



## Review

## Remediation of mercury contaminated sites – A review

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## ABSTRACT

Environmental contamination caused by mercury is a serious problem worldwide. Coal combustion, mercury and gold mining activities and industrial activities have led to an increase in the mercury concentration in soil. The objective of this paper is to present an up-to-date understanding of the available techniques for the remediation of soil contaminated with mercury through considering: mercury contamination in soil, mercury speciation in soil; mercury toxicity to humans, plants and microorganisms, and remediation options. This paper describes the commonly employed and emerging techniques for mercury remediation, namely: stabilization/solidification (S/S), immobilization, vitrification, thermal desorption, nanotechnology, soil washing, electro-remediation, phytostabilization, phytoextraction and phytovolatilization.

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## 1. Introduction

Mercury is regarded as one of the “priority hazardous substances” by the Agency for Toxic Substances and Disease Registry (ATSDR) because of its toxicity, mobility, and long residence time in the atmosphere [1]. The physico-chemical properties of mercury and its compounds are presented in Table 1.

Once mercury is released to the atmosphere it can be retained for between 6 and 24 months and be transported over tens of thousands of kilometers before eventual re-deposition on the Earth's surface [2,3]. Both natural and anthropogenic activities emit mercury to the atmosphere [4]. Mercury in soil generally originates from three major pathways, namely natural processes, anthropogenic activities, and deposition of re-emitted but previously deposited mercury.

Natural activities general constitute the weathering of rocks, volcanic events and geothermal activity [5–9]. Generally, the average background concentration of mercury in soil ranges from 0.03 to 0.1 mg kg<sup>-1</sup> with an average value of 0.06 mg kg<sup>-1</sup>. Anthropogenic activities include coal combustion [10,11], waste incineration [12], metal refining and manufacturing [13,14], chlor-alkali production [15,16], activities which all discharge a large amount of mercury into the environment. The recent estimation of global mercury emissions ranges from 5000 to 8000 metric tons per year [17]. Mercury deposited by dry and wet deposition processes can be trapped by organic matter and thereby become enriched in the surface layers of soil. It is reported that the amount and the quality of organic matter, and the mechanisms regulating the partition of organic matter between aqueous and solid phases, play a major role in the distribution of total mercury in soil and the transport of mercury through soil profiles [18]. Deposited mercury can be transformed by soil bacteria to a more toxic form of mercury, namely methyl mercury (MeHg) [19]. In general, peat cores or sediment cores are used as geological records of atmospheric pollution. Information on atmospheric mercury deposition can be revealed by analyzing these cores [20,21]

Mining activities represent a vector for direct input of mercury into the environment that is not related to the atmospheric contamination. Such activities usually produce large quantities of mine-wastes, which are often abandoned to the environment without any treatment, and can cause direct contamination of adjacent soils with mercury [22].

The contamination of soil with mercury has led to environmental concerns. Mercury can readily be taken up by the plants and be accumulated in the human body through the food chain. It has been demonstrated that crops grown in mercury contaminated soil have an elevated total mercury (THg) concentration in their tissues. Qian et al. [23] found that the total mercury concentration in

vegetables grown mercury-contaminated soil (0.09–0.54 mg kg<sup>-1</sup>) ranged from 0.05 to 0.13 mg kg<sup>-1</sup>. In the Lanmuchang mercury mining area of China, the THg concentration in green cabbages (*Brassica oleracea*) has been shown to reach up to 18 mg kg<sup>-1</sup>. In the Wanshan mercury mining area of China, the THg concentration in rice samples has been recorded as between 4.9 and 215 μg kg<sup>-1</sup> (dry weight). Studies on rice have shown that this plant can assimilate and accumulate MeHg in seed to an unsafe level. MeHg concentration in rice can be as high as 174 μg kg<sup>-1</sup> [24].

The contamination of food crops with mercury poses a direct health risk to local people. Feng et al. [24] showed that the mean MeHg concentrations in hair samples collected from inhabitants of the Wanshan mercury mining area was significantly higher than that from a control site. In this area, rice with an elevated concentration of MeHg was judged to be the main route of mercury exposure. Significant brain damage in rats fed mercury-contaminated rice from the Wanshan mercury mining area was also observed in a study conducted by Cheng et al. [25]. Available data clearly shows that mercury contamination of soil will result in an elevated exposure of mercury to local residents and will consequently pose a direct threat to the health of these people. Due to such environmental and public health concerns, there is great interest in the development of methods to remediate mercury contaminated soils.

The aim of the present work is to review current knowledge on the main aspects concerning mercury contamination in soil, mercury speciation in soil, mercury toxicity to humans, plants and microorganisms, as well as on techniques for remediation of polluted soil together with recent advances in the application of these processes to the detoxification of mercury contamination.

## 2. Mercury contamination in soil

### 2.1. Mercury contamination through mercury mining and metallurgy

In mercury mining districts, soil can become heavily polluted due to the extensive nature of mining and refining activities. Abandoned mercury mine wastes usually contain high mercury concentrations due to inefficient retorting during mining activities [26]. A secondary pathway for mercury release into the environment is through erosion of the primary mine wastes. For example, it has been demonstrated that soluble mercury can leach from calcines (tailings) residual after small-scale refining of the metal [26]. Soils from mercury mines usually present the high concentration of mercury (Table 2). Once discharged into the free environment, mercury can readily methylate by way of a dominantly biotic reaction

**Table 1**  
The physico-chemical properties of mercury and its compounds [2].

Properties	Hg <sup>0</sup>	HgCl <sub>2</sub>	HgO	HgS	CH <sub>3</sub> HgOH
Melting point (°C)	-38.8	277	500 (decomposition)	584 (sublimation)	137
Water-solubility (g L <sup>-1</sup> )	49.6 × 10 <sup>-6</sup> (20 °C)	66 (20 °C)	0.053 (25 °C)	2 × 10 <sup>-24</sup> (25 °C)	-
Boiling point (°C)	356.7	303	-	-	-
Vapor tension (Pa)	0.18	0.009	9.2 × 10 <sup>-12</sup>	nd	0.9

**Table 2**  
Reported mercury concentration in soils at a range of contaminated sites.

Category	Location	Mercury contaminated soil (mg kg <sup>-1</sup> )	References
Wanshan Hg mine	Guizhou, China	5.1–790	[22]
Wuchuan Hg mine	Wuchuan, China	0.33–320	[27]
Lanmuchang Hg mine	Guizhou, China	0.41–610	[28]
Tong guang Gold mine	Shanxi, China	0.9–76	[29]
Dexin Gold mine	Jiangxi, China	–1100	[30]
Artisanal zinc smelting area	Guizhou, China	0.06–0.35	[31]
Usagre Hg mine	Badajoz, Spain	5–778	[32]
Almadén Hg mine	Almadén, Spain	–9000	[33]
Almadén Hg mine	Almadén, Spain	–8898	[34]
Mieres Hg mine	Asturias, Spain	1.7–472.1	[35]
Idrija Hg mine	Idrija, Slovenia	8.4–415	[36]
Podljubelj Hg mine	Podljubelj, Slovenia	0.17–719	[37]
Mine-smelter area	Idrija, Slovenia	2.44–2456	[38]
Chlor-alkali factory	Estarreja, Portugal	0.9–89.2	[39]
Caveira sulfide mine	Grândola, Portugal	1.1–76.5	[39]
Chlor-alkali plant	Estarreja, Portugal	0.01–91	[40]
Hg mine	Alaska, USA	0.05–5326	[41]
Nevada Hg mine	Nevada, USA	–170	[42]
Haliköy Hg mine	Beydağ, Turkey	0.2–33	[43]
Areometer factory	Warsaw, Poland	62–393	[44]
Chlor alkali plants	Germany	1.1–1.7	[45]

that may be stimulated by water temperature [46,47], and is mediated by the presence of obligate anaerobic sulfate-reducing bacteria [48,49]. Thus, elevated methyl mercury levels in soil have been found in rice paddy fields that have become contaminated through adjacent mining activities. For example, in paddy fields near the Wanshan and Wuchuan mercury mines of China, methyl mercury concentrations in soils were 23 and 20 µg kg<sup>-1</sup>, respectively [27,50].

### 2.2. Mercury contamination in gold mines and Zn/Pb smelters

Small-scale gold mining activities are damaging to the environment, in part because of the widespread use of mercury in the gold extraction system. After thorough grinding of a gold-containing ore or silt, mercury is added to the mixture to create a gold amalgam. Subsequent burning of this amalgam concentrates the gold into a pellet but releases elemental mercury into the environment [51]. Feng et al. [29] found that the total mercury concentration ranged from 0.9 to 76 mg kg<sup>-1</sup> in soil samples collected from the Tongguan gold mining area in China. Pataranawat et al. [52] reported that an elevated mercury concentration (10.5 mg kg<sup>-1</sup>) was found in surface soil collected from a small-scale gold mining area in Phichit province, Thailand. In soil samples collected from the Tapajós gold mining reserve, Brazil, the total mercury concentration in soil was nearly 13 times higher than the background sites [53].

Mercury emission from the refining of non-ferrous metals also represents a major source of anthropogenic mercury through the deposition of atmospheric mercury onto soils surrounding metal smelters. Soil samples collected from the Hezhang and Zhuzhou artisanal Zn smelting areas of China showed an average total mercury concentration of 0.38 and 2.27 mg kg<sup>-1</sup>, respectively; values that were significantly higher than the local background values (Hezhang: 0.14–0.15 mg kg<sup>-1</sup>; Zhuzhou: 0.20 mg kg<sup>-1</sup>) [54,55]. Similarly, soil samples collected from the lead smelting town of Příbram in the Czech Republic showed a range of mercury concentration between 0.07 and 2.32 mg kg<sup>-1</sup> [56]. Stafilov et al. [57] reported a wide concentration range for mercury in soil at a lead and zinc industrial region in the Republic of Macedonia (0.01–12 mg kg<sup>-1</sup>). A higher mercury value of 14.6 mg kg<sup>-1</sup> was reported in soil sampled from the Huludao zinc smelting area in China [58].

