

Review



Aqueous Adsorption of Heavy Metals on Metal Sulfide Nanomaterials: Synthesis and Application

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Abstract: Heavy metals pollution of aqueous solutions generates considerable concerns as they adversely impact the environment and health of humans. Among the remediation technologies, adsorption with metal sulfide nanomaterials has proven to be a promising strategy due to their cost-effective, environmentally friendly, surface modulational, and amenable properties. Their excellent adsorption characteristics are attributed to the inherently exposed sulfur atoms that interact with heavy metals through various processes. This work presents a comprehensive overview of the sequestration of heavy metals from water using metal sulfide nanomaterials. The common methods of synthesis, the structures, and the supports for metal sulfide nano-adsorbents are accentuated. The adsorption mechanisms and governing conditions and parameters are stressed. Practical heavy metal remediation application in aqueous media using metal sulfide nanomaterials is highlighted, and the existing research gaps are underscored.



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Keywords:** metal sulfide; nanomaterial; adsorption; heavy metal; aqueous media; transition metal sulfide; cationic exchange; surface complexation; electrostatic attraction

1. Introduction

Most heavy metals (HMs) are soft metals classified as chalcophiles, a group of elements with a specific affinity for soft chalcogenides—S, Se, and Te according to the Pearson acid–base concept. This high sulfide affinity for HMs has been exploited with the emergence of multiple metal sulfide adsorbents (MSAs) [1,2].

Most novel metal sulfides (MSs) and their nanocomposites (NCs) have the advantage of being composed of transition metals with outstanding affinities for many HMs. Transition metal sulfides (TMSs) contain numerous surface vacancies, defects, and reactive sites such as metal-edge sites, S-edge sites, and basal plane sites in their structures [3]. These imperfections allow the presence of copious adsorption active sites for removal mechanisms, including direct ion exchange, redox reaction, precipitation, surface complexation, and electrostatic attraction of HM cations that are capable of spanning and populating these interfaces. The novel synthetic MSs or their NCs, in general, are excellent adsorbents of HMs with direct surface activation. They are amenable to fine-tuning for specific properties such as controlling the interlayer spacing and layer thickness through cation exchange [4] and exfoliation/intercalation using suitable polar micromolecular solvent [5–7]. These processes make the MSs capable of capturing hydrated HMs with hydrated radii larger than the layer *d*-spacing of MSs [8]. The affinities for metals are enhanced by enlarging the interlayer spacing, allowing for HMs sequestration via coordination [9,10], and ion exchange [1].

Many reviews have focused on research works conducted on the synthesis, properties, classifications, and applications of metal sulfide nanomaterials (MS-NMs). However, most are based on other applications [3,12,13] rather than removing HMs from aqueous

solutions. Lately, there has been a significant interest in MSAs for HMs removal from aqueous media. This rise is seen in the continuous increase in published papers as per Web of Science Database searches with keywords "metal sulfides and metal adsorption" (Figure 1A) and searching in the results with keywords "water or wastewater" (Figure 1B). Recent advances in the development and subsequent adsorption investigations of MS-NMs decontamination of aqueous media polluted with HMs utilizing adsorption strategies have not been thoroughly reviewed.



Figure 1. (**A**) Publication results in Web of Science using the keywords "Metal sulfide and metal adsorption". (**B**) Publications from searching in the results with keyword "Water and Wastewater".

Hence, this work is a systematic review of the state-of-the-art progress made in HMs sequestration from aqueous solutions by MS-NMs. Therefore, the aim of this review was to explore the application of MS-NMs for HM abatement from aqueous environments under ambient conditions, focusing on three main aspects: (1) MS-NM structures and preparation, (2) adsorption mechanisms and variables affecting adsorption performance of MS-NMs for HMs, and (3) major gaps and potential research requirements.

2. Structures, Preparation, and Supports of MS-NMs

MSs contain atom(s) of metal(s) chemically bonded to atom(s) of sulfur. The arrangement of atoms is critical in determining the structural stability of MSs with close-packed units in their structures. In order words, the bonds/interactions between the atoms and the ensuing structures are crucial in defining the properties of MSs. They account for their robust adsorption capacities and the possibility to enhance their adsorption characteristics further. Since their structures, compositions, and properties can be fine-tuned for meeting HMs' exceptional removal from water, MSs are widely synthesized. Requirements for enhancing the structures of MSs to meet environmentally friendly and cost-effective sequestration of metal pollutants from aqueous media include strategies to transform them into adsorbents of high selectivity, capacity, stability, and excellent recyclability. Traditional methods do not meet all these requirements. Hence, novel techniques have been developed to generate the requisite structures and properties of MSs, especially TMSs, for environmentally friendly abatement of HMs in water.

2.1. Structures

MSs occur with many stoichiometries and structures. The mono-MSs can be categorized as monosulfides (MS), disulfides (MS₂), trisulfides (MS₃), tetra-sulfides (MS₄), metal-rich sulfides (MxSy, x > y), and sulfur-rich sulfides (MxSy, x < y). The various metal sulfides and their examples are shown in Figure 2A. The monosulfides such as ZnS and CdS mainly crystalize in two motifs: the zinc blende structure in which the sulfide atoms pack in a cubic symmetry and the Zn²⁺ ions occupy half of the tetrahedral holes and wurtzite structure with hexagonal crystal symmetry, respectively [14,15]. Some disulfides are typically known for their two-dimensional (2D) layered graphene-shaped nanosheets (NSs) structures which have been utilized for many purposes [16]. The disulfides follow the CdI₂ system (1T phase). In this system, the metals occupy all of the octahedral holes in the alternating layers structures, with the sulfide anions forming a hexagonal close-packed lattice. Other disulfides have the MoS₂ structure with trigonal prismatic structure (2H and 3R phases) [17] depending on the atomic arrangement and interlayer stacking. The 1T, 2H, and 3R phases have one, two, and three sandwich layers, respectively (Figure 2B,C), and are transformable to each other via annealing, exfoliation, or other means [18,19]. While the 1T and 3R phases, which are seldom seen in nature, are metallic because of the migrant electrons, the 2H phase is the naturally found thermodynamically stable semiconductor [20]. Disulfide structures containing two sulfide ions in each of the octahedral interstices in the cubic motif follow the high symmetric pyrite structure [12]. The trisulfide MoS₃ and some metal-rich or sulfur-rich MSs can be layered amorphous substances with many pores in their structures [21–23].



Figure 2. (A) Classification and examples of metal sulfides; (B) structure and (C) three phases of MoS₂. MMS = monometal sulfides; PMS = polymetal sulfides; MS = monosulfides; MS₂ = disulfides; MS₃ = trisulfide; MRS =metal-rich sulfides; SRS = sulfide-rich sulfides; M₁M₂S = ternary sulfide; M₁M₂M₃S = quaternary sulfide. Figure 2B,C were adapted from Xia et al. [24]. Copyright 2018, Elsevier.

Although MSs contain numerous reactive sites [3], the amount of exposed active sites is critical for achieving efficient adsorption. For example, the active S-sites in some MS-NCs are bridging $S_2^{2^-}$ or apical S^{2^-} species, having more electron binding energies than other active sulfide atoms [25]. However, these sites are active only when the S-sites consisting of unsaturated and interfacial S atoms are exposed [5,26]. This observation explains why moderate deposition of exfoliated units on active sites promotes pollutants salvaging from aqueous solutions, unlike excess loading of the units, which completely covers the reactive sites [25]. HM ions can attack the numerous exposed bridging sulfide groups forming the S-edge sites in MS structures, converting them to metal-loaded terminal sulfide groups [27].

In contrast, there exists few bridging S_2^{2-} and apical S^{2-} because of the limited number of unsaturated sulfide atoms in bulk MoS₂ nanocrystals [28]. However, delamination or exfoliation reduces the number of layers and, coupled with the integration of metal elements to raise the number of active S-sites [29], can enhance adsorption. In general, the structural arrangements and imperfections in MS-NMs structures allow for the requisite cations to reside and be attached in these vacancies [30].

