



Application of Iron-Based Materials for Remediation of Mercury in Water and Soil

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Received: 29 November 2018 / Accepted: 23 January 2019
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Abstract

Mercury contamination in soil and water has become a major concern to environmental quality and human health. Among the existing remediation technologies for mercury pollution control, sorption via iron-based materials has received wide attention as they are environmental friendly and economic, and their reactivity is high and controllable through modulating the morphology and surface properties of particulate materials. This paper aimed to provide a comprehensive overview on environmental application of a variety of iron-based sorbents, namely, zero valent iron, iron oxides, and iron sulfides, for mercury remediation. Techniques to improve the stability of these materials while enhancing mercury sequestration, such as nano-scale size control, surface functionalization, and mechanical support, were summarized. Mechanisms and factors affecting the interaction between mercury and iron-based materials were also discussed. Current knowledge gaps and future research needs are identified to facilitate a better understanding of molecular-level reaction mechanisms between iron-based materials and mercury and the long-term stability of the immobilized mercury.

Keywords Mercury · Heavy metal · Soil remediation · Water treatment · Iron-based sorbents

Introduction

Mercury (Hg) is considered as one of the most pervasive and bioavailable heavy metals in the environment. It is widely applied in industrial processes such as production of chlor-alkali, pulp, plastics and electronics, mining, and rubber processing (Boening 2000). Hg has three valence states (i.e., +I, +II, and 0), and occurs in both inorganic and organic forms. The divalent mercury, Hg(II), is highly soluble and ubiquitous in the environment. Methylmercury (MeHg) is the Hg species of greatest concern due to its ability to bioaccumulate in biota and biomagnify along food chains. The primary source of MeHg is methylation of inorganic Hg(II)

by anaerobic bacteria in natural aquatic environment (Zhang et al. 2014a).

Hg poses a severe threat to living creatures. Long-term exposure to Hg leads to a variety of symptoms, ranging from tremors, loss of vision and hearing, to extreme neurological damages, such as loss of sensation (Hsiao et al. 2011). To date, over 130 countries have agreed to join the United Nation's Minamata Convention for reducing Hg emission and utilization of Hg containing products (AMAP/UNEP 2013). The maximum concentration of Hg in drinking water was recommended at 6 µg/L for inorganic Hg by the World Health Organization (WHO 2017). The US Environmental Protection Agency specifies the maximum contaminant level of inorganic Hg to be 2 µg/L (USEPA 2018). However, Hg contamination in soil and water is prevalent. For instance, Bollen et al. (2008) reported that Hg content in soil reached up to 11,000 mg/kg and Hg concentration in a groundwater plume with a width of 100 m and a length of 1.3 km reached up to 230 µg/L at a former wood impregnation site in Southern Germany. A recent nationwide survey of soil contamination in China revealed that the average Hg content in 1.6% of the detecting points exceeded the regulation level according to the Ministry of Environmental Protection and Ministry of Land and Resources of China (Bulletin on Natural Survey of Soil

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Contamination in 2014). Hence, a growing number of research efforts have focused on improving environmental remediation for Hg contamination.

Existing Hg treatment technologies include ion exchange (Monteagudo and Ortiz 2000), cementation (Ku et al. 2002), chemical precipitation (Blue et al. 2010), and bioremediation (Essa et al. 2002). These techniques are effective to some extent, however, most of them suffer from various drawbacks such as high cost, incomplete removal, operational difficulties, complicated industrial setups, and production of toxic sludge (Roberts and Rowland 1973). Among all the known methods, sorption has emerged as one of the most feasible treatments for Hg contamination since it is easily implemented and widely adaptable.