### 2.3. Mercury contamination in chemicals and allied production facilities

Mercury has been widely used in a range of chemical production facilities such as those involved with the synthesis of chlor-alkali, chloroethylene and acetaldehyde. Prior to the 1990s, chlor-alkali factories around the world produced chlorine and caustic soda using mercury as a liquid cathode. Mercury pollution has occurred at such industrial facilities through both atmospheric mercury emission and the discharge of mercury containing effluents to land and water [15,59]. Biester et al. [60] reported average mercury concentrations in soil between 0.44 and 0.69 mg kg<sup>-1</sup> within 1 km of three chlor-alkali plants in Europe. Southworth et al. [15] reported average mercury concentrations in soil between 0.7 and 9.4 mg kg<sup>-1</sup> within 30–800 m from the cell building of a chlor-alkali plant in USA. Reis et al. [40] assessed the level of contamination around a mercury-cell chlor-alkali factory operated in Estarreja (North-western Portugal). The total mercury concentration in soil was found to be highly variable, ranging between 0.01 and 91 mg kg<sup>-1</sup>. Bernaus et al. [61] investigated the level of mercury contamination around a chlor-alkali plant in the Netherlands and they observed mercury concentrations as high as 1150 mg kg<sup>-1</sup> in the soil.

An environmental legacy has been left by several well-known industrial facilities that last century directly discharged mercury contaminated chemical waste to the environment without any treatment. In Japan, a serious mercury pollution event happened in 1950s, when a chemical company (Chisso Co.) discharged significant volumes of Hg-containing waste water to the sea leading to an infamous outbreak of mercury poisoning today known as Minimata Disease [62]. In China, acetaldehyde producing plants were important mercury pollution sources in 1990s. Guizhou Organic Chemical Plant (GOCP), which used mercury as a catalyst for acetaldehyde production, discharged significant amounts of Hg-containing drainage into local ecosystems [63]. The reported mercury concentration in drainage-impacted paddy fields is at least two orders of magnitude higher than background sites [64].

### 2.4. Mercury contamination in landfills

Worldwide, landfills are an important source of mercury pollution. Mercury-containing wastes deposited into landfills include

batteries, electrical and electronic equipment, blood-pressure meters, fluorescent lamps and thermometers [65]. Li et al. [66] analyzed the mercury concentration in waste at four municipal solid waste landfills in Guiyang and Wuhan City, China. The results of this study showed that the mercury concentration in waste ranged from 0.17 to 46.22 mg kg<sup>-1</sup> with a geometric mean of 0.57 mg kg<sup>-1</sup>. Earle et al. [67] analyzed the mercury concentration in waste at municipal solid waste landfills in Florida, USA. Their results showed that the mercury concentration in waste ranged from 0.03 to 16.8 mg kg<sup>-1</sup> with a geometric mean of 0.17 mg kg<sup>-1</sup>. Kim and Kim [68] found a significantly higher elemental mercury concentration (3.45–2952 ng m<sup>-3</sup>) in the air at the Nan-ji-Do landfill in Korea.

### 2.5. Mercury contamination at military installations

The Y-12 National Security Facility site, located at Oak Ridge, USA, is heavily contaminated with mercury due to elemental mercury that was used for the manufacture of nuclear weapons during the 1950s and early 1960s. It is estimated that nearly 75–150 Mt of mercury was released into the environment [69]. The mercury concentration in the surrounding watershed/soil ranged from 0.01 to 7,700 mg kg<sup>-1</sup> [70]. Bakir et al. [71] analyzed mercury in ground-water samples collected from a military unit in Ankara, Turkey. Their study showed that mercury concentrations exceeded maximum contaminant levels set by the World Health Organization (WHO).

### 2.6. Mercury contamination at wood/forestry impregnation sites

Mercury chloride solution has been historically used by the wood preservation industry due to the antiseptic effect of this chemical. At such wood impregnation sites, improper storage of treated wood or leakage of solution has often led to severe environmental contamination [72]. Bolle et al. [72] collected soil and ground water samples from a former wood impregnation plant in Southern Germany, and showed that the mercury concentration in soil and ground water was in the range of 3–11,000 mg kg<sup>-1</sup> and 0.5–230 µg L<sup>-1</sup>, respectively. Biester and Scholz [73] collected soil samples from a former wood preservation site near the city of

Freiburg, SW Germany and found that mercury concentrations in these soil samples were as high as 144 mg kg<sup>-1</sup>.

### 2.7. Mercury contamination at other sites

A range of studies has found evidence for mercury contamination of soil at other industrial facilities, including coal-fired power plants, and facilities for the production of mercury thermometers, fluorescent lamps, batteries and electrical products. Soil samples collected from a coal-fired power plant in China, showed a mercury concentration ranging from 0.14 to 2.11 mg kg<sup>-1</sup> (with average value of 0.61 mg kg<sup>-1</sup>) [74]. The mercury concentration in effluent, air and soil samples collected from a battery factory have been reported to be 5.2 mg L<sup>-1</sup>, 40,000 ng m<sup>-3</sup> and 472 mg kg<sup>-1</sup>, respectively [75]. Chen et al. [76] collected soil samples from land at a fluorescent lamp company in China and found that the mercury concentration in these samples ranged from 0.03 to 0.19 mg kg<sup>-1</sup>, and were 3.3 times higher than a control site. Karunasagar et al. [77] analyzed the mercury concentration in water, sediment and fish samples from Kodai Lake in India, which suffered mercury contamination due to waste discharged from a thermometer factory. The results of this study showed that the mercury concentration in water, sediment and fish ranged from 356 to 465 ng L<sup>-1</sup>, 276 to 350 µg kg<sup>-1</sup> and 120 to 290 µg kg<sup>-1</sup>, respectively.

## 3. Mercury speciation in soil

It is currently well known that the determination of a total mercury concentration is insufficient for understanding the biogeochemical cycle of the metal and for establishing an appropriate remediation method. This is mainly due to the lack of information concerning the reactivity (transformation/conversion), bioavailability and toxicity of mercury in soil afforded by such a single determination [78]. The study of mercury speciation can be used to predicate and explain the behavior of mercury in soil. Several approaches such as sequential extraction procedures (SEP), pyrolysis, X-ray absorption fine spectroscopy (XAFS), as well as nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) have been used to study mercury speciation in soil [79–83]. Among these methods, SEP, pyrolysis and XAFS are

**Table 3**  
The speciation of mercury in soil as determined by pyrolysis extraction methods.

Samples	Operating conditions	Compounds released	Percentage of total mercury released	Reference
Soils	<180 °C	Hg <sup>0</sup> , Hg <sub>2</sub> Cl <sub>2</sub>	10–30%	[84]
Tailing	<100 °C	Hg <sup>0</sup>	Nd	[79]
	150–250 °C	Matrix bound Hg		
	250–350 °C	Cinnabar		
	>400 °C	HgSO <sub>4</sub> , HgO		
Soils	25–350 °C	Fe-oxhydroxides/clay		[85]
	453 °C	Minerals bound Hg	20–50%	
		Cinnabar	50–80%	
Soils	200–220 °C	Humic acid bound Hg	Nd	[33]
	310 °C	Cinnabar		
Sediments and soils	<100 °C	Hg <sup>0</sup>	–5%	[86]
	150–250 °C	Non cinnabar Hg	–40%	
	250–350 °C	Red Cinnabar	5–30%	
Soils	200–250 °C	Non cinnabar Hg	–79%	[87]
	250–350 °C	Cinnabar	18%	
Soils (Chlor-alkali plant)	<100 °C	Metallic Hg	20%	[73]
	150–250 °C	Matrix-bound Hg	80%	
	350 °C	Cinnabar	–	
Soils (Hg mine)	<100 °C	Metallic Hg	–	
	150–250 °C	Matrix-bound Hg	11%	
	350 °C	Cinnabar	89%	

Nd: lack of data.

**Table 4**  
The speciation of mercury in soil as determined using X-ray absorption spectroscopy methods.

Site description	Sample types	Total mercury mg kg <sup>-1</sup>	Mercury speciation	Percentage of total mercury	Reference
Mercury deposits, California	Mercury mine wastes	230–1060	Cinnabar	16–58%	[81]
			Metacinnabar	39–84%	
			HgCl <sub>2</sub>	–19%	
			HgSO <sub>4</sub>	–11%	
			Hg <sub>3</sub> S <sub>2</sub> Cl <sub>2</sub>	13–34%	
Chlor-alkali plant, Netherlands	Soils	4.3–1150	Hg <sub>2</sub> OCl	10%	[61]
			Cinnabar	26–37%	
			HgO	6–86%	
			HgSO <sub>4</sub>	17–80%	
			Hg <sub>3</sub> S <sub>2</sub> Cl <sub>2</sub>	33–37%	
Val Basento industrial site, Italy	Soils (<2 mm)	7–240	Cinnabar	27–28%	[88] <sup>a</sup>
			Metacinnabar	14–15%	
			Hg <sub>3</sub> S <sub>2</sub> Cl <sub>2</sub>	33–34%	
			Amorphous(Hg, S, Cl)	24–25%	
			Cinnabar	14–24%	
	Soils (<2 μm)		Metacinnabar	18–25%	
			Hg <sub>3</sub> S <sub>2</sub> Cl <sub>2</sub>	18–30%	
			Amorphous(Hg, S, Cl)	28–43%	
			Cinnabar	18–84%	
			Metacinnabar	20–75%	
Mercury mines, California; gold mine, Nevada	Mercury mine wastes (near the Hg depositional environment)	188–19,500	HgO	26–27%	[89]
			HgCl <sub>2</sub>	13–24%	
			Hg <sub>2</sub> OCl	–10%	
			Hg <sub>3</sub> S <sub>2</sub> Cl <sub>2</sub>	13–34%	
			Hg <sub>3</sub> O <sub>2</sub> SO <sub>4</sub>	11–19%	

<sup>a</sup> Metacinnabar and amorphous are measured by XRD (X-ray diffraction).

frequently used in mercury speciation analysis. Results on mercury speciation measured by pyrolysis and XAFS derivatives from different researchers are showed in Tables 3 and 4. In general, soils from mercury mining areas have a low content of bioavailable mercury due to the majority of mercury being present as HgS [83,89]. However, soil from gold mining areas and industry factories presents a relatively high proportion of bioavailable mercury because of the release of mercury into the soil as a soluble form [44,90,91].

Information on the mercury speciation in soil is crucial for establishing any remediation method. In general, a high proportion of bioavailable mercury in soil would demand the use of soil washing, phytoextraction and electro-remediation techniques through which mercury would be removed. For soil with a low bioavailable mercury concentration, metal availability must first be increased to facilitate the use of these methods. For soil with high elemental mercury content, methods such as stabilization/solidification (S/S), vitrification and immobilization are suitable remediation options. For soil with high non-available Hg content, thermal desorption technology may be suitable where mercury can be volatilized at high temperature.

