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Recent Advances in Functional Materials for Heavy Metal Ion Sensing: Progress and Prospects of Thiourea-Based Systems for Water Remediation

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Water pollution caused by heavy metal ions (HMIs) and metal-oxoanions remains a major public health challenge due to their toxicity, persistence, and bioaccumulation. Various functional materials, including metal oxides, carbon-based nanomaterials, porous frameworks, polymers, and biopolymers, have been investigated for HMI sensing and removal. Their performance is governed primarily by the chemical identity, accessibility, and spatial organization of donor groups such as –C=O, –COOH, –NH_2, and –SH, which mediate coordination, electrostatic, and hydrogen bonding (HB) interactions with target analytes. However, most reported systems remain single-purpose platforms focused either on sensing or adsorption, predominantly targeting metal cationic species under idealized laboratory conditions. Direct comparison of sensing and adsorption performance across studies is further complicated by inconsistent reporting units, variations in sample matrices, preconcentration procedures, pH conditions, and limited validation in real-water environments. In this context, sulfur- and nitrogen-containing moieties, particularly thiourea derivatives, are attractive due to their dual donor characteristics. The –C=S group enables strong coordination with soft and borderline metal cations in accordance with Pearson's HSAB principle, whereas the –NH group may potentially participate in directional HB with oxoanions. However, the practical significance of thiourea–NH–mediated oxoanion recognition in aqueous media remains insufficiently validated because strong solvent competition and oxoanion hydration weaken HB interactions. This review provides a critical and chemistry-based evaluation of thiourea-functionalized materials, including metal oxides, carbon-based materials, porous frameworks, and polymeric systems, focusing on how coordination chemistry, HB, hydration effects, charge transfer, and material architecture influence sensing and adsorption performance. Particular attention is given to the effects of competing ions, sample matrices, and experimental conditions on reported detection limits and adsorption capacities. In addition, this review discusses material stability, regeneration, ligand leaching, and environmental safety, highlighting the limited number of studies that evaluate real-water performance, interference resistance, and long-term reusability. Future strategies are proposed based on polymer-supported and solid-state thiourea architectures, preorganized multivalent HB arrays, electron-withdrawing group modulation, and integrated sensing–adsorption platforms capable of operating under realistic environmental conditions. Overall, this review establishes a rational framework for the development of robust, multifunctional thiourea-based materials for sustainable water monitoring and remediation applications aligned with Sustainable Development Goals (SDG) 6 (Clean Water and Sanitation) and 3 (Good Health and Well-Being).

Keywords: Heavy metal ions, functional materials, thiourea derivatives, hydrogen bonding, sensing, adsorption

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Water pollution is a critical environmental challenge with far-reaching consequences for ecosystems and human health, bearing directly on the attainment of SDG 6 (Clean Water and Sanitation) and SDG 3 (Good Health and Well-Being). Heavy metal ions (HMIs) such as mercury (Hg), cadmium (Cd), arsenic (As), lead (Pb), copper (Cu), and chromium (Cr) are among the most hazardous pollutants found in contaminated

water. These pollutants primarily originate from anthropogenic activities, including industrial processes, agricultural runoff, and improper waste disposal [1, 2]. HMIs are characterized by their high atomic weight, non-biodegradability, and strong potential for bioaccumulation and biomagnification within food chains [1, 3]. In aqueous systems, they exist in both cationic (positively charged) and anionic (negatively charged) forms, depending on their oxidation state and solution chemistry. Prolonged exposure to these metal ions has been associated with serious health issues, including neurodegenerative diseases, respiratory problems, central nervous system (CNS) disorders, Wilson's disease, lung cancer, and Parkinson's disease [4, 5]. Therefore, early detection of HMIs is essential for the effective management and mitigation of water pollution.

Traditional methods for detecting HMIs such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma emission spectroscopy (ICP-ES), atomic absorption spectroscopy (AAS), X-ray fluorescence, chromatography, and spectrophotometry are often time-consuming, costly, and require complex sample preparation as well as skilled operators. Such limitations significantly reduce their practicality and ease of implementation in routine or large-scale monitoring [6]. In response to these challenges, conventional methods have evolved through the development of chemosensors incorporating advanced functional materials. These materials are engineered for improved sensitivity, selectivity, and stability, enabling the fabrication of compact, portable devices suitable for field applications. They possess reactive groups such as amine ($–NH_2$), hydroxyl (–OH), carboxyl (–COOH), and thiol (–SH), which can interact with metal ions via coordination bonding, hydrogen bonding (HB), electrostatic forces, ion exchange, or redox reactions. Upon binding, these interactions trigger detectable changes in physical or chemical signals, facilitating target analyte recognition [7]. Common sensing mechanisms include optical (e.g., colour change or fluorescence) and electrochemical (e.g., current change) responses [8].

Despite these advancements, a key challenge remains in developing chemosensors that combine high affinity and selectivity toward HMIs with environmental compatibility and structural versatility. This limitation has led to growing interest in organic receptor-based systems, particularly those offering tuneable chemical functionality and strong binding sites. Among these, thiourea and its derivatives have emerged as promising candidates, owing to their distinctive chemical structure and functional flexibility. The core structure of thiourea features sulfur (–C=S) and nitrogen (–NH) atoms, which serve as electron-rich donor sites. The –C=S moiety typically forms covalent coordination bonds with metal cations, while the –NH group can engage in HB with metal-oxoanions [9]. Thiourea-based materials are now widely used in both optical and electrochemical sensing platforms, and their integration into solid supports such as nanocomposites, polymer matrices, and nanomaterials, enables portable, cost-effective, and highly sensitive detection systems. Additionally, their relatively low toxicity and synthetic tuneability make them attractive for water monitoring and environmental remediation [10].

This review critically examines recent developments in functional materials for HMI detection, elucidates sensing mechanisms, and addresses the influence of functional group chemistry and material architecture on performance. Unlike most existing reviews that focus on cationic metal ions and treat sensing and adsorption as separate functions, this work adopts an integrative approach centred on thiourea-based systems. Special attention is given to the underexplored role of thiourea –NH groups as HB donors for the selective recognition of toxic metal-oxoanions. By correlating functional group chemistry, material architecture, and interaction mechanisms, this review proposes rational design principles for multifunctional materials, with emphasis on polymer-supported and solid-state thiourea platforms capable of simultaneous detection and removal. While real-world applicability, particularly performance in complex water matrices, is increasingly recognised as critical, it remains insufficiently addressed in current studies. This review therefore highlights stability, reusability, and matrix effects as key challenges that must be systematically considered to advance practical implementation. Overall, this work provides a critical assessment of recent progress while outlining a clear framework for the development of robust, multifunctional thiourea-based materials. These research directions are closely aligned with SDG 6 and SDG 3.

METHOD

This review is based on studies published between 2015 and 2025, collected from databases such as ScienceDirect, Google Scholar, Scopus, Web of Science, and SpringerLink. Keywords used in the search include "functional materials," "HMIs and oxoanions," "thiourea derivatives," "sensing and adsorption of HMIs," "advantages and disadvantages of functional materials," and "chemosensors for HMIs," using Boolean operators (AND, OR). Only peer-reviewed articles in English were included. The selection involved three steps comprising screening titles and abstracts, reviewing full texts, and applying set inclusion and exclusion criteria.

RESULTS AND DISCUSSION

FUNCTIONAL MATERIALS FOR HEAVY METAL ION RECOGNITION: PRINCIPLES, PERFORMANCE, AND LIMITATIONS

The effectiveness of functional materials in HMI recognition is governed primarily by the chemical identity, accessibility, and spatial distribution of surface

functional groups rather than the material category itself. Across a wide range of material platforms including metal oxides, carbon nanomaterials, porous frameworks, and polymeric systems, metal–material interactions are governed by a limited set of donor atoms and noncovalent forces: coordination bonding, electrostatic attraction, HB, and charge-transfer interactions [11]. Consequently, differences in sensing performance arise primarily from functional group chemistry rather than the host material alone.

Within this framework, thiourea derivatives have emerged as a versatile yet comparatively underexplored functional motif for HMI recognition. The thiourea unit integrates two complementary donor elements within a single molecular framework: the soft sulfur atom of the –C=S group, which exhibits strong affinity toward soft and borderline metal cations, and –NH groups capable of acting as directional HB donors toward metal-oxoanion species [10]. This dual-donor configuration distinguishes thiourea from conventional ligands that typically rely on a single dominant interaction pathway and underpins its potential for multifunctional sensing platforms capable of interacting with both cationic and anionic species, although experimental validation for oxoanion recognition in aqueous media remains limited. Importantly, thiourea functionalities can be incorporated into diverse material architectures, including metal oxides, carbon nanostructures, porous frameworks, and polymer matrices, where they act as chemically active motifs rather than standalone sensing materials. Accordingly, thiourea is best regarded as a functional component that enhances selectivity, sensitivity, and multifunctionality when integrated into engineered platforms. Nevertheless, current studies predominantly emphasize sulfur-mediated coordination with metal cations, while the contribution of thiourea –NH groups to HB-driven recognition of metal-oxoanions remains relatively underexplored, and warrants more systematic investigation.

Functional materials such as metal oxides, carbon-based nanostructures, porous frameworks, and functional polymers have been extensively studied for HMI detection due to their high surface areas, tuneable porosity, and abundance of accessible binding sites. However, these intrinsic properties alone are often insufficient to achieve high in complex aqueous environments. As a result, sensing performance is frequently enhanced through surface functionalisation, chemical modification, or the development of multifunctional composites that introduce tailored binding sites [12].

Following metal recognition, the interaction must be transduced into a measurable analytical signal. Optical and electrochemical approaches therefore dominate HMI sensing applications. Colorimetric and fluorescence-based sensors rely on binding-induced perturbations of the electronic structure of the sensing material, resulting in detectable changes in light absorption or emission [13]. Electrochemical sensing, in contrast, is based on measurable variations in electrical signals such as current, potential, or impedance, and is typically classified into potentiometric, amperometric and impedimetric modes [14]. Despite differences in transduction mechanisms, overall sensing performance is fundamentally governed by the chemical nature, accessibility, and spatial organisation of active functional groups, particularly nitrogen-, oxygen-, and sulfur-containing donor sites. Therefore, variations in sensing behaviour across material classes primarily reflect differences in surface functional group chemistry rather than sensing modality itself. Rational design and modification of these functional groups are thus essential for achieving enhanced sensitivity, selectivity, and multifunctionality in HMI sensing systems.

Functionalized and Hybrid Metal Oxide Systems

Metal oxides represent a prominent class of functional materials for HMI sensing due to their unique physicochemical properties and tuneable surface chemistry. These materials can be classified into monometallic oxides such as ZnO, Fe_3O_4 and TiO_2, and bimetallic oxides such as $NiFe_2O_4$ and $CoFe_2O_4$, a distinction based on their composition that directly influences sensing performance. Monometallic oxides are known for their high surface area to volume ratios, excellent chemical stability, ease of synthesis, as well as their tuneable optical and electrical characteristics, enabling efficient signal transduction in electrochemical and optical sensing systems [15].