Although a number of sorbents, such as activated carbon, polymers, and biomass materials, have been assessed for Hg sequestration (Yu et al. 2016), iron-based materials including zero valent iron (ZVI) (Lewis et al. 2016; Wilkin and McNeil 2003; Zhou et al. 2013), iron oxides (Lu et al. 2014; Parham et al. 2012; Richard et al. 2016), and iron sulfides (Bower et al. 2008; Han et al. 2014) are considered the most promising and effective sorbents for Hg due to their high reactivity, controllable particle size, low cost and environmental compatibility. The main challenge of in situ application of iron-based materials is the aggregation during preparation process which usually results in large-sized particles with limited mobility and reactivity. The aggregation of iron-based materials in fixed bed column or other dynamic flow systems can cause high-pressure drop, and thus restrict the direct use for field-scale application. A variety of approaches, particularly nanomaterials (Gong et al. 2014) and surface functionalization (Dodi et al. 2012; Oveisi et al. 2017; Wang et al. 2016) have been developed to overcome the abovementioned limitations. Moreover, supporting materials such as graphene oxide (GO) (Huang et al. 2017) and alumina oxide (Sun et al. 2017a), have been used as mechanical supports to restrain the aggregation and enhance the dispersion of particles.

The main purpose of this review was to provide an assessment of the applicability of iron-based materials for Hg remediation under environmental conditions. Specifically, the review aimed to: (1) elucidate the mechanisms and factors affecting Hg sequestration by iron-based materials; (2) assess the technical applicability and limitations; (3) summarize the approaches for improving the performance of iron-based materials; and (4) identify critical knowledge gaps and future research needs.

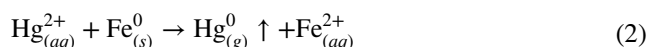
Iron-Based Materials Suitable for Hg Remediation

Zero-Valent Iron

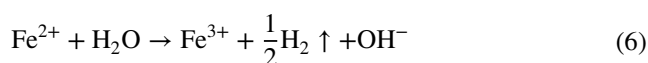
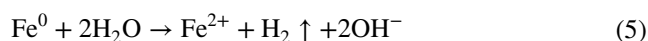
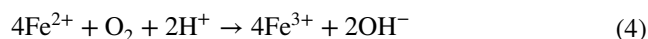
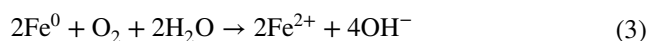
ZVI is a strong reductant with a standard reduction potential (E^0) of -0.440 V (Eq. 1):



Metals with E^0 more positive than Fe^0 are preferentially reduced when reacting with ZVI (Fu et al. 2014). For instance, Hg(II) can be reduced by ZVI to form elemental Hg ($\text{Hg}_{(g)}^0$) (Eq. 2):



ZVI can also react with water under both aerobic and anaerobic conditions to generate Fe^{2+} and Fe^{3+} (Eqs. 3–6), which may further transform to mineral phases, such as oxyhydroxide, on the surface of ZVI, exhibiting strong affinity for Hg (Biernat and Robins 1972; Gu et al. 1999; Kenneke and McCutcheon 2003; Majewski 2006; Sayles et al. 1997).



Successful removal of Hg using ZVI has been demonstrated in different environmental matrices. Zhou et al. (2013) reported that 0.05 g ZVI effectively removed 94.5% of 100 $\mu\text{g/L}$ Hg(II) from wastewater at an initial pH of 5.0. Wilkin and McNeil (2003) added ZVI to synthetic acid mine drainage, and the total Hg concentration was decreased from ~ 3100 to < 70 $\mu\text{g/L}$. When ZVI was utilized in permeable reactive barrier (PRB) in a field experiment, the Hg content in groundwater was reduced from ~ 40 to < 0.1 $\mu\text{g/L}$ (Weisener et al. 2005). Lewis et al. (2016) studied the applicability of ZVI (< 2 mm) as sediment amendments in vegetated laboratory microcosms as well as wetland mesocosms, and the addition of ZVI significantly alleviated MeHg accumulation in pore water and in a freshwater snail.

Despite of the high reactivity of ZVI, challenges remained in environmental application of this materials: (1) the side reaction pathways, such as nitrate and/or oxygen reduction by ZVI, may overcompete the Hg–ZVI interaction and thus compromise the remediation efficiency;

(2) ZVI is not thermodynamically stable in aqueous solution and is subject to corrosion by water molecules; (3) ZVI easily aggregates to form large particles that are less reactive and mobile; and (4) oxidation of ZVI increases the solution pH, which likely leads to precipitation of non-contaminant phases such as calcium carbonate, and decrease the permeability of PRB.

