal ions are reduced at the cathode under an applied potential, forming nanoparticles with relatively clean surfaces and low impurity levels. Ag–Ni and Pd–Fe BNPs fabricated by electrochemical codeposition have exhibited stronger adsorption and catalytic performance than comparable chemically produced materials, mainly because of faster electron transfer at the bimetallic interface (Li *et al.*, 2023). This method also permits direct deposition of BNPs onto conductive supports, including carbon paper and stainless-steel mesh, which is beneficial for designing catalytic reactor systems. Even with these advantages, low production volume and dependence on conductive substrates still restrict the broader industrial use of electrochemical BNP synthesis.

2.5 Laser Ablation and Physical Methods

Laser ablation in liquids (LAL) is an emerging physical technique for producing highly pure BNPs. In this process, a pulsed laser strikes submerged metal targets, generating a plasma plume that cools rapidly and forms nanoparticles in the surrounding liquid. Since the method does not require surfactants or chemical reductants, the resulting BNPs often possess clean, reactive surfaces that are well-suited for catalytic applications (Park *et al.*, 2023). Au–Pt BNPs produced by LAL have shown outstanding Hg(II) adsorption, which is linked to their high surface energy and large number of defect sites (Sharma *et al.*, 2023). The rapid quenching associated with ablation can also generate metastable alloy phases that are difficult to obtain using conventional chemical reduction routes. The principal drawbacks of LAL are its high energy requirement and relatively low production yield, which currently limit its use mainly to specialised applications and mechanistic investigations.

2.6 Seed-Mediated and Core–Shell Architectures

Seed-mediated synthesis offers a high degree of control over BNP architecture. In this method, pre-synthesised monometallic nanoparticles serve as nucleation templates for the controlled growth of a second metal, enabling the formation of core–shell particles, anisotropic nanostructures, or Janus-type systems. Au@Pd BNPs prepared through seed-mediated routes have shown excellent Hg(II) affinity, achieving more than 97% removal as a result of strong Hg–Au metallophilic interactions combined with Pd-assisted catalytic acceleration (Mukherjee *et al.*, 2024). Core–shell designs also improve resistance to oxidation and metal leaching, making them suitable

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for repeated wastewater treatment cycles. However, this approach is limited by the complexity and cost of seed preparation and controlled secondary metal deposition.

2.7 Hydrothermal, solvothermal, and biosynthesis routes

Hydrothermal and solvothermal methods use sealed reactors to promote nucleation, crystallisation, alloying, or oxide formation at elevated temperature and autogenous pressure. Water-based hydrothermal processing is attractive for crystalline Fe-Mn and Fe-Cu oxides, whereas organic-solvent solvothermal processing offers wider control over precursor solubility, reduction rate, morphology, and phase composition. Temperature and residence time generally increase crystallinity and alloy interdiffusion, but excessive values can cause grain growth, loss of surface area, or phase segregation. Solvent choice, filling fraction, precursor hydrolysis, and post-treatment therefore require explicit reporting (Nyabadza *et al.*, 2023). Biosynthesis uses plants, bacteria, fungi, algae, enzymes, or isolated biomolecules as reducing and/or capping systems. It can lower reliance on hazardous reductants and introduce hydroxyl, carboxyl, amine, and phenolic groups that assist metal binding. Its principal limitations are biological variability, uncertain active-reagent concentration, residual organic matter, sterilisation requirements, and difficulty controlling metal ratio and architecture. Green or biological origin should consequently be supported by mass and energy balances, leaching tests, and toxicity assessment rather than assumed from the identity of the reductant (Nizam *et al.*, 2021). **Table 2** shows the comparison of principal BNP synthesis methods and their implications for environmental remediation

2.8 Influence of synthesis variables

Metal ratio controls the abundance and continuity of bimetallic interfaces: too little promoter metal may provide insufficient catalytic sites, whereas excess noble metal can block reactive Fe or Ni sites and raise cost. Reductant strength and addition rate determine whether nucleation is simultaneous or sequential; this distinction often separates alloyed particles from core-shell products (Bhol *et al.*, 2020; Nyabadza *et al.*, 2023). Stabiliser chemistry and concentration regulate aggregation and access to active sites, while pH controls precursor speciation and surface charge. Temperature and reaction time influence reduction completion, crystallinity, interdiffusion, defect density, and particle growth. Meaningful optimisation should therefore use multivariable designs and report final, not only nominal, composition (Mourdikoudis *et al.*, 2018; Nyabadza *et al.*, 2023).

Table 2. Comparison of principal BNP synthesis methods and their implications for environmental remediation (Idris & Roy, 2023; Nyabadza *et al.*, 2023; Sharma *et al.*, 2019).

Synthesis method	Key controls	Main advantage	Primary limitation	Remediation implication
Chemical reduction	Metal ratio, reductant, pH, and capping agent	Rapid synthesis with good composition and size control	Hazardous residues and aggregation	Produces reactive zero-valent phases for electron-transfer reactions
Green/biological synthesis	Biological source, precursor ratio, pH, and temperature	Mild processing using renewable and capping agents	Batch variability and difficult purification	Biogenic groups may enhance adsorption but obstruct catalytic sites

Synthesis method	Key controls	Main advantage	Primary limitation	Remediation implication
Sol-gel/co-precipitation	Hydrolysis, pH, ageing, and calcination	Simple production of porous mixed-metal oxides	Agglomeration and calcination demand	Suitable for redox- and sorption-based oxyanion removal
Hydrothermal/solvothermal	Solvent, temperature, pressure, and reaction time	Strong phase, crystallinity, and morphology control	Energy, solvent, and autoclave requirements	Produces stable phases with tunable catalytic properties
Electrochemical/physical	Current, potential, electrolyte, laser energy, and time	Clean surfaces and precise metal deposition	High equipment and energy costs	Generates accessible interfaces with few chemical residues

2.9 Classification by metallic composition and functional role

Composition provides a useful first classification, but it should be interpreted together with architecture and oxidation state. Fe-based systems typically supply a sacrificial electron donor, magnetic response, and iron-(oxyhydr)oxide sorption phases. Pd-based systems promote hydrogen activation and catalytic electron transfer, usually at higher material cost. Ag-based systems provide soft-metal affinity and antimicrobial activity but require careful control of Ag⁺ release. Cu-based systems accelerate galvanic corrosion and redox cycling, although Cu leaching can create secondary toxicity. Ni-based systems can improve catalytic activity and magnetic separation but raise occupational and ecotoxicological concerns. These roles explain why the same second metal can improve one target reaction yet reduce selectivity or stability in another (Allam *et al.*, 2021; Fu *et al.*, 2015). **Table 3** displays the summary of composition-dependent functions and limitations of BNPs used in water treatment

Table 3. Summary of composition-dependent functions and limitations of BNPs used in water treatment (Allam *et al.*, 2021; Fu *et al.*, 2015).