For instance, Fe_3O_4 functionalized with D-Valine (Fe_3O_4-D-Val) exhibited strong electrostatic interactions with HMIs due to the presence of negatively charged surface functional groups such as –COOH and $–NH_2$ (Figure 1a) [16]. This modification enabled low limits of detection (LOD) at 11.29, 4.59, and 20.07 nM for Cd^{2+}, Pb^{2+}, and Cu^{2+}, respectively, via electrochemical sensing. In another example, TiO_2 modified with thiazolylazopyrimidine (TAP) nanoparticles demonstrated improved detection and recovery of Cu^{2+} ions, attributed to electrostatic interactions involving $–NH_2$, –N=N, and –S groups (Figure 1b) [17]. The colorimetric response was evident as the solution colour changed from yellow to red upon metal complexation. Similarly, ZnO/L-cysteine nanofibres exhibited high sensitivity toward Pb^{2+}, with a LOD of 0.397 µg/L, which was attributed to their porous structure and the Lewis acid-base interactions provided by L-cysteine functional groups [18].

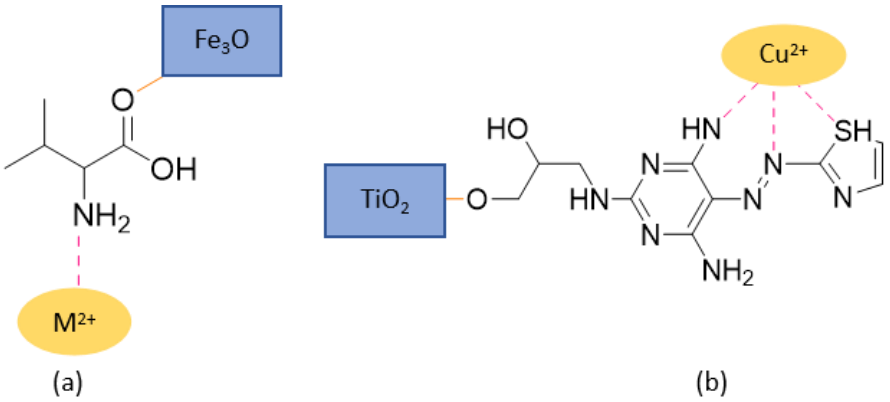

Figure 1. (a) D-valine-functionalized Fe_3O_4 showing interactions between surface –NH groups and HMIs (Cd^{2+}, Pb^{2+}, Cu^{2+}) [16], **(b)** TAP-modified TiO_2 binding Cu^{2+} through $–NH_2$, –N=N, and –S groups, resulting in a colorimetric response [17]. These panels highlight how surface functionalization introduces active binding sites and enables signal generation in metal oxide-based sensing systems.

Despite these promising characteristics, monometallic oxides face limitations such as poor selectivity, relatively low electrical conductivity, and limited long-term stability in aqueous environments [19]. These limitations arise primarily from the nonspecific nature of interactions between metal ions and surface –OH groups. From a mechanistic perspective, the Hard and Soft Acids and Bases (HSAB) principle explains these trends: the hard oxygen donors on oxide surfaces interact preferentially with hard metal ions (Cr^{3+}, Fe^{3+}), while soft metals (Hg^{2+}, Cd^{2+}) are bound less effectively through coordination. Importantly, surface hydration under aqueous conditions competes with analyte binding, creating an outer-sphere adsorption mechanism that reduces selectivity and sensitivity [20]. In contrast, thiourea-based ligands enable inner-sphere coordination through soft sulfur donors and HB –NH groups, facilitating stronger and more selective binding to soft and borderline metal ions. This coordinated binding not only improves selectivity but can also enhance charge transfer processes, thereby contributing to improved sensor performance and stability [17].

To overcome these limitations, bimetallic oxides have been explored as advanced alternatives. The incorporation of two different metal components enhances electronic conductivity, increases surface reactivity, and provides a greater number of active binding sites [19]. For example, $NiFe_2O_4$ nanoparticles incorporated with conductive polypyrrole ($NiFe_2O_4$/PPy) showed enhanced electrochemical performance for selective Pb^{2+} detection within a concentration range of 0.1–2.1 µM. This improved sensing capability was attributed to effective chelation and electrostatic interactions between Pb^{2+} ions (Lewis acid) and –O or –NH donors (Lewis bases) present in the polypyrrole matrix [21]. Similarly, poly(pyrrole-co-*o*-toluidine)/$CoFe_2O_4$ nanocomposites achieved a low detection limit of 0.042 nM for Pb^{2+} highlighting the advantages of hybrid systems in enhancing sensing performance [22]. However, the synthesis processes of bimetallic oxides are more complex, requiring precise control over stoichiometry, morphology, and composition to ensure reproducibility, stability, and scalability. Additionally, structural instability and potential metal ion leaching under extreme pH or redox conditions may affect long-term performance [23].

Consequently, metal oxides are more appropriately regarded as signal transducer platforms rather than standalone selective receptors. While they provide robust frameworks for signal generation, selective recognition typically requires functionalization with organic ligands, polymers, or hybrid materials to introduce specific binding sites such as $–NH_2$, –COOH, or –SH groups [24].

Overall, metal oxide materials offer significant advantages in terms of chemical stability, surface reactivity, sensitivity, and efficient signal transduction. However, their effectiveness in selective HMI detection remains limited without functionalization because interactions with metal ions are often nonspecific. In addition, the rigid inorganic lattices restrict conformational adaptability and cooperative binding, while surface hydration and pH-dependent surface states weaken directional interactions, particularly for highly solvated or polyatomic species [25, 26, 27]. These limitations have driven the exploration of alternative material platforms with greater structural tuneability and electronic flexibility, such as carbon-based materials which offer enhanced conductivity, optical responsiveness, and ease of surface functionalization.

Carbon-based Materials

Carbon-based materials, including zero-dimensional (0D) fullerenes, carbon dots (CDs), and graphene quantum dots (GQDs), as well as two-dimensional (2D) structures such as graphene oxide (GO), have emerged as versatile platforms for HMI sensing due to their outstanding electrical conductivity, optical tuneability, and large accessible surface areas. Surface functionalisation with -O, -N, or -S donor groups enables carbon materials to interact with HMIs via coordination, electrostatic attraction, and π–metal interactions [28].

Among carbon-based materials, quantum dots (QDs) exhibit strong photoluminescence, high photostability, and tuneable emission wavelengths, enabling highly sensitive fluorescence-based detection. In contrast, graphene-based materials provide high electron mobility and mechanical robustness, facilitating efficient signal amplification in electrochemical and optical sensing platforms [29]. Beyond their optical properties, many carbonaceous materials exhibit semiconducting behaviour, allowing the generation of electron–hole pairs under light irradiation. This feature promotes photoinduced charge transfer and redox interactions with metal ions, thereby enhancing sensing performance. For instance, nitrogen-doped carbon dots (N-CDs) dispersed in water-THF systems demonstrated selective detection of Cr^{3+} ions through coordination with protonated –NH groups, achieving an LOD of 0.30 µM (Figure 2a) [30].

Similarly, graphene-based systems exploit surface oxygen functionalities to enable metal ion binding. Indandione oligomer@graphene oxide nanocomposites (HTD@GO) demonstrated detection of Cr^{3+} and Cu^{2+} ions with detection limits of 3.65 µM and 2.25 µM, respectively, primarily via electrostatic interactions with –COOH and –OH groups (Figure 2b) [31]. Incorporation of plasmonic components further enhances sensitivity; for example, AuNPs@GO hybrids achieved an exceptionally low LOD of 1.67 pmol/L for Pb^{2+}, driven by the synergistic effect of localized surface plasmon resonance (LSPR) and strong Pb^{2+} –oxygen interactions [32].

Beyond graphene-based materials, CDs also demonstrate strong signal-transduction capabilities through diverse surface chemistries. Green luminescent CDs have been applied for Cr^{6+} detection (LOD = 0.05–10 mM) via interactions with –S=O, –C–O, and –C–N groups, while hybrid systems such as polyethyleneimine–carbon nanotube/graphene oxide (PEI-CNT/GO) achieved highly sensitive Pb^{2+} detection (LOD = 36 pmol/L) through a combination of coordination, HB, and π–π interactions with –OH, –COOH, –C=O, and –COC groups [33, 34].

Despite these advantages, several intrinsic limitations remain. The heterogeneous and poorly defined distribution of surface functional groups results in non-uniform binding environments, leading to limited selectivity particularly in complex aqueous matrices where competitive ion interference is significant [35]. Additionally, aggregation and π–π stacking reduce accessible surface area and active sites, while photobleaching and limited long-term stability constrain practical deployment [36]. Furthermore, the synthesis of certain carbon nanomaterials, especially heavy-metal-based quantum dots, raises concerns regarding cost, scalability, and environmental toxicity [37].

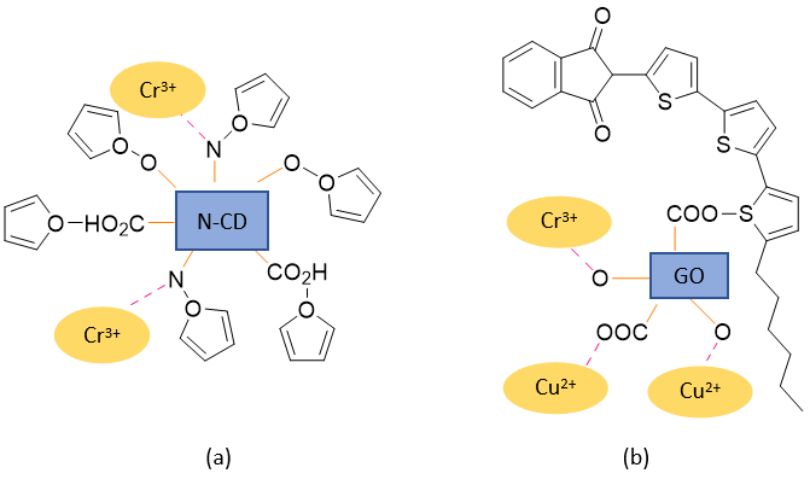

Figure 2. (a) Nitrogen-doped carbon dots (N-CDs) interacting with Cr^{3+} ions via surface nitrogen-containing functional groups in a water–THF system, illustrating fluorescence-based sensing via metal–ligand interactions [30]. **(b)** HTD-functionalized graphene oxide (HTD@GO) showing Cr^{3+} and Cu^{2+} binding through oxygen- and carboxyl-containing groups, enabling electrochemical detection. These examples highlight the role of surface functional groups in governing metal ion recognition in carbon-based sensing platforms [31].

