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Post-Harvest Management of Phytoremediation Technology

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Abstract

Post-harvest management of contaminated phytoremediation byproducts for combating the problem of heavy metal contamination is of utmost significance in recent years. Soil fertility is greatly affected by expensive conventional remedial technologies and subsequently causes negative impacts on the ecosystem. Phytoremediation proved to be a cost effective, environment friendly and aesthetically pleasing approach which is most suitable for developing countries. In spite of these benefits phytoremediation technique contributes huge quantities of contaminated materials to the environment and creates further pollution problems. Post-harvest management of these byproducts through advanced techniques like composting and compaction, combustion and gasification, phytomining and pyrolysis is essential. A lot of contaminated biomass is produced during phytoremediation processes, which uses high biomass weeds. So it needs proper disposal and management to restrict the passage of contaminants into the food chain. The high biomass plant selected for phytoremediation should be non-edible, disease resistant and tolerant plants, which can provide renewable energy. Post-harvest management of phytoremediation technique is an alternative for biomass to biofuel conversion. This enhances the practicability of phytoremediation technology. Postharvest strategies are essential with preharvest approaches for developing a sustainable phytoremediation technology.

Keywords: Bioremediation; Heavy metals; Phytoremediation; Phytomining; Pyrolysis; Rhizoremediation

Introduction

Toxic discharges from industries lead to several detrimental effects on human health and environment [1]. India is one of the developing countries having huge natural resources with emerging industrial avenues for satisfying the growing demands of ever-increasing population. Along with 48.83% arable land, India has significant sources of coal (fourth-largest reserves in the world), bauxite, titanium ore, chromite, natural gas, diamonds, petroleum, and limestone. According to the 2008 Ministry of Mines estimates: 'India has stepped up its production to reach the second rank among the chromite producers of the world. Besides, India ranks 3rd in production of coal and lignite, 2nd in barites, 4th in iron ore, 5th in bauxite and crude steel, 7th in manganese ore and 8th in aluminum. India accounts for 12% of the world's known and economically available thorium. It is the world's largest producer and exporter of mica, accounting for almost 60 percent of the net mica production in the world as per the data obtained from Annual Report (2007-2008), Ministry of Mines, Government of India, National Informatics Centre [1]. Effect of mining activities on environment is provided in the box given below as obtained from Sustainable development Networking Programme (SNDP-New Delhi) [1] (Box 1).

Mehta reported the mining effects on the environment in India as quoted in following box [1] (Box 2).

Huge quantities of pollutants from industrial and mining activities degrade our environment to a great extent [2]. Emission of heavy metals though anthropogenic activities like mining, fossil fuel combustion, application of phosphate fertilizers, military activities and natural processes such as volcanic eruptions, continental dust etc. lead to accumulation of these chemicals in environment [3,4]. The advantage of phytoremediation technique depends on soil metal uptake abilities of root systems of different plants together with its translocation, bioaccumulation and pollutant storage/degradation abilities of the entire plant body. Disposal of contaminated plant material has been one of the hurdles for commercial implementation of phytoremediation. Accumulation of huge quantities of hazardous and contaminated biomass is the consequent step after phytoextraction mechanism. This hazardous biomass should be stored or disposed appropriately so that it does not pose any risk to the environment. These contaminated biomass have main constituents of lignin, hemicellulose, cellulose, mineral matter and ash which possess high moisture and volatile matter constituents, low bulk density with calorific value [3] varies from species to species.

Post-Harvest Management Techniques

The contaminated biomass by-products of phytoremediation technique need volume reduction through various techniques as follows in order to handle it safely.

Composting and compaction

Composting and compaction is one of the post-harvest biomass treatments as reported by some authors [5-8]. Leaching of composted material formed soluble organic compounds that enhanced metal solubility. Hetland et al. [9] showed that composting can significantly reduce the volume of harvested biomass from phytoremediation technology; however metal contaminated plant biomass would still require treatment prior to disposal. Total dry weight loss of contaminated plant biomass by compaction is advantageous, as it will lower cost of transportation to a hazardous waste disposal facility.