BNP class	Representative pairs	Main contribution	Typical targets	Principal limitation
Fe-based	Fe–Cu, Fe–Ni, Fe–Mn, Fe–Ag	Electron donation, magnetic recovery, and oxide-mediated sorption	Cr(VI), As species, Pb(II), and Cd(II)	Passivation and metal leaching
Pd-based	Pd–Fe, Au–Pd	Hydrogen activation and catalytic electron transfer	Redox-active metals and oxyanions	High cost, poisoning, and difficult recovery
Ag-based	Fe–Ag, Ag–Ni, Ag–Cu	Soft-metal affinity, electronic promotion, and antimicrobial activity	Hg(II) and selected divalent metals	Ag ⁺ release and microbial toxicity

Cu-based	Fe–Cu, Cu–Ni, Ag–Cu	Galvanic coupling and redox mediation	Cr(VI) and mixed-metal systems	Cu dissolution and competing reactions
Ni-based	Fe–Ni, Cu–Ni, Ag–Ni	Catalytic promotion, magnetism, and alloy stabilisation	Cr(VI) and other redox-active contaminants	Ni toxicity, leaching, and passivation

3. Mechanisms of Heavy Metal Removal

Bimetallic nanoparticles (BNPs) remove heavy metals from contaminated water through several interconnected processes, including adsorption, catalytic reduction, coprecipitation, and surface-driven redox transformations. Compared with monometallic nanoparticles, BNPs benefit from intermetallic synergy that improves electron-transfer capacity, surface binding affinity, and operational stability. This synergistic behaviour arises from differences in electronegativity, work function, and oxidation tendency between the two metals. When arranged as alloys, heterostructures, or core-shell particles, the electronic structures of the metals interact and generate more reactive surface states. These active states strengthen adsorption, promote electron flow, and support multi-electron reduction reactions, making BNPs highly effective for detoxifying heavy metals in wastewater (Alvarez *et al.*, 2023; Wang *et al.*, 2024). The following subsections explain the major mechanisms involved in metal removal. **Figure 2** illustrates the mechanism of heavy metal removal by bimetallic nanoparticles (BNPs).

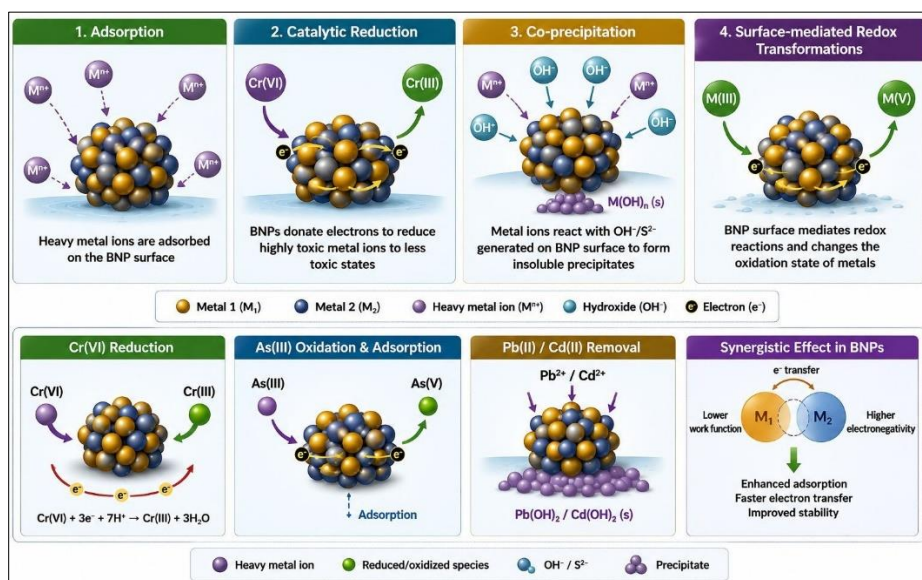


Figure 2. Mechanism of Heavy Metal Removal by Bimetallic Nanoparticles (BNPs).

3.1 Adsorption Mechanism

Adsorption commonly represents the first and most important interaction pathway between heavy metal species and BNP surfaces. During this process, metal ions are retained on nanoparticle surfaces through several binding modes, including electrostatic attraction, inner-sphere complex formation, surface precipitation, π -electron interactions, and metallophilic bonding. The large

specific surface area of BNPs, together with abundant structural defects such as vacancies, edges, kinks, grain boundaries, and lattice distortions, creates numerous reactive sites for metal uptake. These surface irregularities raise the surface free energy and strengthen interactions with both cationic and anionic heavy metal species. In bimetallic nanostructures, adsorption performance is often improved by electronic interactions between the two metals. For instance, Pd–Au BNPs show a strong tendency to bind Hg (II), mainly because Au forms metallophilic interactions with mercury that can produce quasi-covalent surface bonding. Pd further supports this process by increasing electron density at the Au–Pd interface, thereby reinforcing Hg(II) attachment (Li *et al.*, 2023). Similarly, Fe–Ag BNPs enhance Pb (II) uptake because Fe supplies hydroxide-rich reactive sites, while Ag provides favourable binding sites for soft acid metal ions such as Pb (II) (Sharma *et al.*, 2023). The surface charge of BNPs also plays a key role in controlling adsorption behaviour. Under acidic conditions, Fe-based BNPs usually become positively charged, which favours attraction toward oxyanions such as Cr (VI) and As(V). By contrast, at neutral or alkaline pH values, the nanoparticle surface often becomes negatively charged, promoting the uptake of cationic metals such as Cd (II), Pb (II), and Hg (II) (Abbas *et al.*, 2024). Adsorption behaviour is commonly interpreted using Langmuir or the Freundlich isotherm models, and many studies report that BNPs follow Langmuir-type monolayer adsorption because of their well-defined reactive surface sites (Mukherjee *et al.*, 2024). Therefore, adsorption is a central pathway for heavy metal immobilisation, with the superior adsorption capacity of BNPs arising from the combined structural and electronic effects of their paired metallic components. **Figure 3** illustrates the adsorption mechanism involved in heavy-metal removal.

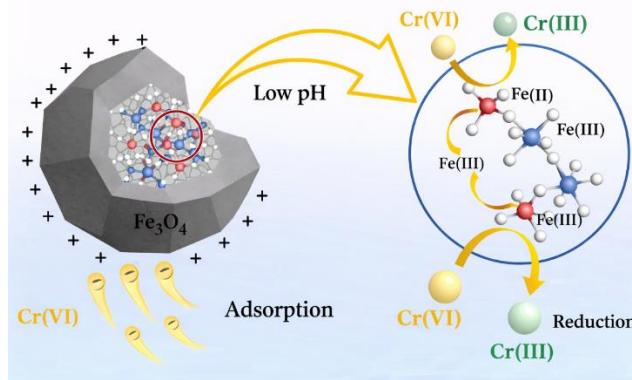


Figure 3. Proposed adsorption and reduction pathways for Cr (VI) removal on a Fe₃O₄-based bi-metallic surface.

3.2 Catalytic Reduction Mechanism

Catalytic reduction is a major pathway for treating oxidised, highly toxic metal species, including Cr(VI), Hg(II), and As(V). BNPs perform particularly well in this process because the interfaces between their two metallic components create electron-rich regions that support rapid electron transfer. These transferred electrons convert toxic metal ions into oxidation states that are less harmful or less mobile. In the case of Cr(VI), Fe–Cu BNPs have shown strong catalytic activity. Fe(0) functions as a sacrificial electron source that reduces Cr(VI) to the less toxic Cr(III), whereas

Cu helps limit iron passivation by supporting Fe(0) regeneration and improving electron transport (Wang *et al.*, 2024). The resulting Cr(III) species can then precipitate as Cr(OH)₃ or become adsorbed onto newly generated Fe(III) hydroxides, thereby increasing total removal efficiency. A similar enhancement is observed during Hg(II) reduction in bimetallic systems. Pd–Au BNPs can promote multi-electron conversion of Hg(II) into elemental mercury (Hg⁰), which subsequently forms amalgam-like surface complexes (Sharma *et al.*, 2023). The strong interaction between Hg and Au improves selectivity, while Pd facilitates faster electron movement across the interface. Arsenic remediation often involves coupled oxidation and reduction steps. For example, Fe–Mn BNPs oxidise As(III) to As(V) through Mn(IV)/Mn(II) redox cycling while Fe-based hydroxides simultaneously capture the generated As(V). Recent mechanistic studies have confirmed this dual function by reporting nearly complete As(III) to As(V) conversion together with high As(V) adsorption capacity (Mukherjee *et al.*, 2024). The overall efficiency of catalytic reduction is influenced by particle size, exposed surface facets, alloy composition, and crystallinity. Smaller BNPs with abundant high-index facets generally provide more active sites for multi-electron transfer, highlighting the importance of nanoscale structural design (Li *et al.*, 2023).