For removing HMs from aqueous media, the essential MSs include sulfides of transition metals such as zinc [14,15], copper [31,32], cobalt [21,22], iron [33–35], and cadmium [14,36,37]. MSs contain localized or migratory sulfide 3d electrons or both, exhibiting hybridization with sulfide 3s and 3p orbitals, stabilizing the closest cation neighbors in the trigonal pyramidal, octahedral, tetrahedral, and other configurations in the anion arrays [30,38]. These configurations facilitate the formation of metal–metal and sulfur–sulfur covalent bonds. The increased covalency and polarization may support layered sheet structures with Van der Waals forces between the sheets [3,34,39]. The atomic arrangements in MSs are usually close-packing combinations, governed by ionic size, charge, and electron configuration [30,40]. However, the entire structure may not display a continuous close packing arrangement. A significant number of sulfides show close-packed units (blocks and rods) in groups connected to nearby structures by interfaces with cuts in a dense arrangement of anions faces that are differently oriented [30].

2.2. Synthesis

Several techniques have been introduced to synthesize and control features of MS-NMs and their NCs [3]. Usually, two general strategies are involved: a top-down approach (in which bulk structures are disintegrated into few-layers or monolayer sheets) and bottomup methods (with which the build-up of an NM atom by atom or layer by layer is achieved). While the bottom-up approach's benefits are the low cost, scalability, and better uniformity of the product, the top-down strategy's advantage is its provision of better control. The conventional synthetic methods for producing MSAs generate bulk substances that exhibit inherent limitations, including inert basal planes [41] and low surface areas [42,43]. The novel synthetic technologies have proven to be promising for fabricating MSAs with more exposed active sites and are among the primary preparation methods for generating a wide range of nano-/micro-structured MSAs. In general, the strategies applied in these new synthetic techniques for tuning MSs to achieve required characteristics include surface adjustment, ligand modulation, solvation regulation during crystal formation, and physical grinding. Table 1 presents some of the methods of MS synthesis and their peculiarities.

Table 1. Methods of synthesis of MSs and their merits, demerits, and product quality.

Synthetic Techniques	Merits	Demerits	Product Quality	Reference					
Top to bottom approaches									
Mechanical exfoliation	Facile synthesis	Low productivity	Perfect surface; high crystallinity	[12,44]					
L.P./chemical exfoliation	Facile synthesis with high-yield; generally single-layer products	Strict operating environment; long reaction times	Small size and Few-layers thickness	[3,12,44]					
Ball milling	Low cost, scalable, facile synthesis, relatively low cost, high productivity	Process-induced damages such as irregular shape product	More crystal defects	[45,46]					
Electrospinning	Controlled formation of complex structures; a variety of fiber size (from submicron to nanometer diameters); flexible materials with a variety of functionalities	High temperatures; expensive to produce large diameter and challenging to generate <10 nm diameter fibers	Highly rough surfaces	[12,47]					
Bottom-up techniques									
Chemical vapor deposition	Adjustable thickness; considerable area growth; rapid reaction rate; flexible design and easy incorporation of new technology to existing producing unit	High-temperature requirement; complex process; usually toxic, explosive, corrosive, and costly precursors	High crystal quality	[3,12,44]					
Hydrothermal (solvothermal) synthesis	Easy to operate; ability to synthesize unstable substances near the melting point; large crystals of high quality.	High energy consumption and cost of equipment; relatively long production cycle	Numerous defects	[3,12,44]					
Cation exchange	tuned products; precise control of the NP phase; rapid reaction rates; high yield	Relative high cost of some chemicals	Numerous defects	[12,38]					

2.2.1. Top-Down Approach

These techniques begin with a bulk material that is disintegrated into a few layers or monolayers [48]. In other words, it refers to successively slicing the bulk material into micro-/nano-sized particles. To generate nano-sized structures, the top-down technique requires lateral patterning of bulk materials using either subtractive or additive processes [49].

Therefore, modern top-down NM synthesis methods may be divided into two groups: (1) transferring a computer-generated design to a bigger piece of bulk material and then physically removing material to produce a nanostructure and (2) rearranging or adding components to a substrate [50]. Photolithographic and lithographic methods are the most often used techniques in top-down approaches. Despite their affordability and speed, photolithographic technologies' resolution is limited by optical diffraction. Although lithographic methods enable the creation of ordered nanostructured arrays with high resolution and excellent control over particle shape and spacing, their output is low, and the process is slow when compared to a parallel technique (such as photolithography), which patterns the entire surface at once [50]. In general, the major drawbacks of top-down techniques are the development of high surface finished materials, and longer etching times [49]. For MS-NM synthesis, the process includes physical and chemical routes including electrospinning, ball milling, and exfoliation. These are discussed below.

Mechanical Exfoliation

Sheets or flakes with few defects can be isolated from natural bulk MoS_2 [51,52] and deposited on Si/SiO₂ substrate via the use of adhesive tape, which when released causes the MS to spread on the substrate surface due to the van der Waals forces [12,44]. This method yields thin MoS_2 sheets of layers ranging from 1 to 5 but repeating the procedure yields flakes of different sizes, forms, and layer counts [53]. Despite the NSs obtained from scotch tape exfoliation having a near-perfect surface and high crystallinity, the main disadvantages are poor yield, limited surface defects, and the need to switch to a different substrate for future use [12,44].

LPE

It is known that the surface atoms in bulk solids play subordinate roles during adsorption. In contrast, thin-film MS-NMs have excellent absorption properties [9,10]. MSs in a solution can be exfoliated by mechanical approaches and ionic intercalation (chemical exfoliation) [12]. Exposure to many active sites by exfoliation in multiple layers or a single layer using ultrasonic LPE can easily be done [5]. For example, bulk MoS_x obtained by thermal decomposition of $(NH_4)_2MOS_4$ can be exfoliated in a suitable polar micromolecular solvent into monolayers or individual nanoflakes using ultrasonic radiation [6,7]. This process creates a force greater than the Van der Waals attraction between the layers, causing the bulk structure to crumble and be sliced into single-layer nanotubes that can easily be dispersed in polar micromolecular solvents. The criteria for selecting a surfactant or solvent are based on the similarity between the liquid's surface tension and the absorbent surface's free energy [54]. LPE results in high exfoliation success on materials with low surface energy and can prevent agglomeration of MS NSs [55] in contrast to mechanical exfoliation, where much of the resulting MSs are multilayer structures, which still blocked the efficient active sites in comparison with that in the well-dispersed single-layer structure [3].

The thickness of the single-layer NSs is typically in sub-nanometers, which increases the number of active sites exposed [6]. However, the thickness and sizes may be in a range of sub-nanometers [56]. Therefore, centrifugation at different speeds may be required to obtain more uniform size. Although LPE produces 2D MS NSs on a large scale, creating flakes of various shapes, sizes, and layers compared to other exfoliation techniques, it is a time-consuming process that creates a lower quality product and leaves the original nanostructure preserved after exfoliation [12,44].

During chemical exfoliation or ion intercalation, a solution of Li⁺ ions is mixed with polar micromolecular solvents to destroy the original 2H-MoS₂ (with only active edges) with a trigonal-prismatic structure forming a 1T octahedral filled phase with both active edge and basal sites [57]. The intercalated Li atoms weaken the bonds between MoS₂ layers. Reacting the intercalated lithium-MoS₂ with excess water separates the layers

essentially into monolayers [3,56] but damages the structure of the NSs due to loss of the semiconducting 2H phase during the intercalation [58].

Electrospinning

Electrospinning is a technique for producing nanofibers in which electrical energy is used to make charged filaments from a polymer solution or melt with a fiber diameter of several hundred nanometers. Several MS-NMs have been successfully synthesized using the electrospinning technique [13,39,59]. The treated MS nanofiber has a high surface to volume ratio and high porosity, which makes it versatile in terms of surface properties, excellent mechanical properties, self-standing structure, and stable sulfur and HM interactions, rendering it ideal for use as an absorbent for remediation of HMs in aqueous solution [36]. The supporting material has a significant effect on the properties of the MS-NMs obtained by electrospinning. They may provide excellent structure, morphology, and surface properties leading to outstanding absorption functionalities of the adsorbent [36,60].