Compaction of harvested plant material was proposed by Blaylock and Huang [10] found essential for processing metal rich phytoextraction residue. Advantages of compaction are similar as composting, the leachate will need to be collected and treated appropriately; in comparison to composting there is little information on compaction. One of the conventional and promising routes to utilize

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1. Air: Surface mines may produce dust from blasting operations and haul roads. Many coal mines release methane, a greenhouse gas. Smelter operations with insufficient safeguards in place have the potential to pollute the air with heavy metals, sulphur dioxide and other pollutants.

2. Water: The mining sector uses large quantities of water, through some mines do reuse much of their water intake. Mining throws sulphide-containing minerals into the air, where they oxidize and react with water to form sulphuric acid. This together with various trace elements impacts groundwater, both from the surface and underground mines.

3. Land: The movement of rocks due to mining activities and overburden (material overlying a mineral deposit that must be removed before mining) in the case of surface mines impacts land severely. These impacts may be temporary where the mining company returns the rock and overburden to the pit from which they were extracted. Many copper mines, for example, extract ore that contains less than 1% copper.

4. Health and Safety: Mining operations range from extremely hazardous to being as safe or as dangerous as any other large scale industrial activity. Underground mining is generally more hazardous than surface mining because of poorer ventilation and visibility and the danger of rock falls. The greatest health risks arise from dust, which may lead to respiratory problems and from exposure to radiation (where applicable).

Source: Sustainable Development Networking Programme (SDNP, India).

Box 1: How Mining Affects Environment.

Effects of Mining on the Environment in India

The mining sector in India is plagued by several environmental and health and safety related problems. Several accidents have taken place in underground and surface mines like coal and stone mines in the last few years, which have killed scores of mineworkers. An example of environmental damage by a mining company in India is the Kudremukh Iron Ore Company Limited (KIOCL) in the Western Ghats Mountain Ranges in Karnataka State in southern India. The operations of KIOCL have caused large-scale destruction of the hills, pollution of groundwater in the neighborhood and have severely affected the Kudermukh National Park.

Since 1973, seven mining disasters have taken place. The latest was in February 2001, when 30 miners lost their lives in an accident in the Bagdigi mines in the eastern Indian State of Bihar. Every year many mine workers lose their lives in mining accidents in India. Wide spread illegal mining and lack of effective government supervision in government and private mines accentuates the problem. While the safety of mineworkers is the most serious problem facing the Indian mining industry, the Directorate General of Mines Safety (DGMS), who is responsible for the supervision and enforcement of mining rules, is unable to do its job effectively because of a shortage of supervisory staff. The main reason for this shortage is the inability of the DGMS to fill its vacancies due to lack of funds. The miners also face health hazards arising out of on-site pollution due to dust, gases, noise and polluted water. Health related issues are increasingly coming into focus.

One of the major environmental challenges facing the mining industry is due to the mine sites which are no longer in use. In the Jharia and Raniganj coal fields in Bihar there are more than 500 abandoned mines covering about 1800 hectares. The sites include subsided areas, excavated pits, overburdens, spoil dumps and areas affected by fire.

Box 2: Effects of Mining on the Environment in India.

biomass produced by phytoremediation in an integrated manner is through thermo chemical conversion process. Phytoextraction can be combined with biomass generation and its commercial utilization as an energy source.

Combustion and gasification

Combustion and gasification processes leads to generation of electrical and thermal energy. Recovery of this energy from by burning the biomass or gasification makes phytoextraction more cost-effective. Phyto extracted biomass residue undergoes thermochemical energy conversion to yields high quantity energy as it cannot be utilized in any other way as fodder and fertilizers. Combustion is a crude method of burning the biomass, under controlled conditions, where volume is reduced to 2-5% and the ash can be disposed properly [8]. Combustion involves burning the metal bearing hazardous waste in open, and releases the toxic gases and particulates to the environment which may be detrimental. So this process of combustion leads to volume reduction only and the heat produced in the process is wasted. Gasification involves a series of chemical changes to yield clean and combustive gas at high thermal efficiencies for generating thermal and electrical energy. The process of gasification of biomass in a gasifier involves drying, heating, thermal decomposition (pyrolysis) simultaneously [11]. Hetland et al. [9] reported possibility of co-firing plant biomass with coal, the results suggested that ashing reduced the mass of lead contaminated plant material by over 90% and partitioned lead into ash. It may be possible to recycle the metal residue from the ash; however there are no estimates of the cost or feasibility of such a process [5].

