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REVIEW ARTICLE

Pollution due to hazardous glass waste

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Abstract Pollution resulting from hazardous glass (HG) is widespread across the globe, both in terms of quantity and associated health risks. In waste cathode ray tube (CRT) and fluorescent lamp glass, mercury and lead are present as the major pollutants. The current review discusses the issues related to quantity and associated risk from the pollutant present in HG and proposes the chemical, biological, thermal, hybrid, and nanotechniques for its management. The hybrid is one of the upcoming research models involving the compatible combination of two or more techniques for better and efficient remediation. Thermal mercury desorption starts at 100 °C but for efficient removal, the temperature should be >460 °C. Involvement of solar energy for this purpose makes the research more viable and ecofriendly. Nanoparticles such as Fe, Se, Cu, Ni, Zn, Ag, and WS_2 alone or with its formulation can immobilize heavy metals present in HG by involving a redox mechanism. Straight-line equation from year-wise sale can provide future sale data in comparison with lifespan which gives future pollutant approximation. Waste compact fluorescent lamps units projected for the year 2015 is 9,300,000,000 units and can emit nearly 9,300 kg of mercury. On the other hand, CRT monitors have been continuously replaced by more improved versions like liquid crystal display and plasma display panel resulting in the production of more waste. Worldwide CRT production was 83,300,000 units in 2002 and can approximately release 83,000 metric tons of lead.

Keywords Hazardous glass pollutant · Hybrid method · Thermal remediation · Nanoremediation · Future waste approximation · CFL · CRT

Introduction

The use of glass products in household and industrial appliances is continuously popular among us from thirty-fifth century BC (Before Christ). In 1994, approximately 9,200,000 tons of post-consumer glass was discharged in the USA alone (Shi and Zheng 2007) and this figure is expected to touch 40,000,000 tons of flat glass as a current global demand (http://www.tatachemicals.com/europe/touching_lives/pdf/glass_industry.pdf). Waste thus obtained can be managed by any of the following techniques:

1. Mechanical recycling (remelting and shaping)
2. As a material resource to make concrete admixture/aggregates (Terro 2006; Disfani et al. 2011a), masonry blocks (Turgut 2008), and ceramic tiles (Matteucci et al. 2002); as flux in metallurgical processes (Mostaghel and Samuelsson 2010), foam glass (Chen et al. 2009), footpath/pavement base material (Arulrajah et al. 2013; Imteaz et al. 2012), road building material (Disfani et al. 2011b; Disfani et al. 2012), and adsorbent (Pant 2009); and for decorative purposes (Nnorom et al. 2011), and;
3. Land filling.

Various colorless glass, such as soda lime, borosilicate, vitreous silica, etc. (McLellan and Shand 1984; Shi and Zheng 2007), are broadly nonhazardous, with respect to metal, and can be managed by any of the above three techniques.

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Fluorescent light (contains hazardous mercury) is made up of various materials with 20–59 wt% of glass, which varies from type (i.e., compact fluorescent to fluorescent lamp), design, and capacity of the lamp. An 11 W capacity fluorescent lamp contains 46 and 14 W compact fluorescent lamp has 65 g glass (Welz et al. 2011). Many other glasses like colored, light-emitting diode, and cathode ray tube (CRT) also contains heavy metals (Cheng et al. 2007; Lim et al. 2013; Romero et al. 2013).

Due to the limitation in proper management system, nearly 78 % of resultant waste is dumped in a municipal landfill (Nnorom et al. 2011). A recent study economically validated closed-loop recycling, pyrometallurgy, and hydrometallurgy techniques (110–450 \$/t) with landfill options (45 \$/t) (Xu et al. 2013). So there is a continuous requirement towards an appropriate management option to extend the applications of these techniques. The current review discusses the issues related to quantity and associated risks from pollutants present in hazardous glass (HG) and proposes a plan for its management.

Heavy metal pollutant in glass

Different heavy metal compounds are mixed in the glass for imparting colors and specific applications (Table 1). Iron, in its trivalent form, in combination with barium oxide, gives a reddish brown color to the glass matrix; in its divalent form, with chromium, produces a deep green color; and with sulfur, it gives a dark amber color. Manganese imparts a purple and a weak yellow or brown color in its trivalent and divalent stages, respectively, and provides stability and strength to the glass object. Chromium(VI) imparts a dark green color, and on excess it gives a black color. It is one of the most powerful coloring and corrosion resistance metals in the glass-making industry. Copper imparts turquoise blue tones to the glass and improves its strength. Cobalt with potash produces a rich blue color and green with iodine. Uranium produces a yellow color and is used in making fluorescent glasses, while with lead it gives a deep red color.

The glass of a fluorescent lamp is coated with phosphor powder containing mercury vapor from the inside. Mercury is added to the lamp in the form of solid, liquid, or amalgam (Parsons 2006). It emits ultraviolet light (Fig. 1) upon excitation by electric current which fluoresces phosphor; the resultant gives an emission of visible light (Hildenbrand and Denissen 2000; Nance et al. 2012). Elemental mercury (Hg^0) during lamp operation is oxidized and adsorbed onto the glass, phosphor powder, and metal component of the lamp (Aucott et al. 2003; Jang et al. 2005; Nance et al. 2012; Hu and Cheng 2012) and makes them polluted. The amount of mercury in fluorescent lamp varies according to lamp type, wattage, brand, and manufacturer (Stahler et al. 2008; Culver 2008; Newmoa 2008). Fluorescent lamps consist of 0.7–115 mg of mercury per lamp (Jang et al. 2005; Johnson et al. 2008). Mercury that is present in different lamps can also vary in different countries because of technology and associated environmental legislations. According to the United Nations Environment Program (UNEP), the mercury used in fluorescent tube lights in the European Union was 15 mg/lamp in 1997 which gets reduced to 10 mg/lamp in 2002. Russia, USA, Canada, and India used 15–45, 10–20, 23–46, and 5–60 mg/lamp in fluorescent tube lights (double end), respectively. In compact fluorescent lamp, mercury content varies accordingly such as 5 mg/lamp in the European Union, 10 mg/lamp in Canada, 12–30 mg/lamp in Russia, and 3–12 mg/lamp in India. High-intensity discharge lamps have more mercury content as compared to fluorescent lamps (Hu et al. 2012).

Mercury is hazardous to both infants as well as adults (Fig. 2). It affects neural development in unborn and growing

Table 1 Heavy metals and their effect towards glass matrix

Metal	Color imparted	Application	Reference
Fe	Reddish with BaO (Fe(III) + BaO) Deep green with Cr (Fe(II) + Cr) Dark amber with S (Fe + S)	Stability	Issitt (2005), Romero et al. (2002)
Mn	Mn (III)—purple Mn (II)—weak yellow or brown	Stability and strength	Issitt (2005), Durga and Veeraiah (2003), Srinivasarao and Veeraiah (2001)
Cr	Dark green in low concentration and black in excess	Corrosion resistance	Issitt (2005), Li et al. (2008)
Cu	Turquoise blue tones	Strength	Issitt (2005), Podgorkova and Melnikov (1976)
Co	Deep blue with K_2CO_3 Shades of pink with B_2O_3:SiO_2 Green with iodine	Enhances thermal property	Issitt (2005)
U	Yellow Deep red with lead	Fluorescence property	Issitt (2005), Brenni (2007)

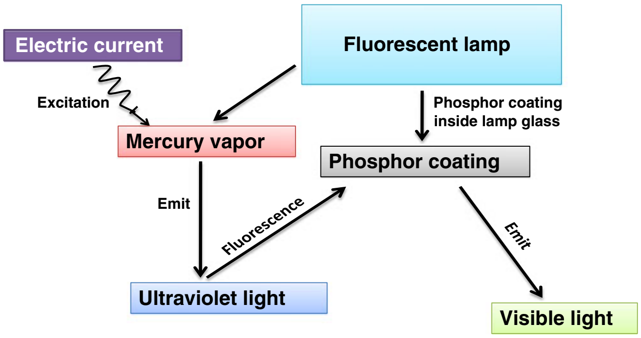


Fig. 1 Mechanism involved in lightening of a fluorescent lamp

children (Johnson et al. 2008; Clarkson 1993; Wang et al. 2011a) and may cause problems to aquatic and terrestrial ecosystems both in organic (methyl mercury) and inorganic (elemental mercury and mercury vapor) forms (Boening 2000; Tchounwou et al. 2003). Inorganic mercury is methylated in aquatic ecosystem and thus being accumulated to a high degree in aquatic food chains resulting in the highest concentration of mercury in marine fish and mammals (Clarkson 1993; Tchounwou et al. 2003; Sams 2007). It can affect the brain, the central nervous system, cause tremor, depression, and behavioral disturbances (Langford and Ferner 1999; Gupta 2007; Tsydenova and Bengtsson 2011; Pant et al. 2012).