Ball Milling

Ball milling is used to synthesize NCs, optimize structural composition, improve material reactivity and uniform spatial distribution of elements through mechanical activation, and prevent the problem of minor admixture formation during air cooling after sintering at high temperatures due to phase instability [61]. This process causes new surface and crystal abnormalities through physical and chemical reactions that change the reaction particles' properties and accelerate the reaction rate [35]. This inexpensive, facile, and scalable mechano-chemical path generates nm-sized hybrids with effective enlargement of the surface area and pore volume [62]. Ball milling induces a rough surface on the synthetic products, which accounts for the high adsorption capacities [33,35].

2.2.2. Bottom-Up Strategy

In bottom-up synthesis approaches, the nanostructures are deposited onto the substrate by assembling atoms generating crystal planes that are further stacked onto each other, leading to the synthesis of the nanostructures. In other words, the building blocks are added to the substrate to form the nanostructures [48]. The most prevalent are bottom-up manufacturing procedures based on the use of a templating substrate, such as chemically or topologically patterned surfaces, inorganic mesoporous structures, and organic supramolecular complexes [50]. This procedure involves the controlled segregation of atoms or molecules with nanostructures (2–10 nm in size) being formed from them. In general, there are two types of bottom-up approaches: synthesis of gaseous and liquid phases, and liquid phase production [49]. Even though bottom-up chemical synthesis has progressed to an astounding level of sophistication, current capacity to produce nanostructured materials from these methods are limited [63]. Some of these approaches as applied to MS-NMs are discussed below.

Cation Exchange

Metal chalcogenides with morphological and structural properties as heterostructures [4,64], the core and shell structures [65], and the metastable phase [66], which are difficult to achieve by conventional synthetic means, are now freely produced by the cation exchange process [38]. Since MS materials have different solubility constants (K_{sp}) in water, they can be transformed via cation exchange into one another. The provision of a selftemplating [67] and easily controllable mechanism to create the multilateral hierarchical structures [68] renders this technique invaluable. MS-NMs can be fabricated readily by inserting the respective metal ions in the precursor MSs synthetic system [15]. The NMs formed by this process are robust adsorbents for HMs remediation, exhibiting high adsorption efficiencies and capacities due to their inherent cation exchange characteristics [69] even in multiple HM polluted aqueous media [15]. The mutual cation exchange properties of HMs can engender their separation via fractional or sequential adsorption on the MS-NMs, with the metal having the most stable sulfide separating first [15]. This fractional or sequential cation exchange could be used to produce MSs in the same order as the manner of their separation. Since ion exchange leads to hollowing or tunneling of solid precursor wires, rods, and spheres without destroying the morphologies and structures [12], the original stability of MSs may be retained in the cation exchange-generated MSs. In general, the cation exchange preparation of MSs is governed by lattice structure stability [70] and defects in the crystal structure [71,72] of the precursor sulfide.

Hydrothermal (Solvothermal) Synthesis

The Hydro-/solvo-thermal technique is used to synthesize a defect-rich product to allow exposure of more active sites. A solvothermal process is a hydrothermal approach with an organic solvent instead of water being used as a precursor solvent. This technique is a simple tool for making MS products with controlled structural properties [73] by reacting the appropriate metal and sulfur precursors under high temperature and pressure conditions. The efficiency of intercalation and stability of the 1T phase of the MoS₂ produced is contingent on the type of solvent used. Li et al. [18] synthesized MoS₂ with the first step using water to produce a 1T/2H mixed phase of MoS₂ consisting of 25% 1T phase and the secondary solvothermal reaction obtaining pure 1T-MoS₂ via ethanol, which was stable in air for over after 360 days and maintaining the same widened interlayer spacing as the MoS₂ mixture.

The percentage of MS-NP detected in the composite may not depend on the amount added during the composite's hydrothermal preparation. Increasing the dosage of precursor only slightly changed the concentration of the core material [74], implying a certain amount of MS-NP may be required to saturate the support after which it is no longer absorbed. Additionally, the hydrothermal design can generate an abundance of unsaturated S atoms in disordered structures and tune the intrinsic adsorption efficiency. MS-NCs with a low surface area may still exhibit high uptake capacity [74], indicating more active sites were introduced by the synthetic method and the support.

Chemical Vapor Deposition

Precursors (usually molybdenum trioxide (MoO₃) or Mo metal and organic sulfides, respectively) containing Mo and S decompose, and the Mo and S atoms then combine via chemical reactions to form a MoS_2 layer on the substrate, usually at temperatures between 700 and 1000 °C, in the Chemical Vapor Deposition (CVD) process [12,54]. However, the temperature range is reduced to 150–300 °C with a modified version of CVD, called the Plasma Enhanced CVD (PECVD) technique, which allows the deposition of NMs on plastic and flexible substrates [75]. NMs prepared by the CVD technique exhibit various tunable properties, including effective control of the active site, thickness, and size during NS growth due to changes in CVD parameters and conditions [44,76,77]. In particular, hydrogen gas is used to accelerate the reaction between sulfide precursors such as diethyl sulfide and Mo precursors, including MoCl₅, and facilitate the formation of single-layer MS-NPs few atoms thick with a large surface area [53,78,79]. Sulfur vapor is rarely composed of one atom, so the flow rate is slow, but with hydrogen sulfide obtained by adding hydrogen, the flow is fast, resulting in the rapid decomposition of sulfur precursors and the formation of MS-NMs with more S defects [3]. Although the NMs synthesized via CVD are crystalline, the complex operational processes limit largescale production [44].

2.3. Functions and Types of Support/Stabilizing Materials for MS-NMs

Due to the inherent difficulties in removing HMs from aqueous media using MSAs, many substances have been studied and utilized as supports or stabilizers to enhance efficient adsorption.

2.3.1. Functions of Support/Stabilizing Materials for MSs

The various supports for core NMs are employed for diverse reasons. However, one primary function of supports for MS-NMs is giving the core material stability in the air. Many MSs, especially FeS, are easily oxidized in the air and consequently require support to limit or prevent the oxidation [34,80,81]. Another critical reason for the use of a support for some nanoparticles of MSs is that they agglomerate rapidly in water, thereby having limited interaction with the targeted HMs [82–84]. Suitable support is usually needed to stabilize them for efficient adsorption in aqueous solutions. A third crucial necessity for adding support to MS-NMs is for the particles to separate from the water quickly without complex filtration or centrifugation systems. This separation is usually accomplished by the use of magnetic support [73,85]. Additionally, most supporting materials contain numerous active sites, and when added to MS-NMs, they synergistically enhanced the adsorption of the HMs [81,86–88].

However, the use of support materials may have some disadvantages. For example, ZVI has the drawback of becoming oxidized readily by aqueous dissolved oxygen, which consumes electrons intended for the target contaminants, resulting in inefficiency [89]. Thus, ZVI becomes an inadequate electron donor, promoting surface iron oxide deposition during the activation of iron (II) ions [90]. Secondly, the addition of support can incur additional costs. The addition of magnetic support to MS-NMs to aid in the easy separation of adsorbent from water may be cost-intensive for largescale applications. Additionally, the support may interfere with the adsorption process, limiting removal efficiency [34].

2.3.2. Types of Supporting Materials

In general, all supporting materials for MSAs can be classified as either organic or inorganic.

Organic Support

Organic supports or stabilizers are abundantly used in NCs due to their many advantages. They usually contain smaller micropore volume, higher specific surface area, abundant functional groups and are low cost [81,86–88]. These supporting materials generally have the merits of excellent water stability and high mechanical strength [91,92], making them invaluable to the adsorption process. Some are noted for their biodegradability, non-toxicity, abundant source, [86], an excellent affinity for HM [93], and are modification coats for metal NPs in preventing aggregation [83,84]. Notable organic supports for MSs includes biochar [88], chitosan [91], and carboxymethylcellulose CMC [92]. In most cases, the organic supports serve as a substrate for the MS NPs to be deposited on or can be used to coat the surface of the adsorbents via the various preparation methods.