3.3 Coprecipitation Mechanism

Coprecipitation represents an important removal route in BNP systems that contain metals such as Fe, Mn, or Mg, since these elements readily generate insoluble hydroxides or mixed-metal precipitates in aqueous media. In Fe-based BNPs, Fe(0) is oxidised to Fe(II) and Fe(III), followed by hydrolysis to form Fe(OH)₂ and Fe(OH)₃. These hydroxide phases act as secondary sorbents because they can strongly bind both cationic metals and oxyanion species. Recent studies have shown that Fe–Mn BNPs immobilise arsenic through the formation of stable Fe–Mn–As complexes that remain in the solid phase and resist re-dissolution under changing pH conditions (Wang *et al.*, 2024). Likewise, during Cr(VI) treatment, the reduced Cr(III) products can co-precipitate with Fe(III) hydroxides to form mixed Fe–Cr hydroxide solids that are readily removed by filtration or sedimentation (Alvarez *et al.*, 2023). This mechanism often operates together with catalytic reduction, as newly reduced species such as Cr(III) and As(V) can rapidly associate with hydroxides produced during BNP surface oxidation. The coupling of redox conversion and precipitation therefore improves removal efficiency and enhances the long-term stability of immobilised contaminants.

3.4 Redox Reactions on BNP Surfaces

Surface-controlled redox reactions are another key process involved in the removal of toxic metal ions. Because BNPs combine metals with different electronegativities and work functions, galvanic interactions can develop at the bimetallic interface. In such systems, the more electropositive metal generally behaves as the anodic component and supplies electrons, whereas the more noble metal acts as the cathodic component and accelerates redox cycling (Zhang *et al.*, 2024). In Fe–Cu BNPs, for instance, Fe(0) serves as the sacrificial anodic phase, oxidising to Fe(II)/Fe(III) and releasing electrons that participate in the reduction of Cr(VI), Hg(II), and As(V). Copper, owing to its higher electronegativity, helps stabilise Fe(0) and improves its electron-transfer capability (Wang *et al.*, 2024). This galvanic coupling promotes multi-electron redox pathways while reducing the likelihood of Fe surface deactivation. Similarly, Ag–Ni BNPs can support rapid electron shuttling because Ni enhances conductivity and increases electron density around Ag sites. This promotes both the binding and partial reduction of Pb(II) and Hg(II) species (Sharma *et al.*, 2023). Redox-mediated pathways are especially valuable in mixed-contaminant waters, where catalytic transformation can convert metals into forms that are more readily adsorbed or precipitated. This close interaction

between redox activity and adsorption is a major reason BNPs often outperform monometallic nanoparticles.

3.5 Integrated binding and transformation pathways

These removal processes usually act together rather than separately. Ions may first be attracted electrostatically to the BNP surface, then form stronger inner-sphere complexes through ligand exchange with hydroxyl, carboxyl, amine, sulfhydryl, or metal sites. Ion exchange, surface precipitation, and coprecipitation may also contribute, especially in metal-oxide, biochar, and zero-valent-iron systems (Pasinszki & Krebsz, 2020; Yin *et al.*, 2020). For redox-active contaminants, galvanic electron transfer can convert pollutants into less toxic or less soluble forms. For instance, Cu-loaded Fe⁰ promotes Cr(VI) reduction to Cr(III), followed by Cr(III)/Fe(III) hydroxide precipitation or coprecipitation (Ye *et al.*, 2021). Mn-containing surfaces can also oxidise As(III) to As(V), which is then strongly retained by Fe-(oxyhydr)oxides (Zhang *et al.*, 2007). Therefore, contaminant removal should not always be labelled simply as adsorption. Confirming the dominant pathway requires solid-phase speciation, mass balance, aqueous chemistry, desorption tests, and post-reaction XPS, XRD, and TEM evidence to distinguish adsorption, redox transformation, precipitation, coprecipitation, or volatilisation (Table 4).

3.6 Characterisation and performance relationships

Characterisation should be conducted before and after treatment, as the reactive nature, oxidation state, morphology, and surface chemistry of BNPs may change during application. XRD is used to detect crystalline phases, alloy formation, oxidation products, and sufficiently crystalline precipitates. TEM and SEM provide information on particle size, structure, aggregation, and surface deposits, while EDX mapping shows spatial elemental distribution and helps confirm metal co-location and changes in elemental ratios (Mourdikoudis *et al.*, 2018). XPS provides surface composition and oxidation-state information and can verify transformations such as Cr(VI) to Cr(III), As(III) to As(V), and Fe⁰ to Fe(II)/Fe(III). For instance, post-reaction XPS of Cu/Fe BNPs confirmed the loss of detectable Cr(VI), the formation of Cr(III), and Fe⁰ oxidation during Cr(VI) removal (Ye *et al.*, 2021). Likewise, spectroscopic evidence for Fe–Mn binary oxides showed that Mn oxide oxidised As(III), whereas Fe oxide supplied binding sites for the resulting As(V) (Zhang *et al.*, 2007). FTIR can indicate changes in oxygen-, nitrogen-, and sulfur-containing functional groups involved in contaminant binding. BET analysis measures specific surface area, pore volume, and pore-size distribution, whereas zeta-potential measurements describe pH-dependent surface charge, electrostatic interactions, aggregation behaviour, and colloidal stability (Mourdikoudis *et al.*, 2018). Nevertheless, no single technique can independently confirm a removal mechanism. Reliable mechanistic interpretation depends on combined evidence from solid-phase characterisation, aqueous speciation, kinetic analysis, desorption tests, dissolved-metal measurements, and contaminant mass balance.

Table 4. Summary of BNP characterisation techniques and their mechanistic relevance (Mourdikoudis *et al.*, 2018; Pasinszki & Krebsz, 2020; Ye *et al.*, 2021).

Technique	Evidence obtained	Performance interpretation	Important limitation
XRD	Alloy/oxide phases; crystallite size; post-reaction precipitates	Confirms phase formation, corrosion products, and immobilisation	Poor sensitivity to amorphous or low-loading phases

TEM/HRTEM	Size, morphology, lattice fringes, core-shell/Janus interfaces	Links interface density and aggregation to accessible reactive area	Small, imaged population may not represent bulk material
SEM-EDX	Surface morphology and elemental maps	Shows dispersion on support and contaminant accumulation	Semi-quantitative; interaction volume can blur nanoscale interfaces
XPS	Surface composition and oxidation states	Tests electron transfer and contaminant redox transformation	Surface-sensitive; vacuum/drying may alter speciation
FTIR	Functional groups and shifts after binding	Supports complexation by hydroxyl/carboxyl/amine groups	Assignments can overlap and do not quantify binding alone
BET	Surface area, pore volume, pore-size distribution	Normalises capacity and reveals pore blocking after use	Dry-state area may differ from hydrated accessibility
Zeta potential	Surface charge versus pH and colloidal stability	Explains electrostatic attraction, aggregation, and pH response	Matrix ions and natural organic matter can shift values

3.7 Electron-transfer pathways, kinetics, facets, and defect density

Electron transfer in BNPs can proceed through direct contact between a contaminant and the less noble metal, through galvanic transfer from an anodic metal (commonly Fe or Ni) to a cathodic promoter (such as Cu, Pd, Ag, or Au), or through adsorbed hydrogen and redox-active surface oxides. The second metal changes the work function and local density of electronic states, thereby shifting adsorption energies and lowering activation barriers. In Fe–Cu and Fe–Ni systems, microgalvanic cells accelerate Fe(0) oxidation and direct electrons toward adsorbed Cr(VI); newly formed Fe(II)/Fe(III) hydroxides then bind or co-precipitate Cr(III). In Fe–Mn systems, the pathway is sequential rather than purely reductive: Mn(IV) sites oxidise As(III), and adjacent Fe-(oxyhydr)oxide sites capture As(V). Dissolved oxygen, proton availability, surface oxide thickness, and competing electron acceptors determine whether useful contaminant conversion or non-productive corrosion dominates (Wang *et al.*, 2024; Yang *et al.*, 2024).