Lead (in the form of PbO) is widely used in CRT glass due to its specific property to protect harmful exposure of X-rays generated from electron gun inside the tube (USEPA 1999; Musson et al. 2000). Lead content in CRT monitor varies from black and white towards colored, older towards newer, size, etc. Black and white and color funnel CRT consists of 2.8–4.4 and 19–23 % PbO, respectively, in terms of net oxide content (Mear et al. 2006). In black and white CRTs, lead is present in the glass part of the panel, funnel, and neck; in colored CRTs, it is present only in the funnel and neck (Corcoran 2001; Andreola et al. 2005a; Mear et al. 2006). The panel, funnel, and neck are joined together with a solder glass called frit which is highly leaded (Monitor 2001). Older CRT monitor contains 2–3 kg lead whereas this amount is decreased to 1 kg in the more recent one (Tsydenova and Bengtsson, 2011). Lead content may also vary according to the size of the television (TV) screen such as 13, 17, 27, and 32 in. contains 0.5, 0.7, 1.8, and 2.9 kg of lead, respectively (Karagiannidis et al. 2005).

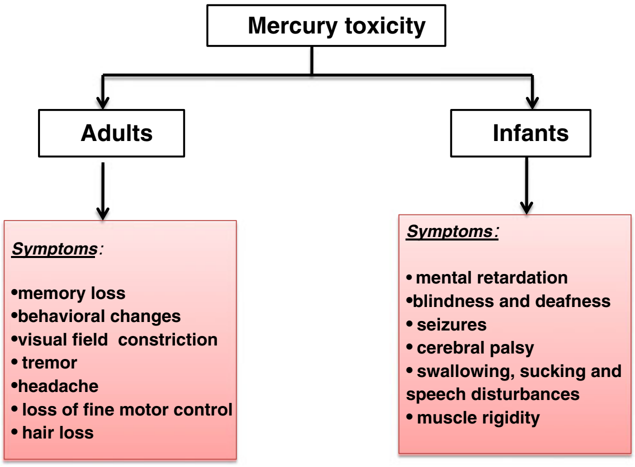


Fig. 2 Mercury toxicity in human adults and infants

The oxide composition in colored CRT glass consist of about 64 % SiO_2, 9 % SrO, 8 % Na_2O, 8 % K_2O, 3 % PbO, 3 % CaO, 2 % BaO, 1 % Al_2O_3, and 2 % of other oxides such as Sb_2O_3, As_2O_3, TiO_2, Li_2O, ZnO, MgO, Fe_2O_3, CeO_2, and ZrO_2 (Brain 1990). The chemical composition of oxides present in CRT glass are classified into three groups: (1) network formers, responsible to form the glassy structure such as SiO_2 and B_2O_3; (2) network modifiers, terminator for glassy network by requiring fewer oxygen to balance the valency such as CaO, MgO, Na_2O, and K_2O; and (3) network intermediates, modify the glass network for its specific application as Al_2O_3 and PbO (Mear et al. 2006, 2007).

Humans can be exposed to lead from air and food in roughly equal proportions (Jarup 2003). Children particularly are very susceptible to lead exposure due to high gastrointestinal (GI) uptake and the permeable blood–brain barrier (INSA 2011). Almost 20–30 % lead in adults and 50 % in children is absorbed through the GI track. Lead can cross blood–brain barrier as well as placental barrier (http://www.atsdr.cdc.gov/toxfaq.html). Pregnant women and young children having iron deficiency (anemia) are more susceptible to lead toxicity (Flora et al. 2006). Exposure to lead can cause intellectual impairment in children and damage either nervous, blood, or reproductive systems in adults (Poon 2008; Barbosa et al. 2005; Chen et al. 2011). Recent data indicates that there may be neurotoxic effects of lead at lower levels of exposure (Jarup 2003). The toxic effects of lead includes anemia, kidney damage, hypertension, cardiac disease, immune system suppression (antibody inhibition), and neurological damage (Quaterman 1986) with skin damage, headache, nausea, gastric, and duodenal ulcers (Monika 2010).

Quantification and risk assessment of pollutant in HG

Environmental pollution caused by mercury is a serious problem around the globe. Elemental mercury can be retained in atmosphere between 6 to 24 months before redeposition on the earth's surface, it can be transported to over tens of thousands of kilometers (Schroeder and Munthe 1998; Dastoor and Larocque 2004; Carpi 1997). Fluorescent glass waste management requires awareness from consumer to manufacturer level so that they do not break or mix this waste with municipal trash bin and hand them over to authorized recycling unit. According to a survey conducted by Raposo and Roeser (2001) in Minas Gerais, Brazil, fluorescent lamps are disposed: (1) straight into garbage bins from public (41 %), hospital (80 %), commercial (100 %), and industrial sources (32 %); (2) recycling by public (51 %) and industrial sources (56 %); and (3) use of other disposal methods including private landfills, old and out of use wells, destroyed and buried in the ground, incinerated with other hazardous materials, dropped in junk yards, burned on corporate dumping grounds, and given away to service companies that replace burned out lamps under contract by public (8 %), hospital (20 %), and industrial sources (12 %).

Table 2 represents the worldwide production and associated waste data of fluorescent devices in terms of real and projected data. Worldwide production of compact fluorescent lamps (CFL) in the year 2001 was 820,000,000 pieces (CPCB 2008). China is the world's largest CFL manufacturer; in the year 2009, it produced over 3,650,000,000 pieces of CFL bulbs out of which 80 % were exported (Chen 2010; Hu and Cheng 2012). The average life span of CFL is usually 8,000 h (Welz et al. 2011; Duff 2012), i.e., approximately 1 year. Straight-line equation from year-wise sales (2001–2006; Fig. 3) gives the future sale data of CFL in comparison with its lifespan that provides the resultant future waste data (Pant 2013a; CPCB 2008).

Technological advancement has been continuously replacing CRT with more improved versions like liquid crystal display (LCD) and plasma display panel thus generating enormous amount of waste CRT (Chen et al. 2009). In 2002, 83,300,000 of CRT was produced worldwide (Socolof et al. 2005). The amount of CRT glass generated in Asia will increase with a factor of 2 and will climb up from 800 to 1,500 metric tons by 2020 (Gregory et al. 2009). China is at the forefront of CRT production and covers about 90 % of the global CRT demand (Widmer et al. 2005; He et al. 2006). International business management estimated that in 2008, about 294,000,000 CRTs were discarded in the USA (Mizuki et al. 1997; Mueller et al. 2012). Asian countries like Japan generated 8,896,000 TVs in 2001, out of which 3,080,000 were taken into recycling facilities and the rest, which is 4,270,000 were exported to other countries (Tasaki et al. 2004). Taiwan generated 1,030,000 units of TV in 2002 (Hsu and Kuo 2005); Korea generated more than 8,000,000 units of TV waste in 2004–2005 out of which less than 3,000,000 units were recycled (Lee et al. 2007). In the USA, approximately 20,000,000 TVs become obsolete each year (Jefferies 2006). Year-wise production of CRT unit (leaded panel, nonleaded panel, and funnel glass) in the USA is represented in Fig. 4 (Monchamp et al. 2001). This figure shows data from the year 1990 to 2000:

Table 2 Worldwide production of CFL (in million units) (CPCB 2008)

Year	World production	Projected waste
2001	820	–
2002	880	820
2003	1,144	880
2004	1,500	1,144
2005	1,930	1,500
2006	2,650	1,930
2007	4,200	2,650
2008	4,900	4,200
2009	6,000[a]	4,900
2010	6,700[a]	6,000
2011	7,300[a]	6,700
2012	8,100[a]	7,300
2013	8,600[a]	8,100
2014	9,300[a]	8,600
2015	10,100[a]	9,300

[a] Based on estimation

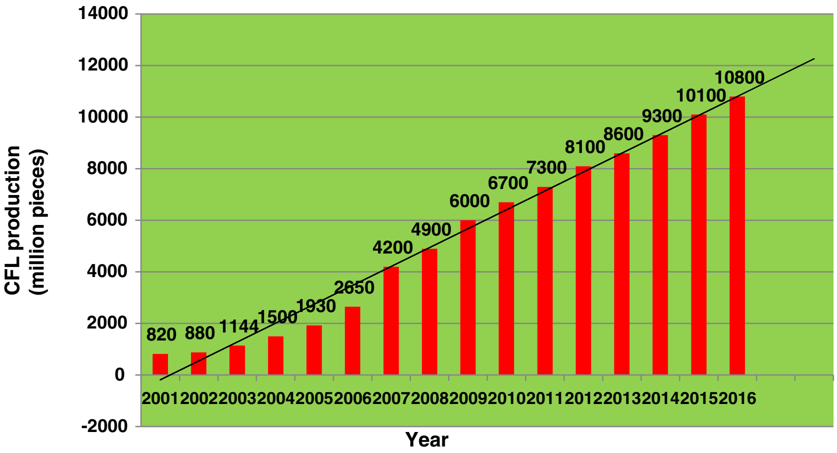
1. There was a continuous increase in CRT glass production from183,565 to 530,904 tons.
2. The amount of leaded panel glass increased up to 1997; then from 1998 to 2000, its production is continuously declined.
3. No-lead panel glass production increases rapidly from 30,137 to 256,358 tons.
4. The amount of funnel glass production increased from 78,967 to 183,906 tons.

