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Manganese Nanoparticles for Heavy Metals Detection, vs. Noble and Base Metal Nanoparticles; Prospects, Limitations, and Applications in Electroanalysis

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Abstract

This review examines the emerging role of manganese-based nanoparticles (Mn-NPs) in detecting heavy metal pollutants in environmental matrices. Heavy metals such as cadmium, lead, zinc, and copper pose serious environmental and health concerns due to their tendency to persist in ecosystems and accumulate in living organisms. As a result, there is a growing need for reliable methods to detect and remove these pollutants. Manganese nanoparticles offer unique advantages that scientists could consider replacing other metal nanoparticles, which may be more expensive or more toxic. The physicochemical properties of Mn-NPs—including their multiple oxidation states, magnetic susceptibility, catalytic capabilities, and semiconductor conductivity—enable the development of multi-modal sensing platforms with exceptional sensitivity and selectivity. While Mn-NPs exhibit inherently low electrical conductivity, strategies such as transition metal doping and the formation of composites with conductive materials have successfully addressed this limitation. Compared to noble metal nanoparticles (Au, Ag, Pd) and other base metal nanoparticles (Bi, Fe_3O_4), Mn-NPs demonstrate competitive performance without the drawbacks of high cost, complex synthesis, poor distribution control, or significant aggregation. Preliminary studies retrieved from the Scopus database highlight promising applications of manganese-based nanomaterials in electrochemical sensing of heavy metals, with recent developments showing detection limits in the sub-ppb range. Future research directions should focus on addressing challenges related to scalability, cost-effectiveness, and integration with existing water treatment infrastructure to accelerate the transition from laboratory findings to practical environmental applications.

Keywords: manganese nanoparticles; noble metal nanoparticles; base metal nanoparticles; electroanalysis; heavy metals

1. Introduction

In recent years, nanoparticles (NPs) have become one of the key materials in the design of modern technologies such as sensors, drug delivery, water treatment, batteries, fuel cells, and others. Heavy metal contamination significantly threatens the environment and public health, making effective remediation strategies necessary. Metals such as cadmium, lead and copper are considered important environmental pollutants of concern due to their non-biodegradable nature, environmental persistence, and bioaccumulative potential, which can lead to long-term ecotoxicological effects at all trophic levels as they tend to accumulate in the food chain, even at very low concentrations, causing multiple health problems [1]. As for zinc, it shares some of these characteristics and is widely recognized for its biocompatibility, resulting in its extensive use in biological and biomedical applications, particularly in the form of ZnO nanoparticles [2] and nanostructures [3,4].

These metal pollutants exist as natural components within environmental matrices. However, anthropogenic activities have significantly enhanced their prevalence and concentration gradients in ecosystems. Such anthropogenic sources include industrial production processes, intensive agricultural methodologies, fossil fuel combustion technologies, agrochemical applications, vehicle emissions, and wastewater discharge mechanisms. These xenobiotics present significant ecotoxicological concerns due to their environmental persistence, non-biodegradability, and tendency to bioaccumulate and bio magnify in trophic hierarchies, thereby potentially causing chronic systemic toxicity to biological organisms after prolonged periods of exposure [5].

On the other hand, nanotechnology has emerged as a prominent research field in recent decades, attracting significant scientific interest due to its revolutionary impact in multiple fields [6,7]. Nanomaterials and nanoparticles (NPs) are fundamental components of nanotechnology, distinguished by their remarkable flexibility, adaptable architecture, and superior performance. According to the literature, nanomaterials, especially those with a size below 100 nm, although still in an early stage of research, show significant prospects for the detection, measurement, and removal of heavy metal pollutants from various environmental samples thanks to their unique physicochemical characteristics combined with the extensive surface-to-volume ratio that gives them unique properties [8].

More specifically, Mn-NPs possess unique characteristics, such as high magnetic susceptibility, remarkable catalytic activity, excellent biocompatibility, and strong adsorption capacities [9], compared to other metal nanoparticles that have been used, such as AuNPs, BiNPs, etc. In comparison, manganese nanoparticles (Mn-NPs) exhibit increased potential as adsorbents due to their significantly larger surface area, higher surface-to-volume ratio, as in the case of Ramat et al., who synthesized a three-dimensional MnO_2 nanofibrous network without the use of any template by a hydrothermal method, with a large surface area [10], and higher number of defect sites. These defect sites refer to structural imperfections in the nanoparticles, which may include surface atoms with unsaturated bonding [11]. Such sites are chemically more reactive than atoms in a perfect crystal lattice, thus enhancing the ability of nanoparticles to adsorb pollutants.

