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Nanomaterials for the removal and detection of heavy metals: a review

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Heavy metal pollution in our water systems has become a global concern. Pollution of heavy metals in water arises from anthropogenic activities such as industrial processes, agricultural runoff, mining, and improper waste disposal. The persistent accumulation of heavy metals in aquatic environments necessitates innovative approaches for remediation. Furthermore, accurate detection and characterization of heavy metals is crucial for proper assessment when evaluating various challenges on water pollution. Emerging applications from the field of nanoscience provide promising developments for both remediation and analytical techniques required for both detection and quantification of heavy metal contaminants. This review provides a comprehensive overview on the current applications of nano-based approaches for heavy metal remediation in water and various analytical techniques based on nanomaterial-based technologies. Important advancement in both removal and characterization of heavy metals provides a holistic outlook on nanomaterials, as well as providing a comprehensive perspective on how nanotechnology can facilitate innovation in water remediation and detection of pollutants.

Environmental significance

The review paper provides a critical review on the utilization of nanomaterials, particularly materials from natural sources, such as cellulosic materials and chitin. It provides insights on how nanomaterials can be utilized to remediate heavy metal pollution, and also to enhance the analysis of trace amounts of heavy metals. The remediation of heavy metals will impact the ecosystem and the health of living systems on planet earth.

1. Introduction

1.1 Background on water pollution

Heavy metal contamination in water is a pressing concern due to pollution from both natural processes and human and industrial activities. Naturally driven processes such as weathering of metal rich rocks, wildfires, volcanic and geothermal activities all lead to the release of heavy metals to water bodies.[1–3] Erosion of metal rich rocks releases metals such as arsenic, cadmium, and lead into both soil and larger bodies of water such as lakes or rivers.[4–6] Additionally, volcanic eruptions and forest fires can release large quantities of metal-laden gases into nearby water bodies.[6] Similarly, there is significant contribution of heavy metal pollution from anthropogenic activities. Many industrial processes are contributors to pollution, such as mining, smelting, and manufacturing activities.[4,7] These processes directly release metals such as lead, mercury, or arsenic into water bodies through effluents, hazardous waste disposal, and atmospheric emissions.[3,5,8–10] Gold mining in particular is known to release significant amounts of mercury, whereas production of steel leads to significant chromium pollution.[9–11] Furthermore, agricultural runoff is also a significant source of pollutants. Specifically, fertilizers and pesticides that contain metallic ions can introduce metallic pollutants into soil which then leach into the groundwater.[12–14] Arsenic and cadmium were historically used in different fertilizers leading to significant leaching of these metals into groundwater and soil.[12–14] Furthermore, increasing urbanization has led to more sources of heavy metal pollution due to improper waste disposal.[15] Lead, mercury, and cadmium in batteries contribute to heavy metal pollution when they are improperly disposed.[15,16] It is important to note that various sources of heavy metal pollution will affect the water bodies. Rivers and lakes are commonly the recipients of industrial discharge and agricultural runoff, and lakes can act as sinks for atmospheric deposition.[13] Sedimentation of heavy metals can lead to long term pollution and is a significant hazard to aquatic life.[13] Furthermore, groundwater contamination can occur due to heavy metal filtration through soil, typically caused by agricultural and industrial activities.[1,2,16] Groundwater

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pollution, in particular, is a critical issue in regions where groundwater is the primary source of potable water.[12,17]

1.2 Background on heavy metals

There is a comprehensive body of studies on the different heavy metals found in water bodies, thus for the purposes of this review, we will focus on the dominant heavy metals of concern, namely arsenic, cadmium, lead, mercury, and chromium. Heavy metals are described as metallic elements that are denser than water and have a large atomic radius.[1,18] These include metalloid elements like arsenic that are typically characterized as severely hazardous for human health even at low concentrations in the parts per billion (ppb) or μg L^{-1}.[1,18] The dangers of heavy metals are made more prevalent due to their persistent half-life.[1,5] Common organic pollutants can be degraded over time, however heavy metals remain in the environment indefinitely and are difficult to be decomposed.[1,5] Lead in particular has been widely studied as a pollutant due to its high toxicity and widespread environmental presence.[16] Lead contamination is widespread due to common contamination sources of lead from plumbing infrastructure and batteries in automobiles.[8,16] Furthermore, lead is highly toxic, with neurodevelopmental, cardiovascular, renal and reproductive health issues at low blood levels of 1–2 μg dL^{-1}.[8] Similarly, chromium is a well-documented pollutant with significant sources from industrial processes such as electroplating.[19] Chromium has been widely reported in the literature, and is known to be highly toxic and is a carcinogen, with the US Environmental Protection Agency (EPA) setting a maximum contaminant level of 100 ppb.[19,20] Furthermore, cadmium is also a common pollutant from industrial activities, with a maximum contaminant level of 5 ppb set by US EPA.[14,20] Mercury is another highly hazardous heavy metal that has been released into the environment by various industrial processes.[10] In aquatic environments, mercury exists in the form of methylmercury, which can be absorbed by aquatic organisms, and this poses a significant risk for human that consumes these contaminated seafood.[10] Lastly, arsenic is a naturally occurring metalloid with severe health risks such as skin lesions, cancer, and various cardiovascular diseases.[2,12,13] It is a common pollutant from agricultural activities since it has been historically used in pesticides, which makes it a severe pollutant for groundwater and in regions that use groundwater for consumption.[2,12,13] The concentration limit of these heavy metals set by the US EPA and their known health hazards are summarized in Table 1. Key takeaways from these summarized findings underscore the severity of potential toxic effects from exposure to these heavy metals as well as the wide range of possible health effects ranging from respiratory, neurological and carcinogenic. Furthermore, the table highlights how each metal has a very low threshold for potential damage emphasizing the critical need for effective remediation strategies given that all five metals are toxic even in the ppb range.

Table 1 Heavy metal health effects and U.S EPA set limits (MCL) in water

Heavy metal	Health hazards[17]	Concentration limit[21]
Arsenic	- Carcinogenic - Skin lesions - Circulatory system damage	10 ppb
Chromium	- Known carcinogen - Severe respiratory effects	100 ppb
Cadmium	- Kidney damage - Severe gastrointestinal effects	5 ppb
Lead	- Neurodevelopmental effects - Kidney damage - Hypertension and heart issues	15 ppb
Mercury	- Kidney damage - Fatal at low concentrations - Neurotoxin	2 ppb

1.3 Current filtration technologies

Due to the prevalence of heavy metal pollution, there has been an abundance of research exploring different technologies for remediation. These techniques include adsorption-based methods, membrane filtration, ion-exchange resins, chemical precipitation, photocatalytic separation, and electrochemical separation.[2,3,6,7] Each of these techniques faces specific challenges and disadvantages. Adsorption and membrane-based methods both require regeneration and reuse of the adsorptive material and the membrane.[2,3,6,7] The cost of regeneration and the loss in efficiency over time are challenges that inhibit widespread use of these methods. Similarly, ion-exchange resins require regeneration in order to maintain efficacy, a process that is costly.[2,3,6,7] Chemical precipitation methods are commonly used for large scale treatment but they face severe challenges due to the generation of hazardous chemical sludge.[2,3,6,7] Electrochemical methods face issues in terms of energy consumption which create a significant barrier to large scale commercialization.[2,3,6,7] Finally photocatalytic methods show promise in terms of effectiveness and environmentally friendly remediation but they face drawbacks in terms of scalability.[2,3,6,7] Furthermore, selective removal of different heavy metals is a challenging issue given that wastewater contains a variety of different pollutants that reduce the removal efficiency.[6,18,21] Similarly, different remediation methods face issues in terms of efficiency under different pH conditions requiring an optimal pH to achieve high filtration efficacy.[6,18,21] From these methods, nanomaterial-based methods are emerging as attractive candidates for remediation. The desirable properties of nanomaterials include their high surface area and large amounts of reactive sites together with tunable surface chemistry that gives nanomaterial-based methods a high degree of efficiency and versatility.[22–24] Furthermore, the use of nanomaterials offers a more cost-effective approach for regeneration, a characteristic that is crucial for scalability.[22–24] The versatility of nanomaterials allows for a variety of mechanisms for heavy metal remediation, such as adsorption, ion-exchange, and photochemical separation.[22–24] Additionally, there is a comprehensive body of literature describing the different functional groups that can be grafted onto nanomaterials such as hydroxyl, thiol, and amino groups, among others that facilitate a wide range of possible adsorption mechanisms.[22–24] There is an abundance of versatile applications and variety of nanomaterials for heavy metal filtration of different types of heavy metals.

1.4 Analysis and detection methods for heavy metals

A crucial aspect in addressing water pollution is the accurate quantification and characterization of heavy metal concentrations in water. Three common areas of analysis are spectroscopic, optical and electrochemical methods. Spectroscopic techniques such as atomic absorption spectroscopy and inductively coupled plasma mass spectrometry are commonly used for the analysis of heavy metals in water.[13,18,21] Similarly, optical strategies such as colorimetric sensors or fluorescence-based spectroscopy are popular due to their ease of use which relies on the quantitative analysis of visible color changes for the detection of different heavy metals.[13,18,21] Finally, electrochemical methods are widely used for on-site heavy metal characterization and detection due to their advantages in terms of rapid response and high sensitivity.[13,18,21] Given the severity of heavy metals on human health in trace amounts, there is strong interest in the improvement and development of methods for heavy metal analysis.[13,18,21] Spectroscopic methods suffer from interference from competing heavy metal ions that diminish their ability to selectively identify heavy metals in highly polluted environmental samples.[13,18,21] Additionally, spectroscopic methods suffer from difficulties in sample preparation and cost of equipment.[13,18,21] Optical methods, while easy to use, suffer from low sensitivity when compared to more expensive analytical techniques.[13,18,21] Furthermore, optical based strategies have limitations in terms of selectivity, for example colorimetric dyes can often bind multiple competing heavy metal ions.[13,18,21] Finally, electrochemical methods suffer from similar issues in terms of detection limits depending on the electrode material and they are sensitive to interference from competing heavy metal ions.[13,18,21] Given that heavy metal pollution is widespread and diverse, there is a significant need for more advanced analytical technology such as the emerging interest in the incorporation of nanomaterials to enhance the sensitivity of different analytical techniques.

