Phytoextraction and the economic perspective of phytomining of heavy metals

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Abstract: The world rapid growing population, expanding economics and anthropogenic activities contribute to heavy metals pollution, which are non-biodegradable, persistent and threaten the environment. The rising level of heavy metals in environment emphasizes on indigenous technologies, but conventional technologies are too expensive, laborious and result in secondary pollution. Phytoremediation/phytoextraction is a plant based technology, which is environmental friendly, economic and effective for heavy metals remediation. The global market of phytoremediation is 34–54 billion US$ and is expanding in the developed countries, providing an opportunity for this green technology. Suitability of phytoextraction depends on biomass production, accumulation rate and tolerance to target metals. Metals uptake can be enhanced by exploring effective hyperaccumulators, expanding phytomining operations and extending molecular studies on accumulation mechanism, tolerance and sensitivity of heavy metals. Hyperaccumulator plants achieve greater performance at low cost than conventional technologies for in situ metal removal. Phytomining generate revenue and provide new research area for biofortification of food and feed, biofuel and metal rich biochar production in future. This review highlights the sources of heavy metals and its effects on plants, enhancing phytoremediation process and increasing economic benefits of phytomining.

Keywords: Cadmium; Environment; Hyperaccumulator; Phytoextraction; Phytomining.

Table of Contents

1. Introduction

Anthropogenic and geogenic activities contribute to heavy metals (HMs) pollution in air, soil and water bodies. Heavy metals having higher densities (>5 gcm^{-3}), include Cd, Pb, Hg, Zn, Cr and As etc., generally refers to metals and metalloids (Li et al., 2014). Heavy metals are considered as toxic, non-biodegradable and extremely persistent elements in the soil and environment (Bharti and Kumar Banerjee, 2012; Luo et al., 2005; Zhao et al., 2010; Zhou et al., 2014). Heavy metals pollution is a worldwide concern, and the number of contaminated sites increasing with the passage of time due to burgeoning populations, disarrayed industrialization and expanding economics (Kaimi et al., 2006).

Industrialization has improved the living standard of man, meanwhile posed numerous health and environmental threats. Global industrialization and technological innovations over the past two centuries has resulted in widespread contamination of the environment. Every factory discharge effluents, mostly containing various contaminants like Cd, Pb, Hg, As, Zn, As, Cu, Ni, Co, Se, and Zn into soil and water resources like sea, rivers and canals (Arias-Estévez et al., 2008; Daud et al., 2013). These contaminants cause catastrophic effects on human, animals and environment due to soil-plant transportation of HMs (Meighan et al., 2011; Vollenweider et al., 2006; Xiong, 1997). Naturally HMs are introduced through the weathering of parent materials, wind-blown dust (erosion), forest fires and atmospheric emissions from volcanic eruptions. Sedimentary rocks (black shale) are considered as the main sources of Cd and Pb containing 0.1-11 and 1-150 $\mu g\ g^{-1}$, respectively. The natural earth crust content of Cd and Pb is ranged between 0.15-0.20 and 10-20 $\mu g\ g^{-1}$, respectively (Arain et al., 2008; Bu et al., 2016).

The conventional methods for remediation of soil heavy metals are ineffective due to high cost, require special treatment plants and release secondary pollutants into the environment. Phytoremediation is cheap and efficient method used for in situ site remediation. Phytoremediation permanently removes the bioavailable fraction of contaminants, minimal site disturbance and is well-suited with risk-based contaminated land management systems (Jiang et al., 2015). The phytoremediation market is assumed to be 34–54 billion US$ and is further expanding with the industrial race among the nations. Number of plants species, like *Sedum alfredii, Thlaspi caerulescens, Helianthus annuus, Brassica juncea* and *Salix* are known to extract Cd and Pb from soil-water system (Escarre et al., 2000; Lomonte et al., 2010; Meighan et al., 2011; Sun et al., 2009b; Zaier et al., 2010b). These hyperaccumulators have the potential to achieve greater performance at low cost than conventional technologies for metals removal (Bolan et al., 2014; Salazar and Pignata, 2013).

The remediation of heavy metals polluted sites through phytoextraction (phytomining) is cheaper and more effective as compared to chemical treatments (Ha et al., 2011; Li et al., 2014). Biofortification of food products, production of biofuel as new energy resource, acquiring reclaimed land for agriculture and commercial purpose and biochar for climate change mitigation, provides a new insight into the phytoremediation of HMs. Phytoremediation indirectly increases soil carbon content, retain nutrients and improve soil biochemical processes (Sheoran et al., 2013). This review gives an overview of the source and potential effects of heavy metals, possibility of enhancing the phytoremediation technology as well as an insight into the economic perspective of reclaiming contaminated sites.

2. Sources of heavy metals and their effects on plants

Anthropogenic sources of HMs include textile, pesticides, petrochemical, energy and power, leather, construction, steel manufacturing, food processing waste disposal, waste incineration, mining and smelting, military operations as well as coal combustion (Bhargava et al., 2012; Mahar et al., 2016; Zhao et al., 2010). A number of natural and anthropogenic activities contributed to Cd and Pb contamination in the environment are presented in Fig. 1.

Figure 1. Natural and anthropogenic sources of heavy metals

2.1. Cadmium (Cd)

Naturally soil Cd content is reported to be 0.1–0.5 mg kg^{-1}, but literature has also reported the highest content up to 150 mg kg^{-1} in sites near batteries, plastics and paint manufacturing, mining, electroplating, alloy preparation, fertilizers, fungicides/pesticide, rubber tires industries, sludge and composting facilities (Gallego et al., 2012). Cd is considered as persistent, inorganic and toxic metal for human and plant at a low concentration (Wahid et al., 2008). Among the heavy metals, Cd is highly soluble, causes soil pollution and adverse effects on plant growth and development. Cd can be taken up by plants as Cd^{+2} from soil solution and enter the food web. If plants exposed to high levels of Cd^{+2}, it can affect water and elemental transportation, absorption, oxidative phosphorylation in mitochondria, photosynthesis, reduce mitochondrial respiration, growth and reproduction of plant (Padmaja et al., 1990). Cd can reduce root growth, cause cell death and chlorosis as well as inhibit auxin homeostasis and enzyme activities (Daud et al., 2013).