However, several critical aspects must be considered to ensure the successful implementation of nanomaterial-based remediation technologies. Recent studies by various scientists suggest that manganese nanoparticles can act as effective nano adsorbents for heavy metal ions, e.g., in aqueous environments, thanks to their high surface-to-volume ratio [12] and abundance of active defect sites [13]. Furthermore, their incorporation into electrochemical and optical sensors has shown promising results for the sensitive and selective detection of trace amounts of heavy metals such as lead and cadmium, MnO_2@RGO Nanocomposite-Based Electrochemical Sensor [14].

Despite these encouraging developments, few works have been published on heavy metal detection. This review aims to fill this gap by providing a systematic overview of the current progress in the synthesis, functionalization, and application of manganese-based nanomaterials in environmental monitoring.

In addition, scalability, cost-effectiveness, and integration with other remediation techniques are key parameters for the practical application and widespread adoption of nanomaterial-based solutions. Furthermore, ongoing research efforts should focus on addressing key challenges such as the stability, longevity, and multifunctionality of nanomaterials to improve their performance and reliability in real-world conditions. Collaboration between key stakeholders in academia, industry, government agencies, and communities is essential to drive innovation, enhance technology transfer, and accelerate the conversion of research findings into actionable solutions for heavy metal detection using advanced nanomaterials such as Mn-NPs.

2. Chemical and Physical Properties of Manganese

Manganese (Mn), one of the most abundant elements in the Earth's crust, ranked twelfth overall and third among transition metals after iron and titanium [15], has already established a prominent position among modern nanomaterials (NMs) [16], although its exploitation is still at an early stage. Beyond its geochemical abundance, manganese is an essential micronutrient, playing a vital role in growth, reproduction, and disease prevention in aquatic and terrestrial organisms [17].

Taking advantage of this physical significance, Mn-NPs exhibit unique physicochemical characteristics that significantly differentiate them from their bulk counterparts, such as improved magnetic susceptibility, superior catalytic functionality, excellent biocompatibility, and remarkable adsorption efficiency. These advantageous properties mainly stem from their nanoscale dimensions, which confer an increased surface-to-volume ratio, increased concentration of active defect sites, and optimized surface-to-volume atom distribution. Among the various manganese nanomaterials, manganese oxide (MnxOy) nanostructures represent a particularly versatile class that exhibits remarkable applicability in diverse scientific and technological fields, including materials engineering, environmental remediation, and biomedical applications [18]. These Mn-NPs are increasingly recognized as promising materials for sustainable nanotechnology due to their exceptional physical and chemical characteristics [15]. Their exceptional utility stems largely from the rich structural and synthetic diversity of manganese oxides, such as MnO, Mn_5O_8, Mn_2O_3, MnO_2, and Mn_3O_4, which distinguishes them among three-dimensional transition metal oxides [19]. MnO_2 nanostructures are one of the most widely used materials for heavy metal detection, as they combine significant advantages such as cost-effectiveness, excellent adsorption capacities, unique nanomorphological structures, biocompatibility, and catalytic properties [20]. Different morphologies of MnO_2, such as nanoparticles, nanocups, and nanotubes, exhibit distinct interaction characteristics when used for heavy metal detection. In particular, the mutual contribution between Cd(II), Pb(II) and Zn(II) [21] ions, and even Cu(II), directly depends on the geometry and surface structure of the nanomaterial. The sensor geometry determines the interactions between different metal ions during detection, and three different morphologies show some regularity in their analytical performance, with MnO_2 nanocups outperforming MnO_2 nanotubes and MnO_2 nanoparticles. This suggests that careful control of nanomaterial morphology is critical for optimizing analytical performance and reducing interference in multi-metal systems [22].

