*Int.J.Curr.Microbiol.App.Sci* (2020) Special Issue-11: 1703-1717

*International Journal of Current Microbiology and Applied Sciences*
*ISSN: 2319-7706* Special Issue-11 pp. 1703-1717
Journal homepage: http://www.ijcmas.com

**Review Article**

# Phytoremediation: A Green Novel Technology to Decontaminate Metal Polluted Sites

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**Keywords**

Phytoremediation, Soil, Pollution, Sustainable agriculture

**A B S T R A C T**

Soil is a very important component of our ecosystem. It plays a very important role in maintaining ecological balance by providing food and shelter to a plethora of living species either directly or indirectly. Unfortunately the rising anthropogenic activities has begin to disrupt its own integrity. Industrialization at large scale, dumping of oil and fuel, over use of agrochemicals like pesticides and fertilizers, civic disorganisation, are among human activities which apart from other harmful substances have contaminated the soils with excess of metals. Such polluted sites remain unfit for agriculture making the land barren. These sites are required to be treated before utilization or any kind of cultivation. Though the conventional strategies have been successful in decontaminating soil up to an extent but simultaneously they may disrupt soil integrity and are expensive as well. Recently, phytoremediation has emerged as a strategy that is biological in nature and hence expected to conserve the soil's integrity. It is based on the fact that there are many plants which are known to sequester or stabilize certain metal elements in their tissues. It is a least expensive remedy that can be brought about mainly by four different methods phytoextraction, phytostabilization, rhizofiltration, phytovolatilization. The present chapter focuses on the problem of metal contamination in soil and phytoremediation as a strategy to overcome it so as to aid in maintaining ecological integrity and sustainable agriculture.

## Introduction

Ever since man started exploring biosphere he knew the significance of soil in providing service to the ecosystem. It has also been referred to as an important component of panchtatva in Indian literature. It has been quoted as the major life supporting system on earth by Purushotham *et al.*, (2012). Not only does it house a huge biodiversity but also stores ingredients for the food production acting as an ultimate source and sink for all cycles (food & nutrient) in the ecosystem. It is very important component of the biosphere and should be well maintained for continuous flow of energy. However it is not the case in today's scenario as soil is facing various deviations from its original composition and integrity due to entry of different pollutants. These pollutants alter different chemical, physical and biological characteristics leading to soil pollution (Yang *et al.*, 2005).

A rise in concentration of heavy metals in the soil is one of the main associated reasons. It is basically an outcome of various anthropogenic activities such as industrialization, mining, agricultural practices increasing fastly with the rapid commercial development. The various by products of such activities and the heavy metals released by them has been reviewed and collectively presented by Lone *et al.,* 2008. Few of all these include semi conductors, petroleum refining for release of As, fossil fuel burning. sewage sludge for Cd, Electroplating industry, smelting and refining for Cu, solid waste, tanneries for Chromium, burning of leaded gasoline, municipal sewage for lead, emissions from industries producing caustic soda, coal, peat for Hg, combustion of fossil fuels, glass manufacturing industry, land fill, forest fire for Nickel (Ni), Electroplating industry, smelting for Zinc (Zn). Not to mention the fact that the above causes are magnifying day by day due to rapid growth in development and population. Hence release of huge quantity of metals is nothing but obvious. Concentrations of different metals in soil have been found in the range of 1 to 100000 mg $kg^{-1}$ (Revathi 2013).

Heavy metals can be strictly defined as transition metals with atomic mass over 20 and specific gravity above $5gcm^{-3}$ (Rascio and Navari-Izzo 2011; Padmavathiamma and Loretta, 2007) while from the standpoint of biology the term heavy metals refers to metals and metalloids that can be toxic to plants and animals even at very low concentrations. Among these so called heavy metals some are considered as non essential due to their no participation in physiological functions of plants e.g As, Cd, Hg, Pb or Se while rest are essential nutients such as Co, Cu, Fe, Mn, Mo, Ni and Zn which are required for normal functioning, growth and metabolic activities of plants (Rascio and Navari-Izzo 2011). As mentioned above the anthropogenic activities particularly releases heavy metals it is hence evident why their enhancement is obvious.