2. Nanomaterials for heavy metal remediation

2.1 Carbon based nanomaterials

2.1.1 Carbon nanotubes. Carbon nanotubes (CNTs) have been shown to be effective in removing toxic organic contaminants and heavy metals.[25–29] CNTs have lengths ranging from a few micrometers to several millimeters, while their diameters are typically in the nanometer range, often between 1 and 100 nanometers, resulting in a larger specific surface area and aspect ratio. It resembles a cylindrical tube with a hollow core, featuring carbon atoms that are sp^2-hybridized and arranged in a hexagonal pattern. These carbon atoms are arranged to form a surface consisting of one or more layers of graphene sheets. CNTs formed by one layer of graphene sheet are single-walled carbon nanotubes (SWCNTs), while those with more layers of graphene sheets form multi-walled carbon nanotubes (MWCNTs), as depicted in Fig. 1. The high surface area, abundant mesopores, layered and hollow structure provide a large surface area for heavy metal adsorption. In addition, CNTs possess a modifiable surface, where it is possible to optimize the removal efficiency of heavy metals *via* modification that increases the surface area and introduces more active adsorption sites.[30–32] The process of removing heavy metals using CNTs is complex and involves several mechanisms. These include electrostatic interactions, formation of surface complexes, ligand exchange and sorption–precipitation between the heavy metal ions and the functional groups on the CNT surface.[33]

Compared to multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs) display higher removal efficiency for heavy metal ions. Non-modified CNTs exhibit low efficiency in removing heavy metal ions from wastewater due to the aggregation of CNTs driven by weak van der Waals interaction between the CNTs.[34,35] The accessible surface area is greater in bundled CNTs compared to individual nanotubes. There are four potential sites for the adsorption of contaminants on the SWCNT bundles as illustrated in Fig. 2. These four adsorption sites consist of the external and internal surface of nanotubes, channels between nanotubes known as the interstitial sites, and outer grooves between the nanotubes.[36] MWCNTs differ from SWCNTs in that they do not form bundles, hence, the active

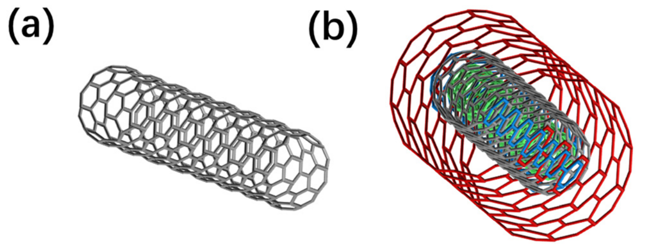

Fig. 1 Structure of single-walled carbon nanotubes (a) and multi-walled carbon nanotubes (b).

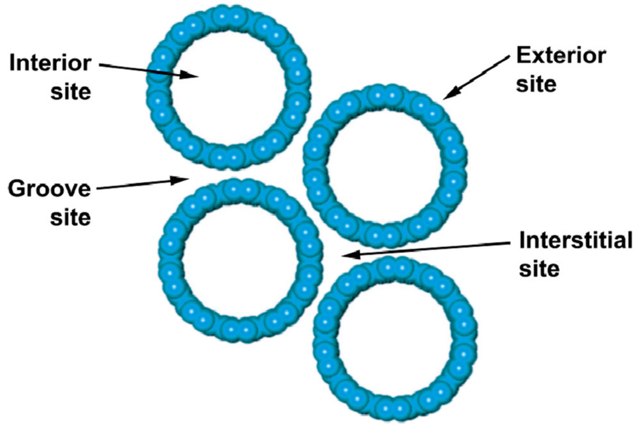

Fig. 2 Schematic model illustrating the potential adsorption sites within a SWCNT bundle.[36]

sites for adsorption are present on both the exterior and interior surfaces of the nanotubes, as well as within the aggregated pores formed by the merging of adjacent tubes.[29,37] Although the aggregation of CNTs increases the accessible binding sites for contaminants, it can also contribute to poor dispersibility which has a negative impact on the removal efficiency.[35]

Therefore, modification of CNTs is a necessary strategy to improve the adsorption performance. One of the common modification methods is to introduce functional groups such as –COOH, –CONH$_2$, –CO and OH onto CNTs to improve the dispersibility and hydrophilicity for the adsorption of heavy metals.[31,38–40] For instance, CNTs with carboxylic functional groups displayed 100% removal efficiency for lead (Pb^{2+}) at neutral pH.[38] The removal efficiency of heavy metal ions such as cadmium (Cd^{2+}), copper (Cu^{2+}), lead (Pb^{2+}) and mercury (Hg^{+}) on SWCNTs is enhanced by the functional groups, such as –COO$^-$, –OH and –CONH$_2$. In the case of CNT-COO$^-$, an adsorption of 120–230% was reported.[39]

In comparison to pristine CNTs, CNT-OH and CNT-CONH$_2$ displayed an adsorption efficiency of 10–47%.[39] The excellent adsorption capacity towards metal ions by CNT-COO$^-$ was also reported by several research groups.[31,41,42] The governing adsorption mechanism of metal ions on CNT-COOH is ion exchange, as illustrated in Fig. 3.[43] Therefore, the adsorption behavior is pH-dependent and metal concentration dependent.[44] At higher pH and initial metal ion concentration, CNTs with –COOH and –OH groups display greater adsorption capacity.[44] Acid treatment or oxidation is one approach to introduce –COO$^-$ and –OH groups, while grafting functional groups onto CNTs is another method to increase oxygen-containing functional groups.[45–48] To enhance the removal of metal ions, multiple functional groups were introduced to CNTs, including grafting ethylenediamine tetraacetic acid (EDTA), amino and carboxyl groups.[49] Functionalization of CNTs by oxidation and ethylenediamine can introduce functional groups, such as –C=O, –OSO$_3$, OH and –CONH–(CH$_2$)$_2$–NH$_2$ to the CNTs.[50] This can be seen in the recent research by Elghamry *et al.* on the production of acid functionalized multiwalled carbon nanotubes.[32] Their work utilized benzimidazole to produce a novel functionalized MWCNT that displayed strong adsorption for both lead and cadmium ions, confirming the versatility of surface modifications of CNTs for heavy metal remediation.[32]

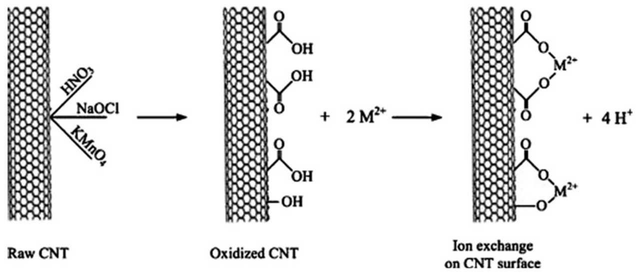

Fig. 3 Adsorption mechanism of heavy metals on CNTs with COOH and OH groups.[43]

In addition to the above modification of introducing active functional groups to the CNTs, the combination of metal oxides and CNTs has generated considerable attention. The enhanced removal of metal ions by the composites of oxidized CNTs and metal oxides is primarily attributed to several mechanisms, such as adsorption, ion exchange, surface complexation and electrostatic interactions, as shown in Fig. 4.[30] The presence of metal oxides on the CNT surface increases the number of active sites for metal ion binding. Specifically, metal oxides such as iron oxide (Fe_3O_4), manganese dioxide (MnO_2), titanium dioxide (TiO_2), aluminum oxide (Al_2O_3) and zinc oxide (ZnO) have a high affinity for certain metal ions due to their ability to form strong bonds with metal cations.[51–56] The combination of magnetic nanoparticles such as Fe_3O_4 and MnO_2 and CNTs makes it easier to separate the adsorbent from the liquid.[56] Moreover, the composites exhibit good stability and reusability, making them suitable for practical applications in removing heavy metal ions. However, challenges remain in optimizing the synthesis methods to ensure uniform distribution of metal oxides.

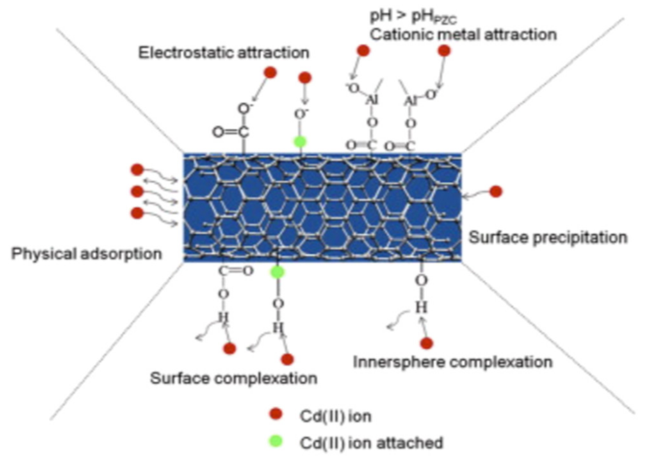

Fig. 4 Schematic showing the interaction of Cd(II) ions with Al_2O_3/MWCNTs.[30]

2.1.2 Graphene and graphene oxide. Graphene has been shown to have great potential in removing heavy metal ions from wastewater due to its large surface area and high stability, however it displays several disadvantages. For CNTs, the van der Waals interactions and π–π stacking between graphene sheets make it difficult to be dispersed in a polar solvent.[55] Graphene oxide, a modified variant of graphene, exhibits good adsorption towards cations like copper and lead.[57] The pronounced hydrophilic nature of the oxygen-containing reactive groups on graphene oxide, including –COOH, –OH and epoxy groups, enables its dispersion in solvents and provides binding sites for the complexation of metal ions, facilitating its adsorption towards metal ions.[58]

In addition, graphene and graphene oxide could be combined with magnetic metal oxide to address the separation problem.[59] The adsorption of TiO_2-graphene oxide toward zinc (Zn^{2+}), Cd^{2+}, and Pb^{2+} approached 88.9 ± 3.3 mg g^{-1}, 72.8 ± 1.6 mg g^{-1} and 65.6 ± 2.7 mg g^{-1} after 12 h, respectively, while graphene oxide exhibited a rather low adsorption capacity for these metal ions of only 30.1 ± 2.5 mg g^{-1} for Zn^{2+}, 14.9 ± 1.5 mg g^{-1} for Cd^{2+}, and 35.6 ± 1.3 mg g^{-1} for Pb^{2+}.[60] In addition to TiO_2, many types of metals or metal oxides can be used to modify graphene oxide, such as Fe_3O_4, MnO_2, silver (Ag), γ-Fe_2O_3, copper oxide (CuO), zinc oxide (ZnO), zirconium dioxide (ZrO_2), iron (Fe), manganese (Mn), nickel oxide (NiO) and gadolinium(III) oxide (Gd_2O_3).[59,61–67] The removal mechanism of graphene/graphene oxide includes adsorption by cation–π interaction, complexation with functional groups containing oxygen, electrostatic interactions between metal ions and ionized oxygen-containing functional groups, ion exchange and reduction of metal ions. The composite of metal oxide and graphene/graphene oxide benefits from the synergistic effects of both components. Aside from the mechanisms described above, it also includes the complexation with metal oxides, ion exchange between the heavy metal ions and ions in the metal oxide lattice and catalysis as summarized in Fig. 5.[68] There are also other materials used in the modification of graphene/graphene oxides for the removal of heavy metal ions, such as silica, β-cyclodextrin, polymethacrylamide, polyethylenimine, CNTs, 3-aminopyrazole, thiosemicarbazide and alginate.[69–77]

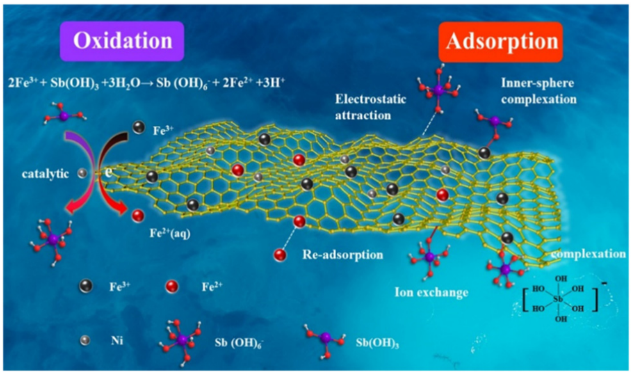

Fig. 5 Removal mechanism of heavy metal ions by graphene and graphene oxide.[68]