The multifunctional nature of these nanomaterials is further enhanced by their distinctive optical properties, characterized by specific fluorescence signatures and unique UV-visible absorption profiles [23], which make them particularly suitable for sensing applications. Furthermore, they exhibit strong catalytic capabilities in facilitating various redox processes [24,25], along with excellent adsorption capabilities [26–28]. For instance, MnFe2O4 is utilized for its high electrochemical activity, exceptional adsorption performance, good water dispersibility, and excellent stability [29]. As a result of these combined characteristics, Mn-NPs exhibit remarkable versatility in a wide range of applications, including molecular sieves, solar cells, batteries, catalysts, magnetic materials, optoelectronics, drug delivery systems, imaging contrast agents, magnetic storage devices, water treatment and purification technologies [30].

Given their exceptional properties—including excellent redox capabilities, high specific surface area, and abundant surface atoms—in combination with their diverse crystalline phases and morphologies, Mn-NPs continue to attract increasing interest for applications in energy storage [31] (batteries, supercapacitors), energy conversion, and environmental catalysis [9].

Manganese-based nanomaterials—especially MnO_2 and related oxides—combine rich redox chemistry, versatile coordination behavior, intrinsic magnetic and catalytic activities, and semiconductor conductivity, all at low cost and environmental benignity. These traits enable multi-modal sensing platforms (electrochemical, colorimetric, magnetic separation) for heavy metals in water, soil, and sediments, with a hallmark study by Siyamthanda et al. demonstrating a MnO_2@RGO electrochemical sensor achieving simultaneous $Zn^{2+}/Cd^{2+}/Cu^{2+}$ detection down to 0.002–0.015 μg L^{-1} (S/N = 3) in surface water [14]. On the other hand, Prashanth et al. developed an electroactive

Mns/graphitic carbon electrode material, with which the simultaneous determination of Pb(II), Cd(II) was successfully achieved. Its advantages and originality include environmental friendliness, long-term storage capability, and operational stability for a period of several months without significant loss of electrocatalytic activity, making it suitable for in situ applications [32]. For biosensor applications, MnO_2-modified carbon electrodes are simple, inexpensive, and non-toxic to prepare, while remaining stable against interfering species like persulfate and oxygen, unlike other modifiers such as Prussian Blue or ferrocene-polyaniline. They function effectively in neutral and slightly alkaline conditions, making them compatible with oxidase-catalyzed reactions and superior in sensitivity to platinum-modified electrodes. This has led to commercial adoption by Roche Diagnostics for glucose, lactate, urea, and creatinine biosensors [33].

2.1. Redox Properties

Manganese exhibits multiple oxidation states ranging from -3 to +7, with the +2 and +4 states being the most thermodynamically stable. Oxidation states of +3 and above readily participate in electron transfer reactions [34,35]. This variability allows manganese to participate in a wide array of redox reactions, making it highly valuable for the development of chemical sensors. The higher oxidation states of the manganese act as strong oxidizing agents, enabling selective interactions with various heavy metal ions. These redox transitions occur at distinct electrochemical potentials, producing unique electrochemical signatures that can be exploited for the selective detection of metal ions [36]. Moreover, manganese oxides possess additional unique features, such as diverse crystal structures, surface nano-architectures, and high surface area, which further enhance their effectiveness in sensor applications through improved analyte interaction and signal transduction [35].

2.2. Magnetic Properties

Manganese-based nanomaterials often exhibit paramagnetic [37] or ferromagnetic behavior, which can be used for magnetic separation, preconcentration of analytes, or the development of magnetic resonance-based detection methods. The inherent magnetic susceptibility of manganese compounds, especially at the nanoscale, facilitates their integration into magnetically assisted detection platforms. This property allows for the efficient separation of target analytes from complex environmental samples, significantly reducing the effects of matrix interference and lowering the detection limits [18].

2.3. Catalytic Activity

Manganese oxides exhibit remarkable catalytic activity [38] and prove to be extremely useful for various oxidation processes, such as the degradation of organic pollutants. Their surface properties and their ability to facilitate electron exchange mechanisms make them effective for such processes.