Iron Oxides

Iron oxides, such as maghemite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), and hematite ($\alpha\text{-Fe}_2\text{O}_3$), possess magnetic properties and can be separated from treated water by a simple external magnetic field. Given their eco-friendliness and low cost, magnetic iron oxides have attracted much attention in the application of treating Hg-contaminated water (Lu et al. 2014; Parham et al. 2012; Richard et al. 2016). Parham et al. (2012) reported that Fe_3O_4 removed 44% of 50 $\mu\text{g/L}$ Hg(II) from aqueous solutions.

Hydrous ferric oxides are highly porous and poorly crystalline iron-based materials, and can serve as sorbents for Hg. Maia et al. (2019) investigated the sorption of Hg(II) by $\delta\text{-FeOOH}$ in aqueous solutions. They reported that Hg(II) was mainly sorbed through surface complexation and the maximum sorption capacity was 35.7 mg/g at pH 7.0.

Fe–Mn binary oxides are ubiquitous in natural aquatic environment and have strong affinity for Hg (Lu et al. 2014). Lu et al. (2014) explored the removal mechanism of trace Hg(II) by in situ formed Fe–Mn oxides in aqueous solution. They reported that 40 mg/L Fe–Mn as Fe (molar ratios of Mn/Fe = 0.33) effectively removed 80% of 30 $\mu\text{g/L}$ Hg(II) at pH 7.0 via concurrent surface complexation and flocculation-precipitation processes.

There are several shortcomings with the application of iron oxides. For example, iron oxides have limited sorption capacity and selectivity for Hg. Also, it is difficult to deliver the materials into the subsurface areas, and thus impeding their use for in situ soil and groundwater remediation.

Iron Sulfides

Hg(II) is a soft Lewis acid that preferentially binds with soft Lewis bases, particularly those with sulfur or thiol groups. Iron sulfides, such as mackinawite (FeS) and pyrite (FeS_2) have been regarded as the most applicable materials for Hg sorption due to their high affinity towards Hg (K_{sp} of $\text{HgS} = 2 \times 10^{-53}$) (Barnett et al. 2001).

Pyrite, as the most abundant metal sulfide in nature, is commonly available and inexpensive (Duan et al. 2016). The surface of pyrite mineral is often comprised of a pyritic area and an oxidized zone with iron hydroxides, and Hg can interact with the pyritic functional groups and/or the hydroxyl groups (Ehrhardt et al. 2000). Bower et al. (2008)

investigated the potential of pyrite as a PRB material to immobilize Hg(II) in groundwater. Batch experiments showed that 2 g/L pyrite removed > 95% of 2 mg/L Hg(II) from aqueous solutions at pH from 4.1 to 10.4, and the maximum sorption was equivalent to 1000 μg Hg/g pyrite. Column experiments demonstrated that Hg(II) was mostly sequestered by a thin reactive barrier of pyrite in a packed column, with breakthrough of Hg(II) in effluent delayed by 15-fold. Moreover, the immobilized Hg was not readily remobilized, indicating the irreversible nature of the reaction, a desirable characteristic of a subsurface PRB.

FeS can be synthesized via simple chemical precipitation of Fe^{2+} and S^{2-} , and immobilizes Hg through chemical precipitation, Hg substitution into metastable FeS compounds, and surface complexation (Gong et al. 2014; Jeong et al. 2007). Liu et al. (2008) investigated sorption of aqueous Hg(II) by synthesized FeS under anaerobic conditions. Batch kinetic tests showed that 0.4 g/L FeS removed nearly 100% of 200 mg/L Hg(II) solution within 20 min at an initial pH of 5.6 and the main reaction products were metacinnabar, cinnabar, and Hg iron sulfides. Han et al. (2014) reported that at pH 8.0, 0.05 g/L FeS completely removed 100 mg/L Hg(II) within 10 min. At higher Hg(II) concentrations (200 and 250 mg/L), longer time was required to reach more than 99% removal. A biphasic sorption behavior was observed, which was probably due to the fast initial transport of Hg(II) to the FeS surface and the slow chemical interactions between Hg(II) and FeS surface.