2.2. Lead (Pb)

The world rapid social and economic development has increased the Pb concentration in urban and industrial areas (Dermont et al., 2008). In 1923, Pb in the form of tetraethyl lead [$(CH_3CH_2)_4Pb$] was introduced as an anti-knocking agent in fuel, which increased the Pb concentration in the atmosphere (Walraven et al., 2014). Pb is released from automobile exhaust (tetraethyl lead), mining and smelters, fertilizers, pesticides, pigments, batteries, ammunition, cable sheathing, fossil fuels, manure, sludge, electricity and heat production. Annual Pb level in air should not exceed 0.5 μgm^{-3} (WHO, 2000). Pb is readily adsorbed in soil, contributes to atmospheric deposition, released by natural weathering processes and considered as a notorious environmental pollutant (Nagajyoti et al., 2010). Pb level in ambient air ranges from 7.6×10^{5} to >10 μgm^{-3} in remote areas (Antarctica) and stationary sources (smelters), respectively (ATSDR, 2007). The Pb concentration even up to 300 mg kg^{-1} is also reported in roadside soils (Chen et al., 2010). The legislations in 1970s in Europe against the use of Pb in petrol, helped in reducing the Pb level within a safe limit (Pacyna et al., 2009). Chemical forms of Pb depend on the source. Like in atmosphere Pb exists in the form of $PbSO_4$ and $PbCO_3$, coal combustion release $PbCl_2$, PbO, PbS and insoluble mineral particles, and oil combustion mainly in the PbO form (Wadge and Hutton, 1987). Pb particle size ranges between 0.1 and 1.0 μm depending on the source of emission. Pb particles in atmosphere are deposited in the terrestrial and aquatic ecosystem by dry or wet deposition (Pan and Wang, 2014). Pb toxicity includes the rapid cessation of root, stunted plant growth and chlorosis. Pb inhibits the activity of enzymes due to its high affinity for sulphydryl groups, disturbs mineral nutrition, water balance and alters plant hormonal status (Gopal and Rizvi, 2008). Pb increases metal containing antioxidant enzyme i.e. superoxide dismutase (SOD).

Due to such adverse effects on plants, the concern over the safe remediation technologies for HMs remediation is growing. Plant based technology is considered as a potentially safe technology to deal the HMs, environment friendly, non-destructive, non-invasive and aesthetically pleasing.

3. Phytoremediation of heavy metals: An environment friendly green technology

Heavy metals pollution has become a global environmental threat, which is caused by a number of metals such as Cd, Pb, Cu and Hg etc. (Xu et al., 2012). Some plants species reported in literature, exhibit tolerance to HMs especially Cd and Pb (Chen et al., 2014; Lomonte et al., 2010; Mahar et al., 2016; Salazar and Pignata, 2013). The rise in Cd and Pb content in environment, caused by anthropogenic activities, stresses the need for a sustainable indigenous remediation technology. Different remediation techniques are practiced for HMs polluted soils as shown in Fig. 2. But most of them are expensive, laborious and cause secondary pollution as well as soil disturbance, thus possess low acceptability among the researcher communities. The conventional remediation techniques include pneumatic fracturing, solidification/stabilization, vitrification, excavation/removal of contaminated soil layer, chemical oxidation, soil washing, chemical precipitation, ion-exchange, adsorption, membrane filtration and electrochemical treatment technologies (Bhargava et al., 2012; Bharti and Kumar Banerjee, 2012; Mahar et al., 2016).

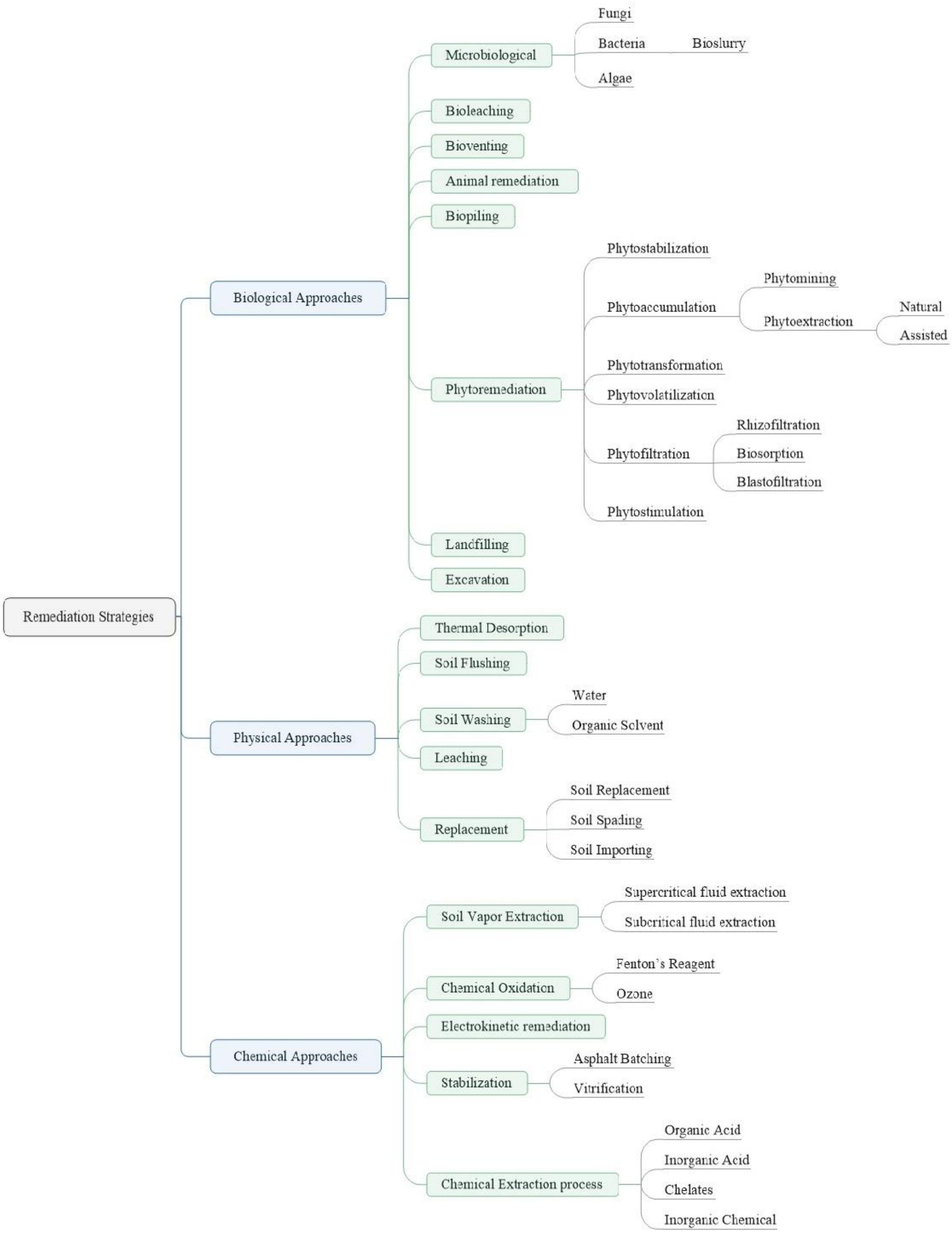

Figure 2. Different remediation strategies used for soil heavy metals treatment.