Manganese-based catalysts have attracted the interest of scientists as economical substitutes for precious metals such as gold, given their flexible functionality and desirable material characteristics. The effectiveness of manganese oxides in catalytic processes depends largely on physical factors such as particle size and geometry, which directly affect their performance in reactions where structure plays a critical role [39]. An additional advantage lies in their natural ability to dissociate interfering compounds in complex sample matrices, which improves the accuracy of sensors and potentially reduces measurement errors from unwanted chemical interactions. So far, a brief review of the literature will indicate a multitude of applications related, for example, to the biomedical sector [27,40,41], while their application in the detection of heavy metals has now begun due to their magnetic properties, low toxicity, and catalytic properties.

2.4. Electrical Conductivity

Electrical conductivity is a critical parameter influencing the performance of electrochemical systems, as it governs charge transfer efficiency and the diffusion kinetics of electrolyte ions across the electrode–electrolyte interface during redox reactions. Although manganese oxides are widely recognized for their favorable redox behavior, their inherently low electrical conductivity [42], typically in the range of 10^{-3} to 10^{-4} S m^{-1}, presents a significant barrier to achieving optimal electrochemical performance [43]. To address this limitation, recent studies have focused on strategies such as doping MnOx with transition metals, including Cu, Ni, Co, and Fe, which serve to enhance electron transport by improving the material's intrinsic conductivity [44]. Additionally, the semiconducting nature of MnOx nanostructures provides distinct advantages in sensing applications. While they do not match the conductivity [45] of noble metals, these materials exhibit suitable band gap energies and charge carrier mobilities that make them highly responsive in conductometric and potentiometric platforms. Upon exposure to heavy metal ions, MnOx-based sensors undergo electronic band structure modifications that lead to measurable variations in conductivity, impedance, or potential. These changes can be quantitatively correlated with analyte concentration, thereby facilitating sensitive and selective detection through modulation of their electronic and redox properties.

2.5. Toxicity and Environmental Considerations of Manganese-Based Nanomaterials

Although manganese is an essential trace element for many biological systems and has been widely utilized in environmental remediation applications due to its high catalytic activity, chronic exposure to elevated levels can result in neurotoxic effects, a condition known as "manganism", characterized by Parkinsonian-like symptoms in humans [46]. Furthermore, the use of manganese-based nanomaterials has raised concerns regarding their environmental safety. Nevertheless, at the nanoscale, manganese may exhibit altered bioavailability and toxicity profiles. Studies have shown that certain Mn-based nanoparticles can induce oxidative stress and neurotoxicity, as well as negatively affect aquatic organisms [47]. Moreover, the potential release of Mn^{2+} ions into the environment is an additional risk factor, directly related to the stability [48] of the nanoparticles under real-world conditions. Therefore, a comprehensive evaluation of manganese nanomaterials is imperative, including dissolution behavior, toxicological assessments, and surface modification strategies to mitigate adverse effects [49].

3. Comparative Analysis of Mn-NPs with Other Metallic Nanoparticles

Recent advances in nanotechnology have led to the widespread replacement of conventional chemical reagents with nanomaterials for the detection of heavy metal ions. Materials such as metal nanoparticles (MNPs) and various metal-based nanostructures offer remarkable physicochemical properties, including a high surface area, enhanced surface energy, and superior electron transfer capabilities. These characteristics significantly contribute to improved sensitivity and selectivity in electrochemical sensing platforms. Researchers have exploited both noble and base metal nanoparticles for heavy-metal sensing, taking advantage of their high surface-to-volume ratios, tunable surface chemistry, and catalytic/optical properties.

3.1. Noble-Metal Nanoparticles

Noble metal nanoparticles (NMNPs), including gold (AuNPs), silver (AgNPs), and palladium (PdNPs), hold significant promise for next-generation point-of-need diagnostic technologies and environmental sensing applications due to their unique physicochemical, optical, thermal, and electronic properties. These properties—such as size, shape, elemental composition, and internal structure—play a critical role in determining their performance as signal reporters and their interactions with target molecules in analyte samples. Their high surface-to-volume ratios, stability, and biocompatibility further enable functionalization with a variety of ligands for the selective detection of clinically relevant biomarkers and heavy metal ions. Therefore, achieving large-scale production of NMNPs with controlled and consistent size and shape is essential for the development of high-performance biosensing platforms [50].