Only few developed countries have effective management program for CRT waste while large quantities are transferred to the developing countries like China for its management (Chen et al. 2009). These countries are deficient in recycling infrastructures and waste is processed in backyard or small workshops using manual disassembly and/or open burning. Such crude recycling techniques creates environmental pollution by affecting the air, soil, and water bodies (Nnorom et al. 2011).

Pollutant management

Mercury-containing glass waste (MCGW) can be managed by dry crushing and heating technology in a fluidized bed reactor. Countries have their own practices for the treatment, collection, and disposal of spent fluorescent lamps. Developed countries like the European Union and the USA have proper legal back up for the safe disposal of mercury-contaminated used lamps. The United States Environmental Protection Agency recommends that fluorescent lamps should be segregated from general waste for recycling or safe disposal (USEPA 1998). The European Union has developed the Waste Electrical and Electronic Equipment and Restriction of Hazardous Substances directives that producers should setup collection system for their household electronic waste. In the USA and Sweden, generator has to hand over the used

Fig. 3 Future sale data of CFL



lamps to authorized recyclers (Luther 2008); in Germany, the used fluorescent lamps are being collected at various collection centers (following the Recovery and Disposal Act for recycling). Russia, China, and Japan follow the regulations of Federal Law-Waste of Production and Consumption, Law of Environmental Protection, and Law for Promotion of Effective Utilization of Resources, respectively (CPCB 2008).

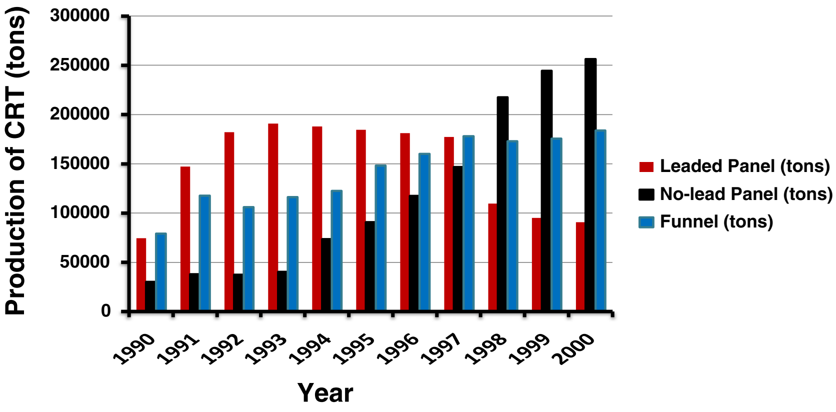
Recycling of waste fluorescent lamps may include the following steps:

1. Feeding of used lamps in a recycling unit and pulverizing it.
2. Sieving/separation of glass, metal, phosphor powder, and mercury vapors.
3. Distillation to recover mercury from phosphor powder.

Other techniques like production of glass ceramics as valuable recycled products are also in practice (Yun et al. 2002). A recent research proposed a low-cost process to remove phosphor powder attached to the glass and removal of mercury by extraction (Rey-Raap and Gallardo 2013).

Lead-containing glass waste (LCGW) can be managed by various strategy involving reusing, recycling, and land filling (Zhang et al. 2000; Nnorom et al. 2007; ICER 2004; Smith et al. 1996; Andreola et al. 2005a). Reusing involves the replacement of previously used electronic gun from the waste CRT to manufacture local brand TVs and screens for video games (Ahluwalia and Nema 2006; Nnorom et al. 2011). Also, the reuse of secondhand TVs in developing countries has been reported as Japan in 2008 exported secondhand TVs to the Philippines (Yoshida and Atsushi 2010). Recycling is another way to manage CRT glasses into various value-added products like flux in metallurgical processes (lead and copper smelting; Mostaghel and Samuelsson 2010; Weitzman 2003; ICF Incorporated Fairfax 1999; Andreola et al. 2008), glass ceramics (Andreola et al. 2005b; Bernardo et al. 2006), glass matrix composites (Bernardo et al. 2003), glass beads for reflective elements and shot peening (Balcar and Dunkirk 1997), cement, clay brick, tile mixture, and glass wool (Lairaksa et al. 2013; Seo et al. 2011; Chen et al. 2002; Dondi et al. 2009; Luz and Ribeiro 2007); aggregate and mortars in concrete (Romero et al. 2013; Maschio et al. 2013); biopolymer-modified concrete (Kim et al. 2005), foam glass (Chen et al. 2009; Bernardo and Albertini 2006; Bernardo et al. 2005), fiber glass highway-reflective products (Dillon 1998), adsorbent (Pant and Singh 2013); and for decorative purposes such as tiles, glass, and lightening products (Nnorom et al. 2011). Smelting, a recycling technique is also used to separate toxic lead from the waste CRT glass

Fig. 4 Production of CRT glass in the USA



(Chatterjee and Kumar 2009). For recycling of CRT, the USA has developed two techniques (Fig. 5; Menad 1999): (1) closed-loop recycling (glass to glass recycling) and (2) open-loop recycling (glass to lead recycling). In closed-loop recycling, whole recovered glass is grounded into cullets and used for the production of new CRT glass; in open-loop recycling, the glass is used for the production of secondary materials (Siikamaki et al. 2002; ICER 2004). Geskin et al. (2002) described the development of recycling technology (water jet technologies) for the efficient recovery of LCGW. This recycling technique involves separation of CRT at the frit line or just below it in order to achieve both high- and low-lead cullet compositions. Land filling methods are potentially unacceptable as it may cause heavy metal pollution which results in contamination of ground water (Noon et al. 2011; Poon 2008). Methods like reduction melting process (Okada and Yonezawa 2013), mechanochemical sulfidization (Yuan et al. 2013a), and mechanical activation as pretreatment followed by nitric acid leaching (Yuan et al. 2013b) are also proposed recently by some researchers to recover Pb from funnel glass of CRT.

The possible remediation techniques to manage hazardous pollutant from glass waste are broadly classified as (Fig. 6):

1. Chemical remediation involving stabilization/solidification and immobilization
2. Biological remediation involving microremediation, phytoremediation, and animal remediation;
3. Thermal desorption
4. Nanotechnology
5. Hybrid technique

Chemical remediation

Chemical remediation technique involves the use of various chemicals for the removal of toxic and hazardous substances from environment. It may be done by the use of acid, base, chelating agents, and inorganic compounds by leaching and/or precipitation.

Remediation of MCGW

Table 3 represents the list of various chemicals used for Hg remediation from waste. It is found that for mercury remediation, EDTA and activated carbon have very extensive research level. Perusal of this table reveals that:

1. Acids like HF and aqua regia, nitric and perchloric acid form soluble compounds with mercury for its removal.
2. Mercury can be precipitated as $Hg(OH)_2$ by using NaOH or at higher pH.
3. Chelating agent increases the concentration and mobility of certain metal atom using coordination (Wenzel et al. 2003). Some biodegradable ligands like diethylene triamine penta-acetate (DTPA), nitrilotriacetic acid (NTA), along with oxalate and citrate have also been used as chelating agents for the extraction of mercury.
4. Various inorganic compounds as KI/I can also be used as leaching agent.
5. Sulfide can be used to remediate Hg by the formation of less toxic HgS (Piao and Bishop 2006; Bower et al. 2008).
6. Various adsorbents like activated carbon, coal and coal fly ash, bamboo charcoal modified with KI , powdered sulfur polymer cement and sulfide, zeolites, sulfur-impregnated activated carbon with zeolites, and rice husk ash can remove mercury from its aqueous solution as well as in vapor form.