Reaction kinetics reflect both intrinsic surface reaction and transport. Apparent pseudo-first-order behaviour is common when the reductant or active surface is in excess, whereas pseudo-second-order fits may indicate that site availability strongly affects uptake; neither empirical fit alone proves a molecular mechanism. Rate constants should therefore be normalised by reactive surface area or metal mass and interpreted together with diffusion, mixing, pH, temperature, and time-resolved speciation. Initial rapid removal may arise from external surface sites, followed by slower intraparticle diffusion, oxide-layer growth, product precipitation, or progressive passivation. Activation-energy measurements and isotope or electrochemical studies can help distinguish surface reaction from transport control (Li *et al.*, 2023; Mukherjee *et al.*, 2024).

Crystal facets and defects determine the coordination environment and electron density of active atoms. High-index facets, steps, edges, vacancies, grain boundaries, and strained bimetallic interfaces generally contain under-coordinated atoms that can bind metal species more strongly

and facilitate charge transfer. However, an excessive defect density can also accelerate non-selective corrosion, dissolution, or irreversible fouling. Particle size has a related but non-monotonic effect: decreasing size usually increases area and interface density, but very small particles may oxidise or aggregate rapidly. Accordingly, facet exposure and defect density should be linked to performance using high-resolution TEM, XPS, electron paramagnetic resonance where appropriate, electrochemical measurements, and density functional theory rather than inferred from size alone (Bose *et al.*, 2024; Zhao *et al.*, 2024).

4. Applications for Heavy Metal Removal

Bimetallic nanoparticles (BNPs) have been extensively applied for the remediation of toxic heavy metals due to their synergistic physicochemical properties, enhanced catalytic behaviour, and improved adsorption capabilities compared to monometallic nanomaterials. Their dual-metal structure creates interfacial active sites that promote electron transfer, accelerate reduction reactions, and increase binding affinity toward both cationic and oxyanionic species. Recent advances (2022–2025) have demonstrated the superior performance of BNPs for the removal of critical pollutants such as Pb(II), Cr(VI), Hg(II), Cd(II), and As(III/V) from industrial wastewater, contaminated groundwater, and municipal effluents. The following subsections provide a detailed overview of BNP applications for each major heavy metal, supported by current experimental findings and mechanistic insights.

4.1 Removal of Lead (Pb)

Lead is one of the most toxic and prevalent heavy metals in water systems, posing severe neurological, developmental, and cardiovascular risks. BNPs have exhibited exceptional Pb(II) removal efficiency due to the combined effects of high surface-area-to-volume ratios and synergistic electronic interactions between the two constituent metals. Among the most effective systems, Fe–Ag BNPs have shown strong adsorption capacity toward Pb(II) because silver forms partial covalent bonds with lead. At the same time, iron provides reactive hydroxide groups that facilitate complexation. A recent study demonstrated that green-synthesised Fe–Ag BNPs achieved over 98% Pb(II) removal from industrial wastewater due to these cooperative mechanisms (Sharma *et al.*, 2023).

Cu–Zn BNPs have also emerged as efficient adsorbents for Pb(II), primarily because Zn promotes surface precipitation of Pb(OH)₂, while Cu enhances electron transfer and stabilises surface complexes. Experiments conducted on Cu–Zn nanoparticles synthesised via chemical reduction reported a maximum adsorption capacity of 185 mg/g, outperforming monometallic Cu or Zn nanoparticles by more than 30% (Zhang *et al.*, 2024). Ag–Ni BNPs synthesised electrochemically demonstrated rapid Pb(II) uptake (within 20 minutes), attributed to Ni-induced conductivity, which enhances electron donation to Pb(II), and Ag-induced metallophilic bonding (Li *et al.*, 2023). These findings underscore the ability of BNPs to remove Pb(II) even in complex wastewater matrices containing competing cations, owing to their strong surface affinity and enhanced redox behaviours. BNPs consistently outperform conventional materials due to their increased density of adsorption-active sites and metal–metal synergistic effects.

4.2 Removal of Chromium (Cr)

Chromium contamination is dominated by the presence of hexavalent chromium (Cr(VI)), a carcinogenic, mobile, and highly toxic oxyanion. Effective removal of Cr(VI) requires both rapid reduction to the less toxic Cr(III) and subsequent immobilisation. BNPs are ideally suited for this dual mechanism because they can simultaneously reduce Cr(VI) and adsorb Cr(III) through surface

hydroxides. Fe–Cu BNPs are among the most efficient materials for Cr(VI) detoxification. Iron serves as a sacrificial anode, donating electrons that reduce Cr(VI) to Cr(III), while Cu accelerates electron transfer and prevents Fe(0) passivation. A recent investigation demonstrated complete Cr(VI) reduction within 30 minutes under mildly acidic conditions using Fe–Cu BNPs synthesised through chemical reduction (Mukherjee *et al.*, 2024). The reduction is followed by precipitation of Cr(OH)₃ or adsorption onto Fe(III) oxyhydroxides formed during iron oxidation. Fe–Ni BNPs also exhibit strong catalytic behaviour because Ni increases the redox cycling rate of Fe(II)/Fe(III), promoting continuous electron transfer. Experiments using Fe–Ni BNPs in simulated industrial wastewater showed a Cr(VI) removal rate of over 90% across five consecutive reuse cycles, demonstrating remarkable stability (Wang *et al.*, 2024). Furthermore, noble-metal BNPs such as Pd–Fe significantly accelerate multi-electron transfer pathways due to palladium's catalytic activity (Alvarez *et al.*, 2023). These findings demonstrate that BNP-mediated Cr(VI) removal is driven by a combination of intrinsic Fe(0) redox activity, intermetallic electron transfer, and surface precipitation of Cr(III), giving BNPs a major advantage over monometallic nanoparticles or bulk iron media.

4.3 Removal of Mercury (Hg)

Mercury is among the most hazardous pollutants due to its extreme neurotoxicity and ability to bioaccumulate in ecosystems. BNPs demonstrate exceptional affinity for Hg(II) because metals such as Au, Ag, and Pd form strong metallophilic or amalgam-like interactions with mercury. Pd–Au BNPs, for example, exhibit a unique synergistic mechanism: Au strongly binds Hg(II) through d-orbital interactions, while Pd accelerates electron transfer, promoting reduction of Hg(II) to elemental Hg(0) (Sharma *et al.*, 2023). This elemental mercury then amalgamates with the Au–Pd surface, ensuring stable immobilisation. Laser-ablated Au–Pt BNPs have demonstrated similarly strong Hg(II) adsorption and reduction behaviours. Because laser ablation generates nanoparticles with clean, ligand-free surfaces and high densities of structural defects, these nanoparticles exhibit increased active site availability and stronger Hg binding energies (Park *et al.*, 2023). Studies reported >95% Hg(II) removal within 10 minutes using such BNPs. Fe–Ag BNPs also show dual-function removal capabilities, initially binding Hg(II) on Ag active sites and subsequently catalysing partial reduction through Fe(0)/Fe(II) cycling. This dual mechanism enhances removal under conditions where competing ions or organic ligands are present. Because many BNP systems reduce Hg(II) to Hg(0), which is strongly retained through amalgamation, they outperform traditional adsorbents and monometallic nanoparticles in both efficiency and metal selectivity.