Sun et al. (2017b) compared the sorption capacity of synthetic FeS and natural pyrite toward Hg(II) in aqueous system. Batch experiments revealed that synthetic FeS offered much greater maximum sorption capacity (769.2 mg/g) compared to pyrite (9.9 mg/g) as FeS had a larger specific surface area with more sorption sites. They proposed that synthetic FeS demonstrated excellent tolerance to pH, chloride and coexisting cations and is a promising sorbent for treatment of high-concentration Hg(II)-containing wastewater (< 20 mg/L), while pyrite can be applied as a long-term adsorbing material in the immobilization of wastewater containing low Hg(II) concentration (< 1 mg/L) due to its cost-effective property and wide availability.

Approaches for Improving the Remediation Performance of Iron-Based Materials

Iron-based materials tend to aggregate rapidly in conventional systems due to van der Waals forces and high specific energy, resulting in a decrease in reactivity and soil deliverability, which limited their practical application, especially for in situ soil remediation in deeper contaminated zones. To overcome these limitations, a variety of approaches have been developed including attaching a stabilizer such as a

soluble polymer on the surface or adding surface functional groups. Moreover, supporting materials, including zeolite, kaolinite, have been widely used as mechanical supports to restrain the aggregation of particles. Through these technologies, more physically stable and chemically reactive iron-based materials were obtained, and their Hg immobilization abilities were enhanced.

Nanomaterials

Compared with bulk particles, nanoparticles have shown great potential for treatment of contaminated groundwater and soil due to the small particle size, large surface area, high reactivity, and controllable soil deliverability. Recent work has demonstrated that preparation of iron-containing minerals in the presence of polyelectrolyte coatings, such as starch, carboxymethyl cellulose (CMC), and chitosan, resulted in nano-sized particles with highly improved stability due to steric hindrance and electrostatic repulsion enabled by the coating. These materials exhibited large sorption capacity for heavy metals (Gong et al. 2012; Xiong et al. 2009).

Gong et al. (2014) compared the aqueous Hg(II) removal of non-stabilized and CMC-stabilized FeS and found that the CMC-stabilized FeS offered a much higher Langmuir sorption capacity (3449 mg/g) at pH 7.0 due to the smaller FeS particles, greater specific surface area, and thus higher abundance of sorption sites. CMC-stabilized FeS nanoparticles have also been successfully applied to treat Hg-contaminated soil/sediment. Xiong et al. (2009) found that at an FeS-to-Hg molar ratio of 26.5, the nanoparticles reduced the water-leachable Hg concentration from a clay loam marine sediment (Hg content = 177 mg/kg) by 97% and reduced the leachability of Hg by 99% according to the toxicity characteristic leaching procedure (TCLP).

Introducing stabilizers to the particles has improved the soil deliverability of the particles. Gong et al. (2012) investigated the soil/sediment deliverability and transport behavior of CMC-stabilized nanoparticles via a series of column breakthrough tests, and they found that the nanoparticles were deliverable in the sediment/soil columns under moderate injection pressure (0.4–0.5 psi) while non-stabilized FeS were completely retained on the top of the soil/sediment bed due to large particle size (1632 nm) (Gong et al. 2012). When a Hg-laden sediment was treated with 160 pore volumes of 0.5 g/L CMC-stabilized FeS (CMC concentration = 0.2 wt%), the water-leachable Hg was reduced by 47%, and the TCLP leachability was reduced by > 75%.