Future experiments focus on development of combustion system and methods to recycle different metals from ash by destroying organic matter and releasing metals as oxides. This method is environment-friendly in consideration to the other disposal technologies.

Gasification is the process through which biomass material can be subjected to series of chemical changes to yield clean and combustive gas at high thermal efficiencies (Figure 1). This mixture of gases called as producer gas and/or pyro-gas that can be combusted for generating thermal and electrical energy. It may be possible to recycle the metal residue from the ash; however there are no estimates of the cost or feasibility of such a process.

Phytomining

Bio harvesting of metals from high biomass plants grown in sub-economic mineralized soil substrates is termed phytomining [12] as shown here (Figure 6).

Phytomining is defined as the uptake and pre-concentration of bioavailable metal species from the environment into the plant biomass in a natural way. Phytomining is the process of commercial metal phytoextraction in which a 'crop' plant is grown to accumulate high metal concentrations. Some of these plants are natural hyper accumulators, and in others the hyper accumulation property is artificially induced (Figure 2). It is a less expensive and environmental-friendly method for recovery of dispersed metals from soils and waters, characterized by simplicity of implementation.

Phytomining offers the possibility of exploiting low grade ore bodies or uneconomic mineralized soils with minimal effect on the environment as compared to opencast mining. Phytomining has several advantages over other mine extraction techniques such as : the area to be mined may be 'ready vegetated'; production of 'bio-ore' with higher metal content than a conventional ore; needs far less space for storage; smelting of low sulphur content of a 'bio-ore' does not contribute significantly to acid rain [12]. Nicks and Chambers [13] reported this process as a second potential use of hyper accumulator plants for economic gain in the mining industry which generate revenue by extracting commercial heavy metals as bio-ore. Hyper accumulation ability of plants varies from species to species. The accumulations may be 100 times more than non-accumulators growing in the same substrates. Most elements have a threshold metal accumulation of 1000 µg g^{-1}(0.1%) dry mass besides zinc (10 000 µg g^{-1}), gold (1 µg g^{-1} and cadmium (100 µg g^{-1}) [14]. On the other hand, high biomass species do not have these limitations and showed higher potential and the extraction capacity can be further increased by use of chelates or soil additives.

A model economic phytomining system differentiating between annual and perennial crops is shown in Figure 3. The success of a phytomining project will probably depend on amount of energy recovered by combustion of raw material obtained from phytoremediation technique. It has been reported that about 300 species are nickel hyper accumulators, 26 cobalt, 24 copper, 19 selenium, 16 zinc, 11 manganese, one thallium and one cadmium hyper accumulator [15] (Table 1). Most of these plants were regarded as scientific curiosities as hyper accumulators until it was proposed [16,17]. Plant species of potential phytomining species for production of commercial 'bio-ore' are reported in Table 2.

Significance of phytomining

Commercial mining of metals is usually performed from ores that have a high concentration of target metals due to high capital investment