In plants these causes oxidative stress by producing free radicals (Ghosh and Singh 2005). It can also replace essential elements interrupting the entire metabolic pathways and affecting the plants in many significant ways. Not only this heavy metals get accumulated in the edible parts. Through food chain these are transferred into the body of humans and animals. These have been found to be carcinogenic in humans (Beyersmann and Hartwig, 2008). It can hamper the process of soil formation and in turn growth of plants. It may generate the want of essential macro and micronutrients. The number of soil micro flora and other biodiversity can get adversely affected due the toxicity of heavy metals which can have a direct impact on decomposition of organic matter. It can also disturb the mineralization of Nitrogen by affecting the soil nitrifying bacteria (Sheoran *et al.,* 2012). To overcome the havoc various techniques have been adopted from time to time. Following is a brief description of the remediation techniques worked out for cleaning the metallic contaminated soil.

## Remediation techniques

The term remediation implies to clean up or to restore. The various techniques of cleaning up the soil can be grouped into three broader categories.

**Physical techniques:** Such techniques involve cleaning of soil by physical means e.g excavation, solidification, mixing, washing of soil (Pierzynski, 1997). This method is in use since past. Though it is rapid yet it is not considered as an appropriate one. It is highly costly and involves a high risk to human health during transportation of contaminants (Williams 1988).

**Chemical remediation:** In such techniques transformation of heavy metals is done by addition of certain chemical compounds in the contaminated soil into forms that are less toxic and difficult to be absorbed by the plants. Thus heavy metals are stabilized in soils (Malik and Biswas, 2012). Though it is a successful method yet it has certain drawbacks. It can affect the significant components of the soil. In addition it requires a high cost (Hinchman 1995) and hence it cannot be applied on large scale.

**Bioremediation:** It involves the use of micro-organisms or material that involves microbes e.g compost and animal manure to degrade the contaminants into less toxic forms. Since it makes use of living material it is an environmentally friendly technique. It requires microbial cultures and biological wastes. It would not be easy to apply it on large scale (Garbisu and Alkorta, 2003; Malik and Biswas, 2012).

**Phytoremediation: A green novel technology**

The technique of phytoremediation involves the use of green plants for decontaminating the polluted site (Baker *et al.,* 1994a). The involvement of green plants explains that the approach is completely eco-friendly and would be no doubt aesthetically pleasing. It includes the process of contaminants' uptake, their sequestration, degradation and metabolization of contaminants (Sebastiani 2004). The technique of phytoremediation can be accomplished by various ways which are explained given below through text and diagrammatically (Fig.1).

**Phytoextraction**

Plants used in this approach accumulates large amount of metals in their aerial parts after translocation from the root system. Such plants are called as hyperaccumulators and are tolerant to high concentration of metals (Rulkens 1998). At maturity shoots can be harvested. This method can be repeated several times until metal concentration in the soil has become quite low. Metals that can be removed through this method are Cd, Cr, Cu, Hg, Pb, Ni Se and Zn (Yong and Ma 2002).

Besides hyperaccumulators plants that produce high biomass can also be used for the purpose of phytoextraction. They are efficient in phytoremediation due to their greater biomass which allows ultimate accumulation of metals at large quantity. Examples of this kind are *Salix* spp., *Populus* spp. (Masarovicova *et al.,* 2012).

**Phytovolatilization**

This method involves accumulator plants that could also convert metals into gaseous form and release them into the atmosphere by volatilization or after conversion into vapours. The soil polluted with Hg, Se, B etc can be remediated by this method (Masarovicova *et al.,* 2009).

**Phytostabilization**

This method involves stabilization of metals in the root zone. The plants used in this approach have low metal uptake potential. By immobilizing metals in the soil, the transfer of metals to food chain is checked which could otherwise leach into aquatic ecosystem. This method can be achieved by mechanisms such as precipitation, complexation, or metal valence reduction. This technique is useful for the removal of Pb, As, Cd, Cr, Cu, and Zn (Jadia and Fulekar, 2009).

**Rhizofiltration**

In this type of phytoremediation the metals are adsorbed or absorbed and retained in the roots. The whole plant is harvested thereafter though the metals are not translocated to the aerial parts (Masarovicova *et al.*, 2009).

**Hyperaccumulation: The basis of most effective phytoremediation technology (Phytoextraction)**

Plants accumulating metals in large concentration in their aerial parts or exhibiting an unusual capacity to accumulate metals are called as hyperaccumulators. They exhibit a characteristic of metal tolerance. In a more precise definition they are plants accumulating metals at a concentration 100 folds greater than that found in ordinary plants or non accumulators (Lasat 2000). Hence such a species will accumulate upto 0.1% (1000mg/kg) of Ni, Cu, Co, Pb or 1% (10,000 mg/kg) of Zn or Mn in the dry matter. For Cadmium and other rare metals it is 0.01% (100mg/kg) by dry matter (Bakers and Brooks 1989). Approximately 500 plant species from 45 plant families are known as hyperaccumulators with different bioaccumulation potential. The hyperaccumulation in plants may depend on several factors such as species, organic matter content, pH of soil, cation exchange capacity, type of heavy metal etc. Some species can hyperaccumulate one metal while others more than one metal each (Lasat 2000).