Phytoremediation involves the use of plants to extract, sequester, and detoxify environmental contaminants (heavy metals, radionuclides, pesticides and polychlorinated biphenyls) from soil. Phytoremediation was introduced as a new discipline in 1970s and developed with the successive discoveries of hyperaccumulators and advancement of analytical techniques in the twentieth century. The concept of moving from 'phytoremediation' to 'phytomining' to recover valuable metals for economic benefits is underway (Ha et al., 2011; Jiang et al., 2015). Phytoremediation costs 25-100 US$ per ton, while conventional excavation/landfill cost is 150-350 US$. Phytoremediation is attracting the attention of research scientists, remediation experts and environmental professionals in different industrial and government sectors, due to its high potential, easiness, efficiency and economic benefits than the other technologies. Phytoremediation can simultaneously detoxify hazardous waste and helps in restoration of polluted sites (Bharti and Kumar Banerjee, 2012; Dermont et al., 2008). Phytoremediation technologies are classified as phytoextraction, phytofiltration, phytostabilization, phytovolatilization, rhizodegradation and phytodesalination (Ali et al., 2013; Ha et al., 2011; Mahar et al., 2016). Different strategies used for remediation and restoration of polluted sites are given in Table 1.

Phytoremediation provides an opportunity for food biofortification with micronutrients (Fe, Zn) and ultimately provide an inorganic supplement for improving human health. Fortification of vegetables with Se gave impressive results (Banuelos, 2006). Biofortification is gaining importance, as large number of international research programs have been recently launched (Qaim et al., 2007). However, medical trials, toxicity and appropriate dosages assessment are needed before biofortified products can be distributed and consumed (Zhao and Mcgrath, 2009). Phytoremediation can generate revenue by the production of biofuels, nonconsumable agricultural products, or wood is economically viable in many countries (Lehmann, 2007). Apart from biofuel, the production of metal rich biochar can provide a new perspective in the remediation of contaminated sites and its application as a fertilizer. The application of biochar can provide plant nutrients, improve soil health, sequester carbon and mitigate climate changes. Phytoremediation provided a niche for native animals and birds in Guadiamar Green Corridor programme (Evangelou and Deram, 2014). Accumulation of heavy metals (Zn and Ni) in plants through phytoremediation provides defense against chewing insects. Phytoremediation with multiple plants specie can counter the adverse soil and environmental condition (Conesa et al., 2012).

Table 1. Summary of phytoremediation techniques

Techniques	Description	References
Phytoextraction (Phytoaccumulation)	Accumulation of pollutants in harvestable biomass i.e., shoots	(Erdei et al., 2005)
Phytofiltration	Sequestration of pollutants from contaminated waters by plants	(Tangahu et al., 2011)
Phytostabilization	Limiting the mobility and bioavailability of pollutants in soil by plant roots	(Tangahu et al., 2011)
Phytovolatilization	Conversion of pollutants to volatile form and their subsequent release to the atmosphere	(Erdei et al., 2005)
Phytodegradation	Degradation of organic xenobiotics by plant enzymes within plant tissues	(Pulford and Watson, 2003)
Rhizodegradation (Phytotransformation)	Degradation of organic xenobiotics in the rhizosphere by rhizospheric microorganisms	(Mahar et al., 2016)
Phytodesalination	Removal of excess salts from saline soils by halophytes	(Ali et al., 2013)

4. Phytoextraction (phytoaccumulation) of Cd and Pb

Phytoextraction is the uptake of contaminants from soil/water via roots and their translocation into the plant shoot, to eradicate contaminants and encourage long-term cleanup of soil or wastewater (Bhargava et al., 2012; Mahar et al., 2016). Among different strategies adopted by plants for the remediation of heavy metals from soil and water, phytoextraction is publicly appealing remediation (green) technology to be practiced at field level (Ali et al., 2013; Mahar et al., 2016). A heavy metal tolerant plant used for the phytoextraction must be capable to grow rapidly with high biomass yield per hectare, metal-hyperaccumulator and has prolific root system.

The identification and selection of appropriate hyperaccumulator plant is vital to phytoextraction process, which can accumulate exceptional concentrations of HMs in aerial parts without evident toxicity signs. Different research studies have reported more than 500 plant species (400 hyperaccumulators) including 101 families of *Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cumouniaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceae, Violaceae* and *Euphobiaceae* as hyperaccumulators (Bolan et al., 2014; Liu et al., 2009).

Hyperaccumulators can concentrate >10,000 mg kg^{-1} Zn and Ni, 1000 mg kg^{-1} Co, Cu, Cr and Pb, 100 mg kg^{-1} Cd, 10 mg kg^{-1} Hg; (2) bioconcentration factor and translocation factor > 1.0 (Ha et al., 2011; Wei et al., 2012). Metal hyperaccumulator species have attracted considerable research interest during the last four decades, because of their evident significance for cleaning contaminated soils (Rascio and Navariizzo, 2011). List of heavy metal hyperaccumulators, especially Cd and Pb is given in Table 2, cited in different scientific literature worldwide (Bech et al., 2012b; Chen et al., 2014; Deng et al., 2014; Salazar and Pignata, 2013; Zhang et al., 2014). During phytoextraction annual crops and grasses are preferred due to their short growth periods and adoptability to environmental stress like water scarcity and high temperature (Ali et al., 2013). Literature has also reported the use of field crops (maize, rice, barley, beetroot, oats, tobacco and sunflower), vegetables (green onion and tomato) and trees (willow, poplar, castor oil and acacia) for soil HMs extraction (He et al., 2009; Luo et al., 2005; Marmiroli et al., 2013).