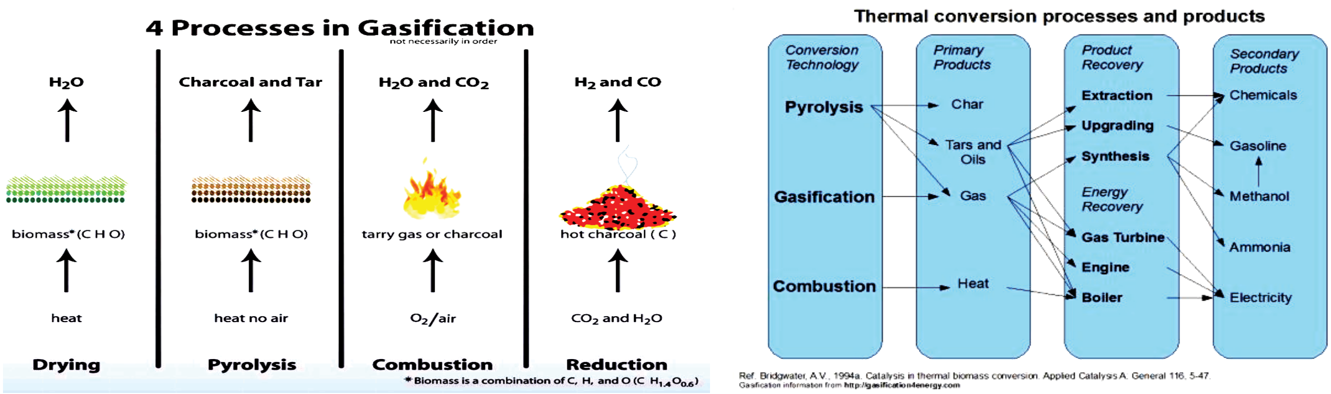

Figure 1: Processes in gasification and thermal conversion processes.

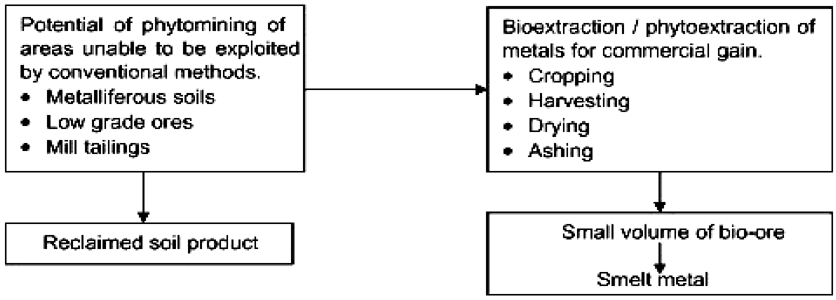

Figure 2: Overall process of phytomining [11].

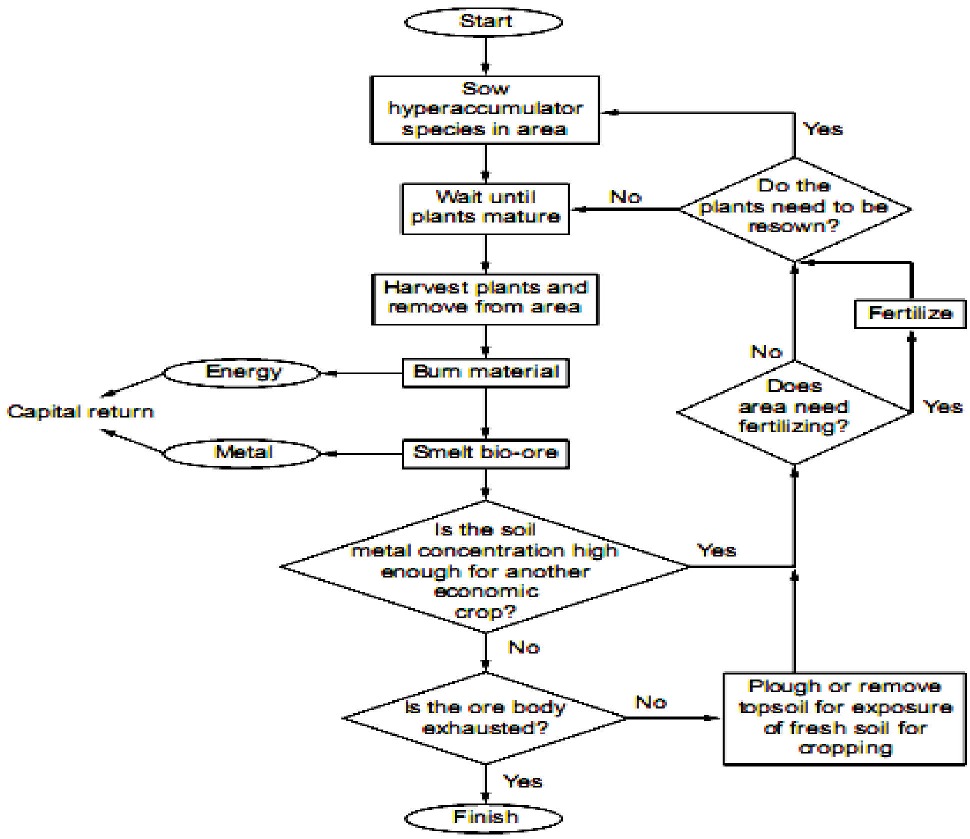

Figure 3: Model of a possible economic phytomining system [11].