#### 4. Mercury toxicity

Mercury in the environment is an increasing health concern. Mercury has been reported to cause various neurodegenerative diseases such as Amyotrophic lateral sclerosis, Alzheimer's diseases and Parkinson's disease [92]. Elemental mercury and inorganic mercury compounds have been reported to damage the immune system and kidneys [93] while MeHg has been reported to pose a threat to the cardiovascular and nervous systems [94,95]. The greatest human health concerns are related to MeHg which has the ability to biomagnify in the food chain. MeHg can be taken up by the aquatic organisms and further accumulate in the fish. Therefore, populations living in areas of mercury contamination that consume a high amount of fish are at greatest risk of MeHg poisoning [62,96]. Recent research has showed that rice will also accumulate MeHg from mercury contaminated soils in mercury mining areas [97].

Rice is now recognized as a major pathway for MeHg exposure in mercury mining areas of China [97] where fish is not a major source of protein [24].

The toxicity of mercury to plants can be summarized as following: (1) affect on the antioxidative system [98]; (2) affect on the photosynthesis system [99]; (3) inhibition of plant growth and yield production and an affect on nutrient uptake and homeostasis [100]; (4) the inducement of genotoxicity [101]. Many researchers have demonstrated that mercury can induce oxidative stress [102] and enhance lipid peroxidation [103,104] in plant cells, and subsequently increase the activity of antioxidant enzymes such as superoxide dismutase (SOD), ascorbate peroxidase (APX), glutathione reductase (GR), peroxidase (POD), as well as reduced glutathione (GSH). A review of the impacts of mercury on antioxidative systems as described by a range of researchers is shown in Table 5. These described antioxidant enzymes and GSH could potentially protect cells from mercury induced damage. A review of the reported effects of mercury on the photosynthetic system as reported by a range of researchers is shown in Table 6. Mercury has been found to affect growth and metabolism of plants to varying degrees depending on the concentration and status of mercury in the plant tissue [100]. Gao et al. [107] found that the biomass of *Jatropha curcas* seedlings (cotyledons, hypocotyls and radicles) increased gradually with increasing mercury concentrations, peaking in seedlings exposed to a mercury concentration of 50 μM, and then decreased beyond this level. In terms of genotoxicity, a number of potentially reactive sites for mercury binding are present in DNA, depending on external conditions such as ionic strength, presence of different competing ions, and base composition [101]. Mercury, where present, could bind with DNA and thus cause damage to chromosomes [114].

Mercury affects all groups of organisms and ecosystem processes, including microbially mediated processes and macro/mezo fauna-mediated processes. The genetic structure and functional diversity of bacterial communities are sensitive to mercury exposure. For example, Ranjard et al. [115] used HgCl<sub>2</sub>-enriched PCA media (plate count agar) to distinguish mercury resistant and sensitive bacteria. In this work, the global population of

**Table 5**  
The affect of mercury on the antioxidative systems of plants.

Plant species	Substrate types	Mercury content	Response of antioxidative system	References
<i>Atriplex codonocarpa</i>	Hydroponics	0.05–1 mg L <sup>-1</sup>	Root: GR activity remained unchanged at 0,0.05,0.1 mg L <sup>-1</sup> and reduced by 65% at 1 mg L <sup>-1</sup> ; APX reached a maximum at 0.05 mg L <sup>-1</sup> ; SOD activity reached a maximum at 0.1 mg L <sup>-1</sup> Hg; Shoot: GR activity remained unchanged at 0,0.05,0.1 mg L <sup>-1</sup> and reduced by 20–30% at 1 mg L <sup>-1</sup> ; APX remained unchanged; SOD activity increased gradually and leveled off at 0.1 mg L <sup>-1</sup> Hg;	[105]
<i>Medicago sativa</i>	Semi-hydroponics system	0–30 μM	Root: GR activity was inhibited; APX activity increased appreciably. Shoot: GR activity was enhanced; APX activity did not change appreciably.	[106]
<i>Pistacia lentiscus</i> . and <i>Tamarix gallica</i>	Hydroponics	0–100 μM	MDA increased both in the root and shoot of the two plant species; total —SH concentration increased in roots of <i>P. lentiscus</i> and in roots and stems of <i>T. gallica</i> .	[104]
<i>Lycopersicon esculentum</i> Mill	Perlite, vermiculite	0–50 μM	H <sub>2</sub> O <sub>2</sub> and MDA content increased both in the leaf and root; SOD, and CAT activities increased with Hg-exposure.	[103]
<i>Sesbania drummondii</i>	Murashige–Skoog (MS) medium	0–50 μM	The contents of GSH and GSH/GSSG ratio increased up to a concentration of 40 μM Hg and then severely declined at 50 μM Hg; The SOD, APX and GR activities followed the same trends as antioxidants, first increased up to a concentration of 40 μM Hg and then declined in the presence of 50 μM Hg.	[98]
<i>J. curcas</i>	Murashige–Skoog (MS) medium	0–400 μM	SOD activities in cotyledons, hypocotyls and radicles reached the maximum at 100 μM; POD activities in the cotyledons and hypocotyls reached peaks at 200 μM, and the highest activity in the radicles was observed at 100 μM; CAT activities in the cotyledons and hypocotyls were significantly induced, and the highest activity in the radicles was observed at 200 μM; PAL activities in the cotyledons and radicles reached peaks at 200 and 100 μM, respectively.	[107]
<i>Chlamydomonas reinhardtii</i>	Nutrient-rich BG-11 medium	0–8 μM	SOD activity increased with Hg concentrations at 1–6 μM but decreased at 8 μM; CAT and APX increased with the Hg concentrations within 2–6 μM but decreased at 8 μM;	[108]
<i>Cucumis sativus</i>	Hydroponics	0–500 μM	For 10-day-old and 15-day-old seedlings, CAT activity peaked at 50 and 250 μM Hg respectively; APX activity was inhibited at concentrations of 250 and 500 μM Hg, both for 10-day-old and 15-day-old seedlings.	[109]
<i>Medicago sativa</i>	Hydroponics	0–40 μM	NADH oxidase and LOX activities increased with Hg expose; SOD, CAT, APX, POD activities increased with Hg concentrations at 1–6 μM but decreased at 10–40 μM;	[110]
<i>Medicago sativa</i>	Hydroponics	0–40 μM	SOD and POD activities increased after Hg treatment of roots. APX activity was stimulated at 40 μM Hg; GR activity was depressed at higher concentrations of Hg (10–20 μM).	[111]

GR, glutathione reductase; APX, ascorbate peroxidase; SOD, superoxide dismutase; MDA, malondialdehyde; CAT, catalase; GSH, reduced glutathione; GSSG, oxidized glutathione; POD, peroxidase; PAL, phenylalanine ammonia-lyase; LOX, lipoxygenase.

the microbial community was decreased, but that of the mercury resistant bacteria (HgR) populations was increased through mercury expose. Soil meso- and macro-fauna constitute a major part of the soil system and have a key role in influencing soil nutrient mineralization processes. Mercury is highly toxic to these fauna and influence their survival, reproduction, growth and behavior. Gudbrandsen et al. [116] reported that the 28-day 50% lethal concentrations (LC<sub>50</sub>) for earthworms (*Eisenia fetida*) exposed to mercury(II) was 170 mg kg<sup>-1</sup>. Lock and Janssen [117] found that the 42-day LC<sub>50</sub> for white worm (*Enchytraeus albidus*) exposed to mercury(II) was 22 mg kg<sup>-1</sup> in a soil mixed with 70% sand, 20% kaolinite clay and 10% finely ground sphagnum peat.

## 5. Remediation techniques

Government, industry, and the public now recognize the potential hazards that mercury poses to the environment. In response to a growing need to address environmental contamination, many efforts have been undertaken to develop remediation technologies to reduce or to manage mercury contamination in soil. These efforts have been undertaken under both laboratory and field conditions. In general, the extraction methods are required to remove mercury from waste containing greater than 260 mg kg<sup>-1</sup>. However, stabilization methods can be used to treat wastes which have mercury concentration less than 260 mg kg<sup>-1</sup>. The requirement of stabilization is that all final waste forms leach less than 0.2 mg L<sup>-1</sup> of

**Table 6**  
The affect of mercury on the photosynthesis system of plants.

Plant species	Substrate types	Mercury content	Damage of Photosynthesis system	References
<i>Cladonia arbuscula subsp. Mitis</i> and <i>Peltigera rufescens</i>	HEPES solutions,	0–500 $\mu\text{M}$	Chlorophyll <i>a</i> decreased in <i>P. rufescens</i> at 50 $\mu\text{M}$ Hg, while in <i>C. arbuscula subsp. mitis</i> at 25 $\mu\text{M}$ Hg; Photosynthetic efficiency decreased at 25 and 50 $\mu\text{M}$ Hg in <i>P. rufescens</i> and <i>C. arbuscula subsp. mitis</i> respectively.	[112]
<i>Pistacia lentiscus</i> . and <i>Tamarix gallica</i>	Hydroponics	0–100 $\mu\text{M}$	Chlorophyll <i>a</i> decreased both in <i>P. lentiscus</i> and <i>T. gallica</i> ; chlorophyll <i>b</i> was less affected by Hg.	[104]
<i>Lycopersicon esculentum</i> Mill	Perlite, vermiculite	0–50 $\mu\text{M}$	Chlorophyll content decreases after 10-days Hg expose in the first and the second leaves.	[103]
<i>Cucumis sativus</i>	Hydroponics	0–500 $\mu\text{M}$	The presence of Hg in the substrate caused a linear decrease of chlorophyll content in the cotyledons; at 500 $\mu\text{M}$ Hg, chlorophyll content was reduced by 59% and 94%, respectively, in 10- and 15-day-old seedlings.	[109]
<i>Spirulina platensis</i>	Zarouk's medium	0–20 $\mu\text{M}$	The increase of Hg concentration led to a decrease in the maximal efficiency of PSII photochemistry, the efficiency of excitation energy capture by the open PSII reaction centers, and the quantum yield of PSII electron transport.	[113]

mercury as assessed by the Toxicity Characteristic Leaching Procedure (TCLP) of the Resource Conservation and Recovery Act (RCRA) [118].