4.4 Removal of Cadmium (Cd)

Cadmium is a highly toxic metal commonly found in wastewater originating from electroplating, battery manufacturing, and pigment production. BNPs remove Cd(II) primarily through surface adsorption, surface complexation, and coprecipitation pathways (Liu *et al.*, 2015; Yin *et al.*, 2020). Ni–Zn BNPs exhibit particularly strong Cd(II) binding capacity because Zn undergoes surface ion exchange with Cd(II), forming insoluble Cd(OH)₂-type surface complexes. Meanwhile, Ni increases the structural stability and electron-transfer ability of the composite, preventing particle dissolution or deactivation. Recent studies reported Cd(II) removal efficiencies exceeding 90% in under one hour, with adsorption capacities surpassing 100 mg/g (Zhang *et al.*, 2024). Fe–Mn BNPs also contribute to Cd removal by forming Mn- and Fe-based hydroxides that bind Cd(II) through inner-sphere complexation. Because Mn can exist in multiple oxidation states (Mn(II), Mn(III), Mn(IV)), it enhances redox-driven surface reactivity, promoting faster metal uptake (Wang *et al.*, 2024). BNPs stabilise Cd(II) through chemical precipitation, complexation, and adsorption, making

them superior to conventional sorbents like activated carbon or ion exchange resins, particularly under variable pH and ionic conditions.

4.5 Removal of Arsenic (As)

Arsenic is frequently present as As(III) and As(V), with As(III) being more toxic, mobile, and difficult to remove. Effective remediation requires oxidation of As(III) to As(V), followed by adsorption onto reactive surfaces. BNPs, particularly Fe–Mn systems, excel in this dual-function approach. Fe–Mn BNPs oxidise As(III) through Mn(IV)/Mn(II) redox cycling. Mn(IV) oxidises As(III) to As(V), while Fe-based oxyhydroxides provide high-affinity adsorption sites for As(V). A recent groundwater simulation study demonstrated over 98% As removal using Fe–Mn BNPs prepared via sol-gel synthesis (Mukherjee *et al.*, 2024). These nanoparticles maintained high performance across multiple regeneration cycles due to their structural integrity and strong Fe–Mn synergy. Fe–Ni BNPs have also been applied in As remediation, with Ni promoting faster redox cycling and iron providing adsorption sites. In 2023, researchers reported that Fe–Ni BNPs achieved complete As(III) → As(V) oxidation within 60 minutes, followed by As(V) adsorption with minimal leaching (Alvarez *et al.*, 2023). BNP-supported biochar and BNP–MOF composites further enhance arsenic removal through increased porosity and additional adsorption functional groups (Zhang *et al.*, 2024).

4.6 Comparative performance and evidence quality

Table 5 compiles representative systems discussed in this review. The values should not be interpreted as a universal ranking because capacity and percentage removal depend strongly on initial concentration, solution volume, dose, pH, ionic strength, temperature, and endpoint definition. Studies that report only percentage removal at high sorbent dose may appear superior to studies that determine equilibrium capacity. Direct comparison therefore requires common protocols, full kinetic and equilibrium data, metal mass balance, and uncertainty estimates (Ye *et al.*, 2021; Yin *et al.*, 2020; Zhang *et al.*, 2007; Zhou *et al.*, 2016).

Table 5. Representative bimetallic and binary-metal nanomaterials used for heavy-metal removal (Ye *et al.*, 2021; Yin *et al.*, 2020; Zhang *et al.*, 2007; Zhou *et al.*, 2016).

BNP position	com-metal	Target metal	Conditions and main outcome	Reuse evidence
Cu/Fe BNPs		Cr(VI)	Chemical reduction; 50–100 nm. Up to 89.2% removal and 689.4 mg g ^{−1} capacity under the investigated conditions (Ye <i>et al.</i> , 2021).	NR
Fe/Ni BNPs		Cr(VI)	Liquid-phase reduction with ultrasound; pH 3–9. Achieved 94.7% removal within 10 min (Zhou <i>et al.</i> , 2016).	Effective after ageing and regeneration; cycle number NR
Fe–Mn binary oxide		As(III)	Oxidation–coprecipitation synthesis. Mn oxide oxidised As(III), while Fe oxide adsorbed the resulting As(V) (Zhang <i>et al.</i> , 2007).	NR
Fe–Mn oxide/biochar		Cd(II)	Ultrasonically assisted loading on biochar; pH 5 and 25 °C. Maximum capacity of 95.23 mg g ^{−1} (Yin <i>et al.</i> , 2020).	NR

*NR: not reported in the cited study or in the data extracted for this review. Outcome wording reflects the cited studies; cross-study numerical ranking is avoided where operating conditions are

not directly comparable. Exact particle-size distributions, uncertainty, and raw regeneration data should be reported in future studies.

4.7 Performance in real wastewater and treatment configurations

Real wastewater contains chloride, sulfate, carbonate, phosphate, hardness ions, dissolved organic matter, suspended solids, oils, surfactants, and co-occurring metals. These constituents can compete for sites, complex the target ion, compress the electrical double layer, foul supported particles, scavenge reactive species, or passivate zero-valent metals. Conversely, carbonate or sulfide can promote precipitation (Lim & Zhu, 2008; Lowry *et al.*, 2012; Wang *et al.*, 2016). Performance should therefore be tested sequentially in synthetic single-solute water, multi-ion model water, spiked real wastewater, and unspiked field samples, with matrix composition reported. Practical systems should immobilise BNPs on biochar, membranes, porous beads, magnetic supports, or packed media to reduce particle release and simplify recovery (Adeleye *et al.*, 2016; Qu *et al.*, 2013). Continuous-flow columns and membrane reactors must be evaluated for breakthrough, residence time distribution, hydraulic loss, fouling, regeneration, and contaminant mass balance. Scale-up decisions should include precursor availability, mixing and heat-transfer limitations, batch reproducibility, worker exposure, energy and water demand, residual handling, and cost per volume treated, rather than nanoparticle cost per gram alone (Adeleye *et al.*, 2016; Miseljić & Olsen, 2014; Nizam *et al.*, 2021).

5. Challenges and Limitations

Although bimetallic nanoparticles (BNPs) have shown strong potential for heavy metal remediation, several scientific, environmental, and operational limitations currently hinder their translation from laboratory research to full-scale industrial wastewater treatment systems. These challenges centre on nanoparticle stability, aggregation tendencies, scalability, reproducibility of synthesis, environmental risks, metal leaching, and variable performance in complex water matrices. Addressing these barriers is essential to ensure that BNP-based remediation is both effective and environmentally sustainable.