Cd is present in most of the Zn contaminated sites. Different plants such as *Impatiens walleriana, Pteris vittata, Sedum alfredii* and *Thlaspi caerulescens* can extract 1168, 6434, 922.6 and 7400 mg kg^{-1} Cd, respectively from soil (Escarre et al., 2000; Wei et al., 2012; Wenhao et al., 2013; Xiao et al., 2008). Many plants can accumulate Pb in a very high concentration in its different parts. *Lepidium bipinnatifidum*, *Thlaspi rotundifolium* and *Zea mays* can be effectively used as a hyperaccumulators for contaminated soils to extract up to 7240, 8200 and 10600 mg kg^{-1} Pb, respectively (Bech et al., 2012a; Huang and Cunningham, 1996; Reeves and Brooks, 1983).

Table 2. List of hyperaccumulator plant species for phytoextraction of Cd and Pb

S #	**Plant species**	**Family**	**Metals**	**Metal accumulation (mg/kg)**	**References**
1	*Arabis paniculata*	*Brassicaceae*	Cd	1662	(Qiu et al., 2009)
2	*Arabis paniculata*	*Brassicaceae*	Pb	2300	(Tang et al., 2009)
3	*Ceratopteris pteridoides*	*Pteridaceae*	Cd	105	(Deng et al., 2014)
4	*Elodea canadensis*	*Hydrocharitaceae*	Cd	300	(Nyquist and Greger, 2009)
5	*Impatiens walleriana*	*Balsaminaceae*	Cd	1168	(Wei et al., 2012)
6	*Ipomoea aquatica*	*Convolvulaceae*	Cd	138	(Wang et al., 2008)
7	*Lepidium sativum*	*Brassicaceae*	Cd	122.4	(Epelde et al., 2009)
8	*Lonicera japonica*	*Caprifoliaceae*	Cd	470.25	(Liu et al., 2009)
9	*Nymphaea aurora*	*Nymphaeaceae*	Cd	140	(Schor-Fumbarov et al., 2003)
10	*Panicum virgatum*	*Poaceae*	Cd	280	(Chen et al., 2012)
11	*Phytolacca americana*	*Phytolaccaceae*	Cd	637, 714	(Liu et al., 2010; Peng et al., 2008)
12	*Populus nigra*	*Salicaceae*	Cd	96.8	(Kirkham, 2006; Marmiroli et al., 2013)
13	*Pteris vittata*	*Pteridaceae*	Cd	6434	(Xiao et al., 2008)

14	*Ricinus communis*	*Euphorbiaceae*	Cd	288	(Zhang et al., 2014)
15	*Salix viminalis*	*Salicaceae*	Cd	200	(Vollenweider et al., 2006)
16	*Sedum alfredii*	*Crassulaceae*	Cd	161.5	(Sun et al., 2009b)
17	*Sedum alfredii*	*Crassulaceae*	Cd	922.6	(Wenhao et al., 2013)
18	*Sedum alfredii Hance*	*Crassulaceae*	Cd	747, 9000	(Liang et al., 2014; Yang and Stoffella, 2004)
19	*Solanum nigrum L.*	*Solanaceae*	Cd	117.2	(Chen et al., 2014)
20	*Tagetes patula*	*Asteraceae*	Cd	324	(Wei et al., 2012)
21	*Thlaspi caerulescens*	*Brassicaceae*	*Cd*	7400, 3000	(Escarre et al., 2000; Reeves et al., 2001)
22	*Wolffia globosa*	*Araceae*	Cd	500	(Xie et al., 2013)
23	*Poa pratensis*	*Poaceae*	Cd,Pb	174, 209	(He et al., 2009)
24	*Thlaspi caerulescens*	*Brassicaceae*	Cd,	380	(Dechamps et al., 2005)
25	*Thlaspi caerulescens*	*Brassicaceae*	Cd,	2120	(Perronnet et al., 2003)
26	*Helianthus annuus*	*Helianthoideae*	Cd	580	(Meighan et al., 2011)
27	*Eleocharis acicularis*	*Cyperaceae*	Cd, Pb	195, 1030	(Ha et al., 2011)
28	*Noea mucronata*	*Amaranthaceae*	Pb	1485	(Chehregani et al., 2009)
29	*Sedum alfredii*	*Crassulaceae*	Cd, Pb	617, 1624	(Zhang et al., 2012)

30	*Bidens pilosa*	*Asteraceae*	Cd, *Pb*	400.7, 100.6	(Salazar and Pignata, 2013; Sun et al., 2009a)
31	*Baccharis latifolia*	*Asteraceae*	Pb	2120-3060	(Bech et al., 2012a)
32	*Onchus oleraceus*	*Asteraceae*	Pb	2180-2900	(Bech et al., 2012a)
33	*Bidens maximowicziana*	*Asteraceae*	Pb	2164.7	(Wang et al., 2007)
34	*Bidens triplinervia*	*Asteraceae*	Pb	5187	(Bech et al., 2012b)
35	*Brassica juncea*	*Brassicaceae*	Pb	2200	(Zaier et al., 2010b)
36	*Buckwheat*	*Polygonaceae*	Pb	2500	(Chen et al., 2004)
37	*Cynara cardunculus*	*Asteraceae*	Pb	1332	(Epelde et al., 2008)
38	*Helianthus annuus*	*Helianthoideae*	Pb	1800	(Chen et al., 2004)
39	*Hemidesmus indicus*	*Apocynaceae*	Pb	1300	(Sekhar et al., 2005)
40	*Lepidium bipinnatifidum*	*Brassicaceae*	Pb	6300-7240	(Bech et al., 2012a)
41	*Indian mustard*	*Brassicaceae*	Pb	2900	(Chen et al., 2004)
42	*Najas indica*	*Brassicaceae*	Pb	3554	(Singh et al., 2010)
43	*Pelargonium*	*Geraniaceae*	Pb	3000	(Arshad et al., 2008)
44	*Piptatherum miliaceum*	*Poaceae*	Pb	8179.8	(García et al., 2004)
45	*Pisum sativum*	*Fabaceae*	Pb	1110	(Chen et al., 2004)