### 5.1. Stabilization/solidification

Solidification/stabilization processes are non-destructive methods to immobilize the hazardous constituents of a matrix while decreasing the waste surface area and permeability. This method involves physically binding or enclosing contaminants within a stabilized mass (solidification) or inducing chemical reactions between the stabilizing agent and the contaminants to reduce their mobility (stabilization) [119]. The stabilization process involves mixing soil or waste with chemical binders such as cement, sulfide and phosphate binders, polyester resins, or polysiloxane compounds to create a slurry, paste, or other semi-liquid state, which is allowed time to cure into a solid form [119]. For mercury, powder reactivated carbon (PAC) and thiol-functionalized zeolite (TFZ) have been used as binders [120,121]. Based on the type of additives through which solidification is achieved, S/S can be categorized into the following groups: cement based, pozzolan based, the thermoplastic method, the organic polymerization method, the encapsulation method, organophilic-clay based [122]. Among these methods, cement-based S/S is of increasing importance as an option for remediating contaminated sites because of its low material and equipment cost. Soil can be treated both *in situ* and *ex situ*. *In situ* S/S techniques are preferred since labor and energy costs are lower. However, there are few vendors of *in situ* processes while many exist for *ex situ* processes since mixing *in situ* is difficult to evaluate [123]. Many studies have reported the treatment of mercury *ex situ*. Zhang and Bishop [120] reported the use of PAC and cement to stabilize and solidify mercury in waste. The mercury was stabilized by reactivated carbon, and then mixed with Portland cement for solidification. The results showed that wastes with up to 1000 mg kg<sup>-1</sup> mercury were stabilized and solidified well enough to pass the TCLP test. Fuhrmann et al. [124] reported the use of powdered sulfur polymer cement (SPC) and sulfide to treat mercury wastes. Subsequent TCLP testing showed that the mercury concentration in the leachate of the treated wastes was nearly 94 times lower than that of the non-treated wastes. Zhuang et al. [125] found that ferric-lignin derivatives (FLD) and Portland cement (PC)

could be used to treat high mercury-contaminated brine purification sludge (BPS). Samples (BPS/PC) after treatment with 7% and 10% FLD, showed a reduction in the TCLP value for mercury from 256 to 35 and 554 to 110  $\mu\text{g L}^{-1}$ , respectively. In this example, the ferric-lignin derivative, which is a lignin-based solid with brown color, is available as a by-product of pulp mill processes. Zhang et al. [121] reported that mercury wastes could be safely disposed of after S/S (thiol-functionalized zeolite and Portland cement). Randall and Chattopadhyay [126] reported the use of chemically bonded phosphate ceramics (CBPC) technology to stabilize mercury in mercury waste mixtures. In this technology, the mercury containing wastes is hosted by magnesium potassium phosphate hydrate (MKP), which is formed by the reaction between magnesium oxide (MgO) and potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>). Common alkali sulfide acts as a binder. The TCLP results from this remediation option showed that the mercury concentration in the leachate of stabilized waste containing an original 50 wt% loading of elemental mercury and HgCl<sub>2</sub> could be reduced to below the 0.2 mg L<sup>-1</sup>. However, wastes containing an initial 70 wt% loading of elemental mercury and HgCl<sub>2</sub> had a final leachate concentration exceeding the regulatory treatment standard of 0.2 mg L<sup>-1</sup>. Sulfur polymer stabilization/solidification (SPSS) is based on sulfur polymer micro-encapsulation and is a mixed-waste treatment technology that was developed at the Brookhaven National Laboratory (BNL). Sulfur polymer cement (SPC) is made with 95 wt% elemental sulfur reacted with 5 wt% of an organic modifier. Two 55 gallon drums of mixed-waste soil containing high concentrations of mercury and about 62 kg of radioactively contaminated elemental mercury were successfully treated by SPSS at Brookhaven National Laboratory. The TCLP tests showed that the mercury concentration in the leachate of the treated wastes meet the requirement set by the US EPA [127].

The materials involved in the S/S technique are inexpensive and commercially available. However, the drawbacks of this remediation option are that: (1) the metals are not removed from the contaminated media; (2) there is a significant increase in waste mass and volume; (3) there is a need for future monitoring of the heavy metals on site; (4) there is a questionable longevity of the solidified/stabilized materials [128].

*Field applications:* S/S is a well established technology and frequently implemented in the USA [129]. According to the US EPA,

S/S of soil and waste that contain mercury has been applied at 12 full-scale and 6 pilot-scale projects. The majority of these full-scale applications are at Superfund sites including metal mining and smelting locations, former chlor-alkali manufacturing plants, chemical and allied product manufacturing facilities and industrial landfills [119]. In addition to US EPA reported information on field scale and pilot-scale application of S/S, there are a range of literature references to S/S of mercury contaminated wastes and soils. Dermont et al. [129] reported the pilot-scale application of S/S to treat mercury-containing wastes at a Sulfur Bank Mercury Mine, at the Lake County superfund Site, California. Zhuang et al. [125] reported the full scale use of an *ex situ* S/S technique to treat mercury contaminated brine purification sludge (BPS) collected from a former chlor-alkali plant in Canada. After treatment, the TCLP mercury was reduced from  $188 \mu\text{g L}^{-1}$  for the untreated BPS to  $17.2 \mu\text{g L}^{-1}$  for the treated BPS. The cost this technology was estimated to be US\$91/Mt of waste.

## 5.2. Immobilization

Immobilization is an *in situ* technology that reduces the potential toxicity, mobility or solubility of mercury by adding stabilizing agents to a contaminated waste or soil. Agents that are used for immobilization can be classified into one of the following groups: (1) sulfur-containing ligands; (2) reducing agents; (3) adsorbing agents. Mercury(II) is a soft Lewis acid and complexes readily with soft Lewis bases such as reduced-S ligands [130]. Adding reduced S to mercury-contaminated soil to precipitate  $\text{HgS(s)}$  has therefore been proposed as a method to stabilize mercury-contaminated soils and materials.  $\text{HgS(s)}$  is relatively insoluble and less volatile than other forms of mercury and is thus potentially less harmful. Piao and Bishop [131] reported the use of sulfide to treat mercury-containing wastes with a mercury concentration as high as  $2,300 \text{ mg kg}^{-1}$ . The TCLP for mercury showed a reduction from  $1900 \mu\text{g L}^{-1}$  for the untreated waste to  $35 \mu\text{g L}^{-1}$  for the treated waste. Kot et al. [132] conducted a pot experiment to investigate the immobilization of mercury by colloidal sulfur. The results indicated that the addition of colloidal sulfur significantly decreased the mercury concentration in soil solution, as well as mercury accumulation by the oats (*Avena sativa*). In another report, the addition of 0.5% granular sulfur to mercury contaminated soil has been found to stabilize 78% of water soluble and exchangeable mercury present in the soil [133]. Liu et al. [134] reported that FeS could effectively immobilize mercury in solution *via* precipitation and adsorption process. Rieser et al. [135] reported to use sulfide and phosphate to treat mercury-containing wastes collected from the Borden Chemicals and Plastics plant (BCP) in Geismar, Louisiana. Their results showed that mercury concentrations in the leachate were significantly reduced for the sulfide treatment, whereas the mercury concentration in leachate was less affected by the phosphate treatment. Bower et al. [130] found that the coordination of mercury with pyrite could form an ordered monolayer of monodentate  $\text{Hg-Cl}$  complexes, and that this thin barrier could inhibit the movement of mercury through a substrate. Reducing agents such as iron chips have been used for the treatment of mercury contaminated soil [136]. The stabilization of mercury by iron chips in soil is dominated by two major pathways. The iron chips could be oxidated, and produce goethite in soil. Mercury in soil solution can be adsorbed onto goethite, a reaction that is promoted in the presence of fulvic acid [137]. But  $\text{Hg}^{2+}$  in soil solution could alternatively be reduced to  $\text{Hg}^0$  by iron chips [136]. Meng et al. [138] investigated the effectiveness of used tire rubber for immobilizing  $\text{Hg(II)}$  in a contaminated soil under field rainwater leaching tests. In the rubber-treated soil, the mercury concentration in the rainwater leachate was  $1.2 \text{ ng mL}^{-1}$ , which was significantly lower than that for the untreated soil ( $84 \text{ ng mL}^{-1}$ ). Furthermore,

the rubber treatment inhibited the evolution of metallic  $\text{Hg}^0$  in the mercury-contaminated soil. Effective stabilization of mercury using tire rubber is best performed under acidic to neutral pH conditions. The reduction of mercury leaching may attribute to the sulfur groups present in the rubber. Mercury could be adsorbed to these sulfur sites through the formation of surface complexes. Qian et al. [139] reported the use of alkali-activated slag (AAS) to stabilize mercury. Soluble mercury ions can be effectively immobilized in the AAS matrix with the leachate meeting the TCLP mercury limit. Physical precipitation was considered to be the controlling mechanism for the immobilization of mercury, by which mercury ions tend to hydrolyze to form a red precipitate of  $\text{HgO}$  in an alkali hydroxide solution or cementitious environment [140,141]. Another reported adsorbing agent for mercury ions is aluminum drinking water treatment residual, which consists of small particles of hydrous oxide which can effectively adsorb free mercury ions [142]. In general, mercury in waste is usually present in a variety of chemical species and the impact of mercury speciation on the performance of this technology should be taken into consideration. For example, the chemical dithiocarbamate (DTC) can be used to stabilize waste contaminated by  $\text{HgS/HgCl}_2/\text{HgO/Hg}^0/\text{C}_6\text{H}_5\text{HgCl}$ , however, calcium polysulfide and sodium borohydride have failed to stabilize any species of mercury in all samples tested [118].

The National Risk Management Research Laboratory (NRMRL) reported the effectiveness of three stabilization technologies for immobilizing mercury in mercury-containing waste. The three stabilization technologies used were: (1) a silica micro encapsulation (SME) process developed by Klean Earth Environmental Company (KEECO), (2) an inorganic sulfide stabilization technology (ENTHRALL<sup>®</sup>) developed by E&C Williams and (3) a generic phosphate treatment. Among the three technologies, the KEECO silica micro encapsulation technology was found to be more effective than the other technologies in reducing mobile mercury ( $<25 \mu\text{m}$ ) concentration. However, the use of silica micro encapsulation technology would increase the mercury levels in the dissolved fraction ( $<0.45 \mu\text{m}$ ) [143].