Inorganic Support

In general, inorganic supports show excellent thermal, chemical, and mechanical stabilities. For MSs, the most prominent inorganic supports include carbon materials, ZVI, and metal oxides. The carbon materials may consist of graphene oxide and other carbon NMs such as carbon nanotubes and nanofibers. Based on their outstanding surface, mechanical, thermal, and optical properties, carbon NMs are widely utilized in many fields, including environmental remediation, energy generation, and water treatment. Inorganic carbon NMs generally exhibit high mechanical strength and thermal stability for MS-base materials, providing mechanic supports to prevent aggregation [74,94]. ZVI adsorbents, on the other hand, have many advantages, including low solid waste product, in situ application, robust removal efficiency independent of changes in the quantity of water treated [95], and safe, environmentally sustainable, and cost-effectiveness for HM species [96,97]. Hence, ZVI can be successfully employed to activate and serve as support for FeS. The primary metal oxides used as supports for MSs include SiO₂, Al₂O₃, and Fe₃O₄. SiO₂ amorphous NMs are used to support MSs due to their high porosity, large surface area, stable structure, and flexibility [60], which ensure immobilization, longevity,

and high recovery. Besides its porous structure and high stability, Al_2O_3 exhibits strong chemical and thermal stability, rendering it suitable for preventing MS aggregation and oxidation [82]. Although Fe₃O₄ adsorbents show high adsorption efficiencies, their major significance is their ability to separate easily from the supernatant after adsorption on their own or via the application of external magnetic fields [73,85].

3. Motivations for Choosing MS-NMs over Bulk Materials and Their HM Adsorption Mechanism

3.1. Motivations for Choosing MS-NMs over Bulk Materials for HM Removal from Water

NMs, which have a particle size range of 1 nm to 100 nm, have been employed to overcome the shortcomings of conventional adsorbents in recent decades [98]. Recently, MS-NMs have been used in environmental remediation. They have been used to remove contaminants like dyes [99], heavy metals [62], pharmaceuticals [81], and radionuclides [80]. However, due of the inherent drawbacks of bulk materials, nanosized materials are receiving a lot of attention. Due to their fine particle size, large surface area, high surface–to-volume ratios, robust sensitivity and reactivity, high adsorption capacity, ease of functionalization, and regulated deliverability, nanoparticles including MS-NMs have shown tremendous promise for treating polluted aquatic systems as compared to bulk particles [82,100]. The binding of inorganic shells and organic molecules to the surface of MS-NMs stabilizes and inhibits the oxidation of nanoparticles [49]. Nanosized MS particles can be composited with other NMs such as carboxymethyl cellulose (CMC) [101], chitosan [91], carbon NMs [102], biochar [87] and ZVI [33] to form NCs with highly improved adsorption functionalities. Most of these supporting structures are locally available, cheap and abundant, and render their MS-NCs inexpensive [86].

NMs are efficient and cost-effective for the fast removal and recovery of metal ions from wastewater effluents due to their large surface areas and excellent magnetic characteristics [49]. The careful balance between the energy from the polar charges, surface area, and elastic deformation results in the diverse shapes and morphologies crucial to the characteristics and efficiency of MS-NMs [82]. Furthermore, the surface functions give locations for the absorption of particular or selective ions, hence improving their removal efficiency [98].

3.2. Adsorption Mechanisms of HMs on MS-NMs

The adsorption process of HMs on MS-NMs ensues via physical and chemical interactions between an adsorbent and an adsorbate and are modified by the reactive environment [33,87,102]. Ionic or covalent bonds form during chemical adsorption, making the process exceedingly specific. Monolayer adsorption will arise from the irreversible chemical interaction [103]. Contrastingly, the physical process involves weak Van der Waals forces between the adsorbate and the adsorbent in a reversible process [103]. Physical adsorption may involve monolayer or multilayer deposition, which is not specific. Some of the specific adsorption mechanisms that explain the attachment of metal ions to NMs include redox reaction, complexation, intraparticle diffusion, surface adsorption, precipitation, electrostatic interaction, and ion exchange and are illustrated in Figure 3.

Based on their redox potentials, distinct HMs' adsorption mechanisms on MS-NMs may be classified as adsorptive removal or redox removal [44]. The adsorptive mechanisms dominate when the heavy metal redox couples are lower than that of MoO_4^{2-} and SO_4^{2-}/MoS_2 pair [58,104]. Otherwise, the adsorption follows redox or adsorptive removal. The process is seen in Figure 4B. MS-NMs could be oxidized via electron loss, which are involved in the reduction of the HMs [105]. The process is illustrated for the adsorption of Ag⁺ by MoS₂ nanosheets in Figure 4A. The adsorption of Cr⁶⁺ from water by reduction to Cr³⁺ by MS-NMs is a classic example of redox removal of HMs by MS-NMs. The adsorption follows the equations such as: $HCrO_4^{-} + 6H^+ + 3e^- \leftrightarrow [Cr(OH)]^{2+} + 3H_2O$ as chromium is usually found as oxyanions in these solutions.



Figure 3. Various adsorption mechanisms of metal ion adsorbate on metal sulfide nanoparticle (MN-NP).

To fully comprehend the mechanism of heavy metals adsorption on MS-NMs, adsorption isotherms, kinetics, and thermodynamics may all be employed. The chemical composition and properties of the material appear to impact adsorption processes on nanoadsorbents. Besides, parameters such as solution pH, initial HM concentration, and contact time have an impact on the adsorption process. These parameters and the specific adsorption mechanisms of HM adsorption on MS-NMs are discussed in detail in the next section.



Figure 4. Schematic illustration of HM adsorption mechanism on MS-NMs (**A**) Ag⁺ adsorption and reduction by MoS_2 nanosheets, reproduced with permission from ref. [105], Copyright 2018, American Chemical Society and (**B**) comparison of reduction potentials of MoO_4^{2-} and SO_4^{2-}/MoS_2 with other pairs common in HM remediation and antioxidation, reproduced with permission from ref. [105], Copyright 2018, American Chemical Society.

4. Application of HMs Sequestration with Selected MS-NMs

Among the MS-NMs, the TMSs are the most prominent used for HM sequestration in recent years. For this reason, this section discusses MS-NM removal of HMs from contaminated water via adsorption processes with TMSs as the archetypal examples.

4.1. Iron Sulfides

FeS adsorbents have emerged as promising materials for a wide range of applications, including removing HMs from water. The main disadvantage of using FeS in situ is particle aggregation, resulting in reduced mobility and reactivity, limiting its direct use in field applications [82]. The agglomeration is due to the magnetic interactions of iron-based materials NPs [87]. The practical application of FeS in the absorption of HMs is also inhibited by rapid oxidation under atmospheric conditions [80]. Various support materials (or stabilizers) have been used to modify the surface of FeS nanoparticles (NPs) to limit inherent shortcomings and to improve their adsorption properties in removing HMs from aqueous solutions (Figure 5A,B and Table 2). The supporting materials used for FeS include biochar [87], plant extract [81], NaBH₄ [34], and others to reduce particle agglomeration

and oxidation and increase recovery efficiency. However, some supports may reduce the removal efficiency of the adsorbent [34]; therefore, suitable materials that do not adversely affect adsorption efficiency are required.



Figure 5. The modified methods of nano-sized FeS particles: (**A**) modification by coating stabilizers and (**B**) modification by physicochemical loading. Adapted and modified from Chen et al. [106], Copyright 2019, Elsevier.

The solution parameters and conditions determine metal adsorption on FeS. The surface charge of the composite and the species distribution of the pollutants, for example, are influenced by pH, as are the rate and capacity of most FeS adsorption [107]. The exact dependence on pH is contingent on the nature of the adsorbent and adsorbate and the parameters and conditions in which adsorption occurs. This phenomenon can be demonstrated by considering the zero point of charge (ZPC), the pH at which the total charge on the adsorbent is zero. Chemical species in FeS NCs are significant in determining the total charge on the adsorbents' surfaces. In aqueous media, this pH is unique to the cations to which the surface oxygen atoms are bound [108]. The opposite charges on pH at different sides of the ZPC become more pronounced farther away from the ZPC, impacting the recovery process. For example, Cr (VI) adsorption efficiency on FeS is high at pH below the ZPC due to the electrostatic attraction of the dominant-negative Cr (VI) oxyanions in the solution to the positive surface of the FeS. However, the removal is reduced at higher pH due to Coulombic repulsion between the anions and the negative FeS surface [62,87].