Given below is a table to show different important hyperaccumulators plants and their bioaccumulation potential (Table 1).

Although phytoextraction has been discussed as the best phytoremediation technology in a vast body of literature yet few questions prevents it from giving a sense of satisfaction to the ecologists. A heavy biomass rich in contaminated waste is produced at the end of the process which cannot be disposed as such because it is a hazardous waste. It becomes very necessary to process it further with methods like composting, compaction, pyrolysis and thereafter with incineration, direct disposal, ashing and liquid extraction etc. (Sas-Nowosielska *et al.*, 2004). This step is necessary to make the most of the input cost.

Determination of phytoextraction capability of plants: The phytoextraction capability can be determined mainly by 4 indices (Masarovicova and Kraova 2012).

- Accumulating capability: To define plants as hyperaccumulators certain threshold values of metal concentrations have been utilised e.g. 10 mg $g^{-1}$ (DW) in shoots for Zn (Salt *et al.*, 1995).
- Bioaccumulation factor (BF Index): It can be defined as the ratio of metal concentration in the shoot tissue to the soil. Non accumulator plants often have metal bioconcentration factors less than 1 (Masarovicova and Kraova, 2012).
- Translocation factor (TF index): It is the ratio of metal concentration in shoots to that in roots. It should be greater than 1.0 for a successful phytoextraction (Mikus *et al.*, 2005).
- Tolerance capability: Hyperaccumulators has high tolerance capability to heavy metals such that they do not show even visible symptoms under a certain toxic concentration (Sun *et al.*, 2009).

A high biomass producing plant is expected to accumulate more of metals as compared to less producing ones. Hence it is advisable to use a crop with a biomass production of 20 tonnes per hectare if it has bioaccumulation factor value as 10.

A crop with a value of 20 of the same could be grown for clean up even though it has a biomass production of 10 tonnes per hectare (Peuke and Rennenberg, 2005).

## Strategies adopted by plants towards metallic environment in soil

The technology of Phytoremediation utilises metal accumulation and exclusion capabilities of plants to remediate areas polluted with heavy metals (Schnoor 2002).

Plants were categorized into three groups according to the strategies adopted by them for growing on metal-contaminated soils by Baker and Walker (1990) which is presented and described below.

The extent of metal concentration in different categories of plants is also explained diagrammatically [Fig 2(a, b & c)].

Metal excluders: Such plants retain a large amount of metals in the roots and prevent their translocation in the aboveground parts. Thus shoots of these plants consists of relatively low concentration of metals. Their metal extraction potential is limited.

Metal accumulators: The potential for metal extraction of these plants is huge. In fact, they accumulate metal ions in aerial tissues at a greater concentration than that present in the soil. The accumulation can be called as bioaccumulation.

Metal Indicators: The accumulation of metals in the plants is proportional to their concentration in the soil. These plants die-off if continue to take up heavy metals. Hence they are considered as metal indicators and therefore find a great importance in ecology in reflecting pollution. They are also used in mining due to this reason.

Various examples of hyperaccumulator species are already presented in Table 1. Few examples of excluders and indicator species and their respective metals are given in Table 2.

## Mechanisms for metal detoxification in hyperaccumulators

Plants that accumulate metals at higher concentrations undergo two main steps to avoid their ill effects i.e firstly complexation/binding of the toxic metals with organic compounds and secondly compartmentation within the cell vacuoles. The various mechanisms of complexation are provided below and presented through figure 3.

**Complexation with amino acids containing SH groups:** There are certain amino acids that contains SH functional groups such as glutathione and Histidine binds to heavy metals when existing free in the cytoplasm and renders them inactive. This type of mechanism has been particularly observed in binding of Nickel (Kramer 2010). *T. Goesingense* and *Alyssum lesbiaccum* are quoted as examples of nickel hyperaccumulators where Ni complexes with histidine to avoid its detoxifying effects (Jain 2007).