The advantages of stabilization are that treated sites can be revegetated and that the technology can be readily applied to large sites. The disadvantages include an increase in the volume of waste and the long-term monitoring the stability of the resulting stabilized waste product.

*Field applications:* Zhuang et al. [125] reported the field scale use of ferric sludge (FS) to immobilize mercury in 9 t of mercury contaminated soils. Ferric sludge (FS) was used at a ratio of 10% of the total weight of soil. Over a period of 60 days, the TCLP mercury was reduced from  $237.5 \mu\text{g L}^{-1}$  for the untreated soils to  $30.4 \mu\text{g L}^{-1}$  for the treated soils.

## 5.3. Vitrification

Vitrification is an immobilization technique that is mainly used to remediate soils contaminated with heavy metals mixed with radioactive elements at military installations. Vitrification involves heating the wastes to form a vitrified end product, into which the contaminants are incorporated and subsequently immobilized [119]. The process may also cause contaminants to volatilize, thereby reducing their concentration in the soil and waste [144]. Cicero and Bickford [145] reported the use of vitrification technology to treat mercury-contaminated soil collected from a TNX pilot-plant facility at the Savannah River site. The results from this study showed that the soil was converted to a durable and leach resistant glass waste and that the optimum waste loading was demonstrated to be 60 wt % wastes with 24 wt %  $\text{Na}_2\text{CO}_3$  and 16 wt%  $\text{CaCO}_3$  used as the glass forming additives. Moreover, mercury in the offgas could be successfully captured by conventional



condensers. The Glass Furnace Technology (GFT) was an *ex situ* technology to treat river sediments contaminated with PCB and other heavy metals. The GFT consisted of two steps: sediment drying and dried-sediment vitrification. The use of this technology to treat sediment from Wisconsin in the USA showed that the mercury concentration in the sediment was significantly decreased (mercury concentration below  $1 \text{ mg kg}^{-1}$ ) [146]. The plasma hearth process (PHP) is a high-temperature thermal process, which has been adapted from a commercial metallurgical technology, for the treatment of mixed waste. The waste is converted into a molten form by heating and a stable glassy and/or crystalline waste form would form when the molten cools. Hazardous organics are destroyed through combustion during the process and the hazardous metals and radioactive components are incorporated in the molten phase [147].

The advantages of this method are that: (1) the treated waste is durable, resistable, and with good long-term stability; (2) the volume of the waste can be reduced; and (3) the treated waste product can be reused. The major disadvantages are high cost and the necessary capture and subsequent treatment of off gases [129].

**Field applications:** Many full-scale and pilot-scale applications of vitrification to treat mercury-containing wastes have been demonstrated [119,129]. For example, at the Parsons chemical/ETM Enterprise Superfund site, Michigan, USA, nearly  $3000 \text{ yd}^3$  of soils and sediments were contaminated with pesticides, mercury and dioxins. The *in situ* vitrification method was applied to treat these Hg-containing wastes. The confirmation core sampling results indicated that the vitrified materials had a mercury and pesticide concentrations below  $40 \mu\text{g kg}^{-1}$  and the TCLP test showed that the concentration of leachable mercury in the vitrified soils was below  $0.23 \mu\text{g L}^{-1}$  [148].

#### 5.4. Thermal desorption

Thermal desorption is a treatment technology that utilizes heat to increase the volatility of contaminants which are subsequently removed (separated) from the solid matrix (typically soil, sludge), but without combustion of the media or contaminants. The desorbed contaminants are then treated in the offgas treatment system to control air emissions [149]. Traditional retorting as practised by small-scale miners is an example of a thermal treatment method that involves distillation or dry distillation [150]. In general, requirements for the retort system are very similar to thermal desorption, except that following desorption there should be some type of condensation system to collect volatilized mercury.

Inorganic mercury is usually present in soil in the elemental state or as mercury(II) compounds such as HgS, HgO and HgCO<sub>3</sub>. When the temperature reaches 600–800 °C, these mercury compounds will be converted into gaseous elemental mercury, which can be recovered [151]. Several mercury thermal desorption experiments have demonstrated the feasibility of mercury removal at temperatures ranging between 127 and 700 °C [151,152] with greater efficiency of mercury removal at relatively high temperature (460–700 °C). Massacci et al. [153] reported that mercury concentrations in soil samples decreased from  $217 \text{ mg kg}^{-1}$  to  $10 \text{ ng g}^{-1}$  after 4 h roasting at 700 °C. Taube et al. [154] used thermal desorption to remediate mercury contaminated soils from a chlor-alkali plant in Sweden. Here, reported mercury removal efficiency was 99% after only 20 min at an operating condition of 460 °C. Busto et al. [155] found that the mercury concentration in the leachate of waste sludge could be decreased to below the threshold value of  $0.2 \text{ mg L}^{-1}$  (TCLP) after treatment at a temperature of 400 °C or higher. Lesa et al. [156] investigated the effect of ultrasound on the thermal remediation of mercury contaminated sludge. The results showed that the application of ultrasound did

not improve desorption and that mercury removal efficiency could reach 90–99% at 297 °C without ultrasound treatment. Recently, the use of solar energy instead of conventional non-renewable sources has been proposed as a more economic energy source during thermal treatment. Navarro et al. [157] used solar energy to remediate mercury-contaminated soils and mine wastes from the Valle del Azogue and Bayarque mines in Spain. Two thermal desorption systems constituting an experimental low-temperature solar furnace (LT-UPC) and a middle-temperature solar furnace (MT-PSA) were designed in the study. The LT-UPC was operated at temperatures ranging between 28 and 280 °C, while the MT-PSA operated with the temperatures ranged between 20 and 502 °C. Results from this study showed that mercury removal efficiencies ranged from 4.5% to 76% and 12.1% to 87%, respectively.

Thermal treatment may greatly alter the soil properties and cause the coexisting contaminants, especially trace metals, to transform and repartition. Huang et al. [158] used thermal treatment to remediate mercury contaminated soil. The results indicated that thermal decontamination at a temperature above 550 °C could reduce the mercury content from 1320 to  $6 \text{ mg kg}^{-1}$ . However, thermal decontamination also caused repartitioning of metals. Heavy metals originally associated with Fe/Mn oxides were transformed into acid-extractable, organic-matter bound and residual forms, and this had a likely profound affect on holistic environmental quality. In addition, the negative effect of high temperature on the physical properties of the thermally treated soil should be taken into the consideration. To counter concerns it has been proposed to operate thermal treatment at a lower temperature but for longer time. Qu et al. [159] reported the use of thermal desorption with operating conditions of 270 °C for 2 h for the treatment of mercury-contaminated soil. The mercury concentration in soil with an initial concentration ranging between 73 and  $132 \text{ mg kg}^{-1}$  could be reduced by 50–90% with minimal effect on the chemistry of essential nutrition elements such as nitrogen (N), phosphorus (P) and potassium (K) in the soil. Kucharski et al. [160] investigated the remediation of mercury-contaminated soil using thermal desorption with operating conditions of 100 °C for 10 days. At the end of this period, the most mobile and toxic mercury species were removed with a reduction of the total mercury concentration in the soil of 32%. In addition, there was no negative effect of heating on soil growth properties. Morris et al. [161] reported the use of a thermal desorption technique to remove mercury from soil of the Lower East Fork Poplar Creek floodplain. Results demonstrated that 90% of the soil mercury load could be successfully removed at an operating temperature of 600 °C. Moreover, mercury and organic substances in the offgas were effectively collected. X-Trax™, which was developed by a chemical waste management corporation and currently marketed by OHM remediation services, is used for the removal of mercury from mercury-containing materials. The system is operated at relatively low temperature and has been demonstrated to reduce mercury concentrations from  $130\text{--}34,000 \text{ mg kg}^{-1}$  to  $1.3\text{--}228 \text{ mg kg}^{-1}$  in soil and sediments [162]. The SepraDyne™-Raduce process is a simple and unique separation technology that removes mercury and other volatiles from non-volatile matrices using a high vacuum rotary retort. Bench-scale test results showed that the mercury removal efficiency of this technology was over 99% and that the mercury concentration in the treated leachate was below the TCLP standard. Moreover, the mercury concentration in the offgas system was well controlled and met all relevant environmental standards [163].

There are many advantages of this method over other remediation methods, including the effective extraction and recovery of mercury, and safety [129,157,164]. The major disadvantages are high energy costs and effectiveness only at rather high total soil mercury concentrations [160].

**Field applications:** Numerous commercial developers are involved in thermal treatment of Hg-contaminated soils and wastes. The Mercury Recovery Services (MRS) system being developed by a Pittsburgh Mineral and Environmental Technology Corporation, has been used to treat mercury contaminated waste at natural gas metering sites in New Mexico and at a mercury recycling facility in Bedford, Ohio, USA. This technology can process soils contaminated with elemental mercury as well as various mercury compounds (oxides, sulfides, organometallics). Bench-scale results have shown mercury removal efficiencies greater than 99% and a final soil mercury concentration less than  $1 \text{ mg kg}^{-1}$ . Moreover, no liquid or solid secondary products are generated and no mercury is released to the air during treatment. The cost of this technology is estimated to be US\$650–1000/t [144].

Many full-scale and pilot-scale applications of thermal desorption to treat mercury-containing wastes have been summarized in other reports or literature [119,129]. Kucharski et al. [160] reported the use of a low-temperature thermal desorption technique to remediate mercury polluted soil near a chemical production facility in southern Poland. Mercury vapors were absorbed in a scrubber. After 10 days of soil heating at a temperature of  $167^\circ\text{C}$ , all water-soluble, exchangeable and elemental mercury fractions were reduced to undetectable levels. Approximately 80% of the soil mercury associated with fulvic/humic acid fraction, 70% associated with the organic/sulfide fraction, and 67% of total mercury was removed. Chang and Yen [151] conducted a full-scale thermal desorption process with operating conditions of  $750^\circ\text{C}$  for 3 h to treat mercury-contaminated soils. A total of 14–16 t of mercury contaminated soil were treated everyday. Over a 1 year test, removal efficiencies were showed to be between 96.12% and 99.84%, and the soil mercury concentration after remediation was below the established environmental criteria ( $2 \text{ mg kg}^{-1}$ ). Over 96% of the exhausted mercury was recovered. The unit cost of this on-site remediation work was estimated to be US\$834  $\text{m}^{-3}$  of soil.