From a critical perspective, the high sensitivity of carbon-based materials arises primarily from their excellent electrical conductivity, optical responsiveness, and large surface areas [38]. However, their sensing performance is still largely governed by nonspecific interactions due to the absence of well-defined and spatially controlled binding sites [39]. This fundamental limitation highlights the need for advanced material platforms that offer greater binding-site density, structural confinement, and precise control over interaction environments. These challenges have driven increasing interest towards porous nanomaterials, which offer well-defined structures, tuneable pore environments, and improved control over analyte recognition.

Porous Nanomaterials: MOFS and COFs

Porous nanomaterials, particularly metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), have attracted considerable attention as advanced platforms for HMI sensing due to their exceptionally high surface areas and tuneable pore architectures. These features provide abundant active sites for metal binding and enable efficient analyte diffusion through interconnected pore networks, resulting in rapid sensing responses. Their modular design allows precise control over pore size, topology, and surface chemistry, facilitating selective recognition of metal ions based on size, charge, and coordination behaviour. In addition, their extended π-conjugated frameworks promote efficient signal transduction upon analyte interaction, while their thermal and chemical stability contribute to reusability and cost-effectiveness [40, 41].

MOFs exhibit remarkable structural diversity which arises from various metal nodes and organic linkers, and provides rich coordination environments and high sensitivity. However, the coordination bonds that underpin MOF architectures are inherently susceptible to hydrolysis, leading to reduced stability under humid, acidic, or strongly basic conditions [42]. In contrast, COFs are constructed through robust covalent bonds between light elements such as C, N, and B, conferring superior chemical stability, structural predictability, and low density. However, they often suffer from limited processability and restricted post-synthetic modification, which can hinder their practical integration into sensing platforms [43].

Both MOFs and COFs have demonstrated outstanding performance in HMI sensing, largely due to their high surface areas, often exceeding 1000 m^2/g, which enhance analyte adsorption and sensitivity. For instance, Bodkhe, *et al.* developed a silver-doped MOF (Ag@ZnBDC) for the selective Hg^{2+} detection, achieving a detection limit of 4.16 nM [44]. In this system, benzene dicarboxylic acid ligands facilitated electrostatic interactions and HB with analytes through –COOH and –OH groups (Figure 3a). In a related study, Feng, *et al.* designed a fluorescent Zr-based MOF sensor for Hg^{2+} detection, achieving a LOD of 0.039 µM, attributed to coordination interactions between Hg^{2+} and donor groups such as the –N of porphyrin and –COOH functionalities (Figure 3b) [45]. In another example, GaOOH-modified UiO-66-NH_2 exhibited exceptional Cd^{2+} detection performance, with an ultralow LOD of 0.006 µM through complexation with –OH and –NH_2 groups [46]. Additionally, a lanthanide-based MOF (Eu-MOF) modified with dipyridylic acid (DPA) and 2,5-dihydroxyterephthalic acid (DHTA) enabled sensitive Hg^{2+} detection with a low LOD of 40 nM, attributed to coordination with –COOH and –N donor sites [47].

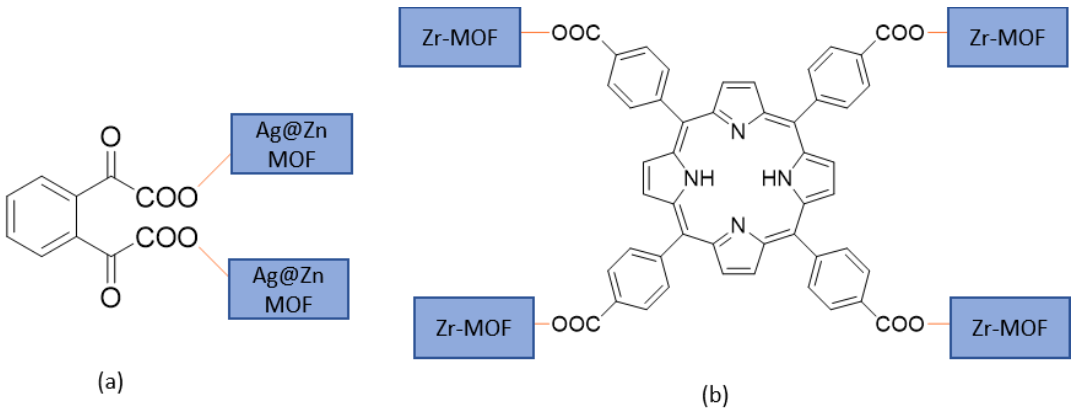

Figure 3. (a) Structural representation of Ag@ZnBDC MOF, showing coordination sites provided by $–COO^-$ groups for Hg^{2+} interaction and sensing [44]. **(b)** A Zr-based MOF incorporating porphyrin linkers with multiple nitrogen and carboxylate donor sites, enabling metal ion binding and fluorescence response [45]. These examples illustrate how tuneable coordination environments in MOFs enhance sensitivity and selectivity in heavy metal sensing.

Despite these advances, several intrinsic limitations persist. The chemical and hydrolytic stability of porous nanomaterials can be compromised, particularly under humid, acidic, or strongly basic conditions [48]. In MOFs, the coordination bonds that enable structural tuneability are inherently weaker than covalent bonds, rendering them susceptible to degradation. Additionally, their synthesis is often complex and energy-intensive, frequently involving toxic solvents or harsh conditions, raising concerns regarding scalability and environmental sustainability [49, 50]. Although COFs exhibit improved chemical and thermal stability due to their covalent frameworks, they often suffer from poor crystallinity, limited processability, and difficulties in dissolution or fabrication using common solvents, hindering their practical integration into sensing platforms [51]. Furthermore, both MOFs and COFs are prone to pore blocking or surface fouling in complex sample matrices, reducing accessibility to internal binding sites and impairing sensing performance [52]. Beyond these practical limitations, their rigid framework architectures restrict conformational adaptability, limiting cooperative binding interactions that are essential for selective recognition. Diffusion constraints within pore networks also hinder mass transport, particularly for larger or highly hydrated metal ions, thereby reducing uptake kinetics and overall sensing efficiency [53]. Collectively, these limitations compromise long-term stability, reusability, and performance under real-world conditions.

From a critical standpoint, the high sensitivity of porous nanomaterials originates from their exceptionally large surface areas, tuneable pore environments, and effective analyte preconcentration, which enhance analyte–surface interactions and host–guest recognition [54]. However, the rigid and preorganized architectures of MOFs and COFs restrict dynamic conformational adjustment, cooperative binding, and mass transport, limiting their ability to accommodate structurally diverse or highly hydrated metal ions in complex matrices [55]. In addition, the fixed spatial arrangement of functional sites reduces multivalent interactions and directional HB efficiency, particularly in systems requiring adaptable coordination environments. Consequently, despite their high sensitivity, porous nanomaterials remain constrained by limited flexibility and functional adaptability under realistic sensing conditions. These limitations highlight the need for more versatile platforms, such as polymer- and biopolymer-based materials, which offer dynamic chain mobility, tuneable architectures, and improved control over binding-site accessibility.

Polymer and Biopolymer Materials

In response to the structural rigidity, limited adaptability, and stability challenges associated with metal oxides, carbon-based materials, and porous frameworks, polymer and biopolymer-based materials have emerged as highly promising alternatives for HMI sensing. Unlike rigid hosts, polymers provide chemically programmable and flexible matrices that enable precise control over functional group density, spatial distribution, and microenvironment polarity. This adaptability facilitates cooperative and directionally controlled interactions with metal ions under aqueous conditions [56].

Synthetic polymers, particularly conducting polymers and engineered polymer composites, may be functionalized with electron-donating functional groups such as –NH, –N=, –COOH, and –SH. These functionalities promote strong coordination, HB, and electrostatic interactions with metal ions, while simultaneously supporting efficient charge transport for electrochemical signal transduction. As a result, polymer–metal interactions can be translated into measurable electrical or optical responses, enabling rapid and sensitive detection [57, 58].

Biopolymer-based materials offer complementary advantages, including sustainability, renewability, and an inherent abundance of functional groups. Natural polymers such as chitosan and cellulose derivatives contain –NH, –OH, –COOH, and $–SO_3$ groups, which enable effective metal ion binding through chelation, ion exchange, and electrostatic interactions [59]. When combined with nanomaterials or optical reporters, these systems can achieve enhanced sensitivity and selectivity.

Representative studies highlight the versatility of polymer-based sensing platforms. Polyaniline (PANI) nanofiber functionalized gold nanoparticles (PANI-AuNPs) demonstrated sensitive detection of As^{3+} with a detection limit of 0.5 ppb, attributed to interactions between nucleophilic nitrogen groups (–NH and =N–) and electrophilic metal ions (Figure 4a) [60]. Similarly, PANI-AuNP composites achieved a detection limit of 1.2 µg/L for Cd^{2+}, reflecting synergistic effects between polymer matrices and metallic nanostructures [61]. In another study, poly(3,4-ethylenedioxythiophene) (PEDOT) systems combined with an NTA lysine-modified electrodes enabled simultaneous detection of Hg^{2+}, Pb^{2+}, and Zn^{2+}, with LODs of 1.73, 2.33, and 1.99 µg/L, respectively, due to strong coordination interactions via –COOH and $–NH_2$ groups (Figure 4b) [62]. Polymer-modified platinum electrodes also demonstrated improved selectivity toward Cd^{2+} and Pb^{2+}, achieving LODs of 0.95 µg/L and 1.84 µg/L, respectively [63]. Likewise, polyglycine-functionalized graphene paste electrodes (PGMGPE) enabled sensitive detection of Hg^{2+} and Pb^{2+} with LODs of 6.6µM and 0.8µM, respectively, due to interactions involving –NH and –C=O groups [64].