Due to their distinctive physicochemical properties, gold nanoparticles (AuNPs) have emerged as significant components in nanotechnology-based sensing applications, particularly for heavy metal detection. Their stability, biocompatibility, and exceptional optical and electronic characteristics, combined with high surface-to-volume ratios, enable functionalization with diverse ligands for selective analyte detection [51].

In environmental monitoring, AuNPs excel at detecting heavy metal ions, including Pb^{2+} and Cd^{2+} [52,53]. When integrated with complementary materials, they form composite systems with enhanced performance for specific metal targets.

The morphology and dimensions of AuNPs significantly influence sensing efficiency. While spherical particles (4-298 nm) predominate in electrochemical applications, various shapes can be synthesized through controlled reaction conditions, as Dutta et al. demonstrated in their work with gold nano-stars [54].

A notable electrode configuration combining AuNPs with l-cysteine and reduced graphene oxide exhibited exceptional performance for cadmium detection across diverse water samples. This same sensor achieved remarkably high sensitivity for Pb(II) detection, illustrating the synergistic benefits of AuNP-nanomaterial combinations in electrochemical sensing applications [53].

Despite their advantages, gold nanoparticles (AuNPs) sensors face significant limitations. Their performance varies considerably with size and shape, affecting optical properties and particle distribution, leading to inconsistent responses [55]. Toxicological concerns persist due to limited information on long-term effects and their ability to circulate without immune rejection [56]. AuNPs can accumulate in ecosystems and enter food chains [57], with toxicity influenced by physicochemical properties [58,59]. Their large surface area-to-volume ratio increases reactivity and cellular penetration [60], potentially enhancing toxicity on a mass dosage basis [33]. Furthermore, economic factors restrict widespread adoption, such as gold’s inherent expense, sophisticated synthesis requirements, and specialized equipment make large-scale production challenging, particularly for environmental monitoring in resource-limited settings.

Silver nanoparticles (AgNPs), a distinct subclass of nanomaterials, have garnered considerable interest as electrode modifiers in the electrochemical detection of heavy metal ions such as Cd(II), Pb(II), and Cu(II) [61,62]. This interest is primarily attributed to their favorable properties, including excellent electrical conductivity, large surface area, and facile synthesis [63]. Numerous studies have demonstrated that integrating nanomaterials with electrochemical methods significantly enhances the speed and efficiency of heavy metal ion detection. While electrodeposition of AgNPs onto the electrode surface offers significant advantages, including the absence of unwanted by-products, elimination of chemical oxidants and reductants, and reduced synthesis time, it also presents notable limitations. These disadvantages include poor control over nanoparticle distribution, time-intensive processing requirements, and the tendency for nanoparticles to aggregate on the electrode surface, potentially compromising the desired functional properties of the modified electrode [64].

Furthermore, palladium nanoparticles (PdNPs) have been extensively investigated as sensing platforms for heavy metal detection. The predominant methodology involves synthesizing porous activated carbon (PAC) followed by decoration with Pd NPs through a one-step thermal reduction process, with minor variations in experimental parameters. Literature reports indicate that spherical Pd nanoparticles (20-30 nm diameter) have been successfully employed for both individual and simultaneous detection of Cd(II), Pb(II), and Cu(II) via square wave anodic stripping voltammetry (SWASV) [65,66]. Although this approach demonstrated efficacy in real environmental sample analyses, a significant limitation was observed: detection limits during simultaneous multi-element measurements were substantially elevated compared to single-metal analyses, thereby compromising analytical performance in complex environmental matrices.

3.2. Base-Metal Nanoparticles

On the other hand, several research groups have investigated bismuth nanoparticles (BiNPs) for the effective detection of heavy metals such as cadmium and lead ions [67,68]. Through the application of anodic square-wave stripping voltammetry and modified bismuth-nano powder electrodes, the detection of zinc, cadmium, and lead ions can be readily achieved [69]. Despite their advantages, bismuth nanoparticles (BiNPs) present certain limitations. A significant challenge is the interference from elevated copper(II) ion concentrations, which can compromise detection accuracy [52,70]. Additionally, the synthesis of particles with uniform size distribution remains a considerable technical challenge.