The specific surface area of adsorption of FeS NPs is greater than those of many other NPs. It is crucial for divalent HM removal from water [109] and offers more active sites in bulk particles [106]. FeS adsorption of divalent HMs may occur by chemical precipitation [105], surface complexation [110,111], and ion exchange [110]. These three processes may occur concurrently [112]. Divalent HMs can also be adsorbed on FeS by chemical coprecipitation and subsequent oxidation reactions [113]. The high HM adsorption is due to HM-S's formation from the dissolution of S₂^{2–} from FeS, caused by the loss of electrons from the Fe.

Support	Effect of Support	HM [I0 (mg/L)]	Ads.Dose (g/L)	% Rem.	Max. Ads. Cap. (mg/g)	SSA (m²/g)	Adsorption Mechanism	pН	Reference
ZVI and PS	Increase recovery rate	Cr ⁶⁺ (35)	0.50	97.0	67.9	19.5	Electrostatic attraction and redox reaction	3–9	[62]
СМ	Prevents iron leaching	Hg ²⁺ (40)	0.33	85.8	104 ^a	72–278	Chemical and physical adsorption	6.5	[102]
СМС	Stabilizes FeS	Cd ²⁺ (1)	0.10	93.0	497.5 mg/L ^b	44.5	Precipitation and surface complexation	7.0	[92]
Date seed extract	Reduces iron sulfate and stabilize FeS	Cr ⁶⁺ (4.5)	0.5	97.0	8.50	51.0	Redox reaction and precipitation	7.0	[80]
Biochar	Provides functional groups	Cr ⁶⁺ (20)	0.80	93.0	23.25	17.6	Electrostatic attraction and redox reaction	5.2	[87]
СМС	Stabilizes FeS	Pb ²⁺ (5.0)	0.05	98.0	77.0	-	Surface complexation and precipitation	7.0	[101]
ZVI	Activates FeS	Sb ⁵⁺ (100)	0.5	≥99.18	214.0	1.65	Chemisorption	2.6-10.6	[33]
ZVI	Activates FeS	As^{3+} As^{5+} (100)	2.0	94.5 (89.3)	101 ^c 58.3 L/mg ^d	-	Surface complexation	3–10	[35]
Chitosan	Stabilizes FeS and provides functional groups	Cr ⁶⁺ /Cr ³⁺ (50)	2.0	90 (total Cr)	119	14.1	Redox reaction, surface complexation and precipitation	3.0	[91]
NaBH ₄	Limits FeS oxidation in air	Cr^{6+} (50) As^{5+} (100)	0.1 1.0	70 56	350 28	-	Redox reaction and precipitation Surface complexation	7.0	[34]
rGO	Stabilizes Fe ₃ S ₄	Pb ²⁺	0.75	99.5	285.7	80.96	Precipitation and surface adsorption	3–6	[94]

Table 2. Support materials, adsor	ption characteristics, and	parameters of some MS NCs.
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 I_0 = initial concentration; ZVI = zero valent iron; PS = peroxydisulfate; CM = carbon micropores; CMC = carboxymethyl cellulose; rGO = reduced graphene oxide; Max. = maximum; ads = adsorption; cap. = capacity; SSA = specific surface area; ^a equilibrium sorption capacity; ^{b & c}Langmuir sorption capacity; ^d calculated from Freundlich isotherm model.

The above results are according to the nature of the intermolecular adsorbate-adsorbent bonds. Both chemical and physical adsorptions ensue during the removal of HMs from an aqueous solution by FeS. In other words, adsorption at the solid–liquid interface follows several mechanisms: ion exchange, electrostatic attraction, hydrophobic bonding, hydrogen bond, surface adsorption, and Van der Waals force [114]. Chen et al. [106] summarized the adsorption mechanisms of FeS NPs or NCs as generally occurring in the form of (1) surface adsorption or complexation due to interactions between the FeS and the pollutants and (2) chemical reactions such as precipitation or ion exchange, especially for the divalent HMs. For example, the adsorption kinetics of FeS NMs for divalent Pb²⁺ is fast due to soft-soft interactions, leading to Pb-S bonds' easy formation and surface adsorption [94]. However, surface complexation between the FeS and Pb (II) also ensues at the surface of FeS NCs [100]. Cr (VI) adsorption is usually achieved due to surface adsorption [62,91] and redox reaction in which Cr (VI) is reduced to Cr (III), and Fe (II) is oxidized to Fe (III), forming mixed iron-chromium oxides/hydroxides [34,62,82,91].

4.2. Zinc Sulfide

The scope of ZnS NMs has widened in recent years, with various toxins recovered from aqueous media using ZnS and its NCs. The adsorption capacity of ZnS NMs is high, and their kinetics are fast. The adsorption capacity of NMs is determined by a range of factors, including the NM's size [69]. For example, Yan et al. [88] found that a thinner sorbent exhibits a faster reaction rate, which was explained by the fact that the reaction time is roughly proportional to the square of the size. This observation was accentuated by Xu et al. [69] using ZnS NCs in recovering Cu²⁺ from water. It was observed that the samples of sizes 20–30 nm, 30–40 nm, and 50–65 nm showed zinc–copper exchange rates of about 98.7%, 97.0%, and 38.5% and surface areas of $15.9 \text{ m}^2/\text{g}$, $13.8 \text{ m}^2/\text{g}$, and $9.5 \text{ m}^2/\text{g}$, respectively. Larger particle agglomerates reduce surface area and adsorption capacity. On the other hand, the chelation of sulfur and HM ions on the particle surface, rather than the ion exchange effect, is responsible for decreasing capacity with increasing NP size [115]. The finer ZnS NPs generate tremendous surface energy leading to a more significant number of coordination vacancies of sulfur atoms on the surface, resulting in a high adsorption capacity. Table 3 shows the primary mechanism, size, and other information relevant to the adsorption of HMs with ZnS NMs.

Adsorbent	Size (nm)	HM	Max. Ads. Cap. and/or Removal Efficiency	Main Ads. Mechanism	Reference
ZnS/alpha-Al ₂ O ₃	20–25	$Hg^{2+}, Cu^{2+}, Pb^{2+}, Pb^{2+}, Cd^{2+}$	99.9% 99.9% 90.8% 66.3%	Cation exchange	[15]
ZnDTC/ZnS	1–2	Cr ⁶⁺	73.2 mg/g; 99.9%	Cation exchange	[115]
Fe ₃ O ₄ @ZnS	750	Pb ²⁺	272 mg/g; 91%	Chemisorption	[85]
Cu/ZnS	9.0	Co ²⁺ Ni ²⁺	57.0 mg/g 53.1 mg/g	Electrostatic attraction	[116]
ZnO/ZnS/biochar	51.6–69.0 (ZnO + ZnS)	Pb ²⁺ Cu ²⁺ Cr ⁶⁺	135.8 mg/g 91.2 mg/g 24.5 mg/g	Surface complexation	[117]
ZnS NPs	-	Cd ²⁺	401 mg/g; >99%	Precipitation	[118]
Biochar/ZnS	7–8	Pb ²⁺	368 mg/g	-	[88]
Dioxa-dithio /ZnS	33	Pb ²⁺	99.6%	Surface complexation Electrostatic attraction	[119]
ZnS/alpha-Al ₂ O ₃	20–30 30–40 50–65	Cu ²⁺	650 mg/g; 98.7% 97.0% 38.5%	Cation exchange	[69]
ZnS/ODA	Length: 5 Diameter: 1.2	Fe ²⁺ Fe ³⁺ Pb ²⁺	-	Cation exchange Surface complexation Precipitation	[120]

Table 3. HM removal characteristics with ZnS NMs.