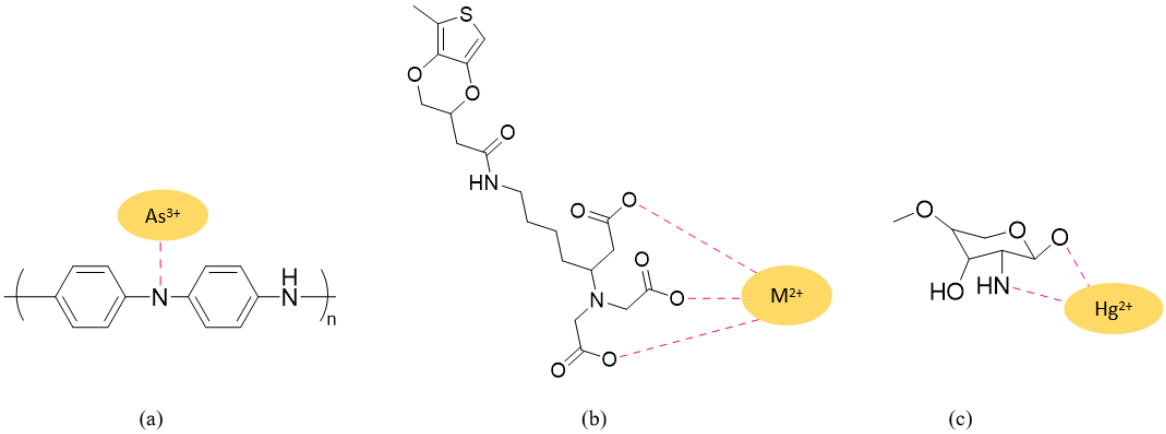

Figure 4. (a) Interaction of polyaniline (PANI) with As^{3+} ions through nitrogen-containing functional groups, enabling electrochemical sensing [60]. **(b)** PEDOT/NTA-lysine system coordinating Hg^{2+}, Pb^{2+}, and Zn^{2+} ions through carboxylate and amine donor groups, contributing to selective detection [62]. **(c)** Chitosan binding Hg^{2+} through –NH and –OH functional groups, supporting fluorescence-based sensing [67]. These examples demonstrate how polymer functional groups provide tuneable binding sites and facilitate signal generation for HMI recognition.

Further examples include a dansyl-tagged dithiocarbamate (DTC)-linked organic polymer, which enabled fluorescence-based detection of multiple metal ions such as Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+} and Fe^{3+}, with detection limits of 13.27, 8.27, 14.36, 14.95, and 15.54 nM, respectively, owing to coordination interactions involving $–NCS_2$, –NH, and –N groups [65]. Ion-imprinted polymer (IIP) systems combined with a quartz crystal microbalance (QCM) sensors also demonstrated selective Hg^{2+} detection through interactions with –OH, –N=, and –C=O groups, achieving a LOD of 14.17 ppb under acidic conditions (pH 3.77) [66].

Biopolymer integration further enhances sensing performance. Rhodamine-functionalised chitosan enabled Hg^{2+} detection through ion-exchange and electrostatic interactions involving –NH and –O groups, achieving a LOD of 3.42 µM (Figure 4c) [67]. Similarly, cellulose-based graphene nanocomposites (PrGO/CMC/Fonda/GC) demonstrated highly sensitive detection of Cd^{2+} and Pb^{2+}, with LODs of 0.28 nM and 0.17 nM, respectively, attributed to coordination with $–SO_3$, –COOH, –OH, and C=O groups [68]. In these systems, the polymer matrix not only provided abundant binding sites but also enhanced electron transfer kinetics and signal amplification, thereby improving overall sensing performance.

Hybridization with nanomaterials such as metal nanoparticles, graphene derivatives, QDs, and MOFs may further enhance sensing performance by leveraging complementary properties. In such systems, polymers contribute flexibility, processability, and controlled functionalisation, while nanomaterials provide high surface area, enhanced conductivity, and signal amplification. This synergistic integration consistently improves sensitivity, selectivity, and response time under diverse environmental conditions [69].

Despite these advantages, polymer-based systems also face certain limitations. Native biopolymers often exhibit low intrinsic conductivity, restricting their standalone application in electrochemical sensing [70]. Their structural integrity may be vulnerable to degradation under fluctuating pH or prolonged aqueous exposure. Conducting polymers, although highly sensitive, may undergo degradation under oxidative conditions and exhibit reduced long-term stability [71]. Overall, polymer- and biopolymer-based materials offer a highly adaptable and versatile platform for HMI sensing, combining structural flexibility, high functional group density, and tuneable physicochemical properties. These characteristics make them particularly suitable for practical sensing applications, especially when integrated with complementary nanomaterials.

To enable direct comparison across studies, Table 1 compiles representative functional materials for HMI detection with LODs normalised to µg L^{-1}, enabling direct comparison across systems. Across material classes, fluorescence- and electrochemical-based techniques dominated, while the sensing performance was fundamentally governed by interfacial coordination chemistry, particularly the nature of donor atoms and their interactions with target metal ions.

A clear trend was observed for sulfur-containing systems, which exhibited superior sensitivity toward soft, polarizable metal ions. For example, the AuNPs@GO platform achieved an

exceptionally low LOD of 0.00035 μg L^{-1} for Pb^{2+} [72], while the graphene quantum dot–thiourea electrode detected Hg^{2+} at 4.71 μg L^{-1} [73]. This enhanced performance arises from strong soft–soft interactions between sulfur donor atoms (–SH, –C=S) and HMIs, which favour efficient orbital overlap and reduced desolvation energy, leading to stable inner-sphere complex formation.

In contrast, oxygen- and nitrogen-dominated systems generally exhibited higher detection limits and broader, less selective binding. For instance, PEI-CNTs/GO detected Pb^{2+} at 16.2 μg L^{-1} [74], while polyglycine-modified electrodes showed significantly poorer sensitivity, with an LOD value of 1324 μg L^{-1} for Hg^{2+} [64]. These systems rely on –COOH, –OH, and –NH functionalities, which are strongly hydrated in aqueous environments. The resulting hydration shells impose thermodynamic barriers to coordination and favour outer-sphere interactions, thereby reducing effective binding strength and selectivity.

The advantage of multidentate and cooperative binding is evident in systems incorporating multiple donor groups. PEDOT/NTA exhibited LOD values of 1.73–2.33 μg L^{-1} for Hg^{2+}, Pb^{2+}, and Zn^{2+} [62], reflecting enhanced binding through chelation. Similarly, PrGO/CMC/Fonda composites achieved LOD values as low as 0.032–0.035 μg L^{-1} for Cd^{2+} and Pb^{2+} [68], where synergistic $–SO_3^-$ and $–COO^-$ groups enabled cooperative coordination. These results highlight the role of the chelate effect, which enhances thermodynamic stability via multidentate interactions.

Hybrid systems integrating conductive nanomaterials further demonstrated improved performance due to enhanced electron-transfer kinetics. For example, AuNPs@GO [72] and UiO-66-NH_2/GaOOH (LOD ~1–5 μg L^{-1}) [46] showed that sensitivity improvements arise not only from increased surface area but also from facilitated charge transfer between the metal–ligand complex and the transducer. This supports the role of LMCT and efficient electron transport pathways in signal amplification.

Solution chemistry imposes additional constraints on sensing behaviour. Most systems operate optimally within a narrow pH range (5–7), as observed across multiple entries, including TiO_2-TAP [75] , PEDOT systems [62, 63], and MOF-based platforms [46]. Under acidic conditions, protonation of donor groups reduces their electron-donating ability, while at higher pH, hydrolysis or precipitation of metal ions limits their availability for coordination.

Importantly, although several systems have been validated in real water matrices, comprehensive evaluation under complex environmental conditions remains limited. Systems such as UiO-66-NH_2/GaOOH [46], AuNPs@GO [72], and Eu-DHTA/DPA [47] demonstrated successful application in real samples, whereas many other materials were evaluated primarily under controlled laboratory conditions. This reflects a key limitation of current sensing platforms, where idealised coordination equilibria may not adequately account for competitive complexation from background ions (e.g., Ca^{2+}, Mg^{2+}). Oxygen-rich systems are particularly susceptible due to strong hydration and non-specific binding interactions.

Recyclability behaviour varied depending on the stability of the binding interaction and structural framework. Electrochemical systems based on conductive polymers generally exhibited stable regeneration due to immobilised coordination sites within conductive matrices. Several systems maintained consistent sensing performance over multiple regeneration cycles, including PEDOT- [62, 63] and PANI-based platforms [61]. Fluorescence-based materials, including rhodamine-functionalised chitosan [67] and Eu-DHTA/DPA MOFs [47], also demonstrated moderate recyclability over repeated sensing cycles, indicating that regeneration behaviour is strongly influenced by framework stability and reversibility of the binding interaction.

Interference behaviour was also consistent with coordination chemistry principles. Sulfur-containing systems (e.g., thiourea-based [73] and dithiocarbamate-linked polymers [76]) exhibited strong selectivity toward soft metal ions, due to high polarizability of sulfur donor atoms. In contrast, nitrogen- and oxygen-dominated systems (e.g., PANI [61], PEDOT [62], cellulose composites [68]) displayed broader binding profiles and cross-sensitivity toward competing ions such as Cu^{2+} and Fe^{3+}. These trends confirmed that selectivity was governed primarily by donor atom identity, electronic density, and coordination environment.

Despite these advances, Table 1 highlights a critical gap: the overwhelming focus on cationic metal ions, with limited attention to metal-oxoanions. Only a few systems, such as N-doped carbon dots for Cr^{6+} detection (LOD 15.6 μg L^{-1}) [77] , addressed anionic species. This bias reflects the dominance of coordination-based sensing strategies, which favour cation binding via lone-pair donation. In contrast, oxoanion recognition requires directional HB and electrostatic complementarity, which are not effectively achieved using conventional functional groups. Furthermore, sensing and adsorption functionalities remain largely decoupled. Materials designed for strong adsorption capacity (e.g., MOFs [44]) often lack efficient signal transduction properties, whereas highly sensitive electrochemical sensors may exhibit limited adsorption capability. This highlights the absence of integrated multi-functional designs that simultaneously optimise binding thermodynamics, reversibility, signal generation and structural stability.

Table 1. Comparative performance, validation parameters, and dominant interaction mechanisms of functional materials for HMI detection.