Iron nanoparticles (Fe3O4) have emerged as prominent candidates among various metal oxides due to their excellent affinity for heavy metal ions, remarkable chemical stability, biocompatibility, superparamagnetism, low toxicity, simplicity of synthesis, high surface-to-volume ratio, and cost-effectiveness [71]. Daniel et al. reported that zero-valent iron nanoparticles have demonstrated significant antibacterial properties, for example against B. subtilis, Pseudomonas fluorescens, and *Gram*-negative *E. coli* [72].

These advantageous properties have allowed Fe_3O_4-based nanoparticles to facilitate the simultaneous detection of multiple heavy metal species such as Zn(II), Pb(II) [73], and Cd(II) from environmental waters and soil matrices. Iron oxide nanoparticles have also been reported as effective adsorbents for highly toxic heavy metals, such as Pb, Zn, and Cd, as well as Hg and Ni, which exhibit harmful effects on plants, animals, and humans even at low concentrations [74–76].

Consequently, Fe_3O_4-derived nanomaterials have been extensively developed as electrochemical sensing platforms, particularly when forming composites with functional materials, including reduced graphene oxide (RGO) [77,78] and EDTA-functionalized polymers [79]. It is worth noting, however, that Fe_3O_4 nanoparticles inherently tend to aggregate, significantly reducing their electrochemical performance capabilities. This limitation explains the relatively limited literature on the applications of unmodified iron oxide nanoparticles in electrochemical sensing systems [80,81].

Table 1. Comparative Summary of Nanoparticles for Heavy Metal Detection: Advantages and Limitations.

Nanoparticle Type	Advantages	Disadvantages	Quantitative Data
MnOx-NPs [27,35,44]	– Multiple oxidation states (−3 to +7) – Magnetic separation – Catalytic activity – Low cost	– Low electrical conductivity – Requires doping for performance	**MnO_2@RGO**, [14] Detection limit: 9.3 ng/L (Cu^{2+}), 13.7 ng/L (Zn^{2+}), 15.1 ng/l (Cd^{2+}) Surface area: 148.7 m^2/g
			MnO2-CT, [82] Detection limit: 50 ng/L (Cd^{2+}), 10ng/L (Pb^{2+}) Surface area: -
			Mn_3O_4, [39] Detection limit: - Surface area: 30–70 m^2/g
			MnO_2, [44] Detection limit: - Surface area: 20-200 m^2/g
			Fe_3O_4/MnO_2, [37]

			Detection limit: - Surface area: 118 m^2/g
AuNPs [51,55]	– Stability, biocompatibility – High optical/electronic response – High surface-to-volume ratio	– Toxicity concerns – High cost	**AuNPs**, [53] Detection limit: 0.0064 ng/L (Cu^{2+}), 99.95 ng/L (Cd2+), 49,73 ng/L (Pb^{2+}) Surface area: -
AgNPs [62,64]	– High conductivity – Simple synthesis	– Aggregation issues – Time-intensive processing	**AgNPs@p-1,8-DAN/GC**, [46] Detection limit: 6 ng/L (Cu^{2+}), 19 ng/L (Cd^{2+}), 30 ng/L (Pb^{2+}) Surface area: -
PdNPs [66]	– Effective for multi-ion detection (Cd^{2+}, Pb^{2+}, Cu^{2+}) – Compatible with SWASV	– Reduced sensitivity in complex matrices	**Pd@PAC**, [51] Detection limit: 31.775 ng/L (Cu2+), 56.205 ng/L (Cd^{2+}), 103.60 ng/L (Pb2+) Surface area: 881.79 m^2/g
BiNPs [67]	– Strong metal affinity – Compatible with SWASV	– Cu^{2+} interference – Size distribution issues	**BiNPs** , [55] Detection limit: 90 ng/L (Cd^{2+}), 170 ng/L (Pb^{2+}) Surface area: 13.47 m^2/g **BiNPs@Ti3C2Tx**, [56] Detection limit: 1.40 ng/L (Cd2+), 2.24 ng/L (Pb^{2+}) Surface area: -
Fe_3O_4NPs [71,77]	– Strong heavy metal affinity – Chemical stability – Biocompatible, superparamagnetic – Low-cost, simple synthesis – Multi-metal detection capability	– Aggregation tendency – Reduced electrochemical performance – Limited applications when unmodified	**Fe_3O_4@MPC**, [57] Detection limit: 2507.12 - 7086.24 ng/Lng/L (Pb^{2+}) Surface area: 75.7 - 238.4 m^2/g