Element	Species	Concentration	Biomass
Cadmium	*Thlaspi caerulescens*	3000 (1)	4
Cobalt	*Haumaniastrum robertii*	10200 (1)	4
Copper	*Haumaniastrum katangense*	8356 (1)	5
Lead	*Thlaspi rotundifolium subsp.*	8200 (5)	4
Manganese	*Macadamia neurophylla*	55000 (400)	30
Nickel	*Alyssum bertolonii*	13400 (2)	9
	Berkheya coddii	17000 (2)	18
Selenium	*Astragalus pattersoni*	6000 (1)	5
Thallium	*Iberis intermedia*	3070 (1)	8
Uranium	*Atriplex confertifolia*	100 (0.5)	10
Zinc	*Thlaspi calaminare*	10000 (100)	4

Concentrations are mean highest elemental values (μg g^{-1} dry matter); Values in parentheses are equivalents for non-accumulator plants; Biomass is $tha^{-1}yr^{-1}$

Table 1: Specific hyperaccumulators that might be used for phytomining [14].

but these ore deposits are concentrated to small areas. Sub- or low-grade ore with low percentage of metal content occupies larger area and required to be economically extracted and smelted by conventional techniques. These low grade ore deposits are scattered throughout the world supporting a characteristic flora called endemic flora. These endemic flora have constitutive (present in most phenotypes) and adaptive (present only in tolerant phenotypes) mechanism for metal accumulation and high metal tolerance.

Factors Influencing Phytomining

Both the external and internal factors are associated with phytomining process. An outline sketch is presented in Figure 4. Success of phytomining process depends on adequate biomass yield and high metal contents in the harvestable parts of hyper accumulators. The metal bioavailability can be increased by bringing modulation in