Complexation with Organic acids: Roots of certain plants exudes carboxylic acids such as malate, citrate and oxaloacetate in the soil which have a tendency to bind to heavy metals due to their acidic groups and make them non functional. Heavy metals can also be bound to them in the apoplasm of roots to prevent further uptake of heavy metals in the plants. The organic acids exudation is also considered to alter the pH of soils and hence affect the bioavailability of heavy metals for plants (Alford *et al.,* 2010). Zinc is considered to bind with malate that is known to shuttle zinc across tonoplast from cytoplasm to vacuole. Thereafter it complexes with citrate and oxaloacetate in the vacuole (Broadley *et al.,* 2007). Such a mechanism is considered to occur in Zn hyperaccumulator *T. caerulescens* (Sarma, 2011).

Binding with Phytic acid: Binding with phytic acid (a phosphate storing compound) in *T.caerulescens* is one more mechanism postulated / quoted in the text for zinc (Jain, 2007).

Metallothioneins - These are small cysteine-rich proteins recently found in plants. They bind heavy metals through the thiol group (SH-groups) of its cysteine residues which represent nearly 30% of its constituent amino acid residues (Sigel and Sigel, 2009).

Binding to phytochelatins: Phytochelatins is a group of thiol-SH rich peptides which are synthesized from glutathione and are considered to shuttle toxic metal from cytoplasm to cell vacuole (Hall 2002). Phytochelatins are well known to chelate cadmium for further detoxification (Cobbett 2000).

## Plant selection criteria for phytoremediation strategy

To accomplish the desired aims and goals through the technique of phytoremediation it is imperative to make a right choice while selecting plants. In addition to the plants great potential to extract metal from soil many other characteristics should be kept in mind. First of all the species selected should possess an inordinate tolerance to the metal/metals present in the contaminated area. The species should be able to grow fastly and yield high biomass. The roots of the plants should have greater surface area so as to extract metals from greater area of land. Furthermore it is important to check whether these plants are tolerant to water logging, drought, salinity and other types of stress that could depreciate their growth rate, biomass production and their capability to uptake metals (Sarma, 2011).

## Advantages of phytoremediation

As it is solar driven it is an inexpensive approach. Vegetation cover in the site facilitates the prevention of soil erosion and improvement of soil nutrition (Wei *et al.*, 2005). This approach can also be used to remove organic pollutants in addition to inorganic pollutants. Since some heavy metals are also essential minerals and that can be deficient in staple food crops, metals can be recovered from the plant tissues and can be utilized in biofortification to improve the nutritional value of these crops. Not to mention the fact that planting green plants makes the site aesthetically pleasing (Mayer *et al.*, 2008).

## Drawbacks associated with phytoremediation

Colonization of numerous species in the contaminated sites becomes slow and difficult because the physical and chemical characters of such sites are altered due to heavy metal contamination. Hence selection of species that could grow easily and fastly should be cautiously done (Wei *et al.*, 2005). This technology can be time taking. Disposal of contaminated plant waste is major concern. There are inadequate numbers of plant species that can remediate the soil. The contaminant may not occur in biologically available form (Lasat, 2000).

In conclusion, heavy metal pollution is emerging as a severe problem with the continually increasing anthropogenic activities. The current review is an endeavour to bring into light the technology that is completely eco-friendly in order to enhance the associated knowledge and understanding which can be utilized in further research. Knowledge on the physiological and biochemical responses helps to adopt different strategies.