2.2 Metal nanoparticles such as titanium dioxide and iron oxide

Nanosized metal oxides (NMOs) have significant potential for use as alternative adsorbents in wastewater treatment processes. Their large surface area, well-defined pore structures, substantial pore volume, and high adsorption capacity make them particularly effective. Additionally, the ability to readily alter their surfaces adds to their distinct advantages as adsorbents.[78] The mechanisms by which metal oxides remove heavy metals are influenced by the functional groups on the NMOs or the type of heavy metal ion being adsorbed and the composition of the NMO itself. For example, it has been reported that the adsorption performance of magnesium oxide (MgO), Al_2O_3, and TiO_2 towards multiple component solutions of Cd^{2+}, Cu^{2+}, nickel (Ni^{2+}), and Pb^{2+} was 594.9, 114.6, and 49.4 mg g^{-1}, respectively.[79] The removal mechanism of MgO is adsorption and precipitation, whereas adsorption is the main mechanism for TiO_2 and Al_2O_3.[79] The adsorption of metal ions on NMOs is achieved by adsorption, ion exchange, complexation with surface hydroxyl groups or other functional groups on the metal oxides, co-precipitation, redox reactions, photocatalysis (in the case of semiconductor oxides, like titanium dioxide, zinc oxide, and cerium oxide), and electrostatic attraction between metal ions and the charged groups on metal oxides, as shown in Fig. 6.[79–84] Iron oxide nanoparticles are one of the most popular NMOs (manganese oxides, aluminum oxides, titanium oxides, zinc oxides, magnesium oxides and cerium oxides) used for the removal of metal ions since they are nontoxic, magnetic, display fast adsorption and are widely found in nature.[85–87] To further enhance the removal of metal ions by iron oxide nanoparticles, some modifications were performed. For instance, Fe_3O_4 coated with ascorbic acid exhibited a maximum adsorption capacity of 16.56 mg g^{-1} for arsenate, As(V), and 46.06 mg g^{-1} for arsenite, As(III), which is due to the increased surface area and improved dispersibility.[88]

Besides NMOs, pure metal nanoparticles could also be used for the removal of heavy metal ions, such as nano zerovalent iron and silver. Typically, iron is highly reactive when exposed to oxygen and water, and this reactivity becomes even more pronounced when its size is reduced to the nanoscale. The surface of nano zerovalent iron comprises of FeO, Fe_2O_3, Fe_3O_4, and FeOOH.[89] The removal mechanism of metal ions by nano zerovalent iron is similar to iron oxides, as shown in Fig. 7.[90] However, the removal efficiency of nano zerovalent iron is significantly impacted by the mass ratio between the nano zerovalent iron and the heavy metal ions and solution pH. When the ratio is 7–9 : 1, the removal amounts of Cd^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+} are 79.33–102 mg g^{-1}, 111.11–142.85 mg g^{-1}, 107.30–137.69 mg g^{-1} and 110.97–

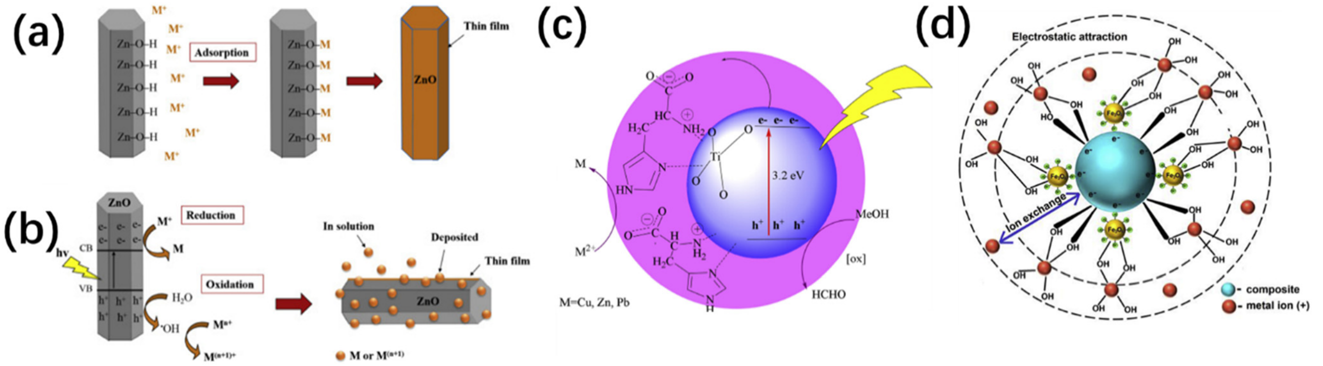

Fig. 6 Mechanisms of heavy metal ion removal using ZnO or TiO_2 particles *via* (a) adsorption on ZnO (ref. 83), (b) reduction/oxidation process on ZnO (ref. 83) and (c) photocatalysis on TiO_2 (ref. 82). d) Potential reactions involved in the adsorption of metal ions by magnetic iron oxide nanoparticles.[84]

142.68 mg g^{-1}, respectively. However, the removal efficiency decreased to very low levels when the ratio was increased to 140–180 : 1, and the heavy metal ions were acidified. This is related to the deposition of iron and the subsequent release of heavy metals.[91] More recent research into nano zerovalent iron (nZVI) focuses on addressing the aggregation of nZVI as this reduces the potential binding sites for heavy metal sorption. A recent study by Awang *et al.* utilized biochar to improve stabilization and reduce aggregation behaviour, which allowed for enhanced filtration of heavy metals such as chromium, cadmium, and lead.[89]

2.3 Biobased nanomaterials

Biobased nanomaterials are derived from natural and renewable sources such as plants, bacteria and algae.[22,92,93] They confer strong advantages in terms of sustainability, environmental friendliness, biocompatibility, and low cost.[22,92,93] Specifically, biobased materials such as cellulose nanocrystals can be extracted from plant sources at a relatively low cost as detailed in Fig. 8.[22,92,93] Additionally, these materials confer specific advantages offered by other nanomaterials such as high surface area and versatile surface chemistry.[22,92,93] There is a significant body of literature describing biobased nanomaterials such as cellulose nanocrystals, cellulose nanofibers, and different nanocomposites based on chitosan and chitin for heavy metal removal with the primary mechanism for remediation being adsorption.[22,92,94–97] Additionally, the abundance of literature in modifying these materials has articulated a comprehensive body of work on how the same biobased nanomaterials can be modified with different functional groups for different applications.[22,92,93]

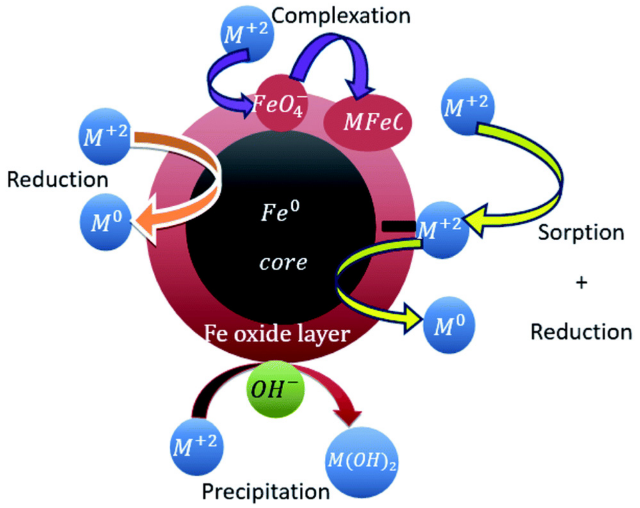

Fig. 7 Removal mechanism of metal ions by nano zerovalent iron.[90]

Cellulose nanocrystals and cellulose nanofibers are two distinct forms of cellulose based nanomaterials.[92,94] Both materials are derived from natural cellulosic materials, the most abundant biopolymer on Earth, with each offering distinct properties for different applications.[92,94,95] Cellulose nanocrystals (CNC) are rod-like nanoparticles with highly crystalline domains and are produced *via* acid hydrolysis of cellulosic sources.[89,92,94] Cellulose nanofibers (CNF) are long flexible nanofibrils produced through mechanical disintegration of cellulose pulp.[22] There is a significant body of work in modifying nanocellulose materials for adsorption of different heavy metals. The high versatility of these modifications includes grafting thiol groups, amino groups, and various types of carboxylic acid moieties onto the surface of nanocellulose.[98–101] This comprehensive body of work presents a wide variety of options for tackling different heavy metal pollutants. For example, Li *et al.* described the use of L-cysteine modified cellulose by chemical grafting of L-cysteine moieties onto the hydroxyl groups of CNC *via* periodate oxidation followed by reductive amination reactions as detailed in Fig. 9.[98] The L-cysteine modified CNC exhibited a high removal efficiency of 93% for mercury (Hg(II) ions) and displayed selective removal of Hg(II) ions with other competing heavy metal ions.[98] The work detailed the importance of using L-cysteine as a green and naturally occurring biosorbent alongside CNC.[98] Furthermore, it is important to highlight the strong binding affinity between the thiol, amino, and carboxyl groups of L-cysteine and

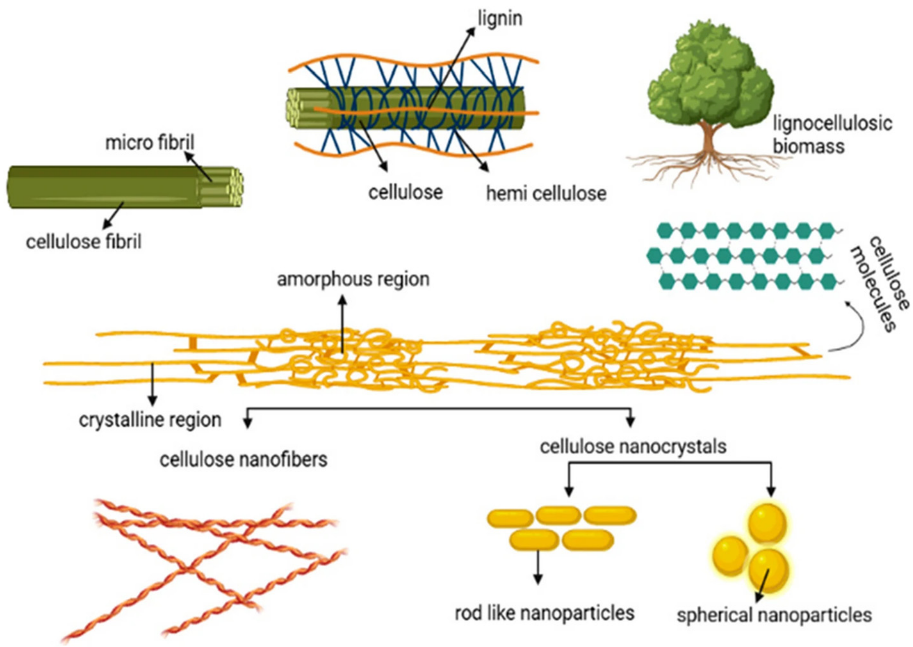

Fig. 8 Extraction and preparation sequences for cellulose nanocrystals (CNC) and cellulose nanofibers (CNF).[22]