Max. = maximum; ads. = adsorption; cap. = capacity; ODA = oxydiacetate.

The mechanism of HM removal from water with ZnS NCs is generally described as a cationic exchange between the metallic pollutant and the zinc in the adsorbent (Table 3). Cation exchange in water treatment involves removing one or more undesirable cationic contaminants by exchange with another non-objectionable or less objectionable cationic substance. The cation exchange is contingent on the size and charge of the pollutant cations, a fixed ionic charge on a supporting material, the permeability of the material to a solution, the structure of the entire composite, and the stability of the resulting product after adsorption. Divalent HMs exhibited cation exchange on ZnS NCs with the metal with the more stable sulfide separating first [15]. For Cu²⁺, the process can be attributed to its similar size and charge as zinc. In contrast, Hg²⁺, Pb²⁺, and Cd²⁺ ions are a little larger than Zn^{2+} ; therefore, the exchange may be due to the ZnS structure's stability and flexibility that allow these ions in the crystal lattice without disintegrating. However, cation-exchange seems to be a more effective mechanism for ZnS adsorbents when there is reasonable charge and radii compatibility between Zn^{2+} and the HM and when NPs of $Zn_{1-x}M_xS$ (M is a divalent HM) develop after adsorption rather than when the pollutant MS is formed [15,69,120].

However, the removal of HMs by ZnS NCs cannot always be explained by cation exchange. Li et al. [117] observed that surface complexation with HMs via hydroxyl ions formation could be responsible for the adsorption of several HMs on ZnS as it is in line with the Freundlich model for heterogeneous adsorbents [117,120]. Further, HMs having mismatch charges or sizes as zinc are usually adsorbed on ZnS NCs via means other than cation exchange (Table 3). For instance, Malakar et al. [115] observed that although cation exchange could explain the removal of Fe^{2+} by wurtzite ZnS nanorods in aqueous solution, Fe^{3+} favors attachment to the S^{2-} and surface complexation forming β -FeOOH oxyhydroxide phases as cation exchange would be energetically unstable due to charge mismatch. Mismatch of sizes between Zn²⁺ (0.785 A°) and Pb²⁺ (1.33 A°) hinders effective ion exchange, rendering removal of Pb²⁺ pollutant from water in the form of PbS precipitation. Electrostatic attraction can also account for the removal of HMs from water by ZnS. It was reported that nano-sized ZnS functionalized with dioxadithio ligands exhibited a negative surface charge at pH 6, where adsorption of Pb²⁺ was maximum [119]. This phenomenon can be explained by assuming electrostatic attraction between the Pb²⁺ ions and the adsorbent's negatively charged surface.

ZnS NCs often have a higher adsorption capacity and are more stable than similar FeS NCs. Wang et al. [118] investigated Cd²⁺ adsorption with FeS and ZnS, observing that FeS and ZnS had adsorption capacities of 116 and 401 mg/g for Cd²⁺, respectively. While ZnS takes longer to reach equilibrium, it has a more effective and stable removal effect. The higher capacity of zinc sulfide may be partly because of the ease with which zinc ($E^0 = -0.763$) can undergo cation exchange and other interactions with HMs via electrons transfer due to it being a more reactive metal than iron ($E^0 = -0.440$). For practical applications in engineered remediation, a low re-release rate of contaminants and high chemical stability are required [118]. With ZnS, no significant amount of captured Cd²⁺ was released after shaking with ultra-pure water for 24 h the and aged ZnS could still achieve >80% removal efficiency of Cd²⁺, significantly greater than those achieved by FeS.

4.3. Molybdenum Sulfides

Two-dimensional layered MoS_2 is an archetypical transition metal dichalcogenide (TMD) material rich in sulfur and has become one of the most popular NMs due to its outstanding optical, electronic, and environmental remediation properties. The adsorption mechanism of HMs on most MoS_2 NMs follows the pseudo-first-order kinetics and the Langmuir isotherm indicating single-layer adsorption/chemisorption. However, the specific adsorption mechanism and high capacity of MoS_2 for HMs are generally attributed to ion exchange, complexation, and electrostatic interaction with the formation of HM-S complex due to the abundant sorption sites on the surface of MoS_2 (Table 4). Since MoS_2 NSs typically have a negative surface charge with H⁺ or Li⁺ as a counterion, the first

possible adsorption process is ion exchange, which leads to metal-sulfur bonding [121,122]. The second primary mechanism is considered to be complexation. Hg^{2+} ions can replace H^+ ions to form complexes with one or two sulfur atoms at high or low Hg-to-MoS₂ ratios. Another potential mechanism is the electrostatic attraction in the outer layer [123]. It is not infrequent for more than one of these adsorption processes to occur concurrently with the same MoS₂ NC [124]. An analysis of the adsorption mechanism showed that the increased Pb (II) removal on the surface of MoS₂ is due to electrostatic interaction, surface diffusion, and the formation of PbMoO₄ on the surface of the adsorbent [125]. The complexation of S with HMs is a key adsorption mechanism of MSs and is controlled by the HM's concentration. For instance, when deficient, Hg^{2+} forms complexes with two S atoms but combines with a single S atom in abundance relative to MoS₂ [9].

Adsorbent	НМ	pН	Co-Existing Ions/Effect	% Rem.	Specific Ads. Mechanism	Kinetic Model/Isotherm	Ref
2D amorphous MoS ₃	$\begin{array}{c}Cu^{2+}\\Cd^{2+}\\Hg^{2+}\end{array}$	6.0	Al ₃ ⁺ , Fe ²⁺ Mg ²⁺ , Ca ²⁺ (% rem. of HM still >90 after 4 cycles)	>99.5	Single-layer adsorption	PSO/Langmuir	[25]
C@MoS ₂ /MMT	Pb ²⁺	6.0	Cu ²⁺ , Cd ²⁺ , Zn ²⁺ , Cr ⁶⁺ (CI have little effect)	>95.0	Electrostatic interaction, surface diffusion and formation of PbMoO4.	PSO/Langmuir	[125]
MoS ₂ /CTAB	Cr ⁶⁺ Ni ²⁺	7.0	$\begin{array}{c} \mathrm{SiO_3^{2-}, SO_4^{2-}, CO_3^{2-},}\\ \mathrm{Mg^{2+}, Ca^{2+}, Na^{2+}} \ (\mathrm{CI} \ \mathrm{have}\\ \mathrm{no} \ \mathrm{effects} \ \mathrm{on} \ \mathrm{Cr^{6+}}\\ \mathrm{adsorption} \ \mathrm{but} \ \mathrm{affected}\\ \mathrm{the} \ \mathrm{Ni^{2+}} \ \mathrm{removal}\\ \mathrm{significantly}) \end{array}$	>99.9	Redox reaction; Electrostatic attraction and outer surface complexation	PSO/Langmuir	[126]
P-PVDF/MoS ₂	Hg ²⁺	4.5-6.0	Pb ² , Cu ²⁺ , Cd ²⁺ , Hg ²⁺ , SO ₄ ²⁻ CH ₃ COO ⁻ , H ₂ PO ₄ ⁻ , Cl ⁻ , NO ₃ ⁻ (little effect: <3% fall in rem. rate)	>95.0	Chelation and precipitation	PSO/Langmuir	[127]
1T-MoS ₂	Cr ⁶⁺	6.0	Na ⁺ , K ⁺ , Cu ²⁺ , Mg ²⁺ , Ca ²⁺ , SO ₄ ²⁻ CO ₃ ²⁻ , Cl ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , AsO ₃ ⁻ (no effect)	>99.9	Redox rxn	PSO/Langmuir	[18]
Ultrathin MoS ₂	$\begin{array}{c} Cd^{2+}\\ Cu^{2+}\\ Ag^{+} \end{array}$	6.0	-	185.2 ^a 169.5 70.4	Physical hole-filling effects and electrostatic interactions	PSO/Langmuir	[128]
MoS ₂ /Fe ₃ O ₄	Hg ²⁺	5.0	Cu^{2+} , Cd^{2+} , Zn^{2+} , Mg^{2+} (little effect only on Pb^{2+})	>99.9	Soft–soft interaction cation exchange and electrostatic interaction	PSO/Langmuir	[124]
A500-MoS ₄	Pb ²⁺ Hg ²⁺	5.0	Na ⁺ , Cu ²⁺ , Mg ²⁺ , Ca ²⁺ (CI have no effect at pH < 1)	>99.5	Soft-soft interaction	PSO/Langmuir	[129]
MoS ₂ NSs	U ⁶⁺ Th ⁴⁺	>7.5 6.0	$Na^+, K^+, Mg^{2+}, ClO_4^-, Cl^-, NO_3^-$ (Effects of CI are significantly higher on U^{6+} than on Th^{4+})	492.72 ^ь 454.72	Electrostatic interaction/inner- sphere surface complexation	PSO/Freundlich	[130]
D-MoS ₂	Cr ⁶⁺	6.0	$\begin{array}{c} SO_4{}^{2-}, CI^-, NO_3{}^{-,} \\ H_2PO_4{}^-, Na^+, Cu^{2+}, Mg^{2+}, \\ Ca^{2+}, Ni^{2+} (No effects, \\ except for highly \\ concentrated Cu^{2+} which \\ lowers Cr^{6+} rem.) \end{array}$	>99.9	Electrostatic interaction and redox rxn	PSO/Langmuir	[131]