For the soils which have high elemental mercury content, methods such as stabilization/solidification and immobilization are suitable remediation options (Wang et al. 2012). It involves chemical reactions between the stabilizing agent and the contaminants to reduce Hg mobility. Powder-activated carbon with cement (Zhang and Bishop 2002) and thiol-functionalized

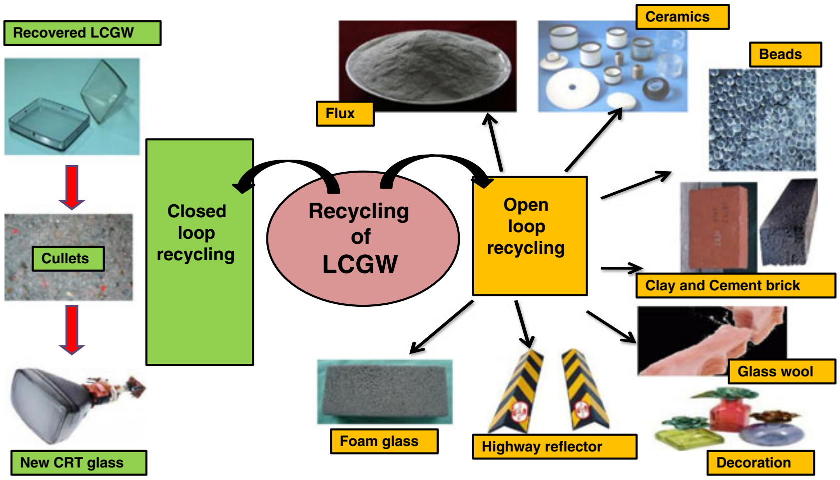


Fig. 5 Open- and closed-loop recycling of LCGW

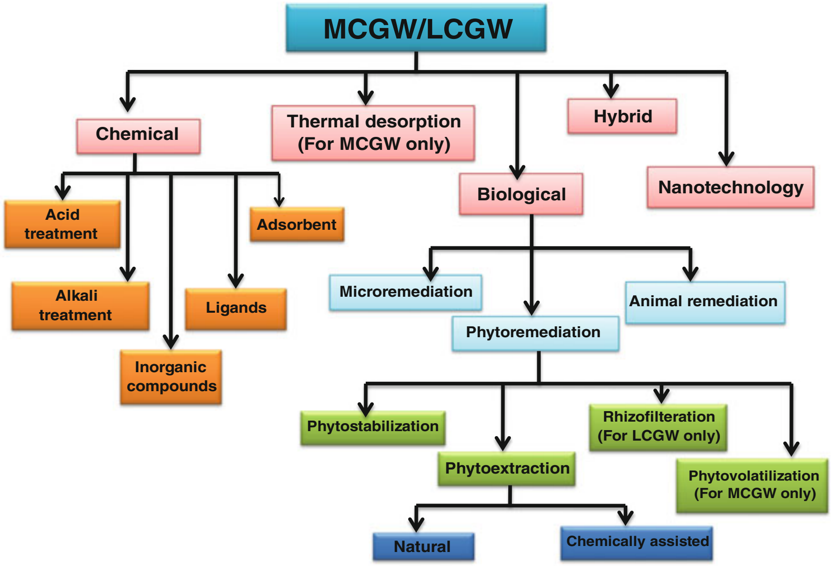


Fig. 6 Management techniques for hazardous metal management from LCGW and MCGW

zeolite (Zhang and Bishop 2002; Zhang et al. 2009) can be used to stabilize mercury.

Chemical remediation technique is primarily applied if the target metal is in the ionic form (Dermont et al. 2008a, b).

Table 3 Chemical remediation of MCGW

S. no.	Technique	Mode of action	Research level	References
1	Acid treatment			
(a)	HF	Leaching	Less extensive	Sladek and Gustin (2003)
(b)	Aqua regia	Leaching	Less extensive	Sladek and Gustin (2003)
(c)	Nitric acid and perchloric acid	Leaching	Less extensive	Harikumar et al. (2011)
2	Alkali treatment			
(a)	NaOH	Leaching/precipitation	Less extensive	Anderson and Twidwell (2008)
(b)	Hypochlorite	Leaching	Extensive	Pedroso et al. (1994)
3	Ligands (chelating agents)			
(a)	EDTA	Leaching	Very extensive	Peters (1999), Cheikh et al. (2010), Hong et al. (2000)
(b)	NTA	Leaching	Less extensive	Elliott and Shastri (1999), Hong et al. (2000)
(c)	DTPA	Leaching	Less extensive	Paez-Hernandez et al. (2005), Hong et al. (2002)
(d)	Citrate and oxalate	Leaching	Less extensive	Peters (1999)
4	Involving inorganic compounds			
(a)	KI/I	Leaching	Extensive	Klasson et al. (1998)
(b)	Sulfide	Lewis base	Extensive	Fuhrmann et al. (2002), Piao and Bishop (2006)
5	Adsorbents			
(a)	Activated carbon	Adsorbent	Very extensive	Inbaraj and Sulochana (2006), Skodrasa et al. (2007), Hafshejani et al. (2012), Oubagaranadin et al. (2007), Ghorishi and Gullett (1998), Yardim et al. (2003), Coolidge (1927), Shabudeen et al. (2013)
(b)	Coal and coal fly ash	Adsorbent	Extensive	Kannan et al. (2010)
(c)	Bamboo charcoal modified with KI	Adsorbent	Less extensive	Tan et al. (2012)
(d)	Zeolites	Adsorbent	Less extensive	Barrer and Whiteman (1967)
(e)	Sulfur-impregnated activated carbon with zeolites	Adsorbent	Less extensive	Steijns et al. (1976), Otani et al. (1998), Gomez-Serrano et al. (1998)
(f)	Powdered sulfur polymer cement and sulfide	Absorbent	Less extensive	Fuhrmann et al. (2002)
(g)	Rice husk ash	Adsorbent	Extensive	Tiwari et al. (1995), Feng et al. (2004)

Sierra et al. (2011) investigated the feasibility of physicochemical procedures by involving physical separation followed by chemical process.

Remediation of LCGW

Table 4 represents the list of various chemicals used for lead removal from waste. EDTA is widely used for Pb removal of the waste with very extensive research level. A perusal of this table reveals that:

1. Acids like HCl, HNO_3 alone/or with H_2SO_4, and acetic acid form soluble compounds with lead for its removal.
2. Extract lead as lead hydroxide by NaOH.
3. Synthetic chelators like DTPA, hydroxylethyl ethylenediamine-triacetic acid (HEDTA), propylene diamine tetraacetic acid, ethyleneglycol-*bis*(2-aminoethylether) tetraacetic acid and biodegradable synthetic chelating agents, such as ethylenediaminedisuccinic acid (EDDS), citric acid and NTA, can also be used for the removal of lead from LCGW.
4. Pyrolusite, calcite, kaolinitic clay, kaolinite with alumina, zeolites, glass, and biosorbents like rice husk ash, *Syzygium cumini* L., and Coir (fibers from *Coco nucifera*) can act as adsorbents for Pb removal.

Biological remediation

Bioremediation technique involves the use of living organisms (microbe, plant, and animal) to remove pollutants from the environment.

Table 4 Chemical remediation of LCGW

S. no.	Technique	Mode of action	Research level	References
1	Acid treatment			
(a)	H_2SO_4 and HNO_3	Leaching	Extensive	Nnorom and Osibanjo (2009), Nnorom et al. (2010)
(b)	HNO_3	Leaching	Extensive	Strzalkowska et al. (2012), Yuan et al. (2013a, b)
(c)	HCl	Leaching	Extensive	Nagib and Inoue (2000), Svehla (2004)
(d)	Acetic acid	Leaching	Extensive	Nagib and Inoue (2000), Rybarikova et al. (2001)
2	Alkali treatment			
(a)	NaOH	Leaching	Less extensive	Nagib and Inoue (2000), Svehla (2004)
3	Ligands (chelating agents)			
(a)	EDTA	Leaching	Very extensive	Peters (1999), Cheikh et al. (2010), Hong et al. (2000), Wu et al. (2010), Wenzel et al. (2003), Niinae et al. (2008)
(b)	DTPA	Leaching	Less extensive	Elliott and Shastri (1999), Hong et al. (2002)
(c)	PDTA	Leaching	Less extensive	Hong et al. (2000), Kocialkowski et al. (1999)
(d)	HEDTA	Leaching	Less extensive	Hong et al. (2000), Kocialkowski et al. (1999)
(e)	EGTA	Leaching	Less extensive	Hong et al. (2000), Kocialkowski et al. (1999)
(f)	NTA	Leaching	Less extensive	Elliott and Shastri (1999), Hong et al. (2000)
(g)	EDDS	Leaching	Less extensive	Nortemann (2005)
(h)	Citrate and oxalate	Leaching	Less extensive	Peters (1999), Elliott and Shastri (1999)
4	Adsorbents			
(a)	Pyrolusite (MnO_2 ore)	Adsorbent	Less extensive	Ajmal et al. (1995)
(b)	Calcite ($CaCO_3$ mineral)	Adsorbent	Less extensive	Reeder (1996)
(c)	Kaolinitic clay	Adsorbent	Less extensive	Orumwense (1996)
(d)	Kaolinite and alumina	Adsorbent	Less extensive	Hall (1998)
(e)	Zeolites	Adsorbent	Less extensive	Yuan et al. (1999)
(f)	Glass	Adsorbent	Less extensive	Pant and Singh (2013)
(g)	Rice husk ash	Sorption	Extensive	Naiya et al. (2009), Feng et al. (2004), Zahra (2012), Nhapi et al. (2011), Zulkali (2006)
(h)	*Syzygium cumini* L. dried leaves	Adsorbent	Less extensive	King et al. (2007), Zahra (2012)
(i)	Coir	Sorbent	Less extensive	Conrad and Hansen, 2007
(j)	Bamboo charcoal (iron coated)	Adsorbent	Less extensive	Zhang et al. (2013)