Classification of material group	Functional material	Method of detection	Analytes	Limit of detection µg L^{-1} [LOD]	Interaction group	Binding mode	pH	Real water	Interference	Recyclability	References
Metal oxide	**D-Valine**-Fe_3O_4	Electrochemical (SWASV)	Pb^{2+} Cd^{2+} Cu^{2+}	0.95 1.27 1.27	–OH, –NH, –SH	Coordination	5.2	Yes	Yes	NR	[78]
	TiO_2-**Thiazolylazopyrimidine** (TiO_2-TAP)	Colorimetric	Cu^{2+}	0.16	$–NH_2$, –S, N=N	Coordination	5	Yes	Yes	Yes	[75]
	ZnO-**L-cysteine** (ZnO-L-cys) nanofiber	Electrochemical (SWASV)	Pb^{2+}	0.397	–SH, $–NH_2$, –COOH	Chelation	-	Yes	Yes	Yes	[79]
	Polypyrrole-$NiFe_2O_4$	Electrochemical	Pb^{2+}	20.7-41.4	–O, –NH	Coordination	-	Yes	Yes	Yes	[80]
	Poly(pyrrole-co-o-toluidine)-$Co_3Fe_2O_4$	Electrochemical	Pb^{2+}	0.0087	–O, –NH	Coordination	-	Yes	Yes	Yes	[81]
Carbon-based	**N-doped carbon dots (N-CDs)**-fullerene	Colorimetric	Cr^{6+}	15.6	$–NH_2$, –COOH, –OH	HB	7	Yes	Yes	NR	[77]
	Graphene quantum dot-**thiourea** ((GQDTU)-IIP-GCE)	Electrochemical	Hg^{2+}	4.71	–N, –S	Chelation	5	Yes	Yes	Yes (3 cycles)	[73]
	2-(5″-hexyl-[2,2′:5′2″ terthiophen]-5-yl) methylene)-1H-indene-1,3(2H)-dione oligomer (HTD)-graphene oxide	Electrochemical (SWASV)	Cr^{3+} Cu^{2+}	189.8 143.0	–COOH, –OH, -π-conjugation	Coordination	-	No	Yes	Yes	[82]

	(GO) (HTD@GO)									
	Gold modified **graphene oxide** (AuNPs@GO)	Electrochemical	Pb^{2+}	0.00035	–COOH, $–NH_2$, –SH	Coordination	7.4	Yes	Yes	Yes (5 cycles)	[72]
	Green luminescent Carbon dots (CDs)	Fluorescent	Cr^{6+}	66560	–COOH, –NH	Charge transfer	7	No	Yes	NR	[83]
	(**PEI**-CNTs/GO)	Electrochemical	Pb^{2+}	16.2	–COOH, –C=O, –OH, –NH	Chelation	3.4	No	NR	Yes (3 cycles)	[74]
Porous nanomaterial	Silver-doped MOF (Zn nodes and **benzene-1,4-dicarboxylate** (BDC) linkers)	Electrochemical	Hg^{2+}	0.02	–COOH	Coordination	4	No	Yes	Yes	[44]
	Zr-MOF	Fluorescence	Hg^{2+}	7.82	-π-π conjugated, –COOH, $–NH_2$	Coordination	7	Yes	Yes	Yes	[84]
	UiO-66-**NH_2** (Zr-MOF)/**GaOOH**	Electrochemical	Cd^{2+} Pb^{2+} Hg^{2+} Cu^{2+}	1.80 5.80 1.20 1.21	–C=O, –NH	Coordination	6	Yes	Yes	Yes	[46]
	Modified biligands **dipyridylic acid (DPA) and 2,5-dihydroxyterephthalic acid (DHTA)-** lanthanide (Eu^{3+}) MOF (Eu-DHTA/DPA)	Ratiometric fluorometric	Hg^{2+}	8.02	–COOH, $–NH_2$	Coordination	6	Yes	Yes	Yes	[47]

Polymer and biopolymer	Au-**PANI**-Fe-CNFs	Electrochemical (SWASV)	As^{3+}	0.5	$–NH_2$, –C=N, –COOH	Chelation	5	No	Yes	NR	[60]
	PEDOT and N_α,N_α-bis-(carboxymethyl)-l-lysine hydrate (NTA lysine) (PEDOT/NTA)	Electrochemical (CV)	Hg^{2+} Pb^{2+} Zn^{2+}	1.73 2.33 1.99	$–NH_2$, –COOH	Chelation	4.5	No	Yes	NR	[62]
	PEDOT modified platinum electrode	Electrochemical (SWV)	Cd^{2+} Pb^{2+}	0.95 1.84	–N=	Coordination	5	No	Yes	Yes (5 cycles)	[63]
	Polyglycine-modified graphene paste electrode (PGMGE)	Electrochemical (CV)	Hg^{2+} Pb^{2+}	1324 166	–NH, –C=O	Chelation	4.5	Yes	Yes	Yes	[64]
	Dansyl-tagged dithiocarbamate (DTC) linked organic polymer	Fluorescence	Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}	0.84 0.49 0.84 0.83 0.87	$–NCS_2$,	Chelation	-	No	Yes	Yes (4 cycles)	[76]
	PANI-gold nanoparticles (PANI-AuNP)	Electrochemical (ASV)	Cd^{2+}	1.2	–NH	Coordination	5	Yes	Yes	NR	[61]
	Rhodamine derivative functionalized chitosan	Fluorescence	Hg^{2+}	686	-NH, -C=O	Coordination	7	Yes	Yes	Yes (5 cycles)	[67]
	Porous graphene/**carboxy methyl cellulose**/ **fondaparinux** nanocomposites (PrGO/CMC/Fonda/ GC)	Electrochemical (SWASV)	Cd^{2+} Pb^{2+}	0.032 0.035	$-SO_3^-$, $-COO^-$	Electrostatic interaction	-	Yes	Yes	Yes (10 cycles)	[68]

Note: *All limits of detection are reported in µg L^{-1}, as indicated in the column header. Values originally reported in different units were converted using the molar mass of the corresponding metal ion, rather than the associated salt species, to ensure consistent comparison across studies. NR = not reported.*

Overall, the limitations identified in Table 1 arise from several fundamental chemical constraints, including hydration effects, donor–acceptor mismatch, non-specific coordination, and limited control over binding environments. Addressing these challenges requires multifunctional systems that integrate soft donor atoms, HB motifs, conductive architecture and stable immobilisation strategies. In this context, thiourea-based materials are particularly promising, as they combine a soft sulfur donor site with directional –NH functionalities within a single framework, potentially advantageous for both cation recognition and oxoanion binding

THIOUREA DERIVATIVES: STRUCTURAL FEATURES, INTERACTION MECHANISMS, AND ROLES IN HMI SENSING AND ADSORPTION

As discussed in the preceding section, the performance of functional materials for HMI recognition is fundamentally dictated by surface functional group chemistry, rather than the material scaffold alone. While conventional donor groups such as –O, –N, and –S have been widely employed across metal oxides, carbon-based materials, porous frameworks, and polymers, ligands capable of integrating multiple interaction modes within a single molecular unit remain comparatively underutilized. In this context, thiourea derivatives have emerged as particularly promising functional motifs due to their strong metal-binding affinity, structural versatility, and compatibility with optical and electrochemical sensing platforms [85,86].

This section highlights thiourea derivatives as versatile building blocks for advanced sensing and adsorption systems. By exploring their structural features, electronic properties, and interaction mechanisms, a clear relationship between molecular design and material performance can be established, with particular emphasis on the development of dual-responsive systems capable of targeting both cationic and oxoanion contaminants in complex aqueous environments.

The thiourea moiety ($(NH_2)_2CS$) is characterised by the coexistence of a sulfur-centered –C=S group and amide –NH functionalities, enabling complementary interaction pathways with metal species. The –C=S group contains a lone pair of electrons in a 3p orbital which acts as a soft Lewis base, forming strong coordination bonds with soft and borderline metal cations such as Hg^{2+}, Pb^{2+}, and Cu^{2+}, consistent with Pearson's HSAB principle [87, 88]. Simultaneously, the –NH groups function as directional HB donors and participate in electrostatic interactions with electron-rich species, including metal-oxoanions [89, 90]. This dual-donor architecture distinguishes thiourea derivatives from conventional ligands that rely predominantly on single interaction mechanisms.

The electronic properties of thiourea may be manipulated by conjugation with π-electron systems (e.g., aromatic rings) or substitution with electron-withdrawing and electron-donating groups. These modifications influence charge distribution, HOMO–LUMO energy levels, and charge-transfer behaviour, thereby directly affecting both binding affinity and sensing performance [91]. In optical sensing systems, metal-induced perturbation of the conjugated framework may generate fluorescence "turn-on" or quenching responses via LMCT or photoinduced electron transfer (PET) processes [92]. In addition, intra- and intermolecular HB, together with resonance stabilisation, promotes binding preorganisation, which enhances selectivity and interaction strength [93].

Structural versatility is achieved through substitution at one or both –NH positions with aromatic, heterocyclic, or alkyl groups, allowing precise control over solubility, binding geometry, and compatibility with different sensing platforms [94]. Importantly, incorporation of thiourea units into polymers, nanomaterials, or solid supports improves stability, minimizes ligand leaching, and enhances the spatial organization of binding sites, thereby increasing reusability and practical applicability. Despite these advantages, current thiourea-based systems remain predominantly focused on cation detection, with sulfur–metal coordination serving as the dominant recognition mechanism. In contrast, the HB potential of thiourea –NH groups, particularly for selective oxoanion recognition in aqueous environments, remains relatively underexplored. In addition, challenges such as aqueous stability, potential ligand leaching, and constraints in solid-state integration continue to hinder real-world application.

Overall, thiourea derivatives provide a versatile molecular platform for designing advanced sensing and adsorption systems. Their dual-donor characteristics, tuneable electronic properties, and structural adaptability enable multifunctional interactions with target analytes. However, further development is required to improve selectivity toward complex species, enhance stability under realistic conditions, and fully exploit HB interactions in aqueous environments.

Performance of Thiourea-Based Materials

Over the past decade, thiourea-functionalized materials have emerged as effective platforms for both sensing and adsorption of HMIs. This dual-functionality arises from the intrinsic chemical architecture of the thiourea group, where sulfur-centred –C=S sites enable strong coordination with soft and borderline metal cations (e.g., Hg^{2+}, Pb^{2+}, and Cu^{2+}), while –NH groups participate in HB and electrostatic interactions. These complementary interaction pathways allow thiourea-based systems to operate at both trace-level detection and bulk ion

capture. In sensing applications, incorporation of thiourea units into conjugated or electron-rich frameworks enhances signal transduction via charge-transfer processes and electronic coupling between recognition and reporter units [89]. Concurrently, immobilisation of thiourea functionalities within high-surface-area supports improves analyte accessibility and adsorption capacity, highlighting the synergistic relationship between molecular recognition and material architecture.

As summarized in Table 2A, all thiourea-based sensing systems operated via –C=S coordination, with Hg^{2+} most frequently targeted, followed by Ag^{+} and Cu^{2+}. This trend is consistent with HSAB principles, where soft acids (Hg^{2+}, Ag^{+}) strongly bind sulfur donors, while Cu^{2+} forms stable complexes through σ-donation and partial back-donation. However, sensitivity is not solely dictated by metal–ligand affinity, as electronic structure and signal transduction efficiency also play critical roles. The lowest LOD (0.8 μg L^{-1} for Cu^{2+}) was achieved by the dimethylaminocinnamaldehyde–aminothiourea (DA) probe, demonstrating that electronic structure and signal transduction efficiency were equally critical.

The lowest detection limit reported in Table 2A (0.8 μg L^{-1} for Cu^{2+}) was achieved by the dimethylaminocinnamaldehyde–aminothiourea (DA) probe [95], which simultaneously detected Hg^{2+} (2.8 μg L^{-1}) and Ag^{+} (1.0 μg L^{-1}). This exceptional sensitivity can be attributed to the donor–acceptor–donor (D–A–D) electronic architecture, where the electron-donating dimethylamino group extends π-conjugation across the cinnamaldehyde–thiourea framework. This extended conjugation reduces the HOMO–LUMO gap and enhances intramolecular charge transfer (ICT) sensitivity. In contrast, the pyridine–substituted thiourea derivative PTB-1 exhibited significantly higher detection limits (396.0 μg L^{-1} for Ag^{+} and 138.4 μg L^{-1} for Hg^{2+}) [96], due to limited electronic coupling caused by non-coplanarity between the pyridine and thiourea units that reduced conjugation efficiency and weakened signal transduction.