4. Overview of Previous Studies

MnNPs demonstrate significant potential across various applications due to their unique structural and electrochemical properties [9]. Preliminary evaluations have shown promising results when using these nanoparticles as electrochemical modifiers for the voltammetric detection of heavy metal ions, particularly lead (Pb^{2+}) and cadmium (Cd^{2+}). This approach represents an important advancement in environmental monitoring technologies.

Although not yet fully exploited, the literature highlights several notable examples demonstrating the application of $MnCo_2O_4$ and related Mn-NPs in environmental monitoring. For example, iron-manganese oxide nanomaterials have been used to remove heavy metals from aqueous media, with their capacity and efficiency being influenced by synthesis methods and environmental conditions [36]. A similar approach was reported by Zhang et al. [26], who used manganese dioxide (MnO_2) nanoparticles supported on biochar (BC@MnO_2) to adsorb Cd(II), Cu(II), Zn(II), and Pb(II) ions from water samples. Hybrid nanosorbents such as HMN-MnO_2 nanoparticles have also shown promising results in the removal of heavy metals from wastewater and the passivation of metal contaminants in soil [83]. In 2017, Junjie et al. successfully used a kind of monodispersed ZnS: Mn/SiO_2 nanoparticles containing a ZnS: Mn core inside them for the detection of copper in seawater. The concentration of Cu^{2+} ions in water samples ranged from 8.16×10^{-8} to 4.96×10^{-4} mol/L, thus providing a highly sensitive fluorescence sensor for the detection of Cu^{2+} in seawater [84]. While Mn_2O_3 nanoparticles assembled into hierarchical hollow spheres (H-Mn_2O_3) were used as nanocarriers for the immobilization of glycoxidase (GOx), horseradish peroxidase (HRP), and sequence signal (S3), forming the S3/H-Mn2O3/HRP/GOx complex. The hierarchical structure of the hollow spheres provides a large specific surface area and efficient loading of biomolecules, while the GOx and HRP enzymes allow the catalytic deposition of polyaniline (PANI) with excellent electrochemical activity, acting as a signal-enhancing label for Pb^{2+} detection [85].

Zhou et al. synthesized and evaluated L-cysteine functionalized mesoporous $MnFe_2O_4$ nanospheres ($MnFe_2O_4$@Cys) for electrochemical detection of Pb(II), Hg(II), Cu(II), and Cd(II) via SWASV. Characterization confirmed the successful functionalization, and electrochemical tests revealed enhanced activity due to the presence of L-cysteine. The sensor showed high sensitivity, especially for Pb(II), and enabled both single and simultaneous detection of multiple ions with remarkable selectivity, stability, and reproducibility, making it a powerful platform for environmental monitoring [86].

A $MnFe_2O_4$/graphene oxide (GO) nanocomposite was also used for sensitive detection of Pb(II) by applying anodic stripping square wave voltammetry (SWASV). The successful incorporation of $MnFe_2O_4$ with GO improved the material surface area, conductivity, and electrochemical activity. The resulting sensor exhibited high sensitivity, low detection limit, and excellent selectivity even in the presence of Zn(II), along with good stability, reproducibility, and practical application for the detection of heavy metal ions [87]. A related advancement was reported by Siyamthanda et al., who developed a modified glassy carbon electrode incorporating MnO_2 supported on reduced graphene oxide (MnO_2@RGO) for the simultaneous detection of Cu(II), Cd(II), and Zn(II) in surface waters using Differential Pulse Anodic Stripping Voltammetry (DPASV). The sensor demonstrated excellent electrocatalytic activity and stability, which were attributed to its high surface area and low charge transfer resistance. Optimization using response surface methodology significantly enhanced its performance, enabling direct analysis of water samples without the need for pretreatment.