Table 5 Bioremediation of MCGW

S. no.	Biological species	Role	Reference
1	Microorganisms		
(a)	*Bacillus cereus*	Immobilization	Sinha et al. (2012)
(b)	*Pseudomonas species*	Biotransformation (Hg^{2+} to Hg^0)	Wagner-dobler et al. (2000)
(c)	*Klebsiella pneumoniae* spp.	Biosorption	Al-Garni et al. (2010)
(d)	*Pseudomonas aeruginosa*	Biosorption	Al-Garni et al. (2010)
(e)	*Saccharomyces cerevisiae* (brewer's yeast)	Biosorption	Yavuz et al. (2006)
(f)	*Chlorophyceae* spp. (*Selenastrum minutum* and *Chlorella fusca*)	Biotransformation (Hg^{2+} to Hg^0)	Kelly et al. (2007)
(g)	*Spirogyra* spp.	Biosorption	Rezaee et al. (2006)
2	Plants		
(a)	*Rumex induratus*	Phytoextraction	Moreno-Jimenez et al. (2006)
(b)	*Marrubium vulgare*	Phytoextraction	Moreno-Jimenez et al. (2006)
(c)	*Hordeum species*	Phytoextraction	Rodriguez et al. (2003, 2007)
(d)	*Lens culinaris*	Phytoextraction	Rodriguez et al. (2003, 2007)
(e)	*Cicer arietinum*	Phytoextraction	Rodriguez et al. (2003, 2007)
(f)	*Lupinus polyphyllus*	Phytoextraction	Rodriguez et al. (2003, 2007)
(g)	*Triticum aestivum*	Phytoextraction	Rodriguez et al. (2003, 2007)
(h)	*Macleaya cordata* L.,	Phytoextraction	Wang et al. (2011a)
(i)	*Achillea millefolium* L.	Phytoextraction	Wang et al. (2011a)
(j)	*Pteris vittata L*.	Phytoextraction	Wang et al. (2011a)
(k)	*Silene vulgaris*	Phytovolatilization	Perez-Sanz et al. (2012)
(l)	*Willow species* (*Salix viminalis* and *Salix schwerinii*)	Phytovolatilization	Wang et al. (2005)
(m)	*Juncus maritimus*	Phytovolatilization	Anjum et al. (2011), Marques et al. (2011)
3	Animal		
(a)	Earthworm (*Eisenia fetida*)	Chelation and complexation	Sinha et al. (2008)

Remediation of MCGW

Table 5 represents the various biological species involved in the remediation of MCGW. Some biological species develop resistance mechanism to overcome Hg toxicity by biosorption, bioleaching, and enzyme-catalyzed transformation. At neutral pH, microbial cell surface carries a net negative charge due to the presence of carboxyl, amine, hydroxyl, phosphate, and sulfhydryl groups able to adsorb positively charged cationic metals. Alginate immobilized mercury-tolerant *Bacillus cereus* cells (Sinha et al. 2012), magnetically modified yeast cells (Yavuz et al. 2006), alga like *Spirogyra* (Rezaee et al. 2006), and autotrophic microorganism like *Thiobacillus* (Lloyd 2002) are some popular microbes used for the biosorption of mercury. Enzyme-catalyzed transformation involves the reduction of the toxic mercuric ion (Ehrlich 1997) Hg(II) to less toxic Hg(0). In some studies, elemental mercury is trapped by using mercury-resistant bacteria like *Pseudomonads* (Wagner-dobler et al. 2000; Lloyd 2002), *Bacillus*, *Closteridium*, and *Escherichia* spp. (Cunningham and Ow 1996) as biofilm in bioreactor.

Phytoremediation is widely viewed as the ecologically responsible alternative to the currently practiced environmental methods (Meagher 2000). Plants can manage mercury by the following three ways:

1. Phytostabilization is the involvement of roots of a plant to limit contaminant mobility and bioavailability in the soil (www.itrcweb.org). It can occur either by the process of complexation, sorption, precipitation, or metal valence reduction (Henry 2000).
2. Phytoextraction is the use of plants to accumulate contaminants in their tissues. Phytoextaction can occur naturally or by the addition of certain chemicals or chelating agents to the plants.
3. Phytovolatilization is the process by which the plant can uptake the volatile metal from the soil. This technique is important for remediation of mercury as some plants may naturally interact with mercury present in the soil (Wang et al. 2012). Five plant species *Lepidium latifolium*, *Artemisia douglasiana*, *Caulanthus* sp., *Fragaria vesca*, and *Eucalyptus*

Table 6 Genetically modified plants involved in phytovolatilization of mercury

MerA modified	MerB modified	MerC modified
Arabidopsis thaliana, *Liriodendron tulipifera*, *Arachis hypogaea*, *Populus deltoides*, *Oryza sativa*, *Spartina alterniflora* and *Chlorophyta* (Huang et al. 2006; Czako et al. 2006; Rugh et al., 1996, 1998; Yang et al. 2003)	*A. thaliana* (Bizily et al. 1999)	*A. thaliana* and *Nicotiana tabacum* (Sasaki et al. 2006)

globules were grown in the soil contaminated with mercury (450–1,605 mg/kg). Among these plant species, *Caulanthus* sp. showed a higher mercury emission rate of 92.6 ng/m^2/h in the daytime (Leonard et al. 1998).

Insertion of bacterial genes to design the genetically engineered plants for detoxifying mercury is another important area of research (Raskin and Ensley 2000). An extensively resistance system based on clustered genes in an operon (i.e., Mer), allows bacteria to detoxify Hg^{2+} into volatile mercury by enzymatic reduction (Komura and Izaki 1971; Summers 1986; Misra 1992; Silver 1996; Barkay et al. 2003). The organic methyl mercury (R-CH$_2$Hg) is the most toxic form than all the other forms of mercury. To detoxify this toxin, transgenic plants (*Arabidopsis* and tobacco) are engineered (Table 6) with bacterial genes merB (organomercurial lyase) and merA (mercuric ion reductase). In these modified plants, merB catalyzes the protonolysis of the carbon–mercury bond with the generation of Hg^{2+} (100 times less toxic than methylmercury) and subsequently MerA converts Hg(II) to Hg(0), a less toxic, volatile element (Heaton et al. 1998; Fox and Walsh 1982; Rugh et al. 1996; Bizily et al. 1999). By genetic engineering, other genes like MerC, MerF, and MerT (membrane transporter genes) are also being introduced in the plants which are involved in the process of translocating Hg^{2+} into the plant cell (Bizily et al. 1999, 2000; Ruiz and Daniell 2009; Liebert et al. 2000; Morby et al. 1995; Wilson et al. 2000; Fig. 7). Recently, two other Mer genes, mer E and mer H (membrane bound), assisting in the membrane transport of mercury has been reported in the bacteria (Kiyono et al. 2009; Schue et al. 2009).

Animal remediation of mercury mainly involves the use of earthworms to biotransform the metals to its less harmful form (Ireland 1983, 1979). They generate and exude carboxylic acid which acidify soil and activate heavy metals. Many earthworm species such as *Eisenia fetida*, *Eisenia tetraedra*, *Lumbricus terrestris*, *Lumbricus rubellus*, and *Allobophora chlorotica* have been used for this purpose (Sinha et al. 2008). Relevant concentration of metal in tissues might prove earthworms as efficient bioindicator of soil contamination by heavy metals (Suthar et al. 2008). Hartenstein et al. (1980) reported that earthworms can bioaccumulate high concentration of metals in their tissues without affecting their physiology.

Remediation of LCGW

Table 7 represents the various biological species involved in the remediation of LCGW. Microbes like *Acidithiobacillus ferrooxidan*, *Acidithiobacillus thiooxidans*, *Aspergillus niger*, *Penicillium bilaiae* and other *Penicillium* sp., and *Aspergillus fumigates* can efficiently leach out Pb from LCGW (Ehrlich 1997; Pant 2013b).