Among Hg^{2+}-selective systems, the 1,8-naphthalimide–thiourea conjugate achieved a detection limit of 16.5 μg L^{-1} [97], leveraging LMCT processes facilitated by the electron-withdrawing imide (–C=O) group, which lowered the LUMO energy of the chromophore. Notably, this system demonstrated dual-mode sensing: fluorescence quenching for Hg^{2+} and colorimetric responses for Fe^{3+} and Pb^{2+}. The markedly higher LOD for Pb^{2+} (1054.6 μg L^{-1}) reflected its borderline softness, resulting in weaker polarisation of the –C=S bond and reduced perturbation of the π-conjugated system [97]. In contrast, Fe^{3+}, a hard Lewis acid, interacts preferentially with oxygen and nitrogen donors, altering ground-state absorbance rather than inducing strong charge-transfer responses.

Multi-analyte detection via *N*,*S*-bidentate coordination is another important feature observed in Table 2A. The thiosemicarbazide–based probe enabled simultaneous detection of Cu^{2+}, Hg^{2+}, and Ag^{+} across a wide pH range (5–12) [98]. This behaviour is mechanistically attributed to the formation of stable five-membered *N*,*S*-chelate rings, which maintain complex stability even under alkaline conditions where metal hydroxide formation would typically limit free ion availability. Similarly, the coumarin–thiourea conjugate exhibited Hg^{2+} detection across pH 1–11 via a PET mechanism, where Hg^{2+} coordination at –C=S suppressed electron donation from nitrogen, restoring fluorescence emission [99]. The wide pH tolerance highlights the dominance of soft acid–soft base interactions over proton competition.

A distinct sensing mechanism was observed in the thiourea-functionalised graphene aerogel, which achieved the lowest Pb^{2+} detection limit (1.51 μg L^{-1}) through electron transfer-mediated fluorescence quenching [100]. Here, the graphene framework acted as a signal amplifier due to its extended π-conjugation, while the three-dimensional porous architecture enhanced accessibility to –C=S binding sites and reduced diffusion limitations. In contrast, the potentiometric bis(trifluoromethyl) thiourea (TPC) probe employed strong electron-withdrawing $–CF_3$ groups to increase –NH acidity, facilitating Cu^{2+} coordination within an ion-selective membrane [101].

Despite these advances, Table 2A reveals several critical limitations. Although several systems demonstrated successful application in real-water matrices, comprehensive validation under environmentally complex conditions remained limited, representing a significant barrier to practical application. In addition, interference studies were incomplete in several cases, and systems targeting multiple soft metal ions (Hg^{2+}, Ag^{+}, Cu^{2+}) via the same –C=S coordination mechanism are inherently susceptible to competitive binding and cross-interference. This highlights a fundamental limitation in selectivity design, where reliance on a single coordination motif constrains discrimination between chemically similar analytes.

Table 2. Thiourea-based functional materials for sensing and adsorption of heavy metal ions.

A. Thiourea-Based Materials for Sensing of Heavy Metal Species

Thiourea-based material	Analyte	Limit of detection, µg L^{-1} [LOD]	Method detection	pH	Dominant interaction	Interaction group	Real Water	Interference	Recyclability	Reference
1-(6-aminopyridin2-yl)-3-phenylthiourea	Hg^{2+} Au^{3+} Ag^{+}	100.5 4.21 79.2	Fluorescent	-	-C=S coordination	–C=S, $–NH_2$	Yes	Yes	NR	[102]
Hydrazinecarbothioamide appended 1,8-naphthalimide	Ag^{+} Hg^{2+}	4.31 4.01	Fluorescent	7.4	-C=S coordination	–C=S, $–NH_2$	Yes	Yes	NR	[103]
Pyridine substituted thiourea derivative (PTB-1)	Ag^{+} Hg^{2+}	396.0 138.4	Fluorescent	5–9	-C=S coordination	–C=S, $–NH_2$, –C=O	No	Yes	NR	[96]
1,8-naphthalimide-thiourea conjugate	Fe^{3+} Pb^{2+} Hg^{2+}	382.7 1054.6 16.5	Colorimetric (Fe^{3+}, Pb^{2+}) Fluorescence (Hg^{2+})	5–9	-C=S coordination	–C=S, $–NH_2$, –C=O	Yes	Yes	Yes (3 cycles)	[97]
1-(4- (pyridine-4-yl) benzylidene) thiosemicarbazide	Cu^{2+} Hg^{2+} Ag^{+}	677.6 2234.6 921.6	Fluorescent Colorimetric	5–12	-C=S coordination	–C=S, $–NH_2$, –N	Yes	Yes	Yes (3 cycles)	[98]
Dimethylaminocinnamaldehyde-aminothiourea (DA)	Cu^{2+} Hg^{2+} Ag^{+}	0.8 2.8 1.0	Fluorescence	5–9	-C=S coordination	–C=S, $–NH_2$, –N	No	Yes	NR	[95]

N1,N3-bis[[3,5-bis(trifluoromethyl)phenyl]carbamothioyl]isophthalamide (TPC)	Cu^{2+}	39.6	Potentiometric	-	-C=S coordination	–C=S, $–NH_2$, –C=O	No	Yes	Yes	[101]
Novel coumarin-thiourea conjugate	Hg^{2+}	29.3	Fluorescent	1–11	-C=S coordination	–C=O, –C=S	No	Yes	NR	[99]
(1-(2-hydroxybenzyl)-3- (naphthalen-1-yl)-1-phenylthiourea)	Hg^{2+}	168.5	Fluorescent	4.7–9	-C=S coordination	–C=S, $–NH_2$	No	Yes	NR	[104]
Thiourea-functionalized graphene aerogel	Pb^{2+}	1.51	Fluorescent	5	-C=S coordination	–C=S, $–NH_2$	No	Yes	NR	[100]

B. Thiourea-Based Materials for Adsorption Applications

Thiourea-based material	**Analyte**	**Adsorption capacity (mg g^{-1})**	**Kinetic/Isotherm**	**pH**	**Binding mode**	**Interaction group**	**Real Water**	**Recyclability**	**Reference**
O-hydroxyphenyl thiourea-modified chitosan (OTCS)	Pb^{2+}	208.33	P-2-O/ Langmuir	7	-C=S coordination	–C=S, $–NH_2$, –OH	No	NR	[105]
Ethylenediamine (EDA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA)–functionalized thiourea (TC) and chitosan (CS)	Hg^{2+}	TC-EDA-CS (217.1) TC-CS (164.8) TC-TETA-CS (149.7) TC-TEPA-CS (140.6)	P-2-O/ Langmuir	4	-C=S coordination	–C=S, $–NH_2$, –OH	No	Yes (5 cycles)	[106]
Thiourea modified chitosan	Cu^{2+}	60.6	P-2-O	-		$–NH_2$	No	NR	[107]

microsphere (TMCM)									
Thiourea-intercalated magadiite; N-(2-methoxyphenyl)-N′-(2-methylphenyl)-thiourea (TMMe) N-(2-methoxyphenyl)-N′- (2-methoxyphenyl)-thiourea (TMM)	Pb^{2+}	Mag/TMMe (19.9) Mag/TMM (33.44)	P-2-O/ Langmuir	75	-C=S coordination	$–OCH_3$, –C=S, $–NH_2$	No	NR	[108]
New resin (PIDTR) containing acyl and thiourea groups	Cu^{2+}	73.7	P-2-O/ Langmuir	5	-C=S coordination	–NH, –C=O, –C=S	No	Yes (5 cycles)	[109]
A hyper-crosslinked resin chemically modified with thiourea (TM-HPS)	Pb^{2+} Cd^{2+} Cu^{2+}	689.65 432.90 290.69	P-2-O/ Langmuir	6 5 5	-C=S coordination	$–NH_2$, –NH, –C=S, –SH	No	Yes	[110]
Thiourea modified D301 resin (TD301)	Hg^{2+} Pb^{2+} Cd^{2+}	454.1 436.6 254.1	P-1-O/ Langmuir	6	-C=S coordination	$–NH_2$, –C=S	Yes	Yes	[111]
Chitosan functionalized with thiourea groups (CHITU)	Cu^{2+} Cd^{2+} Co^{2+} Ni^{2+}	129.8 134 83.4 132.5	P-2-O/Sips	5	-C=S coordination	–C=S, $–NH_2$	No	Yes (3 cycles)	[112]
Thiourea cross-linked three-dimensional graphene aerogel (TCGA-1)	Cu^{2+} Cr^{3+}	25 6	P-2-O	64	-C=S coordination	–COOH	No	Yes	[113]

Thiourea-phenolic resin	Hg^{2+}	285	P-2-O/ Langmuir	4	-C=S coordination	–C=O, –C=S, $–NH_2$	No	Yes (3 cycles)	[114]
Novel flocculant by modification of sodium alginate (SA) with thiosemicarbazide (TSC)	Pb^{2+} Cd^{2+} Cu^{2+}	489 215 160	P-2-O/ Langmuir	2–7	-C=S coordination	–COOH, –C=S, $–NH_2$	No	NR	[115]
Granular hydrogel of chitosan (CTS)/acrylic acid (AA)/N-ally-N'-(2-hydroxyethyl)thiourea (NANHT)	Hg^{2+}	1106.72	P-2-O/ Langmuir	1–2	-C=S coordination	–OH, –NH, –C=S	No	Yes (5 cycles)	[116]
Thiourea-modified Cu_2O	Au^{3+}	1529.4	P-2-O/ Langmuir	1–5	-C=S coordination	–C=S, –NH	No	Yes (5 cycles)	[117]
Thiourea linked COF	Hg^{2+}	960	P-2-O/ Langmuir	4	-C=S coordination	–C=S, –NH	Yes	NR	[118]
Polyamide-amines (PAMAM)-thiourea derivatives integration	Cu^{2+}	158.48	P-2-O/ Langmuir	5	-C=S coordination	–SH, –NH, –COO	No	Yes (7 cycles)	[119]

Note: *All limits of detection are reported in μg L^{-1}, as indicated in the column header. Values originally reported in different units were converted using the molar mass of the corresponding metal ion, rather than the associated salt species, t ensure consistent comparison across studies. NR = not reported.*

Table 2B shows that adsorption performance was similarly dominated by –C=S coordination chemistry, with capacity strongly dependent on metal softness and polarizability. The highest capacity (1529.4 mg g^{-1} for Au^{3+}) was achieved by thiourea-modified Cu_2O, reflecting a combined inner-sphere coordination and, in some cases, redox–coordination coupling [117]. Similarly, the high Hg^{2+} uptake (1106.72 mg g^{-1}) in thiourea–chitosan hydrogels arose from cooperative multi-site interactions, where –C=S provided primary inner-sphere coordination, while –NH and –OH groups contributed secondary stabilisation through HB and electrostatic effects [116]. Other systems, such as TM-HPS (689.65 mg g^{-1} for Pb^{2+}) and TD301 resins (454.1 mg g^{-1} for Hg^{2+}), demonstrated that incorporation of multiple donor groups enhanced adsorption capacity through multidentate coordination and secondary stabilisation effects [110, 111]. Likewise, functionalised chitosan systems (e.g., CHITU) exhibited moderate adsorption capacities across multiple metal ions due to flexible polymer networks and accessible binding sites [112].