5.1 Stability and Aggregation Issues

One of the most significant limitations of BNPs relates to their long-term stability in aqueous environments. BNPs possess high surface energy due to their nanoscale dimensions, making them prone to aggregation, which reduces accessible surface area and diminishes catalytic and adsorption performance. This problem is particularly severe for Fe-containing BNPs (e.g., Fe–Cu, Fe–Mn, Fe–Ni), which undergo rapid oxidation to Fe(III)/Fe(II) hydroxides when exposed to water or dissolved oxygen (Wang *et al.*, 2024). Such surface oxidation can block reactive sites and hinder redox cycling, decreasing removal efficiency over time. Aggregation is further promoted by electrostatic destabilisation in high ionic strength solutions, such as industrial wastewater with abundant Ca^{2+} , Mg^{2+} , chloride, and sulfate ions. (Velasquez *et al.*, 2023) reported that the aggregation rate of Fe–Mn BNPs increased by 40% in saline wastewater, leading to a corresponding drop in adsorption capacity. Surface coatings with polymers (e.g., polyvinylpyrrolidone (PVP) and chitosan) or green capping agents from plant extracts can mitigate aggregation; however, these coatings may partially block catalytically active sites, creating a trade-off between stability and performance (Sharma *et al.*, 2023). Thus, stability challenges remain a major barrier for real-world BNP deployment, requiring innovative surface engineering and stabilising strategies.

5.2 Scalability and Synthesis Reproducibility

While BNPs can be synthesised easily in laboratory environments using chemical reduction, green synthesis, or electrochemical methods, scaling these methods to industrial quantities presents substantial challenges. Laboratory-scale syntheses often rely on small reactors, controlled temperatures, precise reagent additions, and pure chemical environments. When scaled up, reaction kinetics and nucleation behaviour change dramatically, leading to broad size distributions, inconsistent alloy formation, and poor reproducibility. In green synthesis, variability in plant extract composition or microbial metabolism can cause inconsistency in particle size and metal ratio. (Thapa *et al.*, 2024) noted that Fe–Ni BNPs synthesised using microbial routes exhibited up to a 25% variation in particle size depending on microbial growth conditions. Similarly, NADES-mediated BNP synthesis demonstrated excellent laboratory reproducibility but faced mass-transfer limitations when scaled beyond pilot volumes (Abbas *et al.*, 2024). High-precision methods such as laser ablation and electrochemical deposition produce extremely pure BNPs but are too slow or expensive for high-volume manufacturing. (Park *et al.*, 2023) highlighted that LAL systems consume high energy per gram of nanoparticles, making them unsuitable for municipal wastewater scales. Therefore, the lack of scalable, cost-effective, and reproducible industrial synthesis routes remains a major limitation for BNP deployment in real-world treatment facilities.

5.3 Environmental Toxicity and Metal Leaching

Despite their remediation potential, BNPs themselves may introduce environmental risks. The metallic components of BNPs—especially Ni, Ag, Cu, and Co—can exhibit cytotoxic, genotoxic, or ecotoxic effects if released into aquatic ecosystems (Alvarez *et al.*, 2023). Nanoparticle surfaces can undergo dissolution, releasing toxic metal ions (e.g., Ag⁺, Ni²⁺) into treated water. Additionally, dissolved iron from Fe-based BNPs may alter aquatic chemistry, promoting eutrophication or microbial imbalance (Sharma *et al.*, 2023). Long-term nanoparticle fate in natural water systems is poorly understood. BNPs may undergo complex transformations such as sulfidation, carbonation, interaction with humic acids, or incorporation into sediment matrices. These transformations can either immobilise nanoparticles or mobilise them depending on pH, salinity, and redox conditions (Wang *et al.*, 2024). Recent studies show that BNPs may accumulate in benthic organisms, posing potential risks to higher trophic levels (Abbas *et al.*, 2024). Environmental regulations currently lack standardised guidelines for the disposal, recovery, or long-term monitoring of engineered nanomaterials. As such, comprehensive ecotoxicological assessments and life-cycle analyses (LCA) are urgently needed to ensure BNP-based technologies do not create new forms of contamination.

5.3.1 Safety by design, fate, and sustainability assessment

BNP safety assessment should consider nanoparticle release, dissolved metal leaching, reactive oxygen species, and contaminant-bearing spent materials (Adeleye *et al.*, 2016; Grieger *et al.*, 2010). Because ageing processes can either immobilise particles or increase their solubility and bioavailability, evaluation should include metal release, particle transformation, partitioning behaviour, and acute and chronic toxicity tests (Levard *et al.*, 2012; Lowry *et al.*, 2012; Wang *et al.*, 2016). Safer design should favour low-toxicity compositions, immobilised active phases, efficient recovery (Adeleye *et al.*, 2016), limited leaching, and closed-loop regeneration. Green synthesis should not be assumed sustainable unless supported by life-cycle, techno-economic, leaching, and ecotoxicity evidence based on a consistent treatment unit, such as one cubic metre of water treated to a defined standard (Miseljc & Olsen, 2014; Nizam *et al.*, 2021).

5.4 Selectivity Limitations in Complex Wastewater

Although BNPs perform excellently in laboratory conditions, real industrial wastewaters are far more complex, containing competing cations, oxyanions, organic matter, dyes, surfactants, and

suspended solids. These constituents can significantly reduce BNP performance by blocking reactive sites, altering surface charge, or forming stable complexes with target metals. For example, phosphate and bicarbonate ions strongly compete with arsenate for adsorption sites on Fe–Mn BNPs, reducing removal efficiency by up to 35% in real effluents (Mukherjee *et al.*, 2024). Similarly, high chloride concentrations reduce Cr(VI) reduction efficiency by forming Cr–Cl complexes or inhibiting Fe(0) surface reactivity (Park *et al.*, 2023). Natural organic matter (NOM) can also adsorb to BNP surfaces, decreasing pesticide or metal adsorption capacity (Zhang *et al.*, 2024). Real wastewaters thus pose a substantial challenge, requiring selective surface functionalization, integration with membrane systems, or pre-treatment steps to restore BNP effectiveness.

5.5 Recovery, Regeneration, and Reuse Challenges

For BNPs to be sustainable and cost-effective, they must be easily recoverable and reusable. Fe-based BNPs are advantageous because of their magnetic properties, enabling magnetic separation. However, repeated regeneration cycles can degrade BNP structure, induce oxidation, or cause metal leaching. Studies show that Fe–Cu and Fe–Ni BNPs lose 15–35% of their removal capacity after five regeneration cycles due to surface passivation or structural degradation (Wang *et al.*, 2024). Acidic or alkaline regeneration procedures can restore some activity but may dissolve parts of the nanoparticles, reducing their lifespan (Alvarez *et al.*, 2023). Additionally, the complete removal of BNPs from treated water remains challenging. Even with magnetic separation, smaller nanoparticles or dissolved ions may escape into effluents, creating potential environmental risks. Development of BNP-anchored composite materials, such as BNP-biochar, BNP-polymer membranes, and BNP-MOF hybrids, may improve separability and reduce environmental release (Zhang *et al.*, 2024).

5.6 Insufficient Long-Term Toxicological and Environmental Studies

Despite rapid research development, long-term studies on BNP fate, ageing, transport, and biological interactions remain scarce. Most publications report removal performance over hours or days, but very few studies examine BNP transformation across months or years. Environmental processes such as sedimentation, dissolution, aggregation, biofouling, and biotransformation can substantially alter nanoparticle behaviour over time (Abbas *et al.*, 2024). Without long-term ecotoxicological data, including assessments in fish, algae, benthic organisms, and soil microbiota, it is difficult to establish safety guidelines for BNP production, use, or disposal. Addressing this knowledge gap is essential for future regulatory approval and commercialisation.

5.7 Quantitative evidence supporting the principal limitations

The limitations discussed above are supported by the experimental trends summarised in **Table 6**. Although the values provide useful evidence of performance loss, they should not be treated as universal constants because the studies used different particle compositions, water matrices, doses, and ageing protocols. Their main significance is that aggregation, synthesis variability, leaching, matrix interference, and regeneration loss are measurable engineering constraints rather than only theoretical concerns. **Table 6** shows the quantitative findings supporting the challenges and limitations of BNP remediation.

Table 6. Representative quantitative findings supporting the challenges and limitations of BNP remediation.