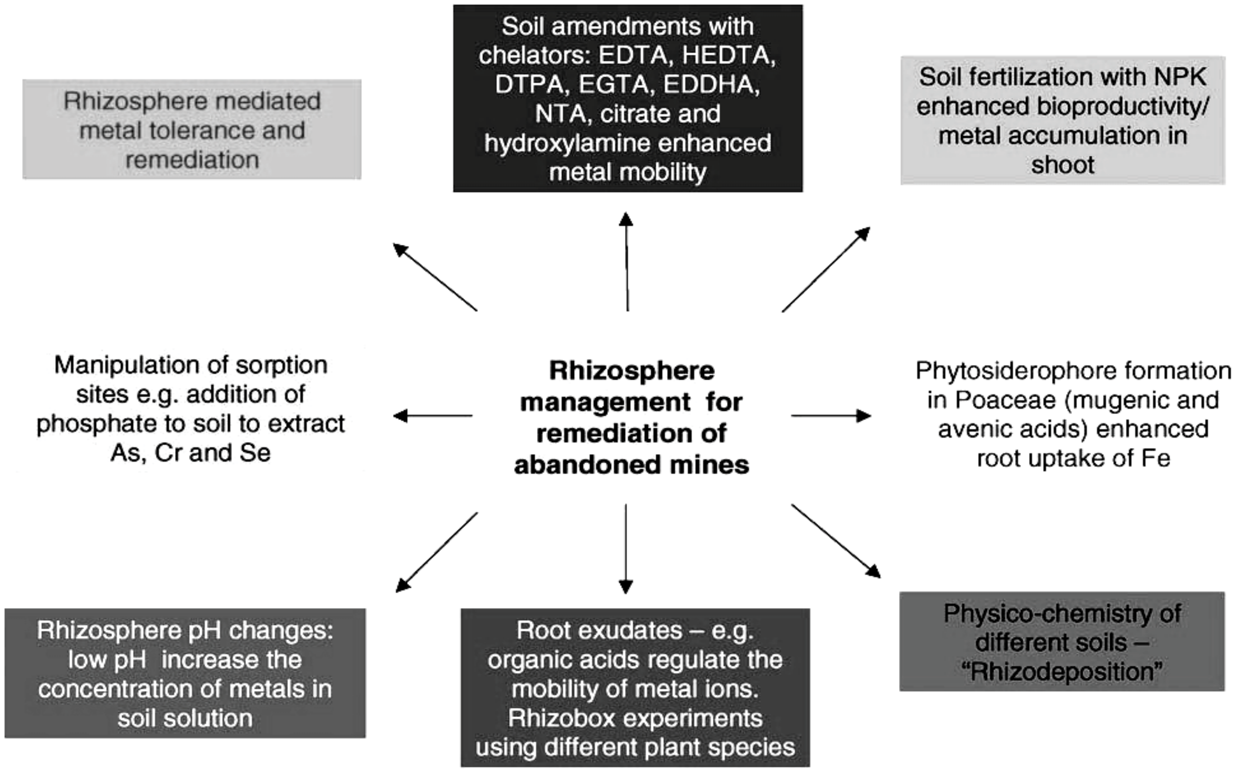

Figure 4: Various factors affecting phytomining process [11].

Metals	Plant species
Cobalt	*Haumaniastrum katangense, Crepidorhopalon perennis, Acalypha cupricola, Anisopapus chinesis*
Manganese	*Macadamia neurophylla, Phytolacca acinosa*
Nickel	*Thlaspi goesingense*
	Psyshotria douarrei
	Sebertia acuminate
	Alyssum narkgrafii
	Alyssum murale
	Phyllanthus species, Euphorbia helenae, Leucocroton flavicans, L. linearifolius
Platinum	*Sinapis alba, Lolium perenne*
Thallium	*B. olerace, Alberis intermedia*
	Hirschfeldia incana, Diplotaxis catholica

Table 2: Plant species of potential phytomining ability of some valuable metals [11].

both internal (plant associated) factors and external (soil associated) factors.

Plant associated factors

Several plant associated factors influence the process of phytomining details of which are shown in Figure 5. The plant species selected for phytomining must be a hyper accumulator i.e., it must be able to accumulate more than 1000 mg/kg of (0.1%) of the concerned metal. Natural metal hyper accumulators release metal chelating compounds (phytochelators/phytosiderophores) e.g., malic, malonic, oxalic acids, acetic acid, succinic acid, sugars, oxalic acids, amino acids and phenolics to enhance accumulation by changing metal speciation. Fungal symbiotic associations enhance root absorption area and stimulate the acquisition of plant nutrients along with metal ions [12].

Soil associated factors

Several factors associated with metal soil properties as discussed below also significantly affect the process of phyto extraction.

pH: Soil pH (acidity or alkalinity) affects the solubility of various trace elements. pH of the rhizospheric soil containing low grade metals depends on species and age-of plants.

Fertilizers: Addition of fertilizers (nitrogen, phosphorus, potash) to soil for supporting the growth of plants decreases the soil pH and hence increases bioavailability of some metals.

Advantages and Limitations of Phytomining

Phytomining is a potential economic method of metal exploitation from low-grade ores, overburdens, mill tailings, or mineralized soil as compared to conventional mining methods with minimal effect on the environment. It also helps in soil remediation and recovery and reuse of the metal with restoration of mined degraded land. Revegetation in degraded mine land minimizes wind erosion and surface run off and thus prevents metal spread. Growing a crop of metal through phytoremediation makes the environment suitable for an increasingly greater and diverse range of species [12].

On the other hand phytomining which directly depends on phytoextraction ability of hyper accumulators has several limitations as discussed below. The process of growing high biomass hyper accumulators is limited by biogeochemical factors viz. rhizobiological