Kinetic and isotherm analyses consistently indicate that adsorption followed PSO kinetics and Langmuir isotherm behaviour, as reported across multiple systems including OTCS, PIDTR, and TM-HPS [105, 109, 110]. This suggests that uptake was dominated by chemisorption via inner-sphere coordination at homogeneous binding sites. Optimal adsorption performance was generally observed within the pH range of 4–7, as demonstrated in systems such as TC-EDA-CS [106] and TM-HPS [110]. At low pH, protonation of –NH and –C=S groups reduces their electron-donating ability, while at higher pH, metal ion hydrolysis limits availability for coordination.

Across both Table 2A and 2B, sensing and adsorption behaviours followed common chemical principles governed by inner-sphere coordination at thiourea –C=S sites. Detection limits as low as 0.8 µg L^{-1} [95] and adsorption capacities exceeding 1500 mg g^{-1} [117] highlight the strong affinity of thiourea toward soft metal ions. However, several limitations remain. Most systems rely on a single –C=S coordination motif, resulting in cross-interference among soft metal ions such as Hg^{2+}, Ag^{+}, and Cu^{2+}. In addition, real-water validation was absent across all reported systems, recyclability was limited in many adsorption materials, and sensing and adsorption functionalities remained largely separated.

Notably, the HB potential of thiourea –NH groups remain underutilised, particularly for oxoanion recognition. In aqueous environments, solvent competition weakens HB interactions, limiting the development of selective anion sensors. This highlights a key opportunity for future design strategies that integrate dual coordination and HB functionalities within a single system.

Limitation and Research Gaps

This study provides valuable insights into recent progress in thiourea-based functional materials for the detection and removal of HMIs. Nonetheless, several critical limitations and research gaps persist. Most existing studies focus predominantly on metal cations, while metal-oxoanions such as CrO_4^{2-}, MnO_4^{-}, and AsO_4^{3-}, have received comparatively little attention despite their environmental relevance, toxicity and persistence in groundwater systems [120,121].

The selective recognition and removal of metal-oxoanions present distinct physicochemical challenges. The large ionic size, high solvation energy, delocalised charge, and tetrahedral geometry of an oxoanion hinders selective binding and receptor accessibility. Compared to metal cations, oxoanions exhibit lower charge densities and weaker electrostatic interactions, while strong hydration shells further limit complex formation [122]. Although thiourea –NH groups can in principle form HB with oxoanions, effective recognition requires precise spatial preorganization and geometric complementarity, and this remain insufficiently developed. In aqueous environments, strong solvent competition further weakens HB interactions, and quantitative binding data for thiourea–oxoanion systems remain scarce [123].

Material stability and recyclability also require more rigorous evaluation. While some systems demonstrate acceptable reuse cycles, the potential leaching of thiourea or degradation products into treated water is rarely assessed, raising concerns for long-term safety and sustainability. In addition, interference studies are typically conducted under simplified laboratory conditions, with limited interference testing and minimal validation in real water matrices. This does not reflect the complexity of real environmental matrices that contain diverse competing ions (e.g., Ca^{2+}, Mg^{2+}, Fe^{3+}) and dissolved organic matter that can significantly affect performance. Consequently, validation in real or certified water matrices and benchmarking against regulatory standards remain largely absent. This is a critical limitation for safe and sustainable water treatment applications aligned with SDG 6.1 and SDG 6.3.

Another key limitation is the lack of multifunctional design. Most thiourea-based materials are developed either as sensing probes or as adsorbents, with little integration of both functions. Existing dual-functional systems remain scarce and are rarely evaluated under realistic conditions. These challenges are further compounded by reduced performance in aqueous environments, where highly dielectric media weaken intermolecular interactions, leading to unstable host–guest complexes and, in some cases, incomplete capture or release of target species. Non-immobilised systems are particularly

susceptible to ligand leaching and secondary contamination [124].

Addressing these limitations requires a shift toward rational material design combined with realistic validation strategies. In particular, the development of preorganised multi–NH binding arrays tailored to accommodate the tetrahedral geometry of oxoanions is essential to improve binding selectivity. This can be further enhanced through the incorporation of electron-withdrawing substituents, which increase HB donor strength and stabilise host–guest interactions. In addition, immobilisation of thiourea functionalities within polymeric or hydrogel frameworks is necessary to enhance structural stability, minimise ligand leaching, and enable repeated use. Equally important is the implementation of comprehensive testing under environmentally relevant conditions, including validation in real-water matrices and systematic evaluation of interference effects from coexisting ions.

Overall, advancing thiourea-based systems will depend on integrating selective oxoanion recognition with robust material design and dual-function capability. Such developments are essential for achieving reliable sensing and efficient remediation in complex environmental systems. These challenges highlight key directions for future research.

Future Perspectives: Design Strategies, Mechanistic Understanding, and Real-World Implementation of Thiourea-Based Functional Materials

Strategic molecular design is essential for achieving selective and efficient oxoanion recognition. A major challenge in anion sensing arises from the intrinsic diversity of anionic species, including variations in geometry, size, charge distribution, solvation energy, and pH-dependent behaviour, all of which complicate selective binding. This challenge is particularly significant for larger tetrahedral metal-oxoanions such as SO_4^{2-}, CrO_4^{2-}, or AsO_4^{3-}, which require precisely tailored receptor architectures for effective recognition [125]. One effective strategy involves enhancing the HB donor strength of thiourea through the incorporation of electron withdrawing groups (EWGs), such as $–NO_2$ or $–CF_3$, onto aromatic frameworks. These substituents reduce electron density on the thiourea –NH groups, thereby increasing their acidity and strengthening HB interactions with oxoanions (Figure 5) [126].

Several studies have demonstrated that thiourea-based receptors containing electron-withdrawing substituents can selectively interact with oxoanions through directional N–H·O hydrogen bonding. For example, nitrophenyl-substituted thiourea systems exhibited sensitive detection of anions such as SO_4^{2-}, F^-, and AcO^- through distinct colorimetric responses from colourless to yellowish, with low LOD values of 4.68×10^{-7} M, 5.12×10^{-7} M, and 3.26×10^{-6} M, respectively [127]. This enhanced performance was attributed to the strong electron-withdrawing effect of the $–NO_2$ group, which increased –NH acidity and strengthened HB donor ability, leading to more stable N–H·O interactions with oxoanions. Similarly, incorporation of additional HB active groups such as $–CONH_2$ into the thiourea framework increased both the number and directionality of interactions, generating more preorganized binding environments with enhanced affinity toward oxoanions [128].

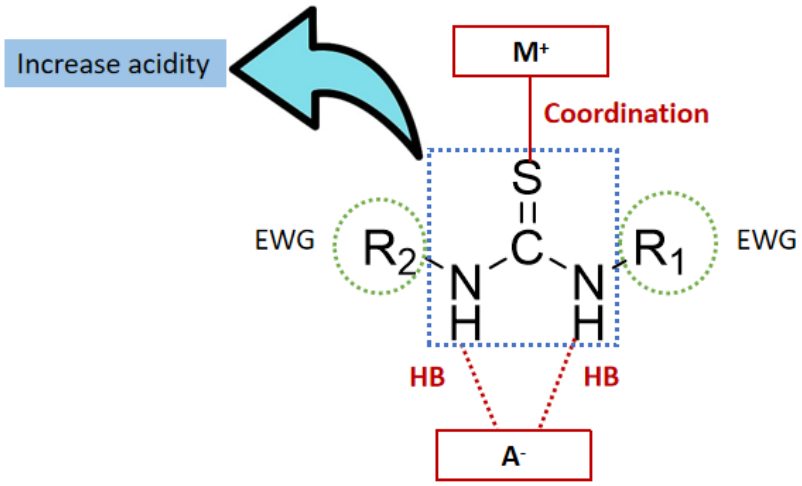

Figure 5. EWG-substituted thiourea framework showing modulation of –NH acidity and dual interaction capability. The C=S group interacts with metal cations (M^+), while –NH groups form HB with anionic species (A^-). EWGs (R_1, R_2) increase –NH acidity, potentially enhancing anion binding. This illustrates a tuneable design strategy for multifunctional sensing.

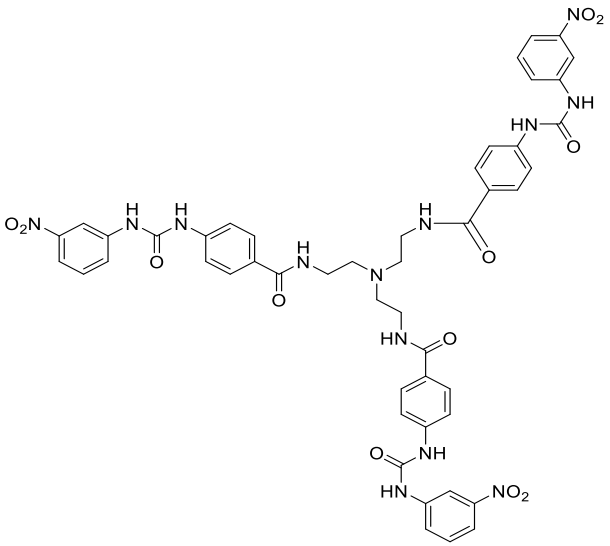

Figure 6. Second-generation amide–urea receptor showing multiple HB donor sites for anion binding. The preorganized framework enables cooperative interactions and improved selectivity toward oxoanions [132].

Receptor geometry also plays a critical role in determining selectivity. Monopodal thiourea receptors, such as 4-nitrophenylthiourea, generally exhibited stronger selectivity toward smaller anions such as F^-, compared to bulkier species including AcO^- and PO_4^{3-} in dimethyl sulfoxide solution [129]. In contrast, dipodal thiourea receptors often displayed reduced selectivity because their flexible conformations permit multiple binding modes and reduced geometric complementarity with tetrahedral oxoanions [130]. Tripodal thiourea receptors, however, provide a more rigid and preorganized three-dimensional cavity that promotes cooperative HB interactions with tetrahedral oxoanions. Such systems have demonstrated selective recognition of SO_4^{2-} and PO_4^{3-} [131], while second-generation amide–thiourea receptors exhibited improved selectivity toward AsO_4^{3-}, through cooperative multidentate HB interactions (Figure 6) [132]. Crystallographic studies further confirmed strong host–guest interactions between the receptor cavity and AsO_4^{3-}, highlighting the importance of geometric complementarity and binding-site preorganization in oxoanion recognition.