mercury ions.[98] Specifically, the lone pair of electrons on each of the sulfur (S), nitrogen (N) and oxygen (O) elements can rapidly complex mercury ions, where there is a high adsorption affinity between thiol groups and mercury ions.[98] Note that the affinity between thiol groups and mercury ions as defined by hard–soft acid base theory facilitates the selective removal of mercury ions in the presence of other heavy metals such as lead, cadmium, zinc and copper. Furthermore, Kardam *et al.* described the use of cellulose nanofibers for the adsorption of cadmium, nickel, and lead *via* appropriate modification of the hydroxyl groups on CNF.[93] Furthermore, acid hydrolysis imparts a negative surface charge that facilitates electrostatic attraction to positively charged heavy metal ions.[93] Also, pH was found to impact the metal binding due to van der Waals forces and ion exchange between CNF and metal cations.[93] The results were promising with high removal efficiencies and regeneration capabilities.[93] Specifically, a high mass loading efficiency for cadmium of 9.7 mg g^{-1}, 9.42 mg g^{-1} for lead, and 8.55 mg g^{-1} for nickel has been reported.[93] Additionally, regeneration studies were performed *via* desorption using acid mixtures, such as mixtures of HCl/HNO_3 and HNO_3 to remove metals from the surface of CNF.[93] Adsorption efficiencies above 80% were maintained for cadmium, nickel and lead for three cycles following desorption, indicating the reusability of the material up to three adsorption cycles.[93] Similarly, Najib and Chrisodoulatos detailed the use of CNF modified with quaternary amine groups to remove arsenic in the form of arsenate As(v).[102] Specifically, glycidyl trimethylammonium chloride was grafted onto CNF, which could then bind As(v) ions *via* electrostatic interactions between the positively charged quaternary ammonium groups and negatively charged arsenate ions.[102] The work reported a high removal efficiency using this process, with removal efficiency of As(v) ions greater than 97% in a pH range of 4–8 and 88% below pH 4. However, there was a marked reduction in removal efficiency to 49% above a pH of 8.[102] It described the importance of pH on the speciation of As(v) displaying varying affinities of As(v) for the CNF depending on the dominant species.[102] Specifically, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} are different species of arsenate ions with the protonated forms existing at lower pH values and with smaller electrostatic attraction compared to the more deprotonated

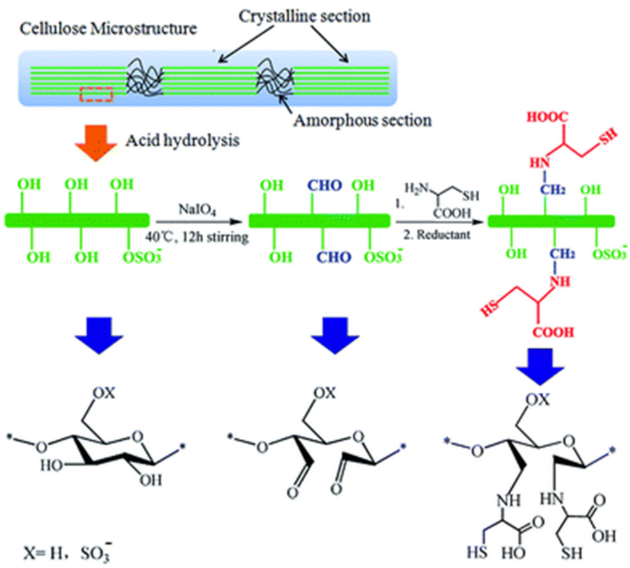

Fig. 9 Example of surface modification of CNC to produce L-cysteine grafted CNC, with dialdehyde cellulose nanocrystals as an intermediate.[98]

forms at higher pH values.[102] Furthermore, at higher pH values there is competition for the affinity of the quaternary amine with hydroxyl ions, thereby lowering the efficacy of arsenate adsorption. These results are consistent across different studies with promising results for removal of different heavy metals that depended on the types of functionalization. Many studies have reported the removal of chromium, mercury, lead, arsenic, cadmium, nickel, and copper with high efficiencies across each pollutant.[93,103–105]

Key takeaways from a comprehensive review of the literature suggest the importance of tunable surface chemistry for selective heavy metal removal. The versatility in removing different heavy metals and the benefits of using biological materials for heavy metal removal are gaining popularity. It is important to note that cellulosic nanomaterials can be derived from different sources including rice husks, coconut coir and various types of pulp fibers, and there is an abundance of sources that can be deployed for the production of heavy metal adsorbents.[106–108] It is also important to note that different nanocomposites can be enhanced *via* the surface chemistry of biobased polymers such as chitosan and chitin.[97,109] Current research focuses heavily on different media in encasing biobased nanomaterials for heavy metal remediation. For example, Kim *et al.* showcased the remediation of chromium ions *via* carboxymethyl cellulose nanofibrils embedded within the macrobeads.[105] Similar advances were reported by Dou *et al.* on utilizing nano calcium carbonate doped chitin hydrogel for the removal of copper and cadmium ions.[94] Given the promising results of biobased nanomaterials for heavy metal removal, there is strong interest in developing the field for commercialization.

2.4 Nanocomposites

Nanocomposites are advanced polyphasic materials made up of two or more types of nanomaterials.[24,110,111] These materials are defined by a structure consisting of multiple phases, with at least one phase having nanoscale dimension.[24,110,111] The nanoscale phase introduces a distinctive high surface area to volume ratio to the nanocomposites, which is crucial in developing adsorption based technologies.[24,110,111] Nanocomposites can be divided into three groups, characterized by the different types of nanomaterials used. Ceramic matrix nanocomposites are materials where one or more ceramic phases are mixed to enhance different properties such as thermal resistance, chemical stability, or mechanical resistance.[111–113] Polymer matrix nanocomposites are nanocomposites containing a polymer matrix mixed with nanofillers and are often used for energy-based applications.[24,110,111] Finally, metal matrix nanocomposites are nanocomposites with different embedded metal materials such as metal nanoparticles and are widely utilized in the automotive industry.[24,110,111]

There is a comprehensive body of literature detailing the various advantages and applications of nanocomposites for heavy metal remediation of a wide range of heavy metals. Nanocomposites possess several desirable qualities that are being exploited for different types of remediation applications. These qualities include high surface area for adsorption and versatile surface modifications to enhance their performance for a specific application.[24,110,111] Nanocomposites also possess desirable physical properties such as enhanced mechanical, thermal & chemical stability and durability.[23,114,115] Furthermore, the combinations of nanomaterials often lead to synergistic effects that enhance their performance.[112,113,116–118] For example, Musico *et al.* described the improvement of lead removal *via* a polymer-based graphene oxide nanocomposite.[119] Specifically, the binding capacity of lead ions was enhanced with increasing amounts of graphene oxide (GO) incorporated into a polymer matrix of poly(*N*-vinylcarbazole) (PVK) as outlined in Fig. 10b.[119] The work attributes the increasing amounts of oxygen containing functional groups with increasing adsorption for lead, achieving a maximum adsorption capacity of 887.98 mg g^{-1}.[119] These results were elucidated by the FT-IR spectra as shown in Fig. 10a.[119] There is a broad peak for the PVK-GO and GO spectra at approximately 3200 cm^{-1} which defines the hydroxyl groups and a sharper peak at 1200 cm^{-1} that represents the carbonyl stretching of the carboxylic acid groups.[119] Subsequent characterization of the PVK-GO nanocomposite before and after exposure to lead (Pb^{2+}) ions *via* ATR-IR shows strong evidence of the hydroxyl groups and carboxylic acid groups in the binding and removal of heavy metal ions.[119] Specifically, there is a marked reduction in the absorbance spectra at 1200 and 3200 cm^{-1} following the exposure to Pb^{2+}, confirming the binding of lead to the hydroxyl and carboxylic acid groups.[119] Furthermore, PVK-GO possesses the common advantages of polymer matrix nanocomposites, such as the versatility of fabrication, polymerization methods, and dispersion.[119,120] The synergistic effects between nanomaterials were also articulated by Pitoniak *et al.* where they reported the use of silica–titania nanocomposites for mercury removal.[121] Specifically, titanium dioxide (TiO_2) possesses photocatalytic properties that facilitate the conversion of elemental mercury (Hg^0) into mercuric oxide (HgO), which is less volatile and therefore less likely to be released to the atmosphere.[121] Silica on the other hand possesses a high surface area that functions as a concentrator for the adsorption of elemental mercury.[121] Once a specific amount of mercury is accumulated on the silica surface, UV light activates the titanium dioxide which photocatalytically oxidizes Hg^0 to HgO.[121] The photocatalytic property of TiO_2 and the high surface area of silica promoted the efficient removal of mercury greater 90% for elemental mercury.[121] Furthermore, both silica and titanium dioxide are natural occurring materials derived from fly ash, making the nanocomposite environmentally friendly.[121] There is a significant body of work detailing how different nanomaterial compositions in the nanocomposites could be extended for the removal of different heavy metals, such as chromium, cadmium, arsenic, mercury, lead and others.[112,118,122–125]

In addition, there are several articles detailing the regeneration of nanocomposites, a feature vital for sustainable and cost-effective approaches for remediation.

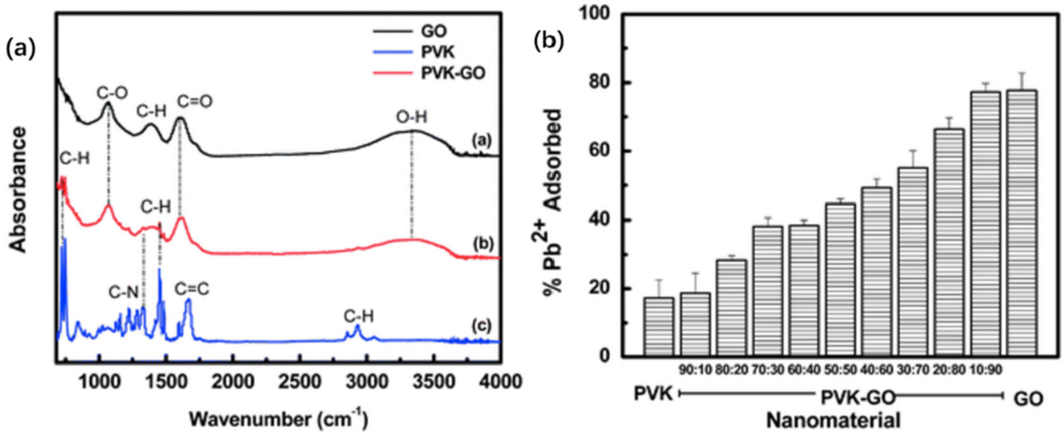

Fig. 10 a) ATR-IR spectra of graphene oxide (GO), poly(*N*-vinylcarbazole) (PVK), and PVK-GO polymer nanocomposite. b) Lead (Pb^{2+}) adsorption at varying PVK-GO concentration ratios.[119]