Challenge	BNP/system	Reported quantitative finding	Reference
Aggregation in saline water	Fe–Mn BNPs	Aggregation rate increased by approximately 40%, with a corresponding decrease in adsorption capacity	(Velasquez <i>et al.</i> , 2023)
Scale-up reproducibility	BNP batches	Particle-size and composition variability of approximately 20–30% between production batches	(Alvarez <i>et al.</i> , 2023)
Metal leaching	Fe–Cu and Fe–Ni BNPs	More than 5% of the secondary metal released after 30 days under mildly acidic conditions	(Wang <i>et al.</i> , 2024)
Complex-matrix interference	Fe-based BNPs	Removal efficiency decreased by approximately 30–50% in industrial wastewater relative to simplified laboratory water	(Abbas <i>et al.</i> , 2024)
Regeneration loss	Representative BNP adsorbents	Removal efficiency declined by approximately 15–25% after three to five regeneration cycles	(Mukherjee <i>et al.</i> , 2024)
Duration of safety evidence	Environmental BNP studies	Most assessments covered less than 90 days, limiting inference about chronic fate and toxicity	(Zhang <i>et al.</i> , 2024)

6. Future Directions

Although bimetallic nanoparticles (BNPs) have shown exceptional capabilities in removing toxic heavy metals from water systems, several scientific and technological developments are still required to transform this promising laboratory-scale technology into a robust, scalable, and environmentally sustainable treatment solution. Future research must address current knowledge gaps in synthesis, functionalization, environmental safety, and mechanistic understanding. It must also explore integration strategies that enhance performance in real wastewater matrices and reduce long-term ecological risks. The following subsections outline the most critical future directions.

6.1 Advancement of Sustainable and High-Precision Synthesis Methods

A major pathway for future development lies in designing sustainable, scalable, and high-precision BNP synthesis routes. Although chemical reduction remains widely used, its reliance on toxic reagents and surfactants limits environmental sustainability. As a result, future work is expected to focus on environmentally benign synthesis techniques such as natural deep eutectic solvents (NADES), plant-derived reductants, microbial biosynthesis, and photo-assisted nanoparticle formation. NADES-based synthesis in particular has attracted significant attention due to its biodegradability, tunability, and ability to stabilise small, uniform BNPs via hydrogen-bonding networks (Abbas *et al.*, 2024).

Bio-inspired strategies present another promising direction. The use of amino acids, peptides, and proteins as templates for nucleation enables precise spatial control over bimetallic growth while avoiding toxic chemicals. Studies on peptide-mediated Fe–Cu and Ag–Ni BNPs have

demonstrated enhanced homogeneity and reduced aggregation due to well-defined molecular recognition during nucleation (Thapa *et al.*, 2024). Continuous-flow microreactor synthesis can also enhance reproducibility and enable scale-up, offering uniform heat and mass transfer that prevents uncontrolled nanoparticle growth (Zhang *et al.*, 2024). Photo-assisted and microwave-assisted synthesis, which allow extremely rapid nucleation and metal-ion reduction under mild conditions, are expected to gain popularity due to their compatibility with green chemistry principles (Sharma *et al.*, 2023). Overall, future synthesis strategies should integrate environmental stewardship, high precision, and industrial scalability.

6.2 Surface Functionalization to Enhance Stability and Selectivity

The surface chemistry of BNPs plays a crucial role in determining their stability, selectivity, colloidal behaviour, and affinity for specific metal ions. Future research must focus on engineered surface modifications that enhance these properties without compromising the catalytic activity of the nanoparticle core. One promising direction is the incorporation of stimuli-responsive polymer coatings that undergo structural rearrangements based on the pH, ionic strength, or pollutant concentration of the solution. Such coatings can protect BNPs during storage and deployment while exposing active sites during adsorption (Rahman & Kim, 2022).

Biopolymer coatings such as chitosan, alginate, gelatin, and tannic acid provide dual benefits of enhanced colloidal stability and additional functional groups for metal complexation. Likewise, ligand-based modifications using thiols, amines, and phosphonates offer highly selective binding environments for soft metals such as Hg(II) and Pb(II) (Sharma *et al.*, 2023). Another cutting-edge direction lies in integrating BNPs with metal-organic frameworks (MOFs) or covalent organic frameworks (COFs) to form hybrid adsorbents with high porosity, tunable selectivity, and increased surface area. These BNP-MOF composites are particularly attractive for oxyanion removal (e.g., As(V), Cr(VI)), where size-exclusion and chemical specificity play key roles (Zhao *et al.*, 2024). However, future research must ensure that functionalization does not block active sites or impede intermetallic electron transfer. Carefully engineered surface layers are therefore essential.

6.3 Development of BNP-Based Hybrid Composites

Hybrid materials containing BNPs and macro-scale support represent a major future direction for practical implementation. BNPs alone, particularly small nanoparticles, can be difficult to recover and reuse; therefore, immobilising them on solid supports can improve separation, prevent environmental release, and enhance operational durability. Promising supports include biochar, graphene oxide, carbon nanotubes, silica frameworks, cellulose fibres, and polymeric membranes (Zhang *et al.*, 2024).

BNP-biochar composites, for example, have shown increased adsorption capacity due to biochar's abundant functional groups and porous structure (Park *et al.*, 2023). BNP-polymer membranes integrate adsorption and filtration simultaneously, while magnetic BNP hybrids allow rapid magnetic recovery after treatment. BNP-graphene systems have demonstrated improved catalytic reduction rates because graphene's conductivity supports fast electron transfer (Alvarez *et al.*, 2023).

Future research must explore mechanical stability, regeneration techniques, and interactions with wastewater components to optimise hybrid material performance.

6.4 Machine Learning and Computational Design of BNPs

The complexity of bimetallic systems creates a vast design space, making computational tools essential for accelerating discovery. Machine learning (ML) and density functional theory (DFT) simulations are emerging as powerful techniques for predicting alloy stability, electron

distribution, surface reactivity, and metal–pollutant binding energies. DFT studies have identified optimal Fe–Mn configurations for Cr(VI) and As(III) reduction, while ML models have been used to predict optimal synthesis conditions for multi-metal nanoparticles (Zhao *et al.*, 2024). Future research may rely on inverse design approaches, where ML models suggest promising BNP structures that maximise performance while minimising toxicity. This would significantly reduce the need for trial-and-error experimentation and expedite the development of next-generation BNP catalysts. **Figure 4** illustrates the ML- and DFT-assisted inverse design strategy for developing optimised bimetallic nanoparticles (BNPs).

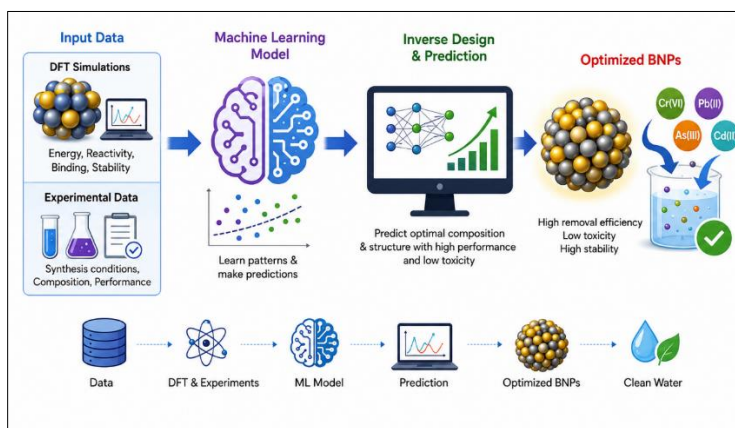


Figure 4. Schematic illustration of the ML- and DFT-assisted inverse design strategy for developing optimised bimetallic nanoparticles (BNPs) for efficient heavy metal remediation in wastewater treatment.