 $\label{eq:remain} \begin{array}{l} \text{Rem} = \text{remain}; \mbox{CI} = \mbox{co-existing ion}; \mbox{CTAB} = \mbox{cetyl trimethyl ammonium bromide}; \mbox{PSO} = \mbox{pseudo second-order}; \mbox{P-PVDF} = \mbox{polyvinylidene} \\ \mbox{fluoride polymer matrix}; \mbox{C@MoS}_2/\mbox{MMT} = \mbox{carbonized glucose} \mbox{MoS}_2/\mbox{montmorillonite}; \mbox{D-A500-MoS}_2 = \mbox{anion resin based amorphous} \\ \mbox{molybdenum sulfide composite}; \mbox{MoS}_2 = \mbox{defect-rich} \mbox{MoS}_2; \mbox{rxn} = \mbox{reaction}; \mbox{NS} = \mbox{nanosheet}; \mbox{adsorption capacity in mg/g}. \end{array}$

Both inner and outer surface complexation have been reported with HM removal on MoS_2 NCs and can be indicated by how strongly the sorption is influenced by pH and ionic strength. When the sorption is strongly affected by pH but not by the ionic strength, the sorption mechanism is predominantly inner-sphere surface complexation; conversely, outer-sphere surface complexation or ion exchange preponderates with the opposite case [132,133].

Li et al. [130] reported that ionic strength had little effect on sorption, implying that inner-sphere surface complexation dominated the sorption processes for the adsorption of U (VI) and Th (IV) on the surface of MoS_2 . On the other hand, outer-sphere complexation may be more responsive to ionic strength fluctuations since the background electrolyte ions are placed in the same plane for outer-sphere complexes [58]. Ionic strength affects the double layer's thickness and the interface potential, influencing the binding of the adsorbed species [134]. Others reported the outer-sphere surface process as the dominant adsorption mechanism for removing HMs from aqueous media using MoS_2 [60,126]. Besides, complexation occurs with the replacement of S atoms by the surface O atoms, which can serve as surface binding sites for HMs [135]. The oxygen-containing groups on the surface of MoS_2 increase with a rise in pH [130]. The increased removal efficiency can be attributed to the robust complexation between the HMs and the oxygen atom [136].

While inner layer chemical complexation may substantially reduce the negative surface charge of MoS_2 and render electrostatic attraction a minor adsorption mechanism [121,137], the latter interaction can still play a significant role in the adsorption of HMs, especially with those that are unable of complexing with MoS_2 [123]. Even with HMs capable of forming complexes with MoS_2 , electrostatic attraction can explain the experimental adsorption capacities that are higher than the theoretical values. Jia et al. [121] confirmed multilayer adsorption of Hg^{2+} from aqueous solution using MoS_2 besides the inner layer complexation that occurred, indicating an attraction of the positive ions to the negative surface of the adsorbent. The specific surface area of sorbents and the interaction between adsorbents and adsorbates affect the sorption capacity, while the rate of water-soluble ions and the degree of electrostatic interaction may be contingent on the strength/value of the surface charge of the sorbent [128]. Increasing the quantity of MoS_2 in the MoS_2 NC increases the adsorbent's negative surface charge and the adsorption capacity [138]. However, the surface area of MoS_2 NC decreased as the wt.% of MoS_2 increased, indicating that the predominant adsorption mechanism was electrostatic interaction.

Additionally, the electrostatic interaction is generally pH-dependent and governed by ionic strength. Due to the elevated negative charges on MoS_2 , there is a more significant electrostatic interaction between MoS_2 and HMs at higher pH, resulting in a rise of HM adsorption. Electrostatic interactions may be responsible for the pH-dependent Cr (VI) on MoS_2 and are the results of protonation and deprotonation of the sorbent surface [126]. This observation is partly validated by the robust effect of ionic strength on the adsorption. The beneficial effects of high ionic strength may be attributed to more efficient shielding of heavily charged surface complexes. A critical Cr (VI)–Cr (VI) intermolecular electrostatic repulsion force exists. However, improved charge shielding at high ionic strength will reduce electrostatic repulsion, resulting in increased Cr (VI) recovery [126]. The adsorption capacity may also be affected by the HM ions' charge values related to the strength of the electrostatic activity between the adsorbate and the adsorbent. With MoS_2 NS, the adsorption capacity of Ag⁺ was much lower than those of Cu²⁺ and Cd²⁺ [128].

MoS₂ has a significant number of available adsorption sites due to its peculiar 2D structure and excess of exposed sulfur atoms and hence has an excellent HM ion removal capacity in water [9,121,123,126,128,130,137,139]. The same sorbent material having different synthetic techniques exhibits different sorption performance for the same adsorbate since the sorbent will have different characteristics such as structures, morphologies, adsorption sites, and thicknesses. However, efficient removal of pollutants from water by adsorption requires optimization of parameters and conditions governing the adsorption process. For example, while rising pH amplifies the negative charges on the surface of MoS₂, a strongly alkaline solution would engender the formation of HM-OH complexes [140,141], reducing the adsorption efficiency of the sorbent. As a result, HM ion adsorption's optimum pH on MoS₂ is found in the range of 4.5–7.5 (Table 4) [126–128,130,139]. Interestingly, the highest limit of around pH 8 may be general for MS-NMs because of the same reason.

Another critical parameter, the time required for arriving at equilibrium (equilibrium contact time), depends on the adsorbent's nature and the adsorbate's concentration. With increasing contact time, the initial rapid increase in removal efficiency of HMs on MoS_2 NCs [84,121,122,124,128,130] can be attributed to abundant vacant adsorbent sites and high solute concentration gradient before equilibrium. The flattening shape of the removal efficiency curve with time could indicate reduced active sites just before equilibrium and a possible HM monolayer deposition on the outer surface with HM diffusion through this coating into the internal cavity of MoS_2 particles. The suggestion of chemisorption being the controlling mechanism is validated by the pseudo-second-order kinetic model's better agreement with most of the studies' experimental data (Table 4).

One of the most crucial process parameters under actual conditions at a watertreatment plant is the adsorbent selectivity. Co-existing ions in the water limit adsorption capacity for HMs removal significantly on adsorbents' active sites. The adverse effect is caused by the competition between the HMs and other ions in the water for the active adsorption sites at the increased ionic strength [142]. Interestingly, MoS₂ can efficiently adsorb various cations and anions of HMs depending on the adsorption conditions [124], [126,130,131]. The effects of various anions and cations on the adsorption of HMs on MoS₂ are shown in Table 4. However, the robust selectivity of MoS₂ towards the HMs and resistance to these foreign ions (strong acids and bases) agrees with the Pearson acid-base concept, i.e., the degree of resistance is proportional to the Pearson hardness of the ions. Chalcophiles exhibit differing affinities for chalcogenides, which may lead to varying adsorption capacities of MoS₂ for HMs depending on the metals' degree of softness. For example, $Hg^{2+} > Pb^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}$ represents the order of removal efficiency of MoS₂/Fe₃O₄ nanohybrid [124,143], relatively consistent with the level of metal softness.