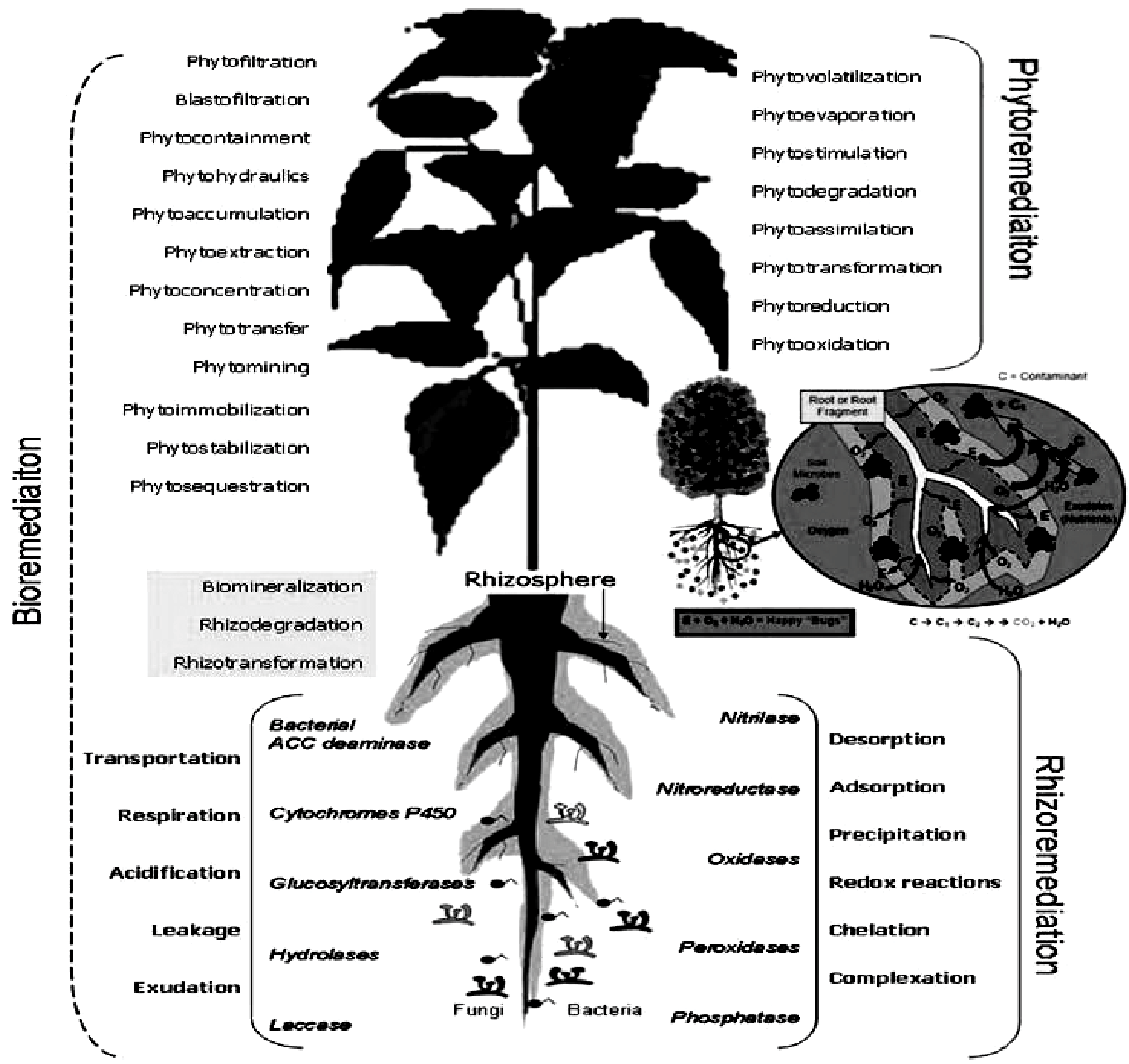

Figure 5: Plant associated factors influencing phytomining process [11].

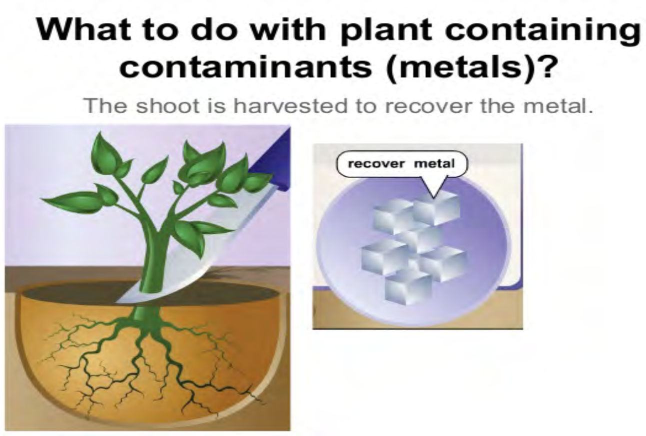

Figure 6: Bio harvesting of metals.

activity, root exudates, temperature, moisture, pH etc. Slow growth rate, small biomass and shallow root system is the characteristic of most of the natural metal hyper accumulators which is a major disadvantage. Quantity of chelators (solubilizing agents) used for increasing metal mobility also create problem if applied in excess. Proper storage of metal contaminated harvested biomass is necessary to prevent its entry to the food chain. It requires a lot of expertise and planning.