### 5.5. Nanotechnology

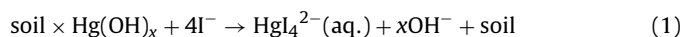
Nanotechnology involves the use of particles with at least one dimension in the range of 1–100 nm, to affect the mobility, toxicity and/or bioavailability of contaminants in their natural environment. Nano-sized particles are characterized by enhanced reactivity and a large surface area to volume ratio, which speeds up sorption kinetics, creating applications in the remediation of groundwater, surface water, and the subsurface [165]. For mercury, stabilized iron sulfide (FeS) nano-particles had been used to immobilize mercury in sediment. Xiong et al. [166] showed that the treatment of a mercury-contaminated substrate with FeS nano-particles at a molar ratio of 26.5 (FeS-to-Hg) reduced the concentration of mercury leached into water by 97% and the TCLP leachability of mercury was reduced by 99%. It must be noticed, however, that knowledge of the fate and transport of nanoparticles in the environment and the potential toxicological effects induced by the nanoparticles themselves is limited. Nanoparticles may indirectly influence human health when they are inhaled, absorbed through skin, or ingested [167]. Once nanoparticles enter the human body, they can migrate to or accumulate in places that larger particles cannot, such as the alveoli in the lungs. This is due to the minute size of nanoparticles [168]. Furthermore an increase in the bioavailability of certain hydrophobic contaminants affected by some nanoparticles has been reported [169].

The major advantages of this method for remediation are low cost, low energy demand and applicability to an *in situ* treatment. However, as described, the potential effects of nanoparticles on the environment have not been fully investigated and this method requires testing under field conditions before it can be considered a viable remediation technique [165].

### 5.6. Soil washing

Soil washing (SW) is an *ex situ* treatment method for separating contaminants (particularly metals) from soil *via* chemical leaching, physical separation or physicochemical procedures [128,129,170]. The specific application of soil washing depends on the form of metal in the waste being remediated. Chemical extraction is primarily applicable when target metal(s) exist in an ionic form, whereas physical separation is suitable for particulate forms [128]. It should be noticed that the particulate metals may resolve from particles during the physical separation process and thus physical separation can be used alone or in combination with chemical leaching [128,129]. Physical separation is based on mineral processing technologies such as size separation, gravity concentration, froth flotation, attrition scrubbing, and magnetic separation. Sierra et al. [171] used physical separation to remediate soil contaminated with pyrite ash which contained As, Pb, Cd, Ni, Cu and Hg. The results of this study indicated that metals present in a grain-size below  $125 \mu\text{m}$  could be effectively separated by hydrocycloning techniques. Sierra et al. [172] investigated the feasibility of washing procedures to physically separate Hg and As from soil contaminated by mining and metallurgical waste in Spain. Their results indicated that the grain-size fraction below  $125 \mu\text{m}$  could be treated with hydrocycloning. However for fractions coarser than  $125 \mu\text{m}$ , milling to below  $125 \mu\text{m}$  was required before treatment. Physical separation is reportedly more appropriate and cost effective for soil with a clay and silt content below 30–50% [128,173]. However, soil with a more dominantly fine-grained matrix can be treated by a method of wet screening or hydrocycloning that combines attrition scrubbing [144].

Solvents are selected on the basis of their ability to solubilize specific contaminants and on their environmental and health effects [174–176]. The addition of  $\text{I}^-$  will increase the solubility of mercury in soil through forming the soluble and stable complex  $\text{HgI}_4^{2-}$  (1) [177].



EDTA is a non-selective extracting agent that can form a strong complex with a variety of metals including alkaline-earth cations such as  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  and target heavy metal(s) such as Pb, Cd, Ni, Zn and Mn [178,179]. EDTA has been suggested as a suitable chemical for use in the remediation (washing) of heavy metal-contaminated soils [128,180–183]. Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), thiosulfate, iodide and nitric acid ( $\text{HNO}_3$ ), *aqua regia*, hydrochloric acid (HCl), sodium hydroxide (NaOH) and potassium iodide (KI) have been tested for their ability to extract mercury from soils [83,184–186]. Among these extractants, iodide, EDTA, and thiosulfate have been found effective in the removal of mercury from soil with an efficiency of about 30% [187] but with limited effect on soil physical and chemical properties. In contrast, stronger chemicals, such as a mixture of 100 mM KI + 50 mM HCl (pH 1.5) can remove nearly 77% of the mercury in soil [177], but with detrimental affect on soil properties. Potassium iodide (KI) (0.4 M) and iodine ( $\text{I}_2$ ) (0.2 M) leaching solutions have been used to remove mercury from stormwater and sewer sediment collected from the Oak Ridge Y-12 site. The mercury concentration in this sediment ( $35,000 \text{ mg kg}^{-1}$ ) could be reduced by 98% with a leachable mercury concentration in the remediated material of 3–10  $\text{mg L}^{-1}$  (TCLP) [188]. The combined effect of the chemicals  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{S}$  has been reported to extract mercury from contaminated soil. This process consists of three steps: (1) the transformation of all waste mercury into mercury salts or mercury oxide by adding  $\text{H}_2\text{O}_2$ ; (2) the formation of soluble mercury complexes with mercury oxide (HgO) or mercury salts through adding  $\text{Na}_2\text{S}_2\text{O}_3$ ; (3) the precipitation and recovery of mercury complexes from solution

through addition of  $\text{Na}_2\text{S}$ . For this study, after remediation, the mercury concentration in the waste was reduced from 2100 to  $270 \text{ mg kg}^{-1}$  [189].

The advantages of soil washing are that: (1) the processes attempts to permanently remove metals from soil and can allow the recycling of metal in certain cases; (2) the processed soil can be returned to the site; and (3) the process duration is typically short to medium-term compared to other metal extraction methods [128]. However, the disadvantages of this method include: (1) the high consumption of water required for making up the washing solution, and of clean water necessary to remove the mobilized metallic species that have been retained in the soil after the remedial treatment; (2) the presence of metal–chelant complexes in the washing solution that must be treated or removed before the water can be safely discharged; (3) difficulty with soils that contain high clay content and high humic content [129,190].

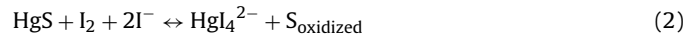
*Field applications:* Physical separation is a more widely used technology to treat waste relative to chemical extraction technology. Dermont et al. [129] reported the use of soil washing to treat mercury contaminated soils at six full-scale sites. In these sites, physical separation technology was frequently used or combined with chemical extraction techniques. US EPA [119] reported eight field applications of soil washing (*via* physical separation or chemical extraction processes) involving remediation of Hg-contaminated soils.

### 5.7. Electro-remediation

Electro-kinetic (EK) remediation consists of the controlled application of low intensity direct current through the soil between appropriately distributed electrodes [191]. The system consists of three compartments; two electrode compartments and a soil compartment placed between these electrodes. The catholyte is separated from the soil by a cation exchange membrane, and the anolyte is separated from the soil by an anion exchange membrane. During electro-kinetic soil treatment, ions can be moved from the soil into the electrode compartment through ion exchange membranes, while no current carrying ions can transport from the electrode compartment into soil [192]. Hydrogen ions ( $\text{H}^+$ ) are generated at the anode due to water electrolysis, and migrate into the bulk of the soil. A low pH develops through the soil (except at the cathode where  $\text{OH}^-$  is generated), causing desorption of metallic contaminants from the soil solid phases. The dissolved metallic ions moved to the electrode by ionic migration [190,193]. Once metallic ions accumulate at electrode, they can pass through the ion exchange membranes and be removed by precipitation.

The difficulty of EK remediation of mercury contaminated soils is the low solubility of mercury in most natural soils [194,195]. An electro-dialytic decontamination experiment carried out on a sand polluted with mercury ( $\text{THg}$ :  $685 \text{ mg kg}^{-1}$ ) from a former chlor-alkali plant showed that the mercury removal rate was only 23%. Mercury removal was attributed to mobilization and reaction of anionic mercury most likely in the form of soluble  $\text{HgI}_4^{2-}$ . As a conclusion to this work, the author suggested that the addition of chloride and oxidizing agents to the soil would mobilize mercury and increase the rate of removal [192]. Thöming et al. [196] reported that the electro-dialytic remediation method alone is not efficient to remove mercury from soil that contains high proportions of elemental mercury. A suggested solution was to add chloride to the soil system. As a result, many studies have been conducted to increase the solubility of mercury through adding chelates, as these would enhance the electro-remediation efficiency. Reddy et al. [197] investigated the effects of different ligands such as  $\text{OH}^-$ ,  $\text{Cl}^-$ , and  $\text{I}^-$  as well as the chelating agent EDTA on the electro-kinetic remediation of Hg(II) spiked kaolin and glacial till soils. The results showed that the application of 0.1 M KI with a

voltage gradient of 1.0V DC/cm could remove 97% and 56% of the mercury from kaolin and glacial till soils, respectively. Cox et al. [195] investigated the use of an iodine/iodide ( $\text{I}_2/\text{I}^-$ ) lixiviant solution located at the cathode for the electro-kinetic remediation of HgS-contaminated soils. Their results indicated that the lixiviant could migrate through the soil to the anode by electro-migration, oxidize the HgS and form the soluble complex  $\text{HgI}_4^{2-}$  (Eqs. (2)–(4)). The  $\text{HgI}_4^{2-}$  then continued to electro migrate toward the anode. By this mechanism nearly 99% of soil mercury could be removed. Studies have shown similar results using field-contaminated soil. Suèr and Lifvergren [198] reported that addition of iodide to the cathode could increase the mercury removal efficiency from a field soil at a chlor-alkali factory in Sweden ( $\text{THg}$   $90 \text{ mg kg}^{-1}$ ).



Shen et al. [194] reported the use of a modified electro-kinetic technique with approaching cathodes (AC-EK) and an  $\text{I}^-/\text{I}_2$  lixiviant to treat mercury polluted soil collected from the Wanshan mercury mine in SW China. These authors showed that nearly 89–92% of the total soil mercury was removed by AC-EK within 5 days. García-Rubio et al. [199] reported that the residual soluble mercury concentration in soil could be significantly increased after iodide enhanced electro-remediation, and that this posed an unacceptable risk to environment. Therefore, acid-enhanced electro-remediation, which has been proven to remove soluble metal from soil, was applied to treat soil with a high soluble mercury concentration [200]. Their results showed that soluble mercury was almost completely removed from areas close to the cathode, but the residual concentration increased with distance in the direction of the anode. Hakansson et al. [201] reported that the soluble mercury complexes produced during electro-kinetic remediation could be precipitated with hydrogen sulfide ( $\text{H}_2\text{S}$ ) which was produced on site by a sulfate-reducing bacteria reactor.