Charpentier *et al.* described the design of magnetic chitosan and carboxymethyl chitosan (CMC) nanoparticles for the removal of lead, copper, and zinc ions.[110] These composite nanoparticles possess unique advantages in terms of the high metal binding capacity of carboxymethylchitosan alongside the desirable quality of being a magnetic adsorbent allowing for easy separation.[110] These qualities facilitated the strong binding of the heavy metals together with the possibility of regenerating the nanoparticles using ethylenediaminetetraacetic acid (EDTA) solution under acidic conditions allowing for their reuse in other water treatment applications.[110] Specifically, EDTA chelation can strip the adsorbed metal ions, whereas the nanoparticles could be removed from water *via* magnetic separation for further use.[110] The magnetic property is imparted *via* the incorporation of iron oxide, with the appearance of the final colloidal CMC nanoparticles being characterized by high resolution TEM.[110] Similarly, Zubair *et al.* outlined the mechanism of arsenic filtration for both As(III) and As(V) *via* mesoporous zerovalent iron-magnetite nanocomposites.[126] Similar to the magnetic based materials developed by Charpentier *et al.*, Zubair *et al.* reported the preparation of unique nanocomposites that possessed many advantageous magnetic properties.[126] Bimetallic oxides exhibited better removal performance for the removal of arsenic due to the synergetic effect between zerovalent iron (Fe^0) and magnetite (Fe_3O_4), as described in Fig. 11.[126] Specifically, there is electron transfer from Fe^0 to Fe_3O_4 *via* the formation of Fe^{2+} on the surface which is believed to improve arsenic remediation.[126] The arsenic uptake *via* iron oxides has been reported to form *via* the inner sphere complexes but there is additional evidence to suggest that a surface redox mechanism partially contributes to the arsenic uptake as shown by the partial redox transformation of As(V) to As(III) on the surface of the nanoparticles.[126] Furthermore, regeneration could be performed *via* a simple procedure with the nanocomposite being dispersed in 0.1 M NaOH and then separated with an external magnet.[126] The composite exhibited excellent adsorption capacity for both As(III) and As(V) at 62.6 and 1000 μmol g^{-1}, respectively, and exhibited exceptional regeneration performance with only a 10 and 6% reduction for As(III) and As(V), respectively, after four repeated uses.[126]

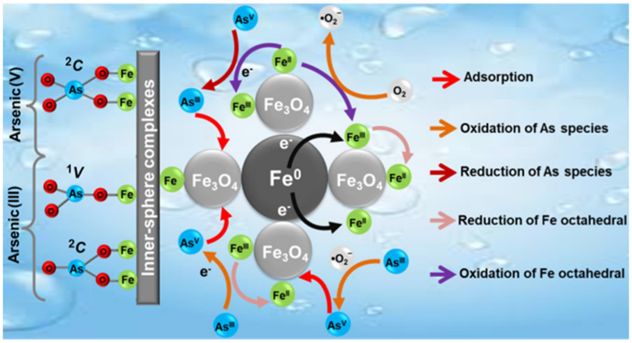

Fig. 11 Mechanism of arsenic removal *via* bimetal oxide materials.[126]

By reviewing the significant body of work on nanocomposites, several key observations on the value of these materials are evident. Firstly, there are several designed nanocomposites that can be regenerated and reused through multiple cycles of adsorption of different heavy metals with minimal loss in efficiency. These materials exhibited promising results for larger scale applications where the cost of materials could be optimized for scalability. Secondly, nanocomposites possess a high degree of versatility in terms of their intended application for heavy metal adsorption, with different types of nanocomposites incorporating different nanomaterials for selective adsorption. Thirdly, they are highly efficient for the selective adsorption of ions due to the synergy of different types of nanomaterials. For example, some nanomaterials could catalyze speciation or photocatalytic conversion of heavy metal ions while other nanomaterials could be used for adsorption. Finally, it is important to note that many nanocomposites have incorporated biobased materials such as chitosan, chitin, or nanocellulose based materials.[109,127–129] For example a recent study by Baruah *et al.* on the utilization of a nanocomposite containing nanocellulose and iron oxide for the remediation of arsenic in groundwater showed promising results.[120] Biobased materials are advantageous in terms of renewability and biodegradability, but they can sometimes be limited in terms of efficiency. The incorporation of biobased materials into nanocomposites has yielded promising results in terms of higher removal efficiency together with the use of more environmentally friendly materials. Table 2 provides an overview of key examples, highlighting their chemical/structural descriptions and mechanisms of action for carbon-based nanomaterials, metal nanoparticles, biobased nanomaterials, and nanocomposites. These nanomaterials share common structural and functional advantages, including high surface area, tunable surface chemistry, and versatile structural morphologies. The summarized mechanisms of action reveal that physical adsorption is the predominant method by which nanomaterials bind heavy metal contaminants. Additionally, other binding mechanisms, such as photocatalysis, precipitation, and ion exchange, are also viable remediation processes. However, the emphasis on physical adsorption underscores the critical role of high surface area for effective remediation.

3. Nanomaterial enhancements for heavy metal analysis

3.1 Spectroscopic based enhancements

Spectroscopic methods are a commonly used analytical tool for heavy metal detection including techniques such as atomic absorption spectroscopy, laser ablation inductively coupled plasma mass spectrometry, and surface-enhanced Raman spectroscopy.[130–132] Spectroscopic methods confer advantages in metal ion analysis in terms of their high sensitivity in both the limit of detection (LOD) and limit of quantification (LOQ).[130–132] However, there are significant drawbacks in using spectroscopic methods such as sample preparation and matrix interference of different species in the wastewater filtrate.[130–132] To address these issues, nanomaterials are emerging as promising candidates to improve and enhance the differentiation between different metal species as well as improving the efficacy of sample preparation. Preconcentration is a vital step in sample preparation for spectroscopic analysis. When analyzing

Table 2 Summary of nanomaterials used towards remediation

Nanomaterial type	Examples	Chemical/structural description	Typical mechanism of action
Carbon based nanomaterials	Carbon nanotubes (multi walled or single walled)	Composed of carbon atoms in different lattice structures[25–29]	Physical and chemical adsorption of different heavy metals *via* van der Waals forces, π–π stacking, electrostatic interactions, formation of surface complexes, ligand and ligand exchange[25–29]
	Graphene	High surface area, electrical conductivity, and mechanical structure[25–29]	Surface functionalization can enhance affinity for different heavy metals[25–29]
	Graphene oxide	Strong covalent bonding arising from sp^2 hybridized structures[25–29]	
Metal nanoparticles	Titanium dioxide	Composed of single metals or metal alloys in crystallized structures such as spheres, rods or plates[79–84]	Typical remediation mechanisms through adsorption and precipitation depending on the nanoparticle[79–84]
	Iron oxide	Versatile electric, optical and catalytic properties from quantum size effects[79–84]	Highly dependent on functional groups present[79–84]
	Nano zerovalent iron		Photocatalytic capabilities of different metals allow for different binding *via* conversion of heavy metal species[79–84]
Biobased nanomaterials	Cellulose nanocrystals	Derived from biopolymers including chitin, cellulose, and chitosan[22,92,93]	Remediation typically through physical adsorption alongside ion exchange mechanisms[22,92,93]
	Cellulose nanofibers	Versatile structures ranging from nanofibers to nanocrystals depending on extraction procedure[22,92,93]	Highly versatile in terms of surface chemistry, with an abundance of literature modifications available for different functional group grafting[22,92,93]
	Chitosan nanoparticles	Possess excellent biocompatible and biodegradable properties[22,92,93]	
Nanocomposites	Ceramic matrix nanocomposites	Polyphasic materials that are a combination of matrix materials such as polymers, metals or ceramic with nanoscale fillers[112,118,122–125]	Versatile binding mechanisms and interactions depending on the type of nanofiller including electrostatic attraction, covalent bonding, and ligand exchange[112,118,122–125]
	Polymer matrix nanocomposites	Possess versatile mechanical, thermal, and chemical properties due to synergy between matrix and nanofiller[112,118,122–125]	Additionally, possess tunable surface chemistry allowing for different preferential binding mechanisms[112,118,122–125]
	Metal matrix nanocomposites		Can be designed to possess catalytic properties enabling oxidation or reduction of heavy metal species which could more readily be adsorbed[112,118,122–125]

wastewater, the desired analyte can often be below the limit of detection and preconcentration of the analyte is required to bring the analyte sample to a detectable limit.[131,133,134] Due to their high surface area and tunable surface chemistry, nanomaterials have been widely exploited for the preconcentration of analyte.[131,133–135] The mechanism for preconcentration by nanomaterials is identical to the mechanisms by which nanomaterials are used for remediation. Specifically, nanomaterials such as carbon nanotubes can be used to selectively adsorb and bind different heavy metals within a given sample for preconcentration, improving the sensitivity of detection and quantification by a preconcentration factor.[131,133,134] For example, Krawcyzk *et al.* utilized multiwalled carbon nanotubes (MWCNT) for the preconcentration of cadmium and lead in water samples for analysis *via* graphite furnace atomic absorption spectrometry, and promising results were obtained.[134] Carbon nanotubes (CNTs) are commonly used as sorbents in solid phase extraction and dispersive micro solid-phase extraction as a mode of separation prior to their use in different types of spectroscopic analyses. The binding *via* electrostatic interaction between positively charged heavy metals and negatively charged CNTs can improve and enhance the preconcentration protocols.[134] Krawcyzk *et al.* described the dispersion of MWCNT in water containing trace amounts of lead and cadmium and following an incubation period, they were introduced into the atomizer for analysis.[134] The analysis could achieve detection limits as low as 0.001 and 0.03 μg L^{-1} and a preconcentration factor of 30 and 15 for cadmium and lead respectively.[134] Furthermore, there is an instantaneous interaction between metal ions and MWCNTs which drastically improves the sample preparation time when compared to the classical solid phase extraction.[134] Similarly, promising results were reported by Yalcinkaya *et al.* on novel hybrid nanomaterials incorporating zirconium dioxide and boron trioxide (ZrO_2/B_2O_3) for the preconcentration of cobalt, copper, and cadmium prior to quantification by flame atomic absorption spectrometry (FAAS).[133] The synthesized composite was characterized *via* TEM and SEM as seen in Fig. 12 to verify the particle size as nanoscale, given the importance of a higher surface area for increased preconcentration performance.[133] The preconcentration procedure utilized a column prepared with the sorbent nanomaterial, with sample solutions of cobalt, copper, and cadmium at concentrations of 5 μg mL^{-1} flowing through the column. Following this, the retained analytes adsorbed onto the nanocomposite were eluted using nitric acid and the analytes were aspirated into air–acetylene flame for quantification *via* FAAS.[133] The methodology was capable of achieving detection limits in the 3 μg L^{-1} range for cobalt, copper, and cadmium.[133]

Another key component of heavy metal analysis in spectroscopy is the speciation of different heavy metals. Metal speciation is the process of distinguishing between different chemical species of a specific metal, with different species having varying toxicity, mobility, and detection limits.[136–138] Nanomaterials are strong candidates for use in various speciation methodologies due to their versatility in terms of engineering different nanomaterials for selective adsorption of varying species of heavy metals.[136–138] For example, Gao *et al.* reported on the synthesis of molybdenum disulfide nanosheets for mercury speciation, which showed promise for the mercury-based detection in wastewater.[139] When coupled with other types of spectroscopic techniques such as high-performance liquid chromatography and atomic