Phytoremediation techniques are found to be effective for the removal of lead from various contaminants (Blaylock and Huang 2000). In 2005, business associated with phytoremediation received 214–370 million dollars in the USA (Henry 2000). Brassicaceae plays a key role in phytoremediation (Blaylock et al. 1997; Kumar et al. 1994); in a report by Henry (2000), *Brassica juncea* is capable of

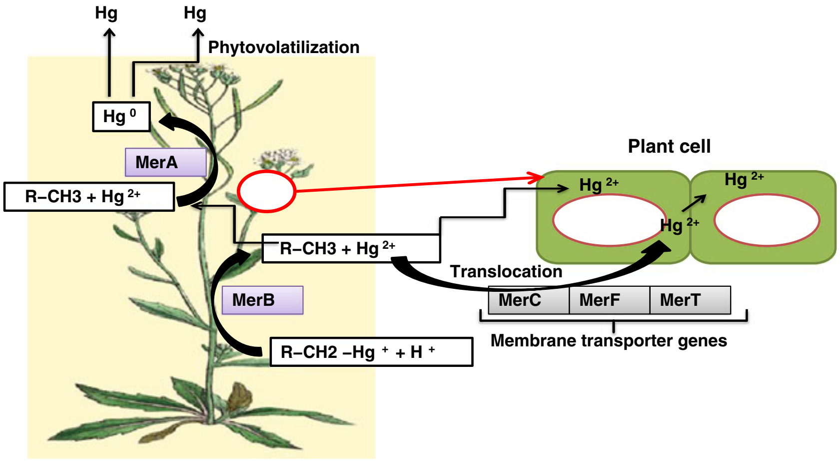


Fig. 7 Involvement of bacterial genes in phytoremediation of mercury

Table 7 Bioremediation of LCGW

S. no.	Biological species	Role	Reference
1	Microorganisms		
(a)	*Acidithiobacillus ferrooxidans*	Leaching	Pacholewska (2004), Brandl et al. (2001), Bayat and Sari (2010a, b), Baba et al. (2011), Sari (2012)
(b)	*Acidithiobacillus thiooxidans*	Leaching	Pacholewska (2004), Brandl et al. (2001)
2	Fungi		
(a)	*A. niger*	Leaching	Brandl et al. (2001), Mulligan and Kamali (2003)
(b)	*Penicillium bilaiae*	Leaching	Arwidsson and Allard (2009), Wasay et al. (1998)
(c)	*Penicillium* sp.	Leaching	Arwidsson and Allard (2009), Wasay et al. (1998), Elliott and Shastri (1999)
(d)	*Aspergillus fumigates*	Leaching	Ramasamy et al. (2011)
3	Algae		
(a)	Freshwater green algae species (*Chlamydomonas reinhardtii*, *Spirogyra species*, *Cladophora fascicularis*)	Biosorption	Wehrheim and Wettern (1994), Schmitt et al. (2001), Tien (2002), Tuzun et al. (2005), Gupta and Rastogi (2008), Deng et al. (2007)
(b)	Marine algae species (*Laminaria japonica*, *Ecklonia radiate*)	Biosorption	Jalali et al. (2002), Luo et al. (2007), Matheickal and Yu (1996), Vilar et al. (2005), Holan and Volesky (1994), Yu et al. (1999)
(c)	Seaweeds (*Ulva*, *Cladophora crispate*, *Caulerpa lentillifera*)	Biosorption	Suzuki et al. (2005), Ozer et al. (1994), Pavasant et al. (2006)
3	Plants		
(a)	Indian mustard (*Brassica juncea*)	Phytoextraction	Kumar et al. (1995)
(b)	Corn (*Zea mays*)	Phytoextraction	Huang and Cunningham (1996)
(c)	Ragweed (*Ambrosia artemisiifilia*)	Phytoextraction	Huang and Cunningham (1996)
(d)	*Atriplex halimus* L.	Phytoextraction	Manousaki and Kalogerakis (2009)
(e)	*Cyperus laevigatus*	Biosorbent	Al-Qahtani (2012)
4(a)	Earthworm	Chelation, complexation and bioaccumulation	Wu et al. (2010), Ireland (1979), Sinha et al. (2008)

removing 11,550 kg of lead per acre. Some other plant species like *Ageratum houstonianum* Mill., *Potamogeton oxyphyllus* Miq. and *Petris vittata* (Ha et al. 2011), *Zea mays* and *Ambrosia artemisiifilia* (Huang and Cunningham 1996), and *Atriplex halimus* L. (Manousaki and Kalogerakis 2009) can also be used for this purpose. Perveen et al. (2011) studied Pb phytoremediation in *Jasminum saambac* and found that the plant accumulate Pb in the root, leaf, and stem. A recent study on the comparison of lead phytoremediation by two plant species *Picea abies* and *Pinus sylvestris* was performed. The result showed that *P. sylvestris* is more suitable for Pb phytoremediation than *P. abies* (Maddah and Moraghebi 2013). The phytoremediation potential of a Mediterranean saltbush *A. halimus* L. was investigated for Pb removal from saline lead-contaminated soils (Manousaki and Kalogerakis 2009). Rhizofiltration is a process to remove toxic substances through the mass of roots from contaminated aqueous samples by absorption, concentration, and precipitation of the metal (Dushenkov et al. 1995). Various wetland species of plants like *Carex pendula* (Yadav et al. 2011), *Pistia stratiotes* L., *Salvinia auriculata* AubL, *Salvinia minima* Baker, and *Azolla filiculoides* Lam (Vesely et al. 2011) can efficiently remove lead from contaminated waste water.

Cellular membranes of the plant are lipophilic in nature so the Pb ion cannot move freely across it. For its movement, it requires transporter proteins and chelating agents like phytochelatin (PC), metallothioniens (MT), and organic acids present within the plant. These transporter molecules consist of extracellular binding domains (–COOH) to which Pb ion binds and forms complexes. This facilitates the transfer of Pb from extracellular to the intracellular environment of the plant cell (Blaylock et al. 1997, 1999; Kagi 1991). A fraction of the metal absorbed in the roots may either be sequestered in the root vacuole or it may pass through xylem and gets translocated from the root to the aerial parts (stem and leaves) of the plants (Figs. 8 and 9).

Many marine algae such as *Laminaria japonica* and *Ecklonia radiate*; green seaweed such as *Ulva*, *Cladophora crispate*, and *Caulerpa lentillifera*; and freshwater green algal species such as *Chlamydomonas reinhardtii*, *Spirogyra species*, and *Cladophora fascicularis* can also be used for the removal of lead through biosorption.

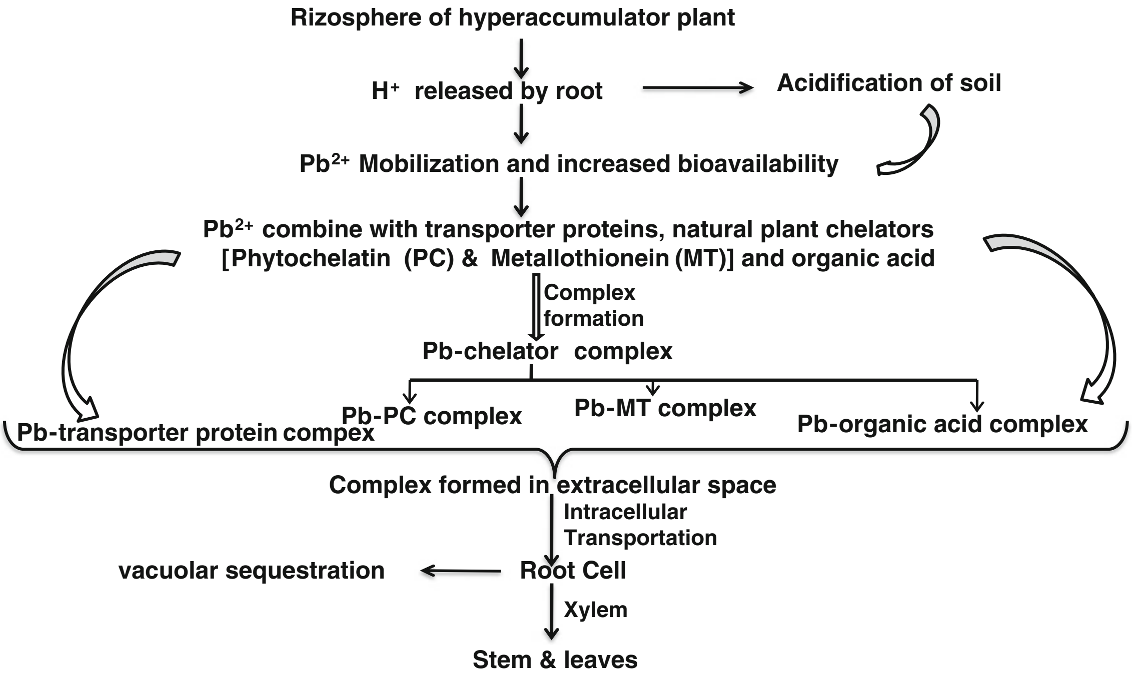


Fig. 8 Uptake, transportation, and translocation of Pb in plant

Earthworm species like as *L. rubellus*, *E. fetida*, *Eudrilus eugeniae*, and *Perionyx excavates* (Udovic and Lestan 2007; Sinha et al. 2008; Pattnaik and Reddy 2011) are also used for the remediation of lead by the formation of Pb–metallothionein complex which gets concentrated in chloragogen cells of the animal (Ireland 1979).

Thermal remediation

Thermal treatment processes are commonly used to treat mercury-contaminated pollutant by thermal desorption, retorting/roasting (Washburn and Hill 2003; George et al. 1995; Kunkel et al. 2006), or distillation under controlled temperature, pressure, and reactor conditions (Yamaguchi et al. 2005). The resultant mercury vapor thus obtained is condensed and collected (Morris et al. 1995). Table 8 represents mercury removal rate at different experimental sites. This table reveals that thermal desorption of mercury is started at 100 °C but for efficient removal, the temperature should be >460 °C. Chang and Yen (2006) performed onsite pilot plant thermal desorption experiments on mercury-contaminated soils from alkali chlorine factory in Taipei at a cost of 834/m^3 US dollar.