**Table.1** Metals and their hyperaccumulator species with bioaccumulation potential

| Metal | Hyperaccumulator plants | Bioaccumulation potential | References |
|---|---|---|---|
| Arsenic (As) | *Pteris vittata* | 22,630 mg $kg^{-1}$ | Ma *et al.*, 2001 |
| | *Pityrogramma calomelanos* | 8,350 µg $g^{-1}$ | Visoottiviseth *et al.*, 2002. |
| Zinc (Zn) | *Gomphrena canescens* | 9,000 µg $g^{-1}$ | Cole *et al.*, 1968 |
| | *Thlaspi caerulescens* | 26,000 ppm | Brown *et al.*, 1995 |
| | *Arabis paniculata* | 20,800 µg $g^{-1}$ | Tang *et al.*, 2009 |
| Lead (Pb) | *Thlaspi (Noccaea) caerulescens* | 30,000 µg $g^{-1}$ | Baker *et al.*, 1994b |
| Copper (Cu) | *Geniosporum tenuiflorum* | 2,299 µg $g^{-1}$ | Rajakaruna and Baker 2006 |
| | *Laportea ruderalis* | Greater than 300 µg $g^{-1}$ up to 600 µg $g^{-1}$ | Brooks *et al.*, 1978 |
| | *Ipomea alpina* | 12,300 ppm | Baker and Walker 1990 |
| Nickel (Ni) | *Sebertia acuminata* | 25% by wt dried sap | Jaffre *et al.*, 1976 |
| Cobalt (Co) | *Haumaniastrum robertii* | 10, 200 ppm | Brooks 1977 |
| | *Phyllanthus species* | 1,100 µg $g^{-1}$ | Reeves 2005 |
| Thallium (Tl) | *Biscutella laevigata* | 15,200 µg $g^{-1}$ | Anderson *et al.*, 1999 |
| | *Iberis intermedia* | 2,810 µg $g^{-1}$ | LaCoste *et al.*, 1999 |
| | *Silene latifolia* | 1,489 µg $g^{-1}$ | Escarre *et al.*, 2011 |
| Manganese (Mn) | *Gossia spp.* | 21,500 µg $g^{-1}$ | Fernando *et al.*, 2009 |
| | *Macadamia neurophylla* | 51,800 µg $g^{-1}$ | Jaffre 1979 |
| | *Maytenus spp.* | 32,000 µg $g^{-1}$ | Fernando *et al.*, 2008 |
| Selenium (Se) | *Astragalus racemosus* | 14,900 ppm | Beath *et al.*, 1937 |
| | *Astragalus bisulcatus, Stanleya pinnata* | 10,000 µg $g^{-1}$ | Freeman 2006 |

**Table.2** Examples of excluders and indicator species and their respective metals

| **Excluders** | | |
|---|---|---|
| **Species** | **Metal** | **References** |
| *Solidago canadensis* | Pb | Yang *et al.*, 2007 |
| *Silene vulgaris, Rumex acetosella* | Ni | Wenzel *et al.*, 2003 |
| *Cyperus exaltatus* L., *Hygrophylla auriculata* | Pb | Mganga *et al.*, 2011 |
| Indicators | | |
| **Species** | **Metal** | **References** |
| *Ageratum conyzoides* | Cu, Zn, Pb, Cd | Deepalakshmi *et al.*, 2014 |
| *Taraxacum officinale,* | Cd, Cr | Petrova *et al.*, 2013 |
| *Azadirachta indica, Tamarindus indica, Saraca Indica, Nerium oleander* | Co, Pb, Ni, Cr, Cd | Aslam *et al.*, 2012 |
| *Agave sisalana* Perr. , *Cyperus articulatus* L. | Zn | Mganga *et al.*, 2011 |

**Fig.1** Various kinds of phytoremediation approaches

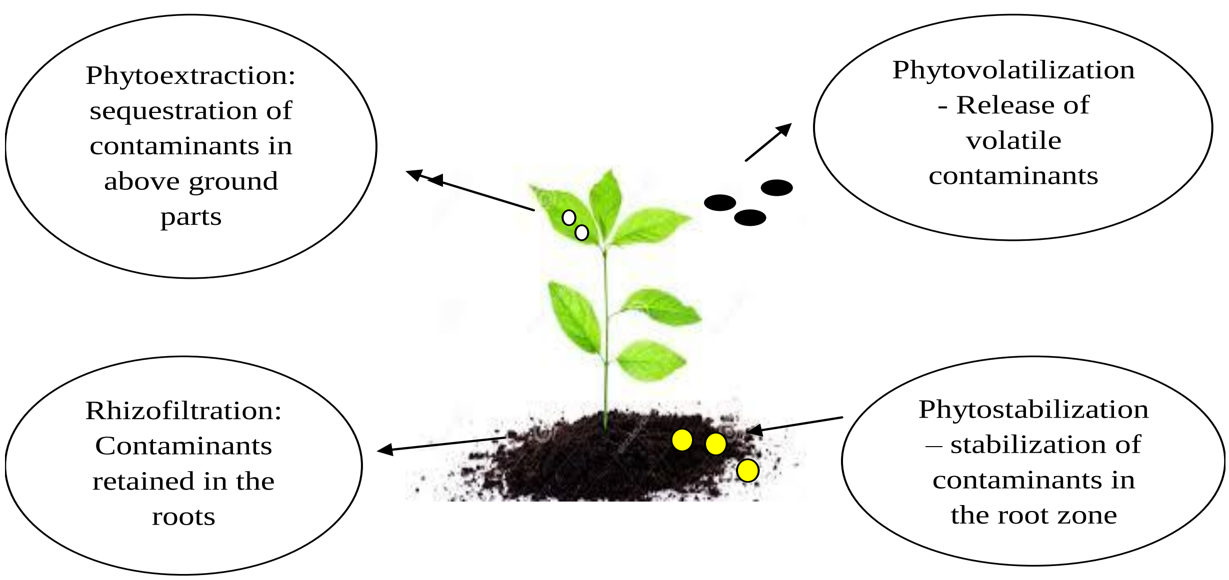


**Fig.2** Different strategies adopted by plants to sustain in metal rich soil (Adopted from Van der Ent *et al.*, 2012, however significantly modified)