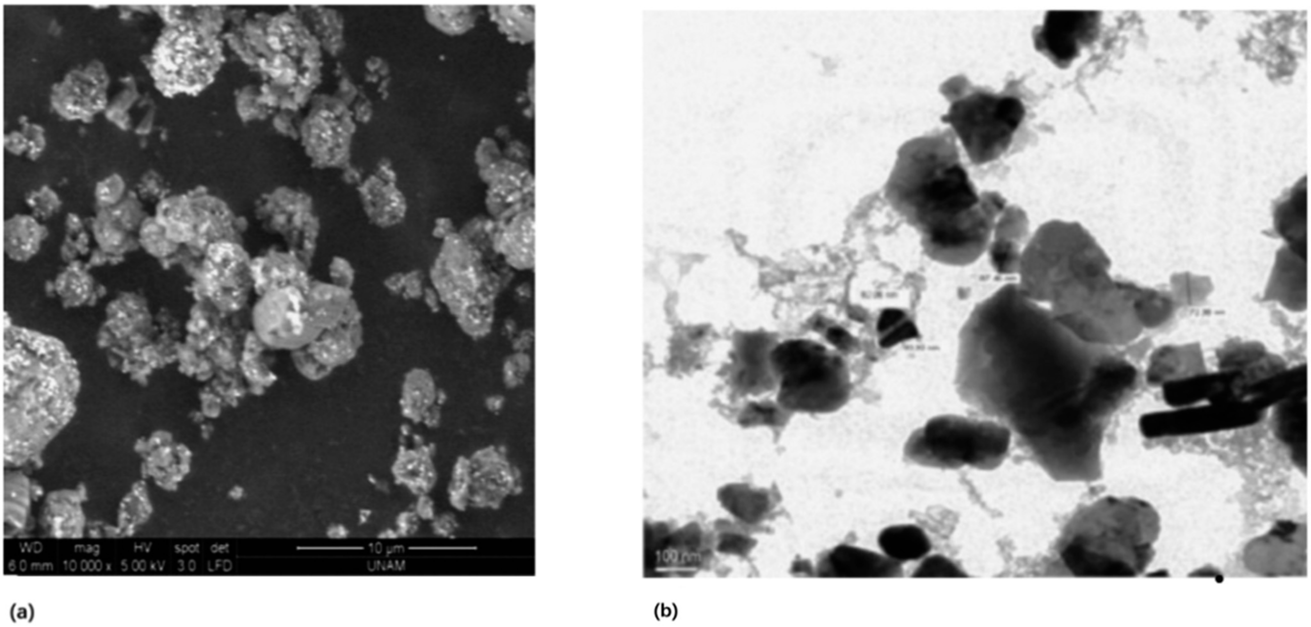

Fig. 12 a) SEM micrograph and b) TEM micrograph of nanocomposite ZrO_2/B_2O_3.[133]

fluorescence spectroscopy, researchers discussed various efficient detection and separation methodologies for mercury ions (Hg^{2+}), methyl mercury ($MeHg^{+}$), and ethyl mercury ($EtHg^{+}$).[139] The utilization of these nanosheets allowed for the detection of limits in the ng mL^{-1} range for Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$.[139] This study is important given that mercury in the organic form is far more toxic compared to the inorganic forms, therefore speciation is vital for pollutant analysis.[136,139] The application of nanomaterials for speciation is especially prominent, where the use of these nanoparticles for separation through photooxidation and photoreduction mechanisms could be exploited.[136,137] In particular, nano-TiO_2 as a photocatalyst has seen widespread use in the speciation of specific oxidation states for elements such as arsenic or chromium.[136]

Another key component of spectroscopy that can be enhanced *via* nanomaterials is photochemical vapor generation, which is an advanced technique for sample introduction in spectroscopy analysis such as atomic absorption spectroscopy or inductively coupled plasma mass spectroscopy.[140–143] There are significant advantages in using this technique for its high selectivity in terms of speciation, high analyte transport efficiency, and ease of operation.[140,141] Nanomaterials play a crucial role in this process by acting as catalysts in vapor generation *via* different nanomaterials possessing photocatalytic capabilities or *via* enhancement of the efficiency of converting metal ions into more volatile species.[140,141] For example Lin *et al.* described the use of a nanocomposite consisting of gold (Au) nanoparticles deposited on TiO_2 nanoparticles for the photocatalytic reduction of arsenic species in the vapor phase.[144] The importance of gold nanoparticles in enhancing the photocatalytic reaction extended the detection limits in the sub μg L^{-1} range for both As(III) and As(V) as shown in Fig. 13.[144] The nanocomposite photocatalytically reduces the arsenic into volatile arsenic hydride species that could be introduced into an inductively coupled plasma-mass spectrometer.[144] The use of titanium dioxide nanoparticles as effective photocatalysts has been extensively exploited where there is an increasing use of this nanomaterial for both speciation and quantification *via* photochemical vapor generation.[144]

3.2 Colorimetric and fluorescence enhancements

Colorimetric sensors are analytical tools used for the detection of specific analytes by measuring the visible color changes. The principle behind these sensors is that the target analytes interact with colorimetric reagents, which produces a color change that can be quantified using different spectrophotometric methods.[145,146] These sensors are often deployed due to the simplicity of the reagent and ease of operation, however they often suffer in terms of sensitivity and selectivity.[145,146] Nanomaterials are rapidly emerging as strong contributors to the field of colorimetric analysis. Nanoparticles in particular possess an optical characteristic known as localized surface plasmon resonance, where conduction electrons on the surface of nanoparticles can

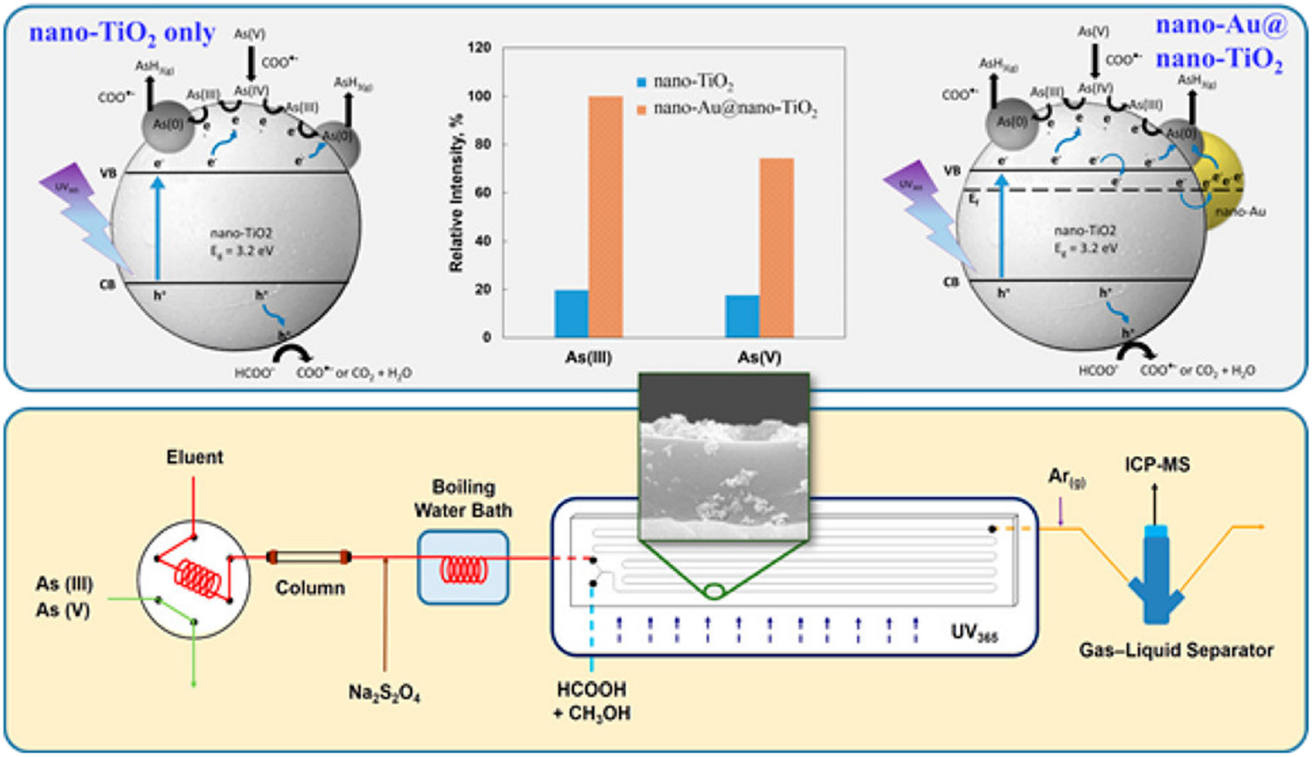

Fig. 13 Nano-TiO_2 and nano-TiO_2–Au composite particles for arsenic reduction.[144]

resonate with incident light at measurable and specific wavelengths.[146–150] For example, Seth prepared L-cysteine functionalized gold nanoparticles and incorporated them into different nanoparticles, where she elucidated their potential for use in the detection of cadmium.[151] Specifically, L-cysteine gold nanoparticles exhibited a dark red colour when individual nanoparticles were dispersed in solution, and when the particles were aggregated in the presence of cadmium, where the color changed from dark red to deep blue.[151] This method allows for an accurate and measurable detection of cadmium that leverages on the unique optical properties of the nanoparticles.[151] Similarly, promising results for the detection of arsenic were reported by Shalvi *et al.* on polyethylene glycol capped gold nanoparticle (PEG-AuNP) composites.[152] Their study described the electrostatic interactions between the PEG-capped gold nanoparticles and As(III), which induced the aggregation of arsenite ions that could be quantified by a hand held colorimetric device.[152] PEG-AuNPs were prepared using gold chloride and PEG solution.[152] With the addition of PEG, trisodium citrate was added to the solution mixture and an observable transition in colour from light yellow to black was observed, which then transitioned to red indicating the successful capping of AuNPs with PEG as shown in Fig. 14.[152] Following this, As(III) ions would aggregate in the presence of hydroxyl groups on the surface of PEG that resulted in the transition from the initial red color to blue that could now be quantified using an integrated hand-held device.[152] This work is especially promising given that the results suggest that it is a highly efficient method for the on-site quantification of arsenic, which is extremely relevant in water pollution analysis.[152] There is a comprehensive set of literature detailing how colorimetric sensors can be constructed using nanomaterial-based technology with good versatility in terms of detection of different heavy metals such as copper, arsenic, mercury, lead, chromium, cadmium and others.[148,149,153–157] These methods are gaining popularity due to the increased sensitivity of detection alongside the fundamental advantages of colorimetric methods such as ease of operation, low cost and flexibility.[148,149,153–157]

Fluorescence spectroscopy is a powerful tool used in the field of analytical chemistry. The technique measures the intensity of light emitted by a given fluorophore following the excitation of the fluorophore by light at a specific wavelength.[154,156,158,159] The intensity of this fluorescence could be measured quantitatively and then correlated to the concentration of the given analyte.[154,156,158,159] Fluorescence sensors have a very high sensitivity and good limits of detection and quantification making these tools extremely attractive for analyzing heavy metal pollution.[154,156,158,159]