46	*Plantago orbignyana*	*Plantaginaceae*	Pb	6070-8240	(Bech et al., 2012a)
47	*Sedum alfredii*	*Crassulaceae*	Pb	2506	(Gupta et al., 2010)
48	*Senecio sp .*	*Asteraceae*	Pb	4253	(Bech et al., 2012a)
49	*Sesuvium portulacastrum*	*Aizoaceae*	Pb	3400	(Zaier et al., 2010a; Zaier et al., 2010b)
50	*Sonchu s oleraceus*	*Asteraceae*	Pb	1113	(Xiong, 1997)
51	*Tagetes minuta L.*	*Asteraceae*	Pb	380.5	(Salazar and Pignata, 2014, 2013)
52	*Thlaspi rotundifolium*	*Brassicaceae*	Pb, Cd	8200, 108	(Reeves and Brooks, 1983; Wenzel and Jockwer, 1999)
53	*Zea mays*	*Poaceae*	Pb	10600	(Huang and Cunningham, 1996)
54	*Phaseolus vulgaris*	*Fabaceae*	Pb, Cd	487, 10.1	(Luo et al., 2005)
55	*Raphanus sativus*	*Brassicaceae*	Pb, Cd	189.52, 326.75	(Chen et al., 2003)
56	*Rorppa globosa*	*Brassicaceae*	Cd	150.1	(Wei and Zhou, 2006)

5. Induced and natural phytoextraction of Cd and Pb

Naturally plants can extract lower concentration of eavy metals from the soil solution and this capacity can be improved by introduction of chelates and complexing agents. Phytoextraction can be induced (chelate assisted) or natural (continuous). Induced phytoextraction is driven by chelates, while, natural phytoextraction is based on the hyperaccumulators with no soil amendments (Hseu et al., 2013; Liang et al., 2014; Saifullah et al., 2010; Schor-Fumbarov et al., 2003).

Chelant-enhanced phytoextraction is cost-effective substitute to conventional techniques for soil HMs remediation. Besides mobilizing metals in soil, chelates also facilitate metal translocation from root to shoot. Chelates help in HMs desorption from soil particles and form metal-chelant complexes in soil, drawn upward by passive apoplastic pathway. The use of chelates is reported in various phytoextraction studies (Epelde et al., 2008; Evangelou et al., 2006; Liang et al., 2014; Zhang et al., 2014), where it enhanced the capability of hyperaccumulator plants to extract higher quantity of HMs (Cd, Pb) from the soil-water system (Freitas et al., 2013; Hadi et al., 2010; Saifullah et al., 2010). The Pb uptake is not improved to the required level by the chelates application. The main reason is supposed to be the root injury caused by chelates. While, the other metals uptake is improved by chelates application in field trials. However, chelates can cause secondary pollution. The excess use of EDTA increase the risk of leaching metallic ions from the soil to groundwater causing severe health hazards and ill effects on the plant biomass and growth (Evangelou et al., 2008).

Natural chelating agents like EDDS and nitrilotriacetic acid (NTA) can be an alternate for EDTA. But it also has leaching and toxicity effects on plants. Thus, proper care should be taken when practicing induced phytoextraction (Evangelou et al., 2008; Song et al., 2012). At phytotoxic level of metals in the soil, lime and organic matter can be a best choice for delaying solubility (Pilonsmits, 2005). The use of citric acid as a chelating agent could be promising, because it has a natural origin and is easily biodegraded in soil. Furthermore, citric acid is nontoxic to plants, therefore plant growth is not restricted (Smolińska and K, 2007). Chelates can be particularly useful in mobilizing heavy metals at high soil pH as the stability of metal-organic complex increases with increasing pH. The common chelates used for enhancing the HMs (Cd, Pb) phytoextraction are presented in Table 3.

Table 3: List of chelates used for inducing Cd and Pb uptake by hyperaccumulators

Chelates or complexing agents	Metals assisted	References
EDDS and NTA	Cd	(Hseu et al., 2013)
Humic acid, EDTA	Cd	(Evangelou et al., 2004; Schor-Fumbarov et al., 2003)
Elemental sulfur, EDTA	Cd, Pb	(Liang et al., 2014; Saifullah et al., 2010)
Citric acid	Cd, Pb	(Freitas et al., 2013; Gao et al., 2012)
EDTA	Pb, Cd	(Gabos et al., 2009; Wang et al., 2007; Wei et al., 2012; Zhang et al., 2014)
EDDS, MGDA	Pb	(Cao et al., 2007)
EDTA, EDDS	Pb, Cd	(Meers et al., 2007)
EDTA, PDTA	Pb	(Cho et al., 2009)
EDTA, EDDS	Pb, Cd	(Luo et al., 2005)
EDTA and EDDS	Pb	(Chen et al., 2004; Epelde et al., 2008)
Na_2-EDTA	Pb	(Evangelou et al., 2006)
HEDTA	Pb	(Huang and Cunningham, 1996)
Citric acid (CA)	Pb, Cd	(Chen et al., 2003)

The suitability of plants for the phytoextraction of heavy metals depends on the following characteristics (Ali et al., 2013; Bhargava et al., 2012; Mahar et al., 2016).

Massive growth potential and high biomass production.

(i) Extensive root system and root developing capacity in adverse condition.

(ii) Ability to grow outside their area of collection.

(iii) Higher accumulation rate of target heavy metals from soil and translocation of the accumulated heavy metals from roots to shoots for successful phytomining.

(iv) Tolerance to the toxic effects of the target heavy metals.

(v) Good adaptation to prevailing environmental and climatic conditions (drought, temperature, humidity, salinity, nutrient deficiency and water logging).

(vi) Easy cultivation, harvest and resistance to pathogens and pests attack.

(vii) Repulsion to herbivores to avoid food chain contamination.

Phytoextraction is an income-generating, solar driven technology, removing precious metals from the soil as bio-ore, generate energy through biomass burning i.e., phytomining (Brooks and Robinson, 1998; Ha et al., 2011; Li et al., 2003). Phytoremediation is the stabilization or recovery of metal contaminants for secure disposal, while phytomining refers to the recovery of precious metals (Au, Pt, Ni and Tl) via growing hyperaccumulators for monetary return (Mcgrath and Zhao, 2003).