Importantly, the practical applicability of these receptors can be further enhanced through immobilisation onto solid supports. For example, thiourea receptors immobilised on TentaGel HBr resin demonstrated visible colorimetric responses (yellow to dark) upon anion binding, highlighting the potential of solid-state thiourea platforms for portable and reusable sensing applications [129]. Nevertheless, most reported thiourea-based oxoanion receptors were evaluated under organic or mixed-solvent conditions. Selective recognition in fully aqueous environments remains considerably more challenging because strong solvent competition and oxoanion hydration weaken HB interactions and reduce binding stability.

Building on these advances, further development of second-generation receptors incorporating both thiourea and complementary HB units, along with electron-withdrawing substituents, represents a promising strategy for enhancing selectivity toward a broader range of tetrahedral oxoanions. To bridge molecular recognition with practical application, these receptors can be immobilized onto polymeric frameworks, enabling multivalent interactions, improved aqueous stability, and dual-function performance as both sensors and adsorbents. Figure 7 presents the schematic design of a second-generation HB receptor functionalized polymer that forms a bifunctional composite that can recognise and absorb tetrahedral oxoanions.

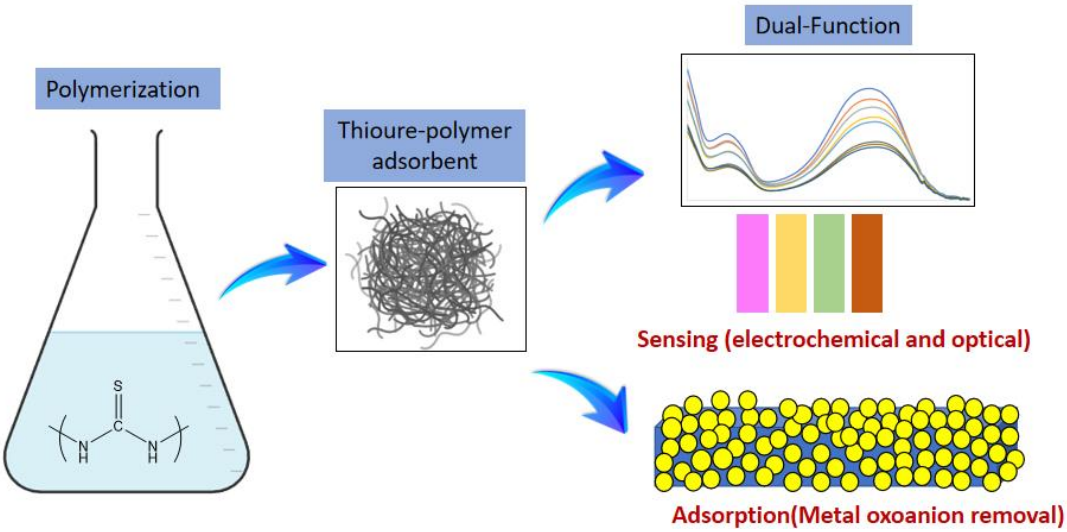

Figure 7. Schematic illustration of thiourea-functionalized polymer design for dual-function sensing and adsorption. Polymerization enables incorporation of thiourea moieties into a polymer backbone, forming a porous adsorbent with accessible binding sites. The thiourea groups provide multivalent interaction sites capable of engaging in HB interactions with tetrahedral oxoanions, supporting both optical/electrochemical sensing and adsorption-driven removal in aqueous systems. This design highlights a multifunctional platform integrating detection and remediation within a single material.

Solid-State Integration

Solid-state integration is crucial for translating thiourea-based systems into practical applications. While many thiourea derivatives have been studied in solution, these systems often suffer from ligand leaching, limited stability, and solvent interference. Immobilisation onto solid supports, such as polymer films, nanofibers, membranes, and electrode surfaces, offers an effective strategy to overcome these limitations.

Solid-supported systems provide enhanced mechanical stability, reusability, and ease of handling. In electrochemical sensing, incorporation of thiourea into electrode materials enables direct signal transduction with improved sensitivity and faster response times. Polymer films and hydrogels further provide high binding-site density and controlled microenvironments that facilitate selective interactions while reducing solvent competition in HB interactions [133]. Additionally, immobilisation minimises ligand loss and enhances durability under continuous operation.

Recent studies highlight the effectiveness of these approaches. For example, chemiresistive sensor arrays based on single-walled carbon nanotubes (SWCNTs) functionalised with thiourea units exhibited high reproducibility and long-term stability due to the presence of well-defined binding sites within the solid matrix [134]. Similarly, polymer-supported thiourea systems showed selective binding toward oxoanions such as $H_2PO_4^-$ and SO_4^{2-} [86]. Covalent attachment of thiourea receptors onto solid supports further preserved binding functionality while enabling reusable sensing interfaces [129].

Despite these advantages, challenges remain in achieving uniform functionalisation, maintaining accessibility of active sites, and ensuring reproducibility during large-scale fabrication. Continued optimisation of material design, fabrication methods, and device integration will be essential for advancing thiourea-based systems toward real-world environment applications.

To further facilitate the translation of thiourea-based materials from laboratory studies to practical applications, the implementation of systematic validation protocols is essential. In this context, Figure 8 presents a recommended validation workflow for thiourea-based sensors and adsorption systems, encompassing key steps from LOD determination in standard solutions, through interference evaluation using multi-ion panels, to validation in real-water matrices. This is followed by assessment of regeneration and recyclability, as well as analysis of leaching and long-term stability. Such a structured framework enables comprehensive performance evaluation under environmentally relevant conditions and supports the development of reliable, stable, and application-ready thiourea-based systems.

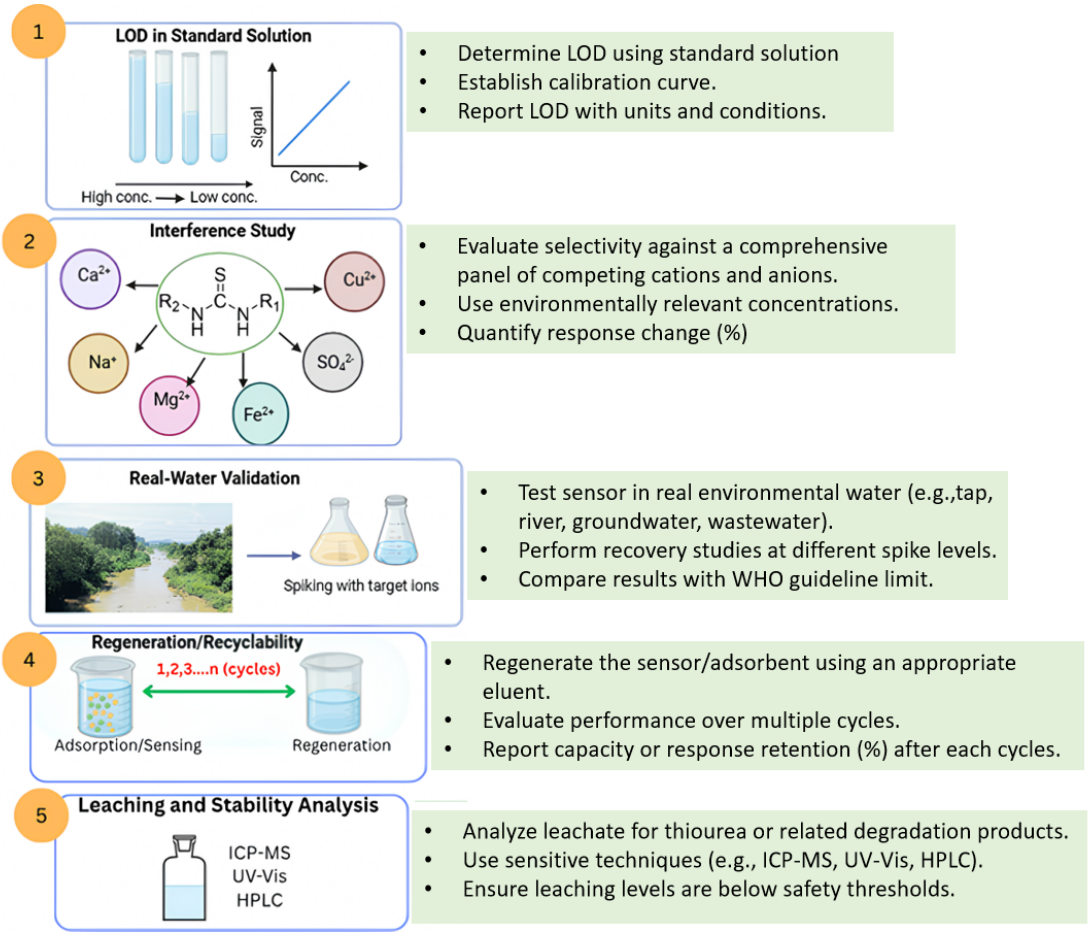

Figure 8. Validation workflow for thiourea-based sensing and adsorption: LOD, selectivity, real-water testing, recyclability, and leaching assessment.

CONCLUSION

This review critically examined recent advances in functional materials for HMI sensing and remediation, with particular emphasis on thiourea-based systems as multifunctional platforms for simultaneous sensing and adsorption. Although significant progress has been achieved, most reported systems were limited to single-function applications, and predominantly designed for cationic metal species under idealized laboratory conditions. Sensing and adsorption performance were governed primarily by donor atom chemistry, binding-site accessibility, and interfacial interaction mechanisms, where sulfur-containing donor groups generally exhibited stronger affinity toward soft and borderline metal ions. Thiourea derivatives are especially promising because the –C=S group enables strong coordination with metal cations, while the –NH group offers potential for HB-driven oxoanion recognition. However, selective oxoanion recognition through the thiourea –NH group remains insufficiently validated in aqueous environments because of solvent competition and hydration effects. In addition, limited real-water validation, insufficient interference studies, and inadequate evaluation of regeneration, stability, and ligand leaching continue to hinder practical application. Future development should therefore focus on multifunctional polymer-supported architectures, preorganized multivalent HB arrays, conductive transducers, and standardized validation workflows under realistic environmental conditions. Overall, thiourea-based materials offer strong potential for the development of next-generation multifunctional platforms for sustainable water monitoring and remediation, in line with SDG 6 and SDG 3.

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CONFLICT OF INTEREST STATEMENT

All authors have read and approved the final manuscript.

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