4.4. Copper Sulfides

Semiconductor chalcogenides, such as copper sulfide (CuS) nanostructures, have recently drawn much interest due to their variety, low cost, and extraordinary electronic and optical properties. However, without a proper surface coating, these nanostructures, like their FeS equivalents, aggregate rapidly in water, reducing efficiency. As a result, a considerable effort has gone into developing appropriate materials for modifying the surface of copper sulfide nanocrystals, with the support or matrix chosen to be crucial. Several investigations have shown that biomolecules are efficient at preventing NM agglomeration [144]. However, CuS NMs demonstrate relatively better air-stability [145] than the FeS, and their oxidation in the air is not as rapid as FeS.

Compared with other transition metal (Zn, Fe, and Mo) sulfides, CuS has been sparingly applied to remove HMs from water in recent years. However, where CuS NMs are employed, they exhibit excellent and unique adsorption characteristics for HMs. For example, Yao et al. [146] synthesized inexpensive CuS NPs, which exhibited highly selective binding and extremely efficient adsorption performance for the noble metals (Au³⁺, Pd^{2+} , and Pt^{4+}). Significantly, after adsorption, CuO/CuS NCs can agglomerate with the contaminant and self-deposit, withdrawing from the supernatant without the use of a complex centrifugation system or an external magnetic field, ushering in a water purification milestone [147]. Due to their porous nature and the close interaction between the HM cations and S^{2-} , some CuS NCs have shown comparatively higher adsorption capacities of 3096 and 2787 mg/g for Hg (II) and Pb (II), respectively [148]. The adsorption with CuS NMs ensues via a variety of adsorption mechanisms, including ion exchange [144,148], and electrostatic interaction [146,149]. Chemical exchange is evidenced by the Langmuir isotherm model, which assumes that monolayer molecules adsorb onto adsorbents' homogeneous active sites or that all adsorption sites have the same affinity for adsorbates. CuS NCs may undergo ion exchange with divalent HMs primarily through the process: $CuS + M^{2+} \rightarrow MS + Cu^{2+}$ [150]. However, the removal efficiency of CuS NCs may drop at pH below the ZPC but rise rapidly as the pH increases, indicating a possible electrostatic attraction [149].

4.5. Other MS-NMs

The structural properties of titanium (IV) sulfide (TiS2) determine its electronic and chemical activity. TiS₂ NPs may have higher binding capacities than other binary titanium compounds due to their layered structure, allowing ion intercalation between layers and electrochemical action. Cantu et al. [151] prepared TiS₂ NPs with a complex morphology made up of arrays of TiS₂ platelets that gave them a flower-like appearance with a thin edge plane at the end of a larger basal plane. These NMs adsorbed Cu²⁺ and Pb²⁺ more efficiently at lower pH than at higher pH, contrasting with the high physisorption (electrostatic attraction) observed with other adsorbents as pH rises [74,94,119]. The adsorption implies that the interaction between the divalent ions and TiS₂ is the formation of a chemical bond rather than just physical sorption.

The pyrite-type material cobalt disulfide (CoS₂) is extensively used in catalysis, supercapacitors, and energy storage [19,152]. CoS₂-based adsorbents are developed with a support that prevents agglomeration, an inherent disadvantage of many MS adsorbents [55,82,87]. Hg²⁺ removal on CoS₂ NCs is weak at low pH [due to repulsion between the protonated surface and Hg (II) ions]. The removal at this point was due to surface complexation between the Hg²⁺ and S²⁻ species. With a rise in pH, the removal efficiency and adsorption capacity increase, indicating that adsorption occurs by electrostatic action. The Langmuir isotherm model with the highest R² implied monolayer adsorption, and the pseudo-second-order kinetic model best fit the experimental data, indicating that chemosorption is the rate-determining process [144,153].

Inexpensive two-dimensional cadmium sulfide (CdS) NPs exhibit an enormous capacity to remove HMs with excellent physicochemical characteristics, including an enhanced exposure and high specific surface area, porous structure abundant in surface-active sites, and high chemical stability [154,155]. CdS NPs removal of Hg²⁺ from aqueous media is very rapid and completed in few minutes due to vacant active sites at the beginning [36,156]. The adsorption behavior is consistent with the Langmuir-type adsorption isotherm model and pseudo-second-order kinetic model. Similarly, with other MSs, the HM's adsorption on these CdS NCs may be pH-dependent, increasing with pH up to between pH 5–7 and falling again [36,149,156] due to precipitation of metal hydroxides.

4.6. A Note on the Controversy of NM Usage and Long-Term Impact on the Environment

It is undeniable that nanoparticles provide a plethora of chances and possibilities for improved health and a cleaner environment. However, the safety and long-term consequences of increased NM usage and disposal in the environment are unknown. However, due to the fact that nanoparticles display extremely high reactivity not seen in corresponding bulk particles, there are significant safety concerns that MS-NMs may be harmful to public health [157,158]. The robust reactivity and other properties of NMs can be used to remove contaminants from water, but these same qualities may also produce undesirable by-products [158]. According to literature reviews [157,158], NMs have the potential to harm living organisms when exposed over lengthy periods of time. However, the surveys reported that the influence of NMs on health is still a source of debate, with some academics claiming toxicity and others disputing it [157,158]. However, as the types and quantities of NMs in the environment rise, it is critical to find a definitive response to the topic of NM environmental toxicity. Formulating and executing research to this purpose can lead to a decisive result.

5. Conclusions and Prospect

This article summarizes the most recent developments in using MS-NMs to recover HMs by adsorption from contaminated water. MS-NMs include some of the most promising two-dimensional layered NMs for offsetting environmental damage, especially the sequestration of HMs from aquatic environments. The structure, synthesis, support material, characterization, and heavy metal adsorption mechanism of MS-NMs have been discussed. Recent advances in MS-NM applications have been identified and highlighted. Their advantages and disadvantages are also mentioned. MS-NMs are a more potent adsorbent for removing HMs from aqueous media than traditional metal adsorbents. Although significant efforts have been made in MS-NMs studies to remove HMs, many unsolved problems and challenges must be overcome before their commercial applications can be implemented. Steps leading to remedying this situation entail addressing some of the gaps and research challenges.

A major disadvantage of most MS-NMs is the failure to separate from the supernatant rapidly. One primary solution is to combine MS-NMs with expensive magnetic NPs. Hence, there is still a great need for research on scalable MS-NMs production at low cost and easy operation while maintaining and enhancing active sites. Additionally, most studies have evaluated the effectiveness of MS-NMs in removing moderately high or very high HM levels in the laboratory. Hence, studies with environmentally relevant HM concentrations should be carried out. As discussed in the current work, it is not uncommon for the water to be contaminated with multiple metals. It is, therefore, appropriate to investigate the effectiveness of MS-NMs with simultaneous contamination. This review shows that most MS-NMs oxidize when in specific solutions or when exposed to air. Consequently, studies on MS-NMs stability and the development or discovery of appropriate support/stabilizing structures for MS-NMs for efficient removal of HMs from water require more attention. Moreover, there is a lack of adequate knowledge on the regeneration and reusability of MS-NMs, which requires further investigation. Relative to MS-NMs, there is a need to establish nanomaterial adsorbents evaluation protocol and life cycle assessment to test NMs at the material discovery stage, considering both adsorption capacity and mass transfer kinetics and to perform long-term testing in real applications. A comparison between the mechanism of heavy metals detection and the methods' sensitivity and selectivity, on one hand, and the commonly used analytic techniques on the other hand, is warranted.

This review has endeavored to present evidence that this category of materials has enormous potential as HM adsorbents. It is anticipated that this analysis will provide a comprehensive overview of the most recent studies on the use of MS-NMs in HM removal and a strong motivation to continue developing these NMs for future and sustainable environmental remediation research, especially in the field of HM abatement in water.

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