6.5 Integration into Real-World Treatment Systems

The practical implementation of BNP-based remediation requires their incorporation into pilot- and full-scale treatment configurations that can operate reliably under real wastewater conditions. Engineering platforms such as continuous-flow reactors, packed-bed adsorption columns, BNP-immobilised membranes, and magnetic recovery units offer feasible routes for transferring BNP performance from laboratory studies to applied water-treatment systems (Velasquez *et al.*, 2023).

Column-based investigations indicate that Fe–Cu and Fe–Mn BNPs can maintain high removal efficiencies for Cr(VI) and As(V); however, issues such as pressure build-up, bed clogging, and possible nanoparticle release remain important barriers (Alvarez *et al.*, 2023). Therefore, future treatment designs should prioritise long-term operational stability, economic feasibility, simple regeneration, and minimal secondary contamination. Another valuable strategy is to combine BNPs with complementary treatment processes, including advanced oxidation processes (AOPs), photocatalysis, and Fenton-like reactions, to achieve broader contaminant removal. Coupling BNPs with photocatalysts such as TiO₂ or g-C₃N₄ may strengthen redox activity, improve reaction efficiency, and lower energy requirements during wastewater treatment (Sharma *et al.*, 2023).

6.6 Environmental Risk Assessment and Life-Cycle Analysis

Responsible use of BNPs also requires a detailed assessment of their environmental safety. Although their removal performance has been widely demonstrated, important uncertainties remain regarding their persistence, transport behaviour, transformation, and ecotoxicological effects in natural ecosystems. Future studies should therefore examine nanoparticle ageing,

dissolution, interactions with natural organic matter, and possible transfer through aquatic food webs (Abbas *et al.*, 2024). Life-cycle assessment (LCA) and broader environmental impact evaluations will be necessary to support evidence-based regulations for BNP production, application, recovery, disposal, and post-treatment monitoring. In addition, the use of biodegradable carriers or environmentally compatible surface coatings may help reduce ecological risks while preserving remediation efficiency.

6.7 Priority research gaps and minimum reporting framework

Future work should move from proof-of-concept batch removal toward reproducible, mechanism-resolved, and risk-informed treatment studies. Priority gaps include long-term structural stability; controlled synthesis at kilogram scale; performance at environmentally relevant concentrations; selectivity in real matrices; continuous-flow validation; standardised kinetic and equilibrium protocols; complete metal mass balance; regeneration with safe residual management; and comparative cost and life-cycle analysis. **Table 7** illustrates the key research gaps and decision criteria for advancing bimetallic nanoparticles (BNPs) in water treatment.

Table 7. Key research gaps and decision criteria for advancing bimetallic nanoparticles (BNPs) in water treatment (Adeleye *et al.*, 2016; Nizam *et al.*, 2021; OECD, 2020, 2021).

Research gap	Recommended action	Minimum decision criterion
Reproducibility	Report synthesis, yield, measured composition, size distribution, and batch variation	Independent batches meet predefined tolerances
Long-term stability	Test ageing, storage, reuse, and continuous operation	Capacity, structure, and leaching remain acceptable
Real-water performance	Progress from single-ion to mixed-ion and real-water tests	Treatment target is achieved without severe interference or fouling
Mechanism validation	Combine mass balance, speciation, desorption, XPS, XRD, and TEM	Adsorption, redox, precipitation, and release are distinguished
Safety and fate	Measure particle release, dissolution, transformation, and ecotoxicity	Leaching and ecological risk satisfy regulatory limits
Regeneration/end-of-life	Quantify retained capacity, metal loss, eluent use, and contaminant recovery	Reuse provides a net benefit over single-use disposal
Cost and scale-up	Conduct TEA and cradle-to-grave LCA per m ³ treated	Cost and environmental impacts are competitive at the required endpoint
Standardisation	Report pH, dose, concentration, time, matrix, controls, and uncertainty	Results permit reliable cross-study comparison

7. Conclusion

Bimetallic nanoparticles (BNPs) are increasingly recognised as highly effective nanomaterials for treating heavy metal contamination in aquatic environments. Their performance is largely derived from cooperative interactions between two metallic components, which provide stronger adsorption, faster catalytic reduction, improved selectivity, and greater structural stability than

many monometallic nanoparticles and conventional treatment materials. During 2022–2025, considerable advances were reported in BNP synthesis, mechanistic interpretation, and environmental application, confirming their potential for addressing water-quality and public-health risks associated with toxic metals such as Pb(II), Cr(VI), Hg(II), Cd(II), and As(III/V) (Abbas *et al.*, 2024; Mukherjee *et al.*, 2024). The findings reviewed here indicate that BNP performance is closely governed by the preparation route, particle architecture, and surface chemical properties. Chemical reduction and coprecipitation continue to be widely adopted because of their operational simplicity and scalability, whereas green synthesis offers a more sustainable route and can introduce functional surface groups that improve metal binding (Sharma *et al.*, 2023; Zhang *et al.*, 2024). More advanced fabrication methods, including laser ablation, electrochemical deposition, and seed-mediated growth, provide finer control over alloy composition, core–shell structures, and catalytically active interfaces, thereby improving removal efficiency toward multiple pollutants (Alvarez *et al.*, 2023; Park *et al.*, 2023). Mechanistic evidence shows that heavy metal removal by BNPs occurs through coupled adsorption, catalytic reduction, coprecipitation, and interfacial redox reactions. These pathways are strengthened by electron exchange between the paired metals, which increases surface reactivity and accelerates multi-electron transformation processes. For instance, Fe–Cu and Fe–Ni BNPs show strong Cr(VI) reduction through Fe(0)/Fe(II)/Fe(III) redox cycling, while Au–Pd and Ag–Ni systems exhibit high affinity toward Hg(II) and Pb(II) through metallophilic bonding and interfacial charge redistribution (Li *et al.*, 2023; Sharma *et al.*, 2023). Despite this progress, the broader application of BNPs is still restricted by several unresolved challenges, including aggregation, loss of structural stability, inconsistent synthesis reproducibility, metal leaching, potential environmental toxicity, and reduced efficiency in complex wastewater matrices (Velasquez *et al.*, 2023; Wang *et al.*, 2024). Overcoming these barriers will require advanced surface functionalisation, robust BNP-supported composites, efficient regeneration approaches, and comprehensive ecotoxicological evaluation. In addition, incorporating BNPs into scalable systems such as continuous-flow reactors, magnetic separation units, and composite filtration membranes will be essential for practical implementation. Future research should place greater emphasis on sustainable synthesis routes, including NADES-assisted preparation, microbial fabrication, computationally guided catalyst design, and integrated life-cycle analysis. Emerging approaches such as machine learning and density functional theory (DFT) modelling may help predict favourable alloy compositions and guide the rational development of next-generation BNPs. At the same time, stronger environmental risk assessments and clearer regulatory frameworks are needed to support the safe production, recovery, application, and disposal of engineered nanomaterials. Overall, BNPs offer a versatile and scientifically supported platform for removing heavy metals from contaminated water. With further optimisation of synthesis strategies, deeper mechanistic understanding, and appropriate environmental safeguards, BNP-based technologies could play an important role in advancing wastewater treatment, protecting public health, and supporting sustainability-oriented circular economy practices.

Author Contributions

Conceptualization, E.V., A.M. and S.A.A.; literature investigation, E.V. and A.M.; writing-original draft preparation, E.V. and A.M.; writing-review and editing, S.A.A.; supervision, S.A.A. All authors have read and agreed to the published version of the manuscript.

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