The application of nanoparticles has evolved into a promising cleanup strategy for in situ remediation of Hg-contaminated soil and groundwater. Stabilized nanoparticles demonstrate unprecedented advantages over

traditional aggregated particles, including enhanced sorption affinity, sorption capacity, and soil deliverability. The nanoparticles can be delivered directly into the contaminated aquifer that is not reachable by conventional materials, potentially reducing remediation cost. Yet, detailed information is lacking pertaining to the environmental fate and transport of stabilized nanoparticles as well as the associated impacts on the in situ biogeochemical conditions.

Surface Functionalization

Hg sorption performance of iron-based materials can be improved by grafting new functional groups mainly amino groups (Chethan and Vishalakshi 2013; Dodi et al. 2012) and thiol groups (Hakami et al. 2012; Huang et al. 2017; Oveisi et al. 2017; Wang et al. 2016; Zhang et al. 2013) onto the surface of the materials (Table 1), thereby, increasing the density of sorption sites and improving the sorption selectivity. At present, most surface functionalized iron-based materials are added into soil in the form of powder or granular particles through mechanical mixing. More information is needed regarding the effect of surface functionalization on the mobility and environmental impacts of these sorbents.

Thiol-functionalized sorbents have strong affinity and high sorption capacity for Hg as a consequence of a soft Lewis acid–base interaction (Stumm and Morgan 1995). 3-mercaptopropyltrimethoxysilane (3-MPTS) is one of the most widely used thiol-modification chemicals (Guimarães et al. 2009; Hakami et al. 2012; He et al. 2012; Yu et al. 2013; Zhang et al. 2013). Huang et al. (2017) developed a novel thiol-functionalized graphene oxide/Fe–Mn (SGO/Fe–Mn) and tested the removal efficiency of aqueous MeHg. 50 mg/L SGO/Fe–Mn effectively removed 91.1% of 50 µg/L MeHg within 3 days at pH 7.0 via concurrent electrostatic attraction and surface complexation. The maximum sorption capacity was determined to be 43.9 mg/g at pH 7.0 and room temperature ($25 \pm 2^\circ\text{C}$), much higher than that of bare GO/Fe–Mn (15.5 mg/g).

Amino groups are involved in metal binding via (a) metal cation chelation in near neutral solutions (through the free electron doublet of nitrogen) and (b) ion-exchange/electrostatic attraction on protonated amino groups (in acidic solutions) (Donia et al. 2012; Elwakeel and Guibal 2015; Guo et al. 2014). A hybrid material was synthesized with chitosan, glycidyl methacrylate and magnetite microparticles, and the amine groups were grafted onto the hybrid material using diethylenetriamine. The resultant amino-modified adsorbent selectively adsorbed Hg(II) from a mixture solution of Hg(II), Co(II), Cu(II), Fe(II), Ni(II), Zn(II) and Mg(II) (Elwakeel and Guibal 2015).

Table 1 Surface modified iron-based materials for Hg removal

Iron-based materials	Hg removal mechanisms	Hg removal capacity	References
Thiol-functionalized Fe ₃ O ₄ -SH	Complexation with thiol and hydroxyl groups	The maximum sorption capacity (Q _{max}) was 344.8 mg/g with an initial Hg(II) concentrations of 25–500 mg/L and pH of 6.0	Oveisi et al. (2017)
Fe ₃ O ₄ @SiO ₂ -SH	Adsorption of Hg ²⁺ , HgOH ⁺ , and Hg(OH) ₂ species by thiol group	Q _{max} was 132.0 mg/g at an initial Hg(II) concentration of 100 mg/L, initial pH 6.0, adsorbent dosage of 0.2 g/L	Wang et al. (2016)
Thiol-functionalized mesoporous silica-Fe ₃ O ₄	Chemical binding through complexation and ion exchange	Q _{max} was 207.7 mg/g with an initial Hg(II) concentrations of 40–1000 µg/L, adsorbent dosage of 4 mg/L, 0.1M NaNO ₃ , initial pH of 6.0, and equilibrium time of 1 h	Hakami et al. (2012)
Thiol-functionalized GO/Fe-Mn	Electrostatic attraction, ligand exchange, and surface complexation	Q _{max} was 43.9 mg/g with an initial CH ₃ Hg ⁺ concentrations of 50–950 µg Hg/L, adsorbent dosage of 50 mg/L, and initial pH 7.0	Huang et al. (2017)
Amino-functionalization			
Amino functionalized Fe ₃ O ₄ -chitosan-glycidyl-methacrylate macromolecular hybrid material	Chelation of cationic Hg species on amino groups or ion exchange of chloroanionic Hg species on protonated amino groups	Q _{max} was 457.3 mg/g with an initial Hg(II) concentrations of 602–2006 mg/L, and the adsorbent dosage was 2500 mg/L, initial pH was 4, and reaction time was 5 h	Elwakeel & Guibal (2015)
Amino functionalized Fe ₃ O ₄ -cellulose	Chemisorption	The maximum Hg(II) sorption capacity was 401.2 mg/g with the adsorbent dosage of 1000 mg/L at 25°C within 5 min	Donia et al. (2012)
Amino functionalized Fe ₃ O ₄ -GO	Chemical precipitation as metal carbonate complexes	The maximum Hg(II) sorption capacity was 167.8 mg/g within 300 min	Guo et al. (2014)