The efficiency of electro-remediation is greatly affected by soil properties, such as pH, the content of carbonates and organic matter which affect the degree of adsorption of mercury to soil constituents, and the geochemical fractionation of mercury particles in the soil [194,197]. It is well known that mercury has a high affinity for organic matter; high organic matter content will decrease the efficiency of mercury removal from soil [194]. One of the most important advantages of the electro-kinetic technique is its efficacy for the treatment of soil of low hydraulic permeability. The major disadvantages of this method are: (1) the acidic conditions that are required for remediation; (2) the amount of time required for remediation; and (3) the interfering effect of non target ions on remedial progress [202].

*Field applications:* Electrokinetic remediation is frequently used to remove metal ions from saturated soils or clay soils. However, very few applications have been reported under field condition. Dermont et al. [129] reported one field application of electrokinetic remediation to remediate mercury-contaminated sites at Savannah River, South Carolina.

### 5.8. Phytostabilization

Phytostabilization is the use of plant roots to prevent metal movement within the soil and occurs by way of biochemical processes that occur in roots or within the root neighborhood [129]. For example, the willow species *Salix viminalis* × *S. schwerinii* has been shown to accumulate bioavailable mercury in its root system and thereby reduce the bioavailable mercury concentration in the rhizosphere, while leaving the concentration of non-available

mercury in the soil relatively unchanged [203]. Some indigenous herbaceous species (red fescue (*Festuca rubra*), meadow grass (*Poa pratensis*), horseradish (*Armoracia lapathifolia*), and Jerusalem sunflower (*Helianthus tuberosus*)) from Poland have proven potential for phytostabilization of soil with moderate mercury contamination [204]. *Silene vulgaris* collected from Spain was demonstrated to be a good candidate for phytostabilization of mercury contaminated soil [205]. The work of Anjum et al. [206] and Marques et al. [207] demonstrated that the salt marsh plant *Juncus maritimus* has a high capacity to stabilize mercury in sediment. Candidate plants for phytostabilization should have an extensive root system and the aboveground biomass should not be available for consumption by animals. Any use of plants to stabilize mercury should take into consideration the toxicity of mercury to plant roots, the survival rate of the plant being used, and the adaptability of the plant to the site-specific environment. Phytostabilization may be effectively combined with immobilization techniques to detoxify mercury in soil.

The major advantages of this method are its low cost, environmentally benign nature, and applicability to the *in situ* treatment of contaminated soil and tailings. However, this method is limited to the depth of the plant root zone and the remediation site should be constantly monitored and managed to preserve active plant growth [129].

### 5.9. Phytoextraction

Phytoextraction is the use of living plants to remove pollutants from the soil. The pollutants are taken up by the roots and transported to the aboveground tissues of the plant. The pollutants can then be removed by harvesting the above-ground tissues. Phytoextraction can be classified as either natural or chemically assisted. Natural phytoextraction involves the use of natural hyperaccumulator plants that have strong metal accumulation capacities, for example, 100 mg kg<sup>-1</sup> for cadmium (Cd) on a dry weight (DW) basis, 1000 mg kg<sup>-1</sup> for arsenic (As), copper (Cu), lead (Pb), or more than 10,000 mg kg<sup>-1</sup> for manganese (Mn), nickel (Ni) or zinc (Zn) DW [208,209,178]. Chemically assisted phytoextraction necessitates the application of chemicals to soil which can promote the solubility of target elements. These soluble elements are then accumulated by plants [83].

#### 5.9.1. Natural phytoextraction

No plant species have been identified as mercury hyperaccumulators. Thus, the natural efficiency for the phytoextraction of mercury from polluted soil is limited. Moreno-Jiménez et al. [210] evaluated the capability of the plant species *Rumex induratus* and *Marrubium vulgare* to extract mercury from a mercury-contaminated soil with a mercury concentration ranging between 122 and 550 mg kg<sup>-1</sup>. The results showed a phytoextraction yield (shoot) of 12.9 g ha<sup>-1</sup> for *R. induratus* and 27.6 g ha<sup>-1</sup> for *M. vulgare*, yields that are too low to warrant application of this technique as a viable remediation system. High biomass crops can be considered as an alternative to hyperaccumulator plants to phytoremediate mercury contaminated soils. The capability of *Hordeum* spp., *Lens culinaris*, *Cicer arietinum*, *Lupinus polyphyllus* and *Triticum aestivum* to accumulate mercury from soils containing from 18.03 and 32.4 mg kg<sup>-1</sup> of mercury were tested in pot experiments. The results showed a phytoextraction yield of 4.7 g ha<sup>-1</sup> for *Hordeum* spp., 2.8 g ha<sup>-1</sup> for *L. culinaris*, 0.4 g ha<sup>-1</sup> for *C. arietinum* and *L. polyphyllus*, and 0.28 g ha<sup>-1</sup> for *T. aestivum* [211,212]. Such amounts of annual mercury extraction are negligible in comparison to the magnitude of mercury contamination in global soils (on global average more than 100 kg ha<sup>-1</sup> of total mercury in the 0–25 cm soil horizon) [211]. The plant species *Macleya cordata* L., *Achillea millefolium* L., and *Pteris vittata* L., which were collected from the Wanshan

mercury mining district, SW China, have been demonstrated to have a relatively high capacity to accumulate mercury in their tissues and therefore may have potential for use in the phytoremediation of soils of the Wanshan mining area. However, no study has been conducted to grow these plants in the greenhouse or field soil [213]. Poor potential for phytoextraction is mainly attributed to the low bioavailability of mercury in soil. Therefore, chemically assisted phytoextraction using high biomass plant species in conjunction with chemical amendments must be relied on to achieve the plant mercury concentrations necessary to more effectively phytoextract mercury from contaminated soil [83].

#### 5.9.2. Chemically assisted phytoextraction

The formation of a heavy-metal complex occurs when a metal ion is coordinately bound to one or more electron donating groups that are called ligands. Many ligands can form bio-stable and water-soluble complexes with metal ions [178]. Many efforts have been made to find ligands (chelators) that can enhance the phytoremediation of heavy metal contaminated soils. Meers et al. [214] conducted a general review of potential soil chelators that can increase the uptake of heavy metals by plants. Chelates such as potassium iodide (KI), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), ammonium thiocyanate (NH<sub>4</sub>SCN), thiourea (SC(NH<sub>2</sub>)<sub>2</sub>), thiocyanate and hydrogen peroxide (SCN+H<sub>2</sub>O<sub>2</sub>), ammonium thiosulfate((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), ethylenediaminetetraacetic acid (EDTA), and urease have all been used to increase the solubility of mercury and to enhance the plant uptake of mercury from soil [83,183,185,186,215,216].

Wang and Geger [215] reported that the addition of 1 mM KI to mercury-contaminated soil increased the mercury concentration in willow by a factor of 5, 3 and 8 times in the leaves, branches and roots, respectively. However, most of the taken up mercury was stored in the root of the plant, with limited translocation to shoots. Moreno et al. [216] found that sodium thiosulfate could dramatically enhance the uptake of mercury by bush bean (*Phaseolus vulgaris*) and Indian mustard (*Brassica juncea*) from mercury-contaminated substrates. In the control pots, the THg concentration in the shoots of both species was below the detection limit, while in roots the values were 5.5 and 9.8 mg kg<sup>-1</sup> respectively. In the sodium thiosulfate treated plants, the THg concentration in the shoots and roots of *P. vulgaris* and *B. juncea* was 9.5 and 113, and 15.2 and 69 mg kg<sup>-1</sup>, respectively. Moreno et al. [185] reported that the THg concentration in the root and shoot biomass of ammonium thiosulfate treated Indian mustard was nearly 13 and >40 times higher than the control pots. Wang et al. [83] conducted a greenhouse experiment to investigate the effect of thiosulfate amendment of soil on mercury uptake by the plant *Chenopodium glaucum* and also studied the effect of phytoextraction on the geochemical fractionation of mercury in the soil. These authors showed that the addition of thiosulfate significantly increases the mercury concentration in plant tissues, and that this increased concentration was significantly correlated with the amount of mercury bound to the Fe/Mn oxide fraction of the soil. They suggested that the Fe/Mn oxide-bound fraction of soil mercury may represent a pool of potentially bioavailable metal which could be transformed into a more available form (complexed) by thiosulfate and subsequently taken up by plants. Thiosulfate demonstrated properties of a good ligand due to its high capacity to enhance the root uptake of mercury and transport this from the root to the aboveground tissues [185,216]. The coordination of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and Hg<sup>2+</sup> in soil would form a soluble complex, likely to be Hg<sub>x</sub>(S<sub>2</sub>O<sub>3</sub>)<sub>y</sub>, and the plant could preferentially absorb this complex over other mercury-bound complexes that would otherwise exist in soil [83].

Optimization of systems to enhance the uptake of mercury by plants using ligands or chelates may come through consideration of the effect of mercury on soil biological parameters.

Mercury is known to inhibit the activity of the soil enzyme urease [183], an inhibition which may affect the phytoextraction process. The addition of urease to a mercury-contaminated soil could increase enzyme activity, and subsequently the mercury concentration in plant tissues [183]. The simultaneous addition of urease with mercury-specific ligands could be a more efficient pathway to mercury uptake than the addition of the chelate alone. Smolinska and Cedzyska [183] reported that the plant species *Lepidium sativum* accumulated about 20% of the total mercury concentration in a soil (soil THg: 2 mg kg<sup>-1</sup>) after simultaneous addition of EDTA and urease.

The potential for leaching of heavy metals to below the root zone of plants should be taken into consideration when considering chemically assisted phytoextraction. EDTA has received considerable attention due to its persistence in the environment and potential to carry heavy metals into groundwater. To the best of our knowledge, no one has used EDTA for the field-scale phytoextraction of mercury polluted soils, and thus the real potential for this risk has yet to be investigated. Nowack et al. [217] used a model to calculate the amount of chelate that is taken up by the plant during the phytoextraction process. These authors showed that nearly 90% of the applied EDTA remains in solution and can be leached to groundwater. Based on this data, Nowack et al. [217] concluded that the pollution of groundwater by EDTA in the course of a phytoextraction procedure is unavoidable except under climatic conditions that completely prevent any leaching of solutes out of the root zone. Under greenhouse conditions, Wang et al. [218] investigated the leaching behavior of mercury during the ammonium thiosulfate assisted phytoextraction of a mercury polluted soil. The mercury concentration in the leachate of the thiosulfate treated pots was nearly 3 times higher than the control pot.