6. Phytomining of heavy metals

It is an environment friendly technology of growing metal hyperaccumulator plants, harvesting the biomass and burning it to produce a bio-ore as shown in Figure 3 (Ha et al., 2011). Phytomining offers the possibility of exploiting ores/mineralized soils that are not economic to explore by conventional techniques. The metal content of bio-ore is greater than conventional ore and requires less storage space due to low density. Moreover, phytomining is an environmentally responsible approach to site remediation. A well-planned phytoremediation/phytomining operation will result in commercially viable metal-enriched bio-ore. The mined soil can be used for agriculture (forestry and horticulture) and commercial use (Sheoran et al., 2009). Research efforts are underway to recognize the economic potential of this green technology. Practicing phytomining will hamper the distribution of HMs by surface runoff and wind, reduce leaching into aquifers, provide vegetation to control water and wind erosion of soil. Phytomining is considered an aesthetic, safe and nondestructive technology, with high public and commercial acceptance (Sheoran et al., 2009).

The pioneering field trial for phytomining was reported by the US Bureau of the Mines, Reno, Nevada on a naturally occurring strain of *Streptanthus polygaloides* which is a specie known to hyperaccumulate nickel (Chaney et al., 1998). Several plant species are renowned as suitable for phytoremediation/phytomining of Ni, Co, Tl, Pb, Cu, Zn, As and Au (Anderson et al., 2005; Boominathan et al., 2004). Phytomining not only provide precious metals, but also increases soil biological activity, nutrients and carbon content (Brooks and Robinson, 1998). Phytomining is less intrusive, requires less energy than traditional mining technology. Phytomining has minimal environmental disturbances and effects due to stabilizing action of the hyperaccumulator plants, when compared with the erosion caused by opencast mining operation (Robinson and Mcgrath, 2003). Vegetation cover can stabilize and accelerate ecological succession (Sheoran et al., 2009).

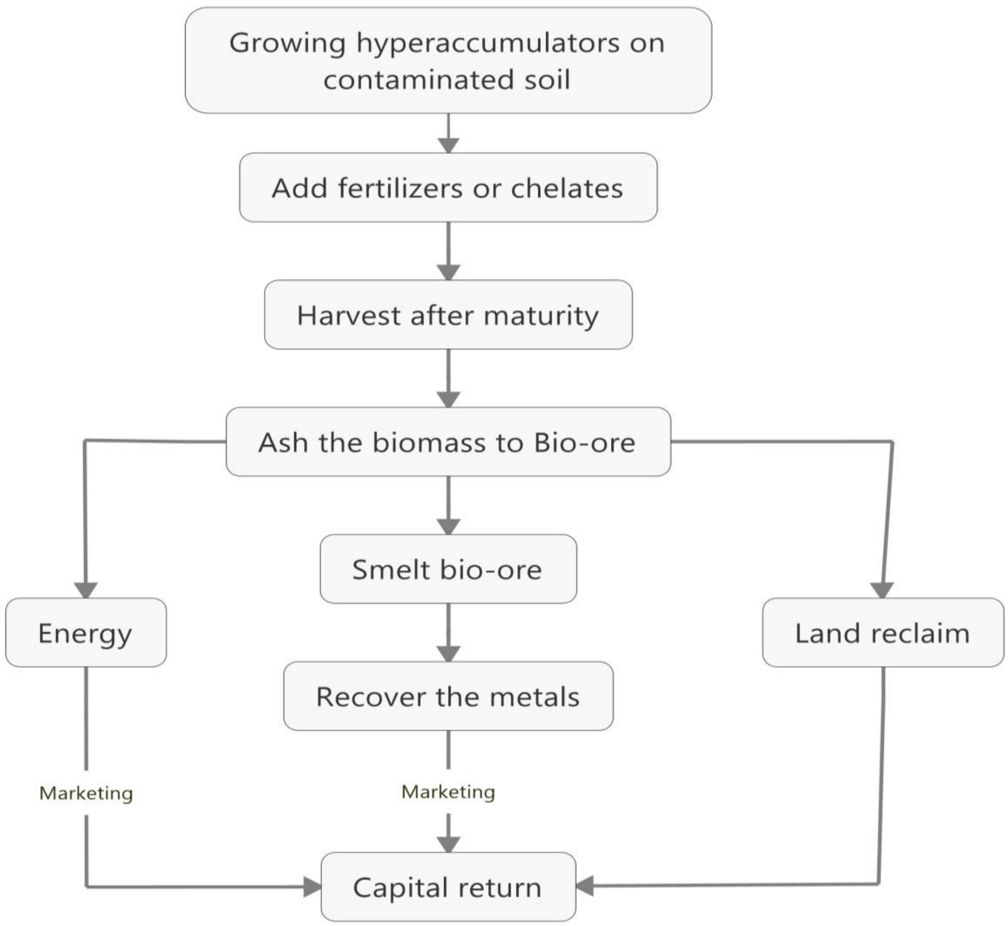

Figure 3. An illustrative model of economical phytomining of heavy metals.

Phytomining faces similar limitations as phytoextraction process, like soil pH, climatic conditions, root depth, solubility and availability of HMs and nutrients affecting plant growth (Li et al., 2003). Phytomining can assist in generating revenue along with rehabilitation and sustainable closure of mining sites (Wilson-Corral et al., 2011).

7. An insight into economics of heavy metals phytomining

Some reclaimed metals (Tl, Au, Co, Ni, Cu, U, Cd, Zn, Pb, Mn, and Se) may provide additional revenue by phytomining (Thangavel and Subbhuraam, 2004). The remediation market around the world is estimated to be nearly 34–54 billion US$ (Evangelou and Deram, 2014). Several companies and scientific research groups are pursuing phytomining strategies. *Berkheya coddii, Daucus carota* and *Brassica juncea* are reported to accumulate as much as 20 mg kg^{-1} of gold after ammonium thiocyanate supplementation (Prasad, 2003). Some companies are gaining profit not just by recovering metals from the biomass, but also using the biomass for energy generation and the ash as a source of carbon and potash as well as gaining benefits from the sale of carbon dioxide credits (Rosenfeld and Henry, 2001; Sheoran et al., 2009). Research showed the extraction of highly pure Ni from Ni-contaminated *Alyssum* biomass, which can be used as substitute for Ni fertilizer. A number of phytomining companies have emerged in US, Canada, Western and Eastern Europe, Japan, Australia, Latin America and an emerging market also exists in Asia (China).