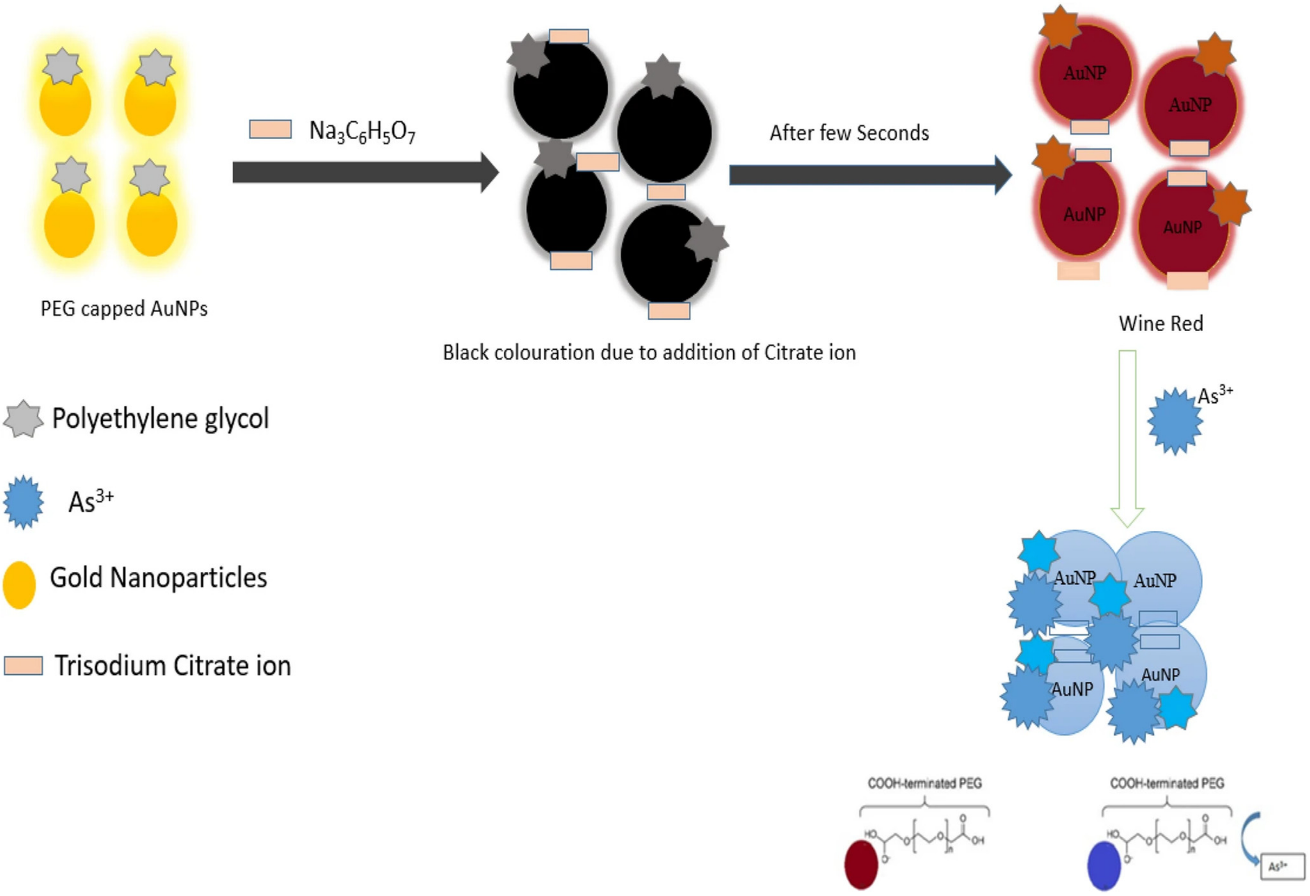

Fig. 14 Mechanism of PEG-AuNP formation and subsequent interaction with As(III) ions for the formation of an observable complex.[152]

Different nanomaterials such as quantum dots, carbon-based nanomaterials, and nanoparticles have the potential to dramatically enhance the analytical capabilities of fluorescence-based methods.[154,156,158,159] For example, Zhang and Chen reported on nitrogen doped carbon quantum dots (N-CQDs), which could be used for the detection of mercury ions.[160] Promising results on analysing mercury ions in lake water samples utilizing N-doped carbon quantum dots as a fluorescent probe were reported.[160] Nitrogen-doped carbon quantum dots possessed high luminescence properties, and they exhibited excitation wavelength-dependent fluorescence.[160] These properties can be leveraged to detect Hg^{2+} ions since Hg^{2+} ions can quench the fluorescence of the N-CQDs.[160] Utilizing these materials to measure the observable reduction in fluorescence with increasing concentrations of Hg^{2+} facilitates the detection of Hg^{2+} at a 0.23 μM detection limit.[160] Furthermore, the sensor demonstrated excellent sensitivity and selectivity even with interference from high concentrations of other metal ions.[160] Similarly, Wang *et al.* demonstrated the capabilities of a quantum dot nanohybrid for cadmium ion detection in water samples.[158] The nanohybrid consisted of a combination of quantum dots which were covalently linked to silica nanoparticles embedded with red emitting quantum dots.[158] The specific mechanism of this composite utilized green-emitting cadmium selenide (CdSe) quantum dots covalently linked to the surface of silica nanoparticles that were covered with red-emitting cadmium telluride (CdTE) quantum dots.[158] Subsequently, EDTA solution was etched onto the surface to quench the green fluorescence characteristics of CdSE quantum dots.[158] This fluorescence quenching effect could be restored *via* the binding of cadmium to the surface of quantum dots, producing a green fluorescence that could be quantified and correlated to the concentration of cadmium ions as shown in Fig. 15.[158] The study provided a strong rationale for the use of these nanohybrids for on-site detection of cadmium ions in lake water, achieving an exceptional detection limit of 25 nM for Cd^{2+}.[158]

3.3 Nanomaterials for electrochemical sensor enhancements

Electrochemical sensors are indispensable tools for the detection and quantification of heavy metal concentrations. These sensors confer significant advantages in terms of high sensitivity, rapid response times, and operating capability under complex environmental conditions such as various types of contaminated wastewater.[161–166] The emergence of nanomaterials has generated an abundance of methods for the enhancement of electrochemical sensor applications.[161–166] Specific properties that are useful to electrochemical sensors include higher surface area, catalytic function, and selective binding to different heavy metals.[161,164,167,168] The utility of nanomaterial-based enhancements can be observed in multiple applications in different types of electrochemical sensors. For example, Mao *et al.* described the application of titanium dioxide nanoparticles and multi-walled carbon nanotubes in glassy carbon electrodes for the analysis of mercury.[169] Glassy carbon electrodes can be used for the determination of trace mercury *via* linear anodic stripping voltammetry which can be enhanced using titanium dioxide MWCNT materials based on the electrocatalytic behaviour of this nanocomposite.[169] Carbon nanotubes, in particular, are extremely useful for electrochemical applications due to characteristics such as strong electrical conductivity, electrocatalytic capabilities, and strong adsorptive properties.[169] CNTs are known to possess unique electronic properties facilitating more effective electron transfer.[169] Additionally, nano TiO_2 has seen widespread application in electrode applications due to its ability to provide more active sites on the surface of the electrode.[169] The proposed enhancement of glassy carbon electrodes *via* nano TiO_2 and MWCNTs can attain high selectivity and determination of mercury even in the presence of common potential interfering metal ions with a detection limit of 0.025 μmol L^{-1}.[169] Singh *et al.* described the use of copper metal organic framework based nanoparticles for use in the detection of mercury *via* differential pulse voltammetry

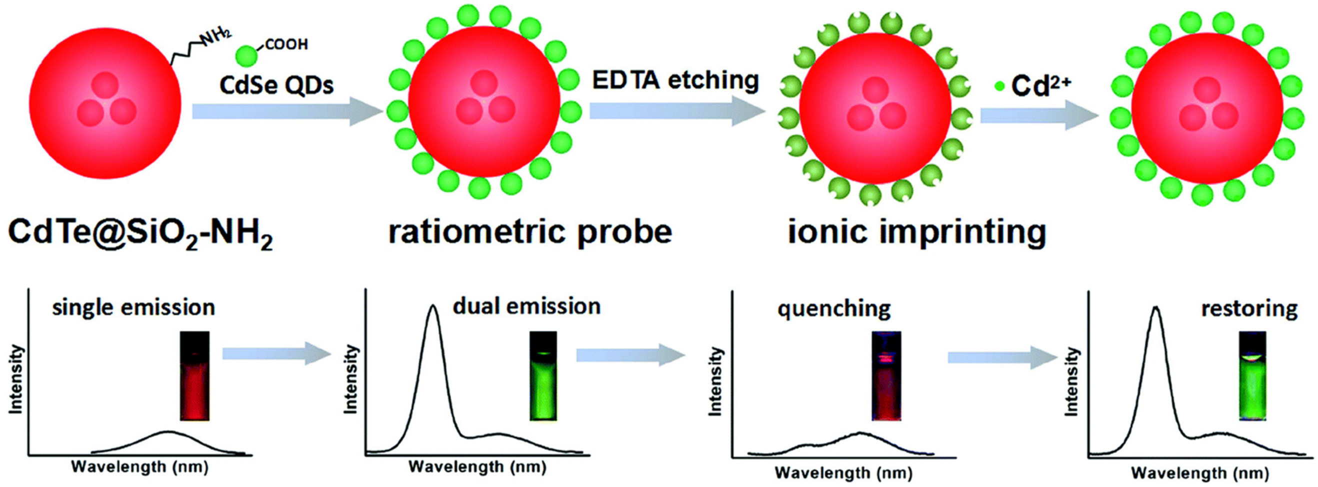

Fig. 15 Schematic description of cadmium absorption and fluorescence measurement *via* a dual emission quantum dot nanohybrid.[158]

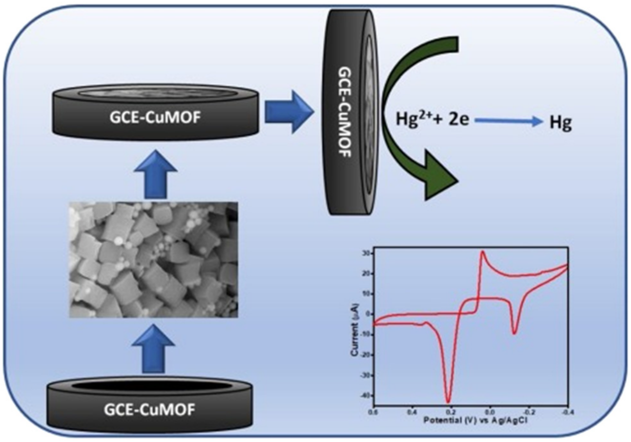

Fig. 16 Schematic diagram of copper metal organic framework nanoparticles for electrochemical detection of mercury (Hg^{2+}).[170]

and cyclic voltammetry.[170] They found similar beneficial qualities using these nanoparticles and when combined with copper metal organic framework (Cu-MOF) nanoparticles, they possess beneficial electrochemical properties with enhanced sensitivity for the detection of metal ions, such as mercury.[170] The specific mechanism of action in the Cu-MOF is detailed in Fig. 16.[170] In detail, cuprous oxide (Cu_2O) nanoparticles are oxidized to form Cu^{2+} and the subsequent electron release aids in the reduction of Hg^{2+} (ref. 170). A subsequent cyclic voltammetry analysis of the Cu-MOF modified electrode can be used to quantify the amount of Hg^{2+} ions as shown in Fig. 16.[171] The sensor was successfully applied for the detection of mercury ions in tap water with a limit of detection of 0.0633 nM.[170]