Supported Iron-Based Materials

Carbon-based materials including carbon nanotubes (CNTs), GO, and biochar, often show high mechanical strength and thermal stability, and thereby have been widely used as mechanic supports to prevent the aggregation of iron-based materials. As summarized in Table 2, the resultant sorbents usually demonstrate large sorption capacity of Hg (Alijani et al. 2015; Mahmoud et al. 2015; Tang et al. 2016; Zandi-Atashbar et al. 2018). CNTs are composed of cylindrical shaped graphite sheets rolled up in a tube like structure, and include single walled carbon nanotubes and multiwalled carbon nanotubes (MWCNTs). Alijani et al. (2015) reported that a MWCNTs supported natural magnetic rock, with Fe_3O_4 being the main component, was an efficient Hg(II) adsorbent with a maximum adsorption capacity of 200 mg-Hg/g. GO have been widely applied in preparation of iron-based composite, showing excellent stability and Hg adsorption performance (Huang et al. 2017). Tang et al. (2016) found that Fe–Mn oxides can be coated on the surface of GO through oxygen-containing functional groups and π - π interactions to form a novel GO/Fe–Mn composite. As the mass

ratio of GO to Fe increased from 0 to 7.5, Hg(II) removal efficiency was enhanced by nearly 20%.

Inorganic minerals, such as SiO_2 and Al_2O_3 , have been applied as supporting materials to prepare novel sorbents for Hg (Table 2) to improve stability and increase reaction active sites of iron-based materials. Aluminum oxide, a white hygroscopic powder with octahedral structure, possesses porous structure, high specific surface area, high stability, and strong moisture sorption characteristics. It is resistant to acid and alkali as well as high temperature (Sun et al. 2017a). Sun et al. (2017a) developed an Al_2O_3 -supported nanoscale FeS ($\text{FeS}/\text{Al}_2\text{O}_3$) to treat Hg contaminated water. FeS was evenly distributed on the surface of Al_2O_3 . Al_2O_3 effectively prevented the aggregation and oxidation of FeS. The maximum sorption capacity of Hg(II) onto $\text{FeS}/\text{Al}_2\text{O}_3$ achieved 313 mgHg/g, significantly higher than bare FeS. Pumice is a porous volcanic rock with large surface area and high mechanical strength. It contains open channels allowing water and ions to travel in and out of the crystal structure. Liu et al. (2014) prepared a pumice-supported ZVI using conventional liquid-phase methods via the reduction of ferric ion by borohydride.