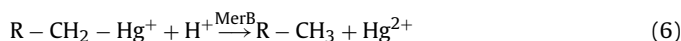
The major advantages of this method are low environmental impacts, easily operated and can be applied at a large scale. The disadvantages such as long time is required for remediation; the remediation efficiency is limited by the bioavailability of metal and the depth of root zone, as well as number of harvest required; the management of the biomass containing mercury may be problematic and may increase the costs of the process; the need of monitoring of the site for the very long period.

**Field applications:** Dermont et al. [129] reported three field applications of phytoextraction to treat soil contaminated with multiple heavy metals (Cd, Cu, Pb, Hg, Zn, Cr). One site, designated ANL-W, is part of the Idaho National Engineering and Environmental Laboratory (INEEL), and is contaminated with mercury (soil mercury concentration 1.5 mg kg<sup>-1</sup>). Many studies have been conducted to investigate the use of phytoextraction technology to remediate this site. Published results indicate that willow (*Salix* sp.) could extract 42% of mercury from soil using a combination of 0.05 M EDTA (40%) and citric acid (60%) as chemical amendments. The estimated cost for the implementation of phytoextraction at this location was US\$300,000 (2-year project) [219,220]. Moreno et al. [221] conducted a field trial to investigate the remediation of mercury contaminated mine tailings using Indian mustard. Small field plots with dimensions of 5 m × 5 m were established at the tailings dam of the abandoned Tui base-metal mine, located in the North Island of New Zealand. The plots were supplied with N, P, K fertilizers and organic matter at a rate of 75 g m<sup>-2</sup> and 3.2 L m<sup>-2</sup>, respectively. The total mercury concentration of the substrate ranged between 1.3 and 4.5 mg kg<sup>-1</sup>. Thiosulfate was applied at a rate of 5 g kg<sup>-1</sup> of substrate. The results of this trial showed that thiosulfate treatment induced a significant increase in root and shoot mercury concentrations relative to control plants, which had shoot and root mercury values below detection levels. The mercury-extraction yield of the thiosulfate treated biomass was in the range of 1.14–24.39 g ha<sup>-1</sup>.

### 5.10. Phytovolatilization

Phytovolatilization is unique to a select group of heavy metals and metalloids including mercury and selenium that have relatively high volatility. Phytovolatilization refers to the uptake and transpiration of such elements by plants. The element is taken up by plant roots, transported through the xylem, and is finally released to the atmosphere from cellular tissues (evaporates or vaporizes). Very few studies have reported the use of plants for the phytovolatilization of mercury, because mercury emission from leaf tissues is strongly affected by environmental parameters such as light intensity and air temperature [222]. Phytovolatilization of mercury is instead considered a natural consequence of the interaction of some plant species with mercury in soil. Leonard et al. [223] investigated the mercury exchange flux between aerial parts of plant and the air. Five plant species (*Lepidium latifolium*, *Artemisia douglasiana*, *Caulanthus* sp., *Fragaria vesca*, *Eucalyptus globulus*) were grown in contaminated soil with a mercury concentration ranging between 450 and 1605 mg kg<sup>-1</sup>. The *Caulanthus* sp. showed a higher mercury emission rate (92.6 ng m<sup>-2</sup> h<sup>-1</sup>) in the daytime than the other plant species. Emissions in the dark were an order of magnitude less than during the daytime for all plant species.

As another alternative, genetic engineering can integrate genes from other organisms to enhance the phytovolatilization capabilities of plants. Of the known bacterial mercury resistance systems, the Mer (mercuric ion resistance) determinant is unique in terms of the orientation of the mercury transporter it encodes [224]. Mercuric reductase, which is encoded by the merA gene, can reduce mercuric ions (Hg<sup>2+</sup>) to the less toxic and volatile elemental mercury form [225] (5). Another important enzyme-organomercurial lyase (MerB) catalyzes the protonolysis of the carbon-mercury bond. The products of this reaction are a less toxic inorganic species and a reduced carbon compound [226] (6).



The MerA gene has been successfully manipulated in the genetic engineering of plants for the remediation of mercury [227]. Both dicotyledon and monocotyledon plants such as *Arabidopsis thaliana*, *Liriodendron tulipifera*, *Arachis hypogaea*, *Populus deltoides*, *Oryza sativa*, *Spartina alterniflora* and *Chlorophyta* have been modified with the MerA gene, and have been shown to be resistant to levels of up to 0.04–100 mM HgCl<sub>2</sub> [228–233]. The MerA mediated mercury reduction and volatilization mechanisms have been successfully integrated for the phytoremediation of mercury-contaminated substrates [226,231,232,234,235]. Unfortunately, the MerA gene fails to protect against the more toxic and environmentally relevant organic-mercury [227]. Both the MerA and the MerB genes are needed to protect cells from organic-mercury [227]. MerA and MerB modified *A. thaliana* can resist up to 5 mM phenylmercury acetate (PMA) and 10 mM CH<sub>3</sub>Hg [236]. Hussein et al. [237] reported that transgenic tobacco plants engineered with MerA and MerB genes *via* the chloroplast can accelerate the plant uptake of mercury from the substrate.

However, phytovolatilization of mercury has caused public anxiety due to the secondary contamination of the environment with elemental mercury. Therefore, another option to promote greater efficiency of phytoextraction could be the expression of other Mer genes in plants to produce plants that can accumulate mercury without releasing Hg<sup>0</sup> into the atmosphere. Besides the genes MerA and MerB, MerC, MerF and MerT are known as membrane transporter genes involved in the process of translocating Hg<sup>2+</sup> into the cell [238–240]. Plants transformed with these genes have greater capacity to accumulate mercury into their tissues than wild

type plants. For example, MerC modified *A. thaliana* and *Nicotiana tabacum* are hypersensitive to  $Hg^{2+}$  and they accumulate approximately twice as much  $Hg^{2+}$  ion as the wild type plants [224]. The gene MerP encodes polyphosphate kinase (ppk), a key enzyme for polyphosphate (polyP) biosynthesis. PolyP is regarded as important in the reduction of the cytotoxicity of  $Hg^{2+}$  via chelate formation. Transgenic tobacco expressing polyP has been shown to accumulate significantly more mercury than the wild-type [241,242]. Moreover, the periplasmic protein encoded by MerP is always physically associated with MerT and enhances  $Hg^{2+}$  uptake. Nagata et al. [241] observed that the expression of MerT in ppk-transgenic tobacco resulted in accelerated and enhanced mercury uptake into tobacco. In addition, tobacco expressing MerT and polyP accumulated significantly more mercury than the ppk-transgenic tobacco from a medium containing a wide range of low concentrations of  $Hg^{2+}$ . Ruiz and Daniell [227] suggested that new mercury phytoremediation technologies would rely on different gene combinations to enhance uptake, translocation, chelation or detoxification and would manipulate the plant-mediated release of  $Hg^0$  into the atmosphere.

The advantages of this method are environmental sound, easily operated and can be applied at a large scale, whereas, the disadvantages such as the secondary contamination of environment by the elemental mercury and the adaptability of the gene-modified plant to the environment, etc.

## 6. Future perspectives

Traditionally, the most common method for the remediation of mercury-contaminated soil is excavation and disposal. But these methods are costly and crude. In addition, they are only useful if the mercury is tightly localized. Therefore, recent efforts have focused on developing better remediation routes for soil contaminated with mercury. Methods such as stabilization/solidification, vitrification, electro-remediation, soil washing, thermal desorption, immobilization, phytostabilization, phytoextraction and phytovolatilization have been tested to treat mercury contaminated soils.

Vitrification is mainly used to treat soil or wastes at military sites such as DOE land in the USA [129] because this technology is well proven for the treatment of heavy metals mixed with radioactive elements. Stabilization/solidification is frequently used to stabilize metals. Many S/S technologies have been developed and patented by commercial companies [119]. These S/S techniques are successful but significant monitoring is required, because the solidification process is influenced by waste characteristics such as organic matter content. *Ex situ* S/S is well established as pollutants and reagents can mix and react thoroughly and therefore produce a stable waste matrix. However, the long-term stability and integrity of the solidified/stabilized matrix is unknown and re-vegetation of the final material is not encouraged [129]. Recently, *in situ* S/S technology was considered as an alternative option to *ex situ* S/S, because of its cost advantage and the option of site re-vegetation. Immobilization and phytostabilization technologies are *in situ* techniques that are still in the research and development stage. For practically use these two techniques, many studies should be focused on: (1) more studies to understand fundamental mechanisms of immobilization and phytostabilization of mercury [129]; (2) more efforts should be conducted to test these techniques in the field; (3) More tests to investigate the stability of the immobilized soil matrix. Although the remediation system is less complex than stabilization/solidification, these technologies may be suitable for the treatment of soils and wastes contaminated with mining waste (tailings), especially within mercury mining district.

Soil washing, electro-remediation, thermal desorption and phytoextraction are used to extract pollutants from waste. Among

these technologies, thermal desorption is frequently used to recover mercury due to the volatility of elemental mercury. Many commercial technologies have been developed such as the Mercury Recovery Services (MRS) system [144]. However, the negative effects of thermal processes on soil properties should be further investigated. Although both soil washing and electro-remediation are commercially available, the application of these technologies is limited for mercury treatment. More field demonstrations are needed before these technologies can be widely implemented.

Phytoextraction is a cleanup technology that is still under development. For phytoextraction to be worthwhile, many efforts should be conducted: (1) more studies to select mercury accumulator/hyperaccumulator plant species; (2) more studies to understand fundamental mechanisms involving plant uptake mercury; (3) more efforts should be conducted to investigate the emission of mercury to the air during the phytoextraction process; (4) more tests should be conducted to translate controlled experimental data to field conditions. The suggested research should be done in parallel with further consideration of the effect of the MerA gene in genetically modified plants which imparts the ability for plants to reduce mercuric ions ( $Hg^{2+}$ ) to the less toxic and volatile form of elemental mercury. The combination of other genes such as MerB, MerC, MerF and MerT could prevent mercury volatilization and enhance plant uptake mercury.

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