The versatility of nanomaterial-based enhancement is demonstrated in various types of heavy metal sensors constructed using nanomaterials. For example, Liu *et al.* described the use of a nanocomposite for the development of a highly selective sensor for lead(II) detection.[171] They reported the development of a complex aptasensor using a nanocomposite built from nitrogen doped graphene gold nanoparticles functionalized with 2,2′-((1*E*)-((4-((2-mercaptoethyl)thio)-1,2-phenylene)bis(azanylylidene))bis(methanylylidene))diphenol (ETBD) incorporated alongside iron oxide titanium dioxide core–shell nanoparticles.[171] Liu *et al.* demonstrated the findings in terms of synergistic effects of the iron oxide titanium dioxide nanoparticles alongside the enhanced electrical conductivity of gold nanoparticles.[171] They demonstrated an application in the selective detection of lead ions at detection and quantification limits of between 4×10^{-13} and 2×10^{-8} mol L^{-1}.[171] A similar

Table 3 Summary of analytical methods and nanomaterial enhancements

Analytical method	Description of technique	Nanomaterial applications
Spectroscopic methods	Detection of specific wavelengths of light or mass signal emission, absorbed, or reflected by different heavy metal ions[130–132]	Spectroscopic methods often require preconcentration of heavy metal samples to a quantifiable limit. Nanomaterials *via* adsorption and tunable surface chemistry of intended materials have strong applications for preconcentration[130–132]
	Common techniques include atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP MS)[130–132]	Speciation of heavy metals and different competing heavy metal effects can be challenging for spectroscopic identification. Nanomaterials have versatile surface chemistry allowing for the selective binding of different species of heavy metal, allowing for improved speciation[130–132] Advanced spectroscopic techniques such as photochemical vapor generation can be facilitated using the photocatalytic capabilities of different nanomaterials[130–132]
Colorimetric and fluorescence enhancements	For colorimetric methods, a visible color change is quantified when heavy metals interact with specific reagents[148,149,153–157]	Nanoparticles possess localized surface plasmon resonance where conduction electrons on the surface of nanoparticles can resonate with light at wavelengths which are quantifiable. This facilitates versatile colorimetric methods[148,149,153–157]
	Fluorescence methods utilize different fluorescent dyes or probes that emit a quantifiable amount of light upon their interaction with heavy metals[154,156,158,159]	Different nanomaterials such as quantum dots, carbon-based nanomaterials and nanoparticles possess luminescence properties and fluorescence capabilities, which allow for dramatic enhancements of current fluorescence based spectroscopic methods[154,156,158,159]
Electrochemical sensors	Operates *via* quantification of heavy metal species as either an oxidation or a reduction current[161–166]	Nanomaterials possess beneficial properties for electrochemical sensors such as catalytic function, electric conductivity, and selective binding of different heavy metals[161–166]
	Additionally, quantification of heavy metal ions *via* electrical potential or conductivity changes[161–166]	Carbon nanotubes in particular possess unique electronic properties for facilitating more efficient electron transfer[161–166]
	Includes techniques such as anodic stripping voltammetry *via* electrodes, as well as potentiometric or conductometric sensors[161–166]	Nanomaterials such as titanium dioxide can often be incorporated onto electrodes due to the electrocatalytic capabilities of the nanomaterial[161–166]

study was demonstrated by Ma *et al.* on a portable microfluidic electrochemical sensor for lead detection using a nanocomposite consisting of silver graphene oxide nanoparticles.[172] The system possessed advantages in terms of portable analysis while still maintaining a high detection of limit of 0.00464 $\mu g\ L^{-1}$.[172] The body of work reported in the literature provides a strong foundation for research on how nanomaterials can enhance the electrochemical methods for sensing and quantification. Different research groups were able to leverage different nanomaterials and nanocomposites in a wide variety of sensor applications with the literature elucidating the various electrochemical properties possessed by different nanomaterials.[173–175] Table 3 summarizes the various characterization techniques and the potential roles nanomaterials can play in enhancing their detection performance. The review of nanomaterial enhancements highlights their versatility and the distinct mechanistic advantages they bring to each of the three techniques discussed above. For spectroscopic methods, properties such as high surface area and adaptable surface chemistry enable the selective physical adsorption of heavy metals, addressing challenges like preconcentration and matrix interference. In fluorescence and colorimetric techniques, the unique optical properties of different nanomaterials can be leveraged for a broad range of sensor applications. For electrochemical techniques, many nanomaterials exhibit properties like enhanced conductivity and electrocatalytic activity, which improve the electrode performance in electrochemical sensors. Overall, Table 3 underscores the broad potential of nanomaterials in enhancing the characterization techniques through various mechanisms.

4. Outlook and perspectives

4.1 Nanomaterial based remediation methods

Nanomaterials are increasingly being incorporated into systems for the remediation of heavy metals in water. They offer many beneficial properties such as high surface area, tunable surface chemistry and interactions with contaminants revealing their effectiveness at the nanoscale. There are many advantages and disadvantages for each type of nanomaterial, which were discussed and elucidated in the literature. As discussed earlier, Table 2 provides a comprehensive overview of the shared mechanistic advantages of nanomaterials in facilitating heavy metal remediation. It particularly highlights the critical role of high surface area, as physical adsorption is the predominant mechanism for heavy metal removal. While all nanomaterials share these common advantages, each type offers unique properties that enhance their effectiveness in remediation. Carbon based nanomaterials such as carbon nanotubes and graphene oxides display strong adsorption capacities and high efficiency in terms of heavy metal removal due to their broad functionalities. However, carbon-based nanotechnology has limitations in terms of scalability and production costs, which limit its potential for commercialization. Metal nanoparticles possess a wide range of remediation of metallic pollutants in terms of adsorption-based methods and photocatalytic characteristics. The regeneration and reuse of metal nanoparticles extend and enhance their lifespan for many applications. However, metal nanoparticles have some limitations in terms of synthesis, which can hinder their long-term use. Specifically, metal nanoparticle synthesis can often be energy intensive and involves hazardous chemicals, which can be counter intuitive for pollutant-based applications. Biobased nanomaterials such as CNC and CNF are environmentally friendly since they are extracted from renewable sources. Additionally, CNC and CNF possess a wide array of surface modifications allowing for different types of heavy metal remediation. However, limitations for biobased nanomaterials are associated with their relatively low removal efficiency compared to other nanomaterial-based filtration materials. Nanocomposites offer several advantages in terms of their enhanced performance for water treatment applications due to the synergistic effects of different nanomaterials being considered. Additionally, nanocomposites have shown remarkable regeneration capabilities offering promising results for sustainable materials for long-term water treatment. However, these regeneration capabilities are limited by the intensive and complex synthesis of the nanocomposites. Additionally, nanocomposites have high production costs due to their more complex preparation procedures, thus the major limitation of nanomaterials used for water treatment applications is the production of the nanomaterials. Given that heavy metal pollution is a widespread phenomenon, there is interest in developing sustainable and scalable solutions for water remediation. Water pollution tends to have a greater impact on developing countries necessitating cost efficient methods for their treatment. As the field continues to develop, special consideration should be given to the scalability and production of the nanomaterials as well as the more potent development of biobased nanomaterials for remediation, given that biobased nanomaterials offer a more sustainable long-term solution.

4.2 Nanomaterial based analysis methods

Analysis and detection are a fundamental aspect of water remediation. Given that different countries have very stringent rules for the heavy metal present in water, thus special focus needs to be devoted to the different methodologies for the characterization of heavy metals in water. This is especially prevalent given that heavy metals are hazardous at extremely low concentrations and therefore the detection needs to be precise for low levels of contaminants. Nanomaterials are rapidly emerging as important systems for the analytical determination of heavy metals, with nanomaterials offering key enhancements in terms of sensitivity, selectivity, and efficiency. Special consideration was given to nanomaterial-based enhancements for spectroscopic tools, colorimetric and fluorescence based methods, and electrochemical sensor applications. Table 3 provides a summary of each technique, and its applications associated with nanomaterial-based enhancements. The summary highlights the versatility of nanomaterials in wastewater analysis, showcasing how each characterization method leverages distinct properties of nanoscale materials. The current field of spectroscopic based methods for heavy metals focuses heavily on reliable methods for preconcentration, speciation of different heavy metals, and photochemical vapor generation for precise injection into different spectroscopic instruments. Nanomaterials have application in the detection and analysis of heavy metals due to their exceptional adsorption capabilities for preconcentration, highly tunable selectivity to enhance speciation, and different photooxidative and photoreductive capabilities that facilitate photochemical vapor generation. Furthermore, given the high selectivity of different fluorescence methods for heavy metal detection and the ease in using colorimetric methods, there is increasing interest in enhancing these methods for higher selectivity and sensitivity. Nanomaterials play a crucial role in this development due to their unique optical properties such as localized surface plasmon resonance by different nanoparticles, or fluorescence based properties of quantum dots. These properties facilitate enhanced detection and sensitivity for different colorimetric and fluorescence based methods when the nanomaterials are incorporated into different sensor applications. Finally, nanomaterials are finding increasing application in different electrochemical based sensors. Electrochemical sensors are widely sought after for heavy metal analysis given their rapid response and potential for on-site use. In this regard, nanomaterial-based enhancements are becoming more popular due to the different catalytic properties, selective adsorption capacities, and electrochemical activity. There is a significant body of literature describing how nanomaterial-based applications can enhance both the selectivity and sensitivity of different electrochemical sensors and electrodes. In terms of the limitations for nanomaterials for heavy metal remediation, there are significant drawbacks in the use of nanomaterials for analysis due to issues with scalability and production costs of these materials. As the field of nanoscience continues to develop, the interest in nanomaterials will continue to increase, and advancements made in this field will drive down cost and increase the sensitivity of detection.

5. Conclusions

Nanoscience is an emerging field with an endless capacity of untapped potential. Current research into heavy metal remediation in water describes several key mechanisms and applications of nanomaterials used in these applications. As heavy metal pollution is a critical global issue, thus there is an increased need for sustainable, effective solutions for both remediation and analysis. Once the production and scalability of nanomaterials are addressed, we should expect a higher degree of interest in applying nanomaterials for heavy metal remediation on a large scale. Its notable that studying nanomaterials for analysis as well as remediation offers a holistic approach to understand the mechanisms of the nanomaterials with heavy metals. The application and review of both remediation and analysis offer vital insight into different prospective applications for nanomaterial utilization, with their being a great deal of potential utility in the field.

Data availability

No new data were generated or analysed as part of this review. All data discussed within the text of the manuscript, included in figures or presented in tables, are sourced from previously published articles, which are cited accordingly. All figures are referenced accordingly and appropriate permissions have been granted.

Conflicts of interest

There are no conflicts to declare.

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