Table 2 Supported iron based materials for Hg removal

Iron based materials	Hg immobilization mechanisms	Hg sorption capacity	References
Carbon materials			
Multiwalled carbon nanotubes-magnetic rock	Chemical and physical adsorptions	Q_{\max} was 200 mg/g with Hg(II) concentrations of 0.5–80 mg/L within 90 min	Alijani et al. (2015)
Activated carbon @ Fe_3O_4 -baker's yeast	Electrostatic interaction and physical adsorption	Q_{\max} was 160.5 mg/g with Hg(II) concentrations of 2–100 mg/L at pH 7 within 30 min	Mahmoud et al. (2015)
$\text{Fe}_2\text{CuO}_4/\text{rGO}$	A monolayer adsorption	Q_{\max} of Hg(II) was 1250 mg/g at pH 7 within 60 min	Zandi-Atashbar et al. (2018)
GO/Fe–Mn	Ligand exchange and surface complexation	Q_{\max} was 32.9 mg/g with initial Hg(II) concentrations of 0.1–5 mg/L at pH 7	Tang et al. (2016)
$\text{CoFe}_2\text{O}_4\text{-rGO}$	Monolayer chemisorption	Q_{\max} was 157.9 mg/g at pH of 4.6 and 25°C	Zhang et al. (2014b)
Resin– Fe_3O_4 – β -cyclodextrin–GO	Chelation or ion exchange	Q_{\max} was 88.4 mg/g at pH of 7.1 and 50°C within 30 min	Cui et al. (2015)
$\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ -biochar	Chemisorption, surface complexation, and co-precipitation	The adsorption capacity was 167.2 mg/g in 200 mg/L Hg(II) at pH of 6.5 and 30°C with 6 h	Wang et al. (2018)
Inorganic minerals			
$\text{FeS}/\text{Al}_2\text{O}_3$	Precipitation and surface complexation	Q_{\max} was 313.0 mg/g at pH 6 and 30°C	Sun et al. (2017a)
Pumice–NZVI	Physical adsorption and chemical reduction	The adsorption capacity was 332.4 mg Hg/g Fe in 100 mg/L Hg(II) and 60 min	Liu et al. (2014)
Azolla–OH–NZVI	Coupled Fe(0)–Hg(II) redox reaction and adsorption	Q_{\max} was 459.3 mg/g with Hg(II) concentrations of 2.5–300 mg/L and 1000 mg/L of adsorbent at 25°C	Arshadi et al. (2017)

ZVI particles with a mean diameter of 31 nm were uniformly distributed on the pumice surface. The thermal stability, mechanical strength, and Hg removal capacity of the material was greatly enhanced.

However, similar to surface functionalized iron materials, the application of supported iron-based materials are restricted by the soil deliverability, and are currently suitable for Hg remediation in shallow soils. Moreover, there is limited information available on the regeneration and reusability of these materials.

Conclusions and Future Research Needs

Due to natural and anthropogenic activities, Hg contamination has become one of the major environmental issues all around the world. Iron-based materials can effectively immobilize Hg in water and soil. This review presents the latest development and current limitation of the application of ZVI, iron oxides, and iron sulfides for Hg immobilization. Approaches that improve particle stability and enhance sorption selectivity can help overcome these limitations. To advance the Hg remediation technology enabled by iron-based materials, future research should address the following research gaps and challenges:

1. More studies should be performed to reveal the molecular-level reaction mechanisms between iron-based materials and Hg.
2. The majority of researches has evaluated the performance of iron-based sorbents in removing relatively or extremely high concentrations of Hg in the laboratory. There is a need to work at Hg concentrations which are environmentally relevant.
3. It has been a rule rather than exception that water and soil are polluted with multiple pollutants including metals and organic chemicals. It is imperative to assess the efficacy of iron-based materials on co-contamination.
4. Pilot-scale experiments and field demonstration studies are needed to assess the applicability of iron-based materials for in situ Hg remediation.
5. Information on the long-term stability of stabilized Hg by iron-based materials is very limited. Long-term monitoring data, particularly under field conditions, are critical to evaluate the technology effectiveness.

Acknowledgements This research was supported by the National Natural Science Foundation of China (Grant Nos. 41503085, 41603099), the Natural Science Foundation of Tianjin (Grant No. 17JCYBJC23100), and the Fundamental Research Funds for the Central Universities.

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