The economics of phytomining is influenced by a number of factors, i.e., the metal content in soil and plant, annual biomass production and whether the energy of combustion of the biomass can be recovered and sold. The biomass production plays an important role in adaptation of hyperaccumulator for phytomining operation in future agrofarming. The most important factor, however, is worldwide price of metal being phytomined (Brooks and Robinson, 1998; Harris et al., 2009). Metal value ranges from \$1.793 to \$39368.59 kg^{-1} for Pb and gold, respectively (March, 2016 shown in Table 4). The best candidate metals for phytomining are Au, Tl, Co, and Ni due to their high market prices and metal concentration in biomass of hyperaccumulators. Though, the price of uranium and gold are comparatively high among the candidate metals, but its reported metal concentration (100, 10 mg kg^{-1}) in biomass (10000, 20000 kg ha^{-1}) is low, which makes *Atriplex confertifolia*, *Berkheya coddii* it uneconomical for phytomining (Mahar et al., 2016; Sheoran et al., 2009). The high market value can compensate to some extent the low biomass, but low biomass can reduce the yield of the metal in the bio-ore and hence reduce the profit. The price of Mn was low (\$1.91 kg^{-1}) but plant concentration (1650 $mgkg^{-1}$) was high in *Macadamia neurophylla*, making it more practical than *Haumaniastrum katangense and Atriplex confertifolia* used for Cu and Uranium, respectively (Jaffré, 1980). Metals prices are subjected to global economics condition and current low/high value of a metal cannot ensure its consideration for permanent phytomining. The produced biomass could be combusted to ash, stored until the world price hikes (Brooks and Robinson, 1998). Reviewing the published scientific literature, the plant species reported for phytoextraction of precious metals (Tl, Au, Co, Ni, Cu, U, Cd, Zn, Pb, Mn, and Se) may be used for phytomining purpose after field trials. The revenue (US$) to the grower is presented in Table 4 at the harvest time and at current, based on the price of the metals (March, 2016).

Table 4. Economic benefits of phytomining of precious metals

S #	Hyperaccumulators	Metals	Biomass (kg/ha)	Metal concentration (mg/kg)	(kg/ha)	Price $/kg March, 2016	Profit $/ha	References
1	Iberis intermedia	Tl	8000	4055	32.44	7.03	228.05	(Brooks, 1977)
2	*Iberis intermedia*	Tl	10000	4000	40	7.03	281.2	(Leblanc et al., 1999)
3	*Biscutella*	Tl	4000	14000	56	7.03	393.68	(Leblanc et al., 1999)
4	*Iberis intermedia*	Tl	8000	3070	24.56	7.03	172.6568	(Leblanc et al., 1999)
5	*Berkheya coddii*	Au	20000	10	0.2	39368.59	7873.72	(Msuya et al., 2000)
6	*Daucus carota*	Au	-----	3.8	0.779	39368.59	30668.13	(Msuya et al., 2000)
7	*Daucus carota* (induced)	Au	-----	3.8	1.45	39368.59	57084.46	(Msuya et al., 2000)
8	*Haumaniastrum robertii*	Co	4000	10200	40.8	23.205	946.76	(Brooks, 1977)
9	*Alyssum murale*	Ni	20000	22000	440	8.62	3792.80	(Li et al., 2003)
10	*Alyssum corsicum*	Ni	90000	800	72	8.62	620.64	(Li et al., 2003)
11	*Streptanthus polygaloides*	Ni	10000	10000	100	8.62	862.00	(Chaney et al., 1998)

12	*Alyssum bertolonii*	Ni	9000	8000	72	8.62	620.64	(Robinson et al., 1997)
13	*Berkheya coddii*	Ni	22000	5500	121	8.62	1043.02	(Robinson et al., 1997)
14	*Alyssum serpyllifolium*	Ni	9370	6515	61.05	8.62	526.21	(Morais et al., 2015)
15	*Alyssum serpyllifolium*	Ni	8890	7037	62.55	8.62	539.26	(Morais et al., 2015)
16	*Haumaniastrum katangense*	Cu	5000	8356	41.78	5.06	211.41	(Brooks, 1977)
17	*Atriplex confertifolia*	U	10000	100	1	63.382	63.38	(Cannon, 1964)
18	*Thlaspi caerulescens*	Cd	4000	3000	12	2.06	247.2	(Reeves et al., 1996)
19	*Thlaspi rotundifolium*	Pb	4000	8200	32.8	1.793	58.81	(Reeves and Brooks, 1983)
20	*Macadamia neurophylla*	Mn	30000	55000	1650	1.91	3151.50	(Jaffré, 1980)
21	*Astragalus pattersoni*	Se	5000	6000	30	14.68	14.68	(Cannon, 1964)

8. Factors affecting phytoextract on (phytomining)

The efficiency of hyperaccumulator plants used in phytoextraction of HMs depends on the favorable soil and environmental factors; like salinity, pH, nutrients deficiency, HMs toxicity, speciation and bioavailability, flooding, temperature, humidity, water logging, desiccation and resistant to drought conditions (Ali et al., 2013).

The increase in clay content (clay type specially and surface area) has a negative impact on the mobility and availability of metals in soil due to fixation in clay matrix and the uptake is also pH dependent (Saifullah et al., 2010). The exchangeable and soil solution pool of metals is considered to be readily available for plant uptake (Meers et al., 2007). pH and organic matter are two of the most important soil factors that control Cd availability (Kirkham, 2006). Bioavailability of the heavy metals increases at low soil pH, since metal salts are soluble in acidic media. In acidic soils, metal desorption from soil binding sites into solution is stimulated due to H^+ competition for binding sites. Soil pH affects not only metal bioavailability, but also every process of metal uptake into roots. This effect appears to be metal specific. For example, in *Thlaspi caerulescens*, Zn uptake in roots showed small pH dependence, whereas uptake of Mn and Cd was more dependent. The CEC is a function of the amount and types of organic matter and clay minerals in the soil. The uptake of Cd by wheat was highest in plants grown in soils with a low CEC and vice versa. Apparently, in the soil with a high CEC, more Cd was adsorbed to the exchange complexes, and hence, less Cd was available for uptake by the wheat plants. In general, sorption to soil particles reduces the activity of metals in the system. Thus, the higher the cation exchange capacity (CEC) of the soil, the greater the sorption and immobilization of the metals.