Solar energy can also be used for thermal remediation of mercury from contaminants (Navarro et al. 2009). Two thermal desorption systems, constituting low-temperature solar furnace (28–280 °C) and a middle-temperature solar furnace

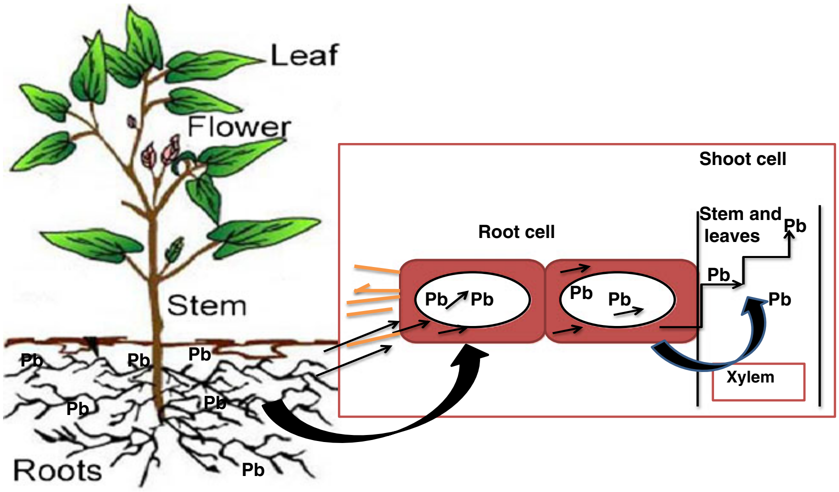


Fig. 9 Cellular uptake, transport, and translocation of Pb in plants

Table 8 Thermal removal of mercury from the contaminated sites

S. no.	Source	Temperature (°C)	Removal parameter	Reference
1	Soil from mining and metallurgical treatment of cinnabar	700	4 h, 99 %	Massacci et al. (2000)
2	Contaminated soil from chlor-alkaline industry	460	20 min, 99 %	Taube et al. (2008)
3	Leachetes of waste sludge from chlor-alkaline industry	≥400	Hg content below the US EPA regulations	Busto et al. (2011)
4	Waste sludge from chlor-alkaline industry	800	1 h, Hg content below the US EPA regulations	Busto et al. (2011)
5	Mercury-contaminated soil	>550	99 %	Huang et al. (2011)
6	Contaminated soil from Guizhou Organic Chemistry Company	270	2 h, 50–90 %	Qu et al. (2004)
7	Contaminated soil from chemical production facility, Poland	100	10 days, 32 %	Kucharski et al. (2005)
8	Contaminated soil from floodplain Soils of Lower East Fork Poplar Creek	600	90 %	Morris et al. (1995)
9	Used fluorescent lamp glass	600	100 %	Wijesekara et al. (2011)

(20–502 °C) were designed for this purpose with removal rate of 4.5–76 and 12.1–87 %, respectively.

Nanotechnology

The advantages of nanotechnology in the field of environmental remediation are inevitable. Nanoparticles have unique properties like their size (10–100 nm), larger surface area, high surface reactivity, and adsorptivity along with photoelectronic and photocatalytic properties which assists in analytical detection and effective remediation of environmental pollutants (Cabrejo and Phillips 2010; Stone et al. 2010; Wang et al. 2010; Nurmi et al. 2009; Liu et al. 2011). Many researchers proved significance of nanoscale zerovalent iron particles for remediation of various heavy metals including lead and mercury, using redox reaction (Eqs. 1, 2, and 3), where metals are reduced while nanoparticles get oxidized (Zhang 2003; Tratnyek and Johnson 2006; Karn et al. 2009). Iron sulfide (FeS) nanoparticles can be used to immobilize mercury in the mercury-contaminated sites (Wang et al. 2012; Fig. 10). As the standard reduction potential (E^0) of mercury (Hg^{2+}/Hg) is 0.85 V which is more than zerovalent iron nanoparticles (Fe2+/Fe=−0.44 V) so it can be reasonably reduced by zerovalent iron nanoparticles.

$$Fe^0 \rightarrow Fe^{2+} + 2e- \quad (1)$$

$$Hg^{2+} + Fe^0 \rightarrow Fe^{2+} + Hg^0 \quad (2)$$

$$Pb^{2+} + Fe^0 \rightarrow Fe^{2+} + Pb^0 \quad (3)$$

According to Xiong et al. (2009), FeS nanoparticles (molar ratio of 26.5 FeS to Hg) has the potential to reduce the concentration of mercury up to 97 % in mercury-contaminated substrates, while nanosorbent Fe_3O_4–silica shows a removal efficiency of 97.34 and 90 % for Pb(II) and Hg(II), respectively (Ambashta and Sillanpaa 2010). Nanoscale formulations of S, Se, Cu, Ni, Zn, Ag, and WS_2 were used for in situ capture of Hg vapor from broken CFLs. It is found that unstabilized nanoselenium in two forms (dry powder and impregnated cloth) gave the best result over the other sorbents (Johnson et al. 2008). Functionalized nanoporous ceramic sorbents (mercaptopropyl–trismethoxy silane) having pore sizes (2–10 nm) and very high surface areas (~1,000 m^2/g) are used for the removal of mercury from aqueous waste streams (Mattigod et al. 2006). Citrate-coated

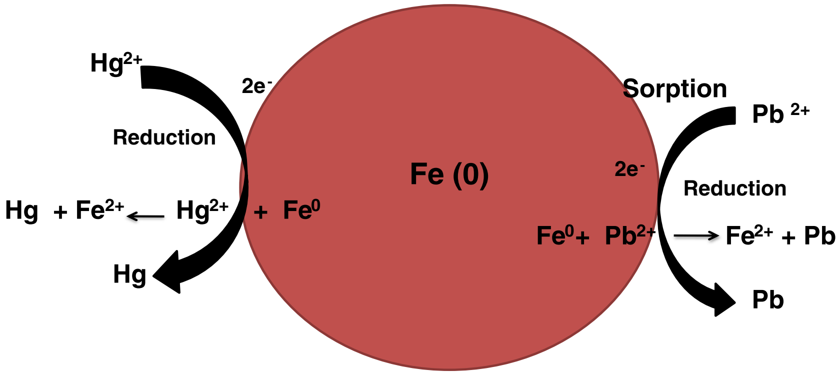


Fig. 10 Nanotechnology for the management of MCGW and LCGW

Table 9 Hybrid technique for remediation of MCGW

Name of the plant	Chemical added	Mercury concentration in plant (mg/kg)	Reference
Lepidium sativum	EDTA and urease	20 % of Hg from soil	Smolinska and Cedzynska (2007)
Willow (*Salix* sp.)	0.05 M EDTA (40 %) and citric acid (60 %)	42 % Hg from soil	Henry (2000)
Willow	1 mM KI	Leaves—5 times Branches—3 times Roots—8 times	Wang and Greger (2006)
Bush bean (*Phaseolus vulgaris*)	Sodium thiosulfate	Shoots—9.5 mg/kg Roots—113 mg/kg	Moreno et al. (2005b)
Indian mustard (*Brassica juncea*)	Sodium thiosulfate	Shoots—15.2 mg/kg Roots—69 mg/kg	Moreno et al. (2005b)

gold nanoparticles are used as scavengers for removal of mercury (II) from polluted water (Ojea-Jimenez et al. 2012). In a study by Parham et al. (2012), a method was proposed for fast and efficient removal of mercury from water samples using magnetic iron oxide nanoparticles modified with 2-mercaptobenzothiazole.

The E^0 of lead (Pb^{2+}/Pb) is −0.13 V which is more than zerovalent iron (Fe2+/Fe) −0.44 V hence it is possible to reduce lead of LCGW by using zerovalent iron nanoparticles (Fig. 10). Kaolinite-supported nanoscale zerovalent iron can be used to remove high concentration of Pb^{2+} from aqueous solution with 98 % removal efficiency (Zhang et al. 2010). Resin-supported zero-valent iron nanoparticles (Ponder et al. 2000, 2001) rapidly separate and immobilize Pb(II) from aqueous solution reducing Pb(II) to Pb(0). It was found that the maximum adsorption capacity for Pb(II) ions was 36.0 mg/g by Fe_3O_4 nanoparticles, which was much higher than that of reported low-cost adsorbents (Nassar 2010).

In addition to self-aggregation, nanoparticles could associate with suspended solids or sediment, thereby can bioaccumulate and enter the food chain or drinking water sources (Karn et al. 2009; Xu et al. 2012). Such uncertainties complicate the assessment of the risks involved in technology over environment and human health (Kotnala 2009).