Pyrolysis

Bridgewater et al. [18] reported that pyrolysis is a novel method of municipal waste treatment that might also be used for decomposition of contaminated plant material under anaerobic condition. The final products are pyrolytic fluid oil and coke; heavy metals will remain in the coke, which could be used in smelter. High cost of installation and operation can be a limiting factor for treatment if used solely for plant disposal. To avoid this plant material can be processed in existing facilities together with municipal waste. Pyrolysis is known as decomposition of organic matter, e.g., solid residues, wastes (saw dust, wood chips, wood pieces) in an oxygen-deficient atmosphere or in absence of oxygen at high temperature (200-500°C). Products of pyrolysis are gases, organic liquids and charcoal. Koppolua et al. [19] reported that 99% of the metal recovered in the product stream was concentrated in the char formed by pyrolysing the synthetic hyperaccumulator biomass used in the pilot scale reactor. The metal component was concentrated by 3.2-6 times in the char, compared to feed. Study of the fate of the metals in various feeds during pyrolysis has been addressed in literature in different context, but results on pyrolysis of phytoextraction plant biomass are limited. Helson et al. [20] conducted low temperature pyrolysis experiments with chromium, copper and arsenate treated wood and it was concluded that most of the metal was retained in the pyrolysis residue. Influence of metal ions on the pyrolysis of wood has been studied extensively by many authors [8]. High cost of installation and operation can be a limiting factor for treatment if used solely for plant disposal. To avoid this plant material can be processed in existing facilities together with municipal waste. The gases that are produced during the process of pyrolysis can be converted or synthesized into methanol and liquids which are used as fuels.

Biomass to Bioenergy

Biomass is the best alternative source of energy as it is available in plenty and production of energy from biomass is also less costly. The world stock of non-renewable natural sources is decreasing and there is necessity of renewable alternative energy resources. Biomass is one of such important resources. Fire wood, charcoal, agricultural residues, vegetable wastes, cow dung, urban and industrial wastes, forest residues are the main sources of this non-commercial renewable energy (43.5%) vs. commercial energy sources (56.5%).

The most efficient utilization of these resources comes when they are converted to bioenergy by appropriate technologies. Biomass to Bioenergy conversion technology includes:

Non-Biological Process (Thermo-chemical)

- Direct combustiuon
- Pyrolysis
- Destructive distillation
- Gasification
- Liquefaction

Biological Process (Bio-conversion)

- A naerobic Bio-gasification
- Bio-hydrogen production
- Alcoholic fermentation

Biomass-based energy (bio-energy), derived from sun via biological routes, has been fulfilling the human need for centuries as fossil fuel.

Most of the work has been done in US, Africa and Asia [21]. Though phytoremediation has shown promising results as an innovative cleanup technology still it is in a developmental stage. Intensive pilot scale research work is needed to manage post-harvest stages of this remediation technology. Ongoing bench-scale studies and field demonstrations are being conducted throughout the United States in order to better understand and implement this technology [21]. As phytoremediation progresses it is expected to increase its share in the environmental cleanup market. D. Glass Associates, Inc. has already estimated a projected market for the field of phytoremediation [21]. For 1998, the projected market was $16.5-$29.5 million, the year 2000 market was estimated at $55-$103 million, and by the year 2005, it has been estimated to reach $214-$370 million [21].

Conclusion

The future of post-harvest management of phytoremediation products though phytomining practices are still in research and developmental phase. There are many technical barriers which need to be addressed. Optimization of agronomic management practices and plant genetic abilities need to be developed as commercially useful practices. Many metal hyper accumulators remain to be discovered. Optimization of the phytomining process with its cost-benefit analysis should be addressed. Phytomining is still a challenge for most developing and developed country for effective and safe handling of phytoremediation by-products with commercial gain. The detailed information (advantages, disadvantages, operational parameters, costs, examples of applying should be added to each technique) are not available so far as the post-harvest management techniques are under practice in developed and developing countries.

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