9. Limitations of phytoextraction (Phytomining)

Although the remediation of heavy metals is effective by hyperaccumulators, but the process is limited by biogeochemical factors viz. rhizobiological activity, exudates release, prevailing temperature, soil moisture and pH, competing ions affecting plant growth and solubility and availability of the metals in the soil-water system (Ali et al., 2013; Bhargava et al., 2012; Mahar et al., 2016).

The major limitations of most metal phytoextraction processes are:

- Bioavailability of only target metal(s).
- Plants accumulate metals within above ground biomass, which is low.
- Polluted site must be large enough to carry out phytomining.
- Extended time for remediation process.
- Limited to low and medium metal contaminant concentrations.
- Climate dependent/variable; seasonal effectiveness.
- Risk of metals transfer by food chain (to animals or air).
- Introduction of non-native species may affect biodiversity (competition/allelopathy).
- Tightly bound fraction of metals in soil clay requires higher chelate application rates, leading to ground water pollution.
- The contaminants must be in the root zone (rhizosphere) to be drawn up by plants.
- Most of the hyperaccumulators are not suitable for field applications due to low biomass and slow growth.

10. Conclusion and Recommendations

The growing world population requires more food, infrastructure, transportation and industrial growth to meet their daily requirements. These activities will intensify the use of agro-chemicals in the agriculture sector, exploration of mining sites for energy and infrastructure, manufacturing of automobile for public transportation and production of households in the coming years. As a result, these activities will contribute to higher metal release into soil, air and water, leading to environmental pollution. All the known conventional remediation technologies for HMs have secondary pollution. An environment friendly and green technology known as "phytoremediation" for in situ remediation of polluted sites is easy, economical and compatible alternate to conventional technologies. Effective phytoremediation (phytoextraction) depends on phytoavailable portion of metals in soil solution, metal uptake in plant tissue and plant biomass. The metal ions are present in soil solution but the plant option for specific ion reduces the uptake capacity of plants. Metals like Pb can form carbonates, hydroxides and phosphates in soil and thus reduces the phytoextraction efficiency, making the natural process difficult to continue. Phytoextraction (phytomining) depends on environmental and soil properties with some limitations, like low biomass and slow growth of hyperaccumulators. But still, progressive as compared to conventional methods, as it is solar driven, low secondary pollution, hyperaccumulators used as fuel and maintain the greenery of environment. Phytomining not only generates revenue for the grower but also provides mineral supplementation and biofuel as well as increases soil health and mitigate climate changes.

Based on the previous studies the following recommendations can be made.

(i) Further exploration of hyperaccumulator plants for enhanced phytoextraction of heavy metals is needed.

(ii) The establishment of hyperaccumulators seed bank must be encouraged, for the expansion of phytoextraction/phytomining studies in different ecological zones. The findings at different ecological zones will help in further understanding of phytoextraction/phytomining for the remediation of pollutants.

(iii) Extensive and precise research is required in the application of chelates assisted phytoextraction in order to reduce secondary pollution of soil and air.

(iv) Experimentation on cost to benefit ratios (economics) and time consumption is required to reach a final conclusion.

(v) The use of constructed wetland for improving water quality by practicing phytoextraction is required.

(vi) Molecular studies on the mechanisms of hyperaccumulation, translocation, distribution, tolerance and sensitivity of heavy metals in different plants need further attention.

(vii) Molecular techniques for the gene identification and introduction into the desired plants for effective phytoextraction.

(viii) The extraction of metals in the target sites during the phytomining need special considerations to trafficking and toxicity of heavy metals through food chain from water, soil, plant and animal to human.

(ix) Need further studies on the rhizosphere for the enhanced phytoextraction.

(x) Biofortification of vegetables with micronutrients requires authentic medical trials, precise toxicity assessment and appropriate dosages prescription.

(xi) The conversion of biomass produced by hyperaccumulator plants into biofuel and biochar need investment and technical experience to meet the economic requirements.

(xii) Measurements for protection and conservation of native plant diversity before introduction of alien plants for phytomining.

11. Future Perspective

Phytoremediation is a slow and time consuming process. Since hyperaccumulators have low biomass and can extract minute quantity of HMs from the soil, which doesn't meet the remediation requirements on large scale within a short time span. It can be improved by exploration of fast growing plants, which yield high biomass and extract high concentration of HMs. Plant species with short growth period, capable of rotation and resistant to environmental stress should be identified for effective phytoextraction. Assisted phytoextraction can be possible cost effective commercial technology for phytomining of HMs in future, which can enhance metal uptake and reduces the environmental risks and time for remediation process. In order to solve the problem of low solubility, soil pH and fixation in clay, new research dimensions with respect to rhizosphere should be explored. Exploration of plant growth regulators (cytokinins, gibberellic acid, indolebutyric acid, naphthylacetic acid and indole-3-acetic acid) and rhizobacteria (P solubilizing) provide a new research area with respect to the mechanism of HMs uptake and stabilization for a safe and green environment. The role of biotechnology and genetic engineering for improving the phytomining can't be ignored. Many genes are involved in metal accumulation, translocation and sequestration. Gene transfer into candidate plant is a possible strategy for genetic engineering of plants. Selection of individuals with genetic coding for high metal content, high biomass production and superior tolerance to soil heavy metal content will augment metal crops. The isolation of genetic materials may allow the genetic manipulation of high biomass plants such as *Zea mays*, to produce a plant that will extract large quantities of metals. Genetic engineering is currently being used to improve metal hyperaccumulation in plants by changing oxidation state of metals, enhancing metal transporters and chelators, encoding metal sequestration proteins i.e., MTs and PCs (metallothioneins and phytochelatins), transport proteins such as ZIP family proteins (zinc–iron permease) and ZAT (Zn transporter). Environment friendly and biodegradable chelates should be developed. If phytomining proceed beyond the theoretical and pilot stage. Plants can be harvested and feedstock can be used for incineration. This could supply steam for electricity production. Biofortification of food and feed will meet the nutritional requirements of human and animals. Production of biofuel and metal rich biochar provide a new research area for soil nutritionist and economist in future. Before phytoremediation is fully commercialized, further research is needed to assure that tissues of plants used for phytoremediation do not have adverse environmental effects if eaten by wildlife or human. Further, explorations of efficient hyperaccumulator that produce more biomass stress the need for commercial smelting to extract the metals from plant biomass.

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