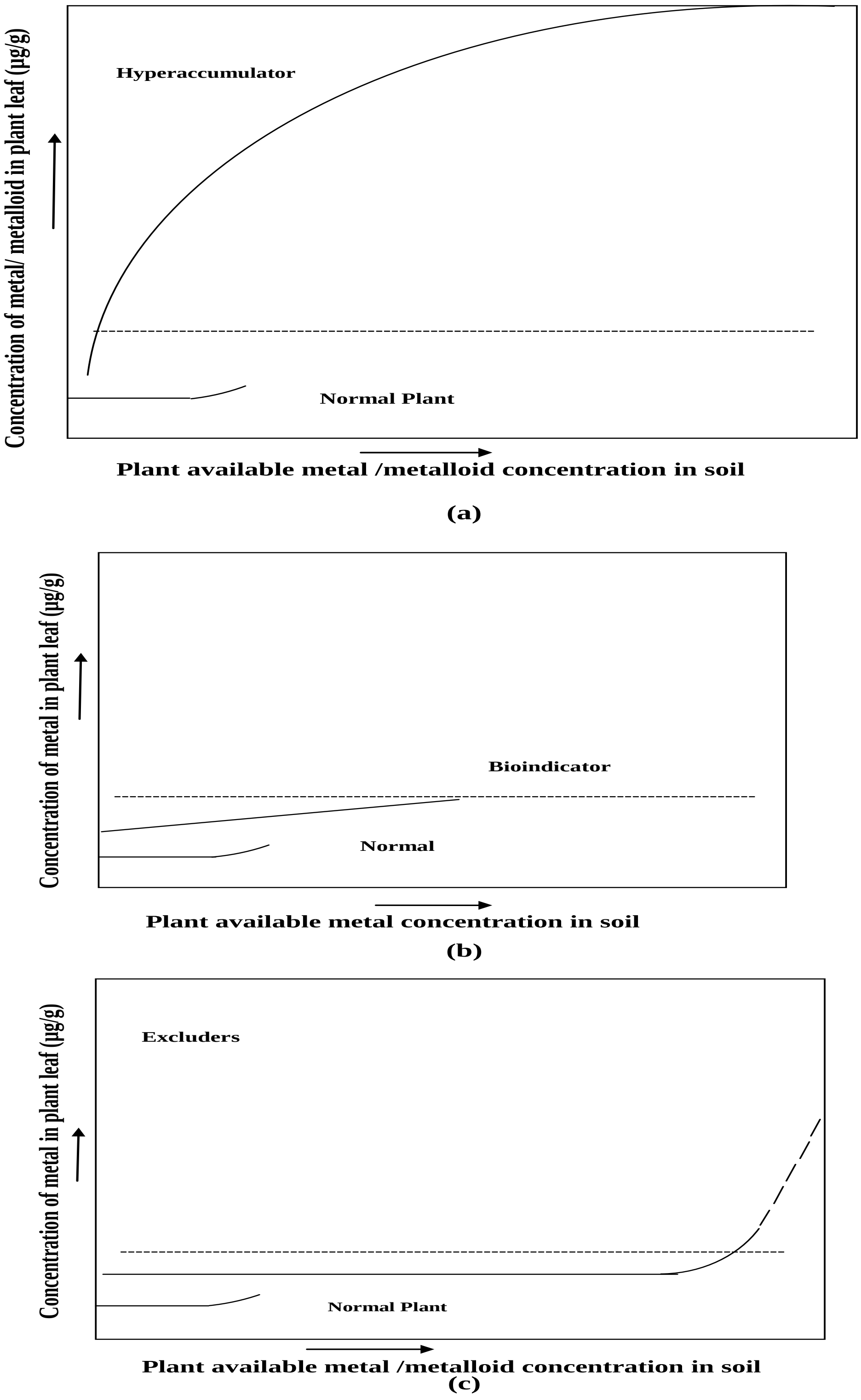