Furthermore, Mn_2O_3 nanoparticles were synthesized and used to modify a carbon paste electrode, creating a highly sensitive sensor for the detection of Cd(II) and Pb(II) ions. The sensor demonstrated excellent detection limits and was successfully applied to real wastewater samples, achieving recovery rates between 80–95%, further confirming its potential for environmental applications [88]. Transition metal oxide nanoparticles, such as MnO_2 (and Fe_2O_3) are also widely used in energy storage devices, such as lithium batteries and supercapacitors, due to their high capacity and large surface area, and offer performance and safety benefits in defense applications [89].

Amany et al. in their published work incorporated MnO_2 nanoparticles, aiming to enhance the electrochemical properties of the 5-BHAHS@NC they had already synthesized. This low-cost detection platform, 5-BHAHS@NC/MnO_2 CPE, was successfully used for the rapid and simultaneous determination of cadmium and lead ions in fish samples, tap water, and wastewater [90].

In another study, a simple colorimetric method uses octahedral Mn3O4 nanoparticles as nanozymes with oxidase-mimicking activity. Oligonucleotides inhibit the catalytic activity of Mn3O4 NPs through noncompetitive inhibition. When heavy metals like Hg(II) and Cd(II) bind to oligonucleotides, they change the oligonucleotide conformation, restoring the nanozyme activity and producing visible color changes. The method requires no hydrogen peroxide, making the color response stable and intuitive. This simple system contains only unmodified octahedral Mn_3O_4 NPs and oligonucleotides, offering a cost-effective approach for environmental and agricultural monitoring that can be extended to other nanozymes and detection targets [91]. On the other hand, Mei et al. reported that materials such as FeOOH and FMBO prepared by the oxidation-co-precipitation method gave satisfactory results in the removal of Cd(II), Ni(II), and Pb(II) in single and multiple systems [92].

Overall, these findings highlight the significant potential of manganese-based nanomaterials as advanced electrochemical sensing platforms for routine environmental monitoring of heavy metal pollutants. When combined with voltammetric techniques, Mn-NPs have demonstrated high efficiency in the detection and quantification of heavy metal ions, particularly Cd(II) and Pb(II), in various aqueous matrices, including distilled water, tap water, and river samples. Their characteristic porous, flower-like morphology enhances the interaction of analytes, making these materials particularly suitable for environmental monitoring applications [93].

5. Conclusions

Mn-NPs have emerged as a promising class of materials for the detection of heavy metals in environmental matrices, offering an exciting alternative to more extensively studied nanomaterials. Their unique combination of redox flexibility, magnetic properties, catalytic activity, and environmental compatibility provides significant advantages in sensing applications. The redox chemistry of manganese, spanning oxidation states from -3 to +7, enables dynamic interactions with target analytes, thereby enhancing both the sensitivity and specificity of detection.

Compared to noble metal nanoparticles such as gold, silver, and palladium, as well as base metal alternatives like bismuth and iron oxide (Fe_3O_4), Mn-NPs demonstrate competitive performance at lower cost and with simpler synthesis processes. Moreover, they offer improved control over particle distribution and reduced aggregation. Although their inherently low electrical conductivity poses a challenge, this limitation can be effectively addressed through strategies such as doping with transition metals and forming composites with conductive materials.

Electrochemical techniques have shown that Mn-NPs can achieve highly sensitive detection of toxic heavy metals—including Cd(II), Pb(II), Cu(II), and Zn(II)—with detection limits reaching the sub-ppb range. These characteristics make them particularly attractive for environmental monitoring, where high sensitivity, selectivity, and cost-effectiveness are essential.

Despite these advantages, challenges remain regarding the long-term stability, standardization, and field deployment of Mn-NP-based sensors. Ongoing research should focus on enhancing sensor robustness, developing scalable fabrication techniques, and integrating these systems into existing monitoring infrastructure. Furthermore, advanced surface functionalization strategies may facilitate the development of multifunctional nanocomposites capable of both detecting and removing heavy metal pollutants.

To fully realize the potential of Mn-NPs in addressing global heavy metal contamination, collaborative efforts among academia, industry, and regulatory agencies are crucial. Additionally, considerations such as scalability, cost-effectiveness, and integration with complementary remediation technologies are key to the practical implementation and widespread adoption of Mn-NPs-based environmental solutions.

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