Hybrid technique

Both chemical and biological remediation of heavy metals have their own limitations as biological leaching (involving microbes) is time taking and complete recovery of metal alone is not possible; on the other hand, chemical leaching have its own environmental consequences. These problems can be overcome by a compatible combination of chemical with biological techniques and these techniques are proposed to be hybrid (Pant et al. 2012). Various chemicals such as EDTA, sodium thiosulfate, thiosulfate, aqua regia, iodide and nitric acid, hydrochloric acid, sodium hydroxide, and potassium iodide have been tested for their ability to uptake and transport mercury from plants (Wang et al. 2011b; Moreno et al. 2004, 2005a; Wallschlger et al. 1998; Wang and Greger 2006). Some possible combinations of hybrid technique for mercury removal are as follows:

1. Chemical leaching (HCl and $FeCl_3$) and volatilization of mercury by bacteria (Nakamura et al. 1999).
2. Addition of 1 mM KI to mercury-contaminated soil increased the mercury concentration in Willow plant by a factor of 5, 3, and 8 times in the leaves, branches, and roots, respectively (Wang and Greger 2006).
3. Chemicals as sodium thiosulfate, ammonium thiocyanate, potassium iodide, EDTA, NTA, dimercaptosuccinic acid, mercaptopropionic acid, mercaptoethanol, thiourea, thiocyanate and hydrogen peroxide, ammonium thiosulfate, and urease for chelating mercury have been used widely to enhance the plant uptake of mercury (Meers et al. 2009; Moreno et al. 2004, 2005a, b; Wang et al. 2011b, Ohki et al. 2003). These chemicals increase the solubility of mercury and enhance the plant uptake of mercury from the soil (Table 9).

Table 10 represents various hybrid combination for Pb removal with either chemical with microbial or plant combination. Chemical and microbial combinations involving the use of EDTA (Wasay et al. 1998) with either *Acidithiobacillus ferrooxidans* (Cheikh et al. 2010) or bacterial strain DSM 9103 (Satroutdinov et al. 2000). Many fungi (*A. niger*, *P. bilaiae*, and other *Penicillium* sp.) secrets various organic acids like citric, tartaric, and oxalic acids which can act as chelating agents hence employed for the extraction of Pb (Arwidsson and Allard 2009; Wasay et al. 1998; Elliott and Shastri 1999). Oxalate along with ammonium citrate can be used for the extraction of Pb (Wasay et al. 1998); the efficiency of this process is reasonably enhanced by adding *A. niger* or *Penicillium* species (Arwidsson and Allard 2009). Hybrid

Table 10 Hybrid technique for the remediation of LCGW

S. no.	Chemical	Biological	References
1	Chemical reagent + microbe		
(a)	EDTA	*Acidithiobacillus ferrooxidans*	Cheikh et al. (2010)
(b)	EDTA	Bacterial strain DSM 9103	Satroutdinov et al. (2000)
(c)	Citrate	*Penicillium bilaiae*, *Penicillium* sp.	Wasay et al. (1998), Arwidsson and Allard (2009)
(d)	Tartrate	*Penicillium sp*., *Aspergillus niger*	Arwidsson and Allard (2009)
(e)	Oxalate + ammonium-citrate	*Aspergillus niger*, *Penicillium* sp.	Arwidsson and Allard (2009), Wasay et al. (1998)
(f)	DTPA	*Candida albicans*	Hong et al. (2000)
2	Chemical reagent + plant		
(a)	EDTA + acetic acid	Indian mustard (*Brassica juncea* L.)	Blaylock et al. (1997)
(b)	EDTA	Indian mustard (*Brassica juncea* L.)	Vassil et al. (1998), Kumar et al. (2011), Meers et al. (2009)
(c)	EDTA	Rainbow pink (*Dianthus chinensis*)	Lai and Chen (2005, 2007),
(d)	EDTA	Vetiver grass	Lai and Chen (2004)
(e)	EDTA and EDDS	Chinese cabbage	Grcman et al. (2003)
(f)	EDDS	Sunflower	Tandy et al. (2006)
(g)	EDTA	Sunflower (*Helianthus annuus* L.)	Azhar et al. (2006)

combination involving chemically assisted phytoextraction is nowadays in practice for the removal and detoxification of Pb from the contaminated sites (Ghosh and Singh 2005; Blaylock and Huang 1999). In order to enhance the availability of Pb in soil and translocation from root to shoot, chelating agents are applied in small doses such as EDTA, DTPA, NTA, CDTA, EDDS, and citric acid (Huang et al. 1997; Saifullah et al. 2009; Grcman et al. 2001, 2003; Puschenreiter et al. 2001; Shen et al. 2002; Kos and Lestan 2003; Luo et al. 2006a, b; Meers et al. 2004, 2005; Tandy et al. 2006). EDTA being the most efficient chelator for Pb is used widely to solubilize Pb in the soil (Salt et al. 1998; Marschner 1995; Vassil et al. 1998). The order of effectiveness in increasing Pb desorption from the soil was EDTA > HEDTA > DTPA > EDDHA (ethylenediamine di(*o*-hyroxyphenylacetic acid) (Huang et al. 1997). There was a twofold increase in the accumulation of Pb by applying EDTA with acetic acid in Indian mustard shoots as compared with the application of EDTA alone (Blaylock et al. 1997). Plant waste adsorbents like rice husks, spent grain, sugarcane bagasse, fruit wastes, and weeds can be modified chemically by mineral and organic acids, bases, oxidizing agents, and organic compound for the removal of Pb from wastewater (Ngah and Hanafia 2008).

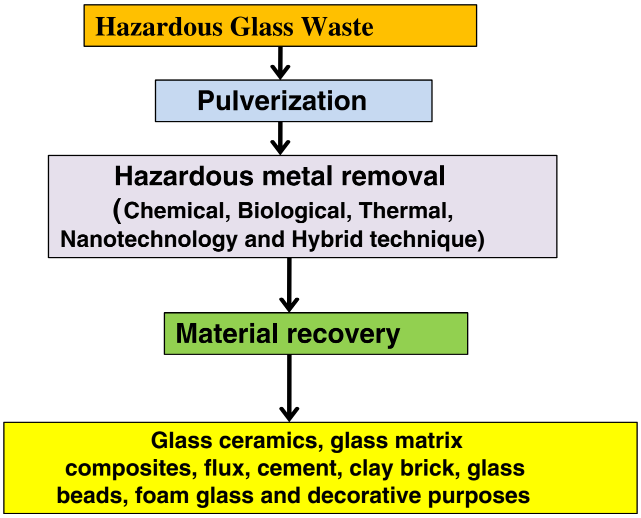


Fig. 11 Hazardous glass waste management

Conclusion

Management issues of heavy metal pollutant from HG are still unimpaired and require special attention due to its hazardous nature. This research proposes possible plans for the management of hazardous glass waste (Fig. 11) by pollutant recovery techniques followed by mechanical treatment. Pollutant recoveries are broadly chemical or biological techniques and can be modified by thermal, nano, and/or hybrid combination. Furthermore, the study has the following outcomes:

1. Mercury pollutants can be managed by dry crushing and heating technology in a fluidized bed reactor, while reduction melting process and mechanochemical sulfidization technique are proposed to recover Pb from funnel glass of CRT.
2. High elemental mercury content can remediate by stabilization/solidification and immobilization involving chemical reactions between the stabilizing agent and the contaminants to reduce Hg mobility.
3. For mercury detoxification, transgenic plants (*Arabidopsis* and tobacco) are engineered with bacterial genes merB and merA. In these modified plants, merB

catalyzes the protonolysis of the carbon–mercury bond with the generation of Hg^{2+} (100 times less toxic than methyl mercury) and subsequently MerA converts Hg(II) to Hg(0) a less toxic, volatile element.

4. Transporter proteins and chelating agents like PC, MT, and organic acids present within the plant facilitates the transfer of Pb from extracellular to the intracellular environment of the plant cell. These transporter molecules consist of extracellular binding domains (–COOH) to which Pb ion binds and form complexes.
5. In chemical remediation technique, the use of sodium hypochlorite, EDTA, KI/I, coal and coal fly ash, and rice fly ash are found to be more applicable.
6. Thermal treatment processes that are commonly used to treat volatile metals like mercury from contaminated wastes are thermal desorption, retorting/roasting, at a cost of around $834/m^3.
7. Solar furnace, constituting low temperature (28–280 °C) and a middle temperature (20–502 °C) have mercury removal capacity of 4.5–76 and 12.1–87 % respectively.
8. Nanoparticles efficiently remove heavy metals by immobilization; for example, nanoscale formulations of S, Se, Cu, Ni, Zn, Ag, and WS_2 were used for in situ capture of Hg vapor from broken CFLs, while kaolinite-supported nanoscale zero-valent iron can be used to remove high concentration of Pb^{2+} from aqueous solution with 98 % removal efficiency.
9. Hybrid combination involves various compatible combination techniques for better and safe removal of metal pollutant from glass. These techniques are found to be most promising both in terms of efficiency and environmental issues. For example, there was a twofold increase in the accumulation of Pb by applying EDTA with acetic acid in Indian mustard shoots as compared with the application of EDTA alone.
10. Plant waste adsorbents like rice husks, spent grain, sugarcane bagasse, fruit wastes, and weeds can be modified chemically by mineral and organic acids, bases, oxidizing agents, and organic compound for the removal of Pb from wastewater.

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