Development of Novel Nanomaterials for Sensing and Removal of Heavy Metals from Foods: A Review

Seham Ebrahem Mohamed Madi

Chemistry Department, Faculty of Science, Bani Waleed University Libya

*Corresponding author email: sehammady88@gmail.com

الملخص:

يُشكل تلوث السلسلة الغذائية بالمعادن الثقيلة السامة، مثل الرصاص (Pb)، والكادميوم (Cd)، والزئبق (Hg)، والزرنيخ (As)، خطرًا صحيًا عالميًا كبيرًا. غالبًا ما تفتقر طرق التحليل والمعالجة التقليدية إلى الحساسية والانتقائية والكفاءة اللازمة لمعايير سلامة الأغذية الحديثة. تُقدم التطورات الحديثة في تكنولوجيا النانو نموذجًا مُبتكرًا لمواجهة هذا التحدي. تدرس هذه المراجعة بشكل شامل تطوير وتطبيق مواد نانوية جديدة لتحقيق وظيفتين: الاستشعار فائق الحساسية والمعالجة الفعالة للمعادن الثقيلة من مصفوفات الأغذية المعقدة. نناقش الخصائص الفيزيائية والكيميائية الفريدة لمختلف المواد النانوية، بما في ذلك المواد الكربونية (الجرافين، الأنابيب النانوية الكربونية)، والمعادن، وجسيمات أكسيد المعادن النانوية والمركبات النانوية، مما يجعلها مثالية لهذه المهام. للاستشعار، نستكشف المستشعرات النانوية اللونية والكيميائية الكهربائية والفلورية، مع تسليط الضوء على آلياتها وحدود الكشف (حدود الكشف). أما بالنسبة للإزالة، فنُفصّل استخدام المواد النانوية كمواد ماصة متطورة وعوامل ترشيح، مع التركيز على مساحتها السطحية العالية وكيمياء سطحها القابلة للضبط. وأخيرًا، نتناول التحديات الحرجة المتعلقة بسمية المواد النانوية، والامتثال للوائح التنظيمية، وقابلية التوسع، مع تقديم وجهات نظر حول اتجاهات البحث المستقبلية الهادفة إلى ضمان التكامل الآمن والفعال لتكنولوجيا النانو في بروتوكولات سلامة الأغذية.

الكلمات الافتتاحية: المواد النانوية، المعادن الثقيلة، سلامة الأغذية، المستشعرات الحيوية، الامتزاز، المركبات النانوية، تلوث الأغذية.

Abstract

The contamination of the food chain by toxic heavy metals such as lead Pb), cadmium (Cd), mercury Hg), and arsenic As) poses a significant global health risk. Traditional analytical and remediation methods often lack the sensitivity, selectivity, and efficiency required for modern food safety standards. Recent advancements in nanotechnology offer a disruptive paradigm to address this challenge. This review comprehensively examines the development and application of novel nanomaterials for the dual functions of ultrasensitive sensing and efficient remediation of heavy metals from complex food matrices. We discuss the unique physicochemical properties of various nanomaterials, including carbon-based materials (graphene, CNTs), metal and metal oxide nanoparticles, and nanocomposites, that render them ideal for these tasks. For sensing, we explore colorimetric, electrochemical, and fluorescent nanosensors, highlighting their mechanisms and limits of detection LODs). For removal, we detail the use of nanomaterials as advanced sorbents and filtration agents, focusing on their high surface area and tunable surface chemistry. Finally, we address the critical challenges of nanomaterial toxicity, regulatory compliance, and scalability, while providing perspectives on future research directions aimed at ensuring the safe and effective integration of nanotechnology into food safety protocols.

Keywords: Nanomaterials, Heavy Metals, Food Safety, Biosensors, Adsorption, Nanocomposites, Food Contamination.

1. Introduction

The persistence of heavy metals in the environment—originating from industrial discharge, wastewater irrigation, and mining activities—results in their bioaccumulation throughout terrestrial and aquatic food chains. Elements such as Pb, Cd, and Hg are recognized as non-biodegradable toxins that, even at low concentrations, can induce severe neurological, renal, and developmental disorders in humans (Bharti & Sharma, 2022; Ulusoy, 2023). Contamination is a documented reality across various food types, including:

a) **Seafood:** Canned tuna, a widely consumed product, has been consistently scrutinized for its potential methylmercury MeHg) content, a form that readily bioaccumulates in predatory fish (Dehghani et al, 2022; Ulusoy, 2023).
b) **Staple Crops:** Studies confirm that essential crops like the date palm fruit are vulnerable to contamination by metals such as Pb and Cd, directly threatening both human health and food security in arid regions (Dehghani et al, 2022; Shahid et al., 2017).
c) **Dairy:** Pasteurized milk, a critical nutritional source, must be monitored for contaminants like Pb, with recent analyses indicating a constant need for assessment to ensure compliance with international safety standards (Salem et al., 2023).

Conventional techniques, such as Atomic Absorption Spectrometry AAS) and Inductively Coupled Plasma Mass Spectrometry ICP-MS), offer high accuracy but are often restricted by high operating costs, long analysis times, and a lack of portability (Welz & Sperling, 2008). In contrast, materials engineered at the nanoscale 1-100 nm) exhibit extraordinary physicochemical properties, including superior surface-to-volume ratios, enhanced catalytic activity, and unique optical behavior. These characteristics allow nanomaterials to be utilized for ultrasensitive detection and highly efficient decontamination, offering a paradigm shift in food safety management.

This review synthesizes recent advances in the application of novel nanomaterials, categorized into (1) Sensing and Detection and (2) Adsorption and Removal of heavy metals from food systems, concluding with a discussion on critical challenges and future research directions.

Table 1: Comparison of Conventional Methods vs. Nanomaterial-Based Approaches for Heavy Metal Management in Food

Feature	Conventional Methods (e.g., AAS, ICP-MS, Ion Exchange)	Nanomaterial-Based Approaches
Sensitivity/LOD (Limit of Detection)	High (ppb-ppt range), but limited by instrument noise and matrix interference.	Ultra-high (ppt and sub-ppt range), capable of detecting levels below conventional AAS limits.
Analysis Speed	Slow (hours), requires complex sample pre-treatment.	Rapid (minutes), facilitates high-throughput screening and on-site analysis.
Portability	Low (lab-based, requires high infrastructure).	High (potential for handheld devices and field deployment).
Removal Efficiency	Moderate to High, but often produces secondary sludge or waste.	Very High, and often enables material regeneration and reuse (e.g., magnetic separation).

2. Nanomaterials for Sensing and Detection of Heavy Metals

The enhanced surface area and tailored surface chemistry of nanomaterials enable their functionalization with highly specific recognition elements (chelating agents, aptamers), leading to a new generation of high-performance biosensors.

2.1. Electrochemical Nanosensors

These sensors transduce a chemical binding event into a measurable electrical signal. Nanomaterials like Graphene Oxide GO) and Carbon Nanotubes CNTs) enhance electrode conductivity and surface area, significantly increasing the signal-to-noise ratio.

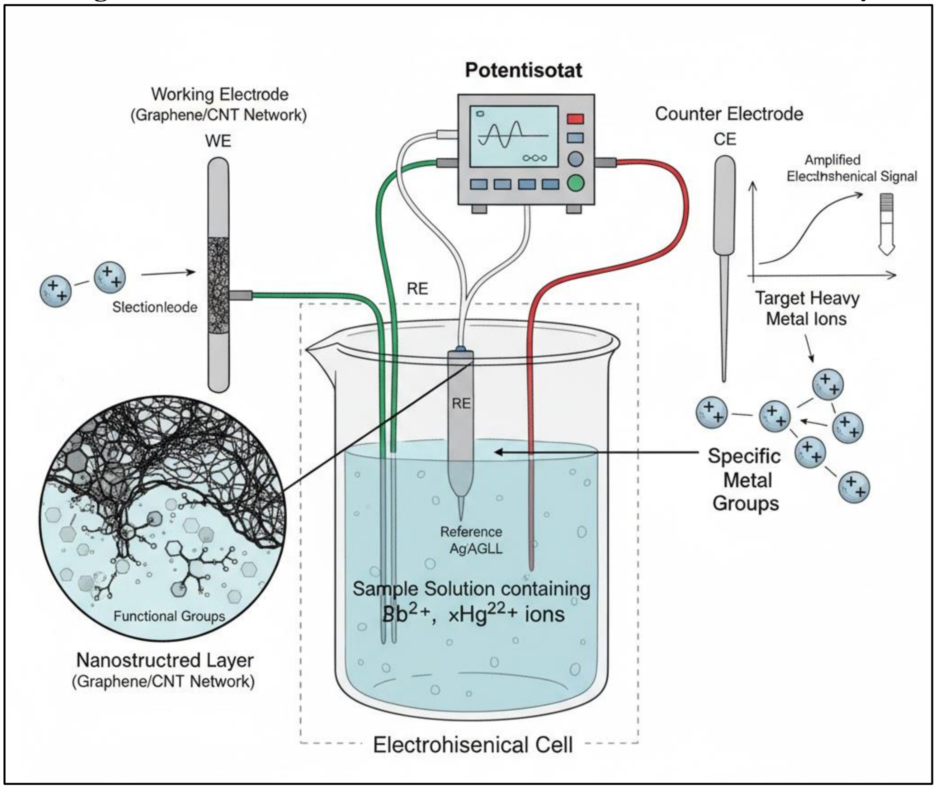
a) **Mechanism:** Nanomaterial-modified electrodes (e.g., glassy carbon electrodes coated with GO and bismuth nanoparticles) are particularly effective for simultaneous multimetal analysis using Anodic Stripping Voltammetry ASV). This approach has demonstrated high sensitivity for Zn^{2+}, Cd^{2+}, and Pb^{2+} in complex matrices such as canned tuna samples (Buica et al., 2019).
b) **Addressing Conventional Limitations:** The need for nanosensors is underlined by the limits of traditional techniques; for example, Flame AAS has been reported to yield "Non-Detectable ND)" results for Cd in pasteurized milk samples, underscoring the inadequate sensitivity of conventional methods for regulatory monitoring of specific toxic metals (Salem et al., 2023).

2.2. Optical Nanosensors (Colorimetric and Fluorescent)

These sensors provide rapid, often visual, detection based on changes in light absorption or emission.

a) **Colorimetric Nanosensors:** They capitalize on the characteristic Surface Plasmon Resonance SPR) of metal nanoparticles, especially Gold Nanoparticles AuNPs). The presence of target ions Cd^{2+} or Pb^{2+} can induce AuNP aggregation, resulting in a quantifiable and often visible shift in color (e.g., from red to blue).
b) **Fluorescent Nanosensors:** Quantum Dots QDs) and Carbon Dots CDs) serve as excellent fluorophores. Heavy metal ions can selectively quench or enhance their fluorescence. For instance, Nitrogen-doped Carbon Dots N-CDs) exhibit selective fluorescence quenching for Hg^{2+}, enabling detection at ppt levels (Wang et al., 2021).

Figure 1: Schematic diagram of a nanomaterial-based electrochemical sensor for heavy metal detection.



3. Nanomaterials for the Removal of Heavy Metals

The high surface area and chemical tunability of nanomaterials make them exceptionally efficient adsorbents for decontamination, offering a potent alternative to conventional precipitation and ion exchange methods.

3.1. Nanomaterials for Heavy Metal Remediation

1. Carbon-Based Nanomaterials

This category focuses on Graphene Oxide (GO) and Carbon Nanotubes (CNTs).

a) **Structure/Function:** These materials are easily decorated with oxygen-containing functional groups like -COOH (carboxyl) and -OH (hydroxyl).
b) Mechanism: These groups act as strong binding sites for positively charged metal cations (like Pb^{2+}) through chelation and electrostatic attraction (adsorption).
c) **Application Highlight:** GO-based filters have shown exceptional efficacy, removing over 99% of Pb^{2+} and As^{3+} (Arsenic) from contaminated water.

2. Magnetic Nanoparticles (Metal Oxides)

This category specifically discusses Magnetite (Fe_3O_4) nanoparticles.

a) **Mechanism:** They are highly effective adsorbents for heavy metals.

b) **Key Advantage: Magnetic Separation:** The crucial advantage is the ability to use a magnet for easy recovery of the adsorbent after the heavy metals have been bound. This reduces secondary waste and simplifies the treatment process.

c) **Application Highlight:** Fe_3O_4 nanoparticles coated with biopolymers have been successfully used to remove Cu^{2+} and Cd^{2+} from food simulants.

3. Zero-Valent Iron (nZVI)

This category involves **nanoscale zero-valent iron (nZVI)**.

a) **Mechanism:** Unlike the first two, which primarily use adsorption, nZVI provides a **remediation pathway through reduction**. The highly reactive Fe^0 (zero-valent iron) donates electrons.

b) **Application Highlight:** The most notable application is the reduction of **highly toxic Chromium (VI)** (Cr (VI)) to the less toxic and less mobile Chromium(III) (Cr(III)). This chemical transformation permanently detoxifies the contaminant.

3.2. Nanocomposites and Metal-Organic Frameworks MOFs)

Combining different nanomaterials into nanocomposites (e.g., GO/Fe_3O_4) creates synergistic properties, such as high adsorption capacity combined with magnetic recoverability (Yu et al., 2020). MOFs, characterized by ultra-high porosity and tunable organic linkers, represent a frontier in adsorption, achieving record-breaking capacities for specific metal capture (e.g., Hg^{2+}).

Table 2: Adsorption Capacities of Selected Nanomaterials for Various Heavy Metals

Nanomaterial	Target Heavy Metal	Maximum Adsorption Capacity (mg/g)	Reference (Example)
Graphene Oxide (GO)	Pb^{2+}	842	(Ali, 2019)
Magnetic Fe_3O_4	As(V)	112	(Zhou et al., 2022)
Carbon Nanotubes (CNTs)	Cd^{2+}	97.1	(Yu et al., 2020)
Nano Zero-Valent Iron (nZVI)	Cr(VI)	180.5	(Liu et al., 2020)
UiO-66 MOF	Hg^{2+}	769	(Wang et al., 2021)

4. Challenges and Future Perspectives

Despite the scientific promise, several complex hurdles must be overcome for the widespread commercial application of nanomaterials in food safety.

4.1. Toxicity, Bioaccumulation, and Safety

The critical challenge is the potential for nanotoxicity—the inherent risk of nanoparticles leaching into food and their long-term effects *in vivo*. The problem is compounded by the behavior of highly toxic species like MeHg, which bioaccumulates up the marine food chain (Dehghani et al, 2022). Future research must prioritize:

1. **Comprehensive Risk Assessment:** Full life-cycle analysis and *in vivo* toxicity profiling of nanomaterials intended for food contact applications.
2. **Biocompatibility:** Development of synthesis methods that utilize food-grade or inherently **biodegradable** components to eliminate toxicity concerns.

4.2. Regulatory Harmonization and Industrial Scale-Up

Currently, a unified global regulatory framework governing the use of nanomaterials in food contact materials remains absent. Furthermore, the cost-effective and environmentally benign mass production (Green Synthesis) of high-quality, functionalized nanomaterials is an ongoing engineering challenge that limits industrial adoption.

4.3. Future Directions

a) **Multifunctional Platforms:** Creating integrated "all-in-one" systems that can simultaneously detect a wide range of contaminants, perform selective removal, and be easily regenerated or disposed of.
b) **New Materials:** Exploration of cutting-edge materials such as Covalent Organic Frameworks COFs) and MXenes for their tailored porosity and exceptional surface reactivity.
c) **Targeted Monitoring:** Developing specialized nanosensors for rapid, on-site monitoring of critical contaminants in staple crops and locally sourced foods, addressing concerns specific to regional food systems (e.g., Pb and Cd in date palm fruit).

5. Conclusion and Recommendations

Nanomaterials have demonstrated unparalleled potential for revolutionizing heavy metal management in foods, offering superior sensitivity in detection and enhanced efficiency in removal compared to conventional techniques. However, the translation of this laboratory promise into commercial practice is contingent upon successfully resolving fundamental issues related to long-term safety, regulatory oversight, and economic scalability.

We recommend the following:

a) For Researchers: Prioritize the development of biodegradable nanosensors and sorbents using sustainable (green) synthesis methods, alongside intensified research on the *in vivo* fate of these materials.
b) For Regulators (e.g., FDA, EFSA): Establish clear, science-based, and globally harmonized guidelines for the evaluation and approval of nanomaterials intended for food contact and processing.
c) For Industry: Invest in pilot-scale studies to validate the long-term efficacy and economic viability of these new technologies in real-world food production lines.

By fostering collaboration across these domains, the immense promise of nanotechnology can be safely harnessed to ensure a safer and more resilient global food supply.

References

Abdel-Rahman, G. N., Salem, S. H., Saleh, E. M., & Marrez, D. A. (2022). *Evaluation of the Sewi dates safety produced by the traditional method.* Egyptian Journal of Chemistry, 65(12), 239–249.

Ali, I. (2019). Graphene oxide based materials for the decontamination of heavy metals from water. *Journal of Environmental Chemical Engineering, 7*(1), 102845.

Bharti, R., & Sharma, R. (2022). Effect of heavy metals: An overview. *Materials Today: Proceedings, 51*, 880–885.

Buica, G.-O., Ungureanu, E.-M., & Diaconu, I. (2019). Electrochemical sensors based on nanomaterial-modified electrodes for heavy metal detection in food and water. *Current Opinion in Electrochemistry, 14*, 100-108.

Dehghani, R., Mostafaeii, G., Akbari, H., Pour Abbasi, M. S., Asadi, F., Rezaei, M., Kashani, Z., Hoseini, M., & Takhtfiroozeh, S. (2022). *Lead, cadmium, tin and other heavy metals in the most widely used brands of canned tuna fish in Kashan, Iran. Journal of Chemical Health Risks, 12*(1), 15–24.

El-Shaer, M. K., El-Kholie, E. A., & Abdel-Allah, S. H. (2022). Migration of iron and some toxic metals to foodstuffs during storage, including canned tuna. *Journal of Home Economics*, 32(2), 64–79

Liu, J., Wang, X., & Wang, T. (2020). Functionalized gold nanoparticles as probes for the detection of heavy metals in food. *Analytical Methods, 12*(5), 565-573.

Salem, M. O. A., Saeed, I. A., Amheisen, A. A., Abujarida, A. R. A., & Emhmmed Moammer, E. M. (2023). Health risk assessment of some heavy metals in pasteurized milk available for consumption in Bani Waleed City - Libya. *African Journal of Advanced Pure and Applied Sciences (AJAPAS), 2*(4), 14-21.

Shahid, M., Dumat, C., Khalid, S., Schreck, E., Xiong, T., & Niazi, N. K. (2017). Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. *Journal of Hazardous Materials, 325*, 36–58.

Ulusoy, S. (2023). Determination of toxic metals in canned tuna sold in developed and developing countries: Health risk assessment associated with human consumption. *Marine Pollution Bulletin, 187*, 114518.

Wang, Y., Hu, J., & Zhuang, Q. (2021). Carbon dots for fluorescent detection of mercury ions: A review. *Microchimica Acta, 188*(8), 258.

Welz, B., & Sperling, M. (2008). *Atomic absorption spectrometry*. John Wiley & Sons.

Yu, S., Wang, X., & Pang, H. (2020). A review on the application of graphene oxide/magnetite nanocomposites for heavy metal removal. *Journal of Molecular Liquids, 301*, 112417.

Zhou, Y., Zhang, L., & Wang, Z. (2022). Efficient removal of heavy metals from food simulants using magnetite nanoparticles coated with biopolymers. *Food Chemistry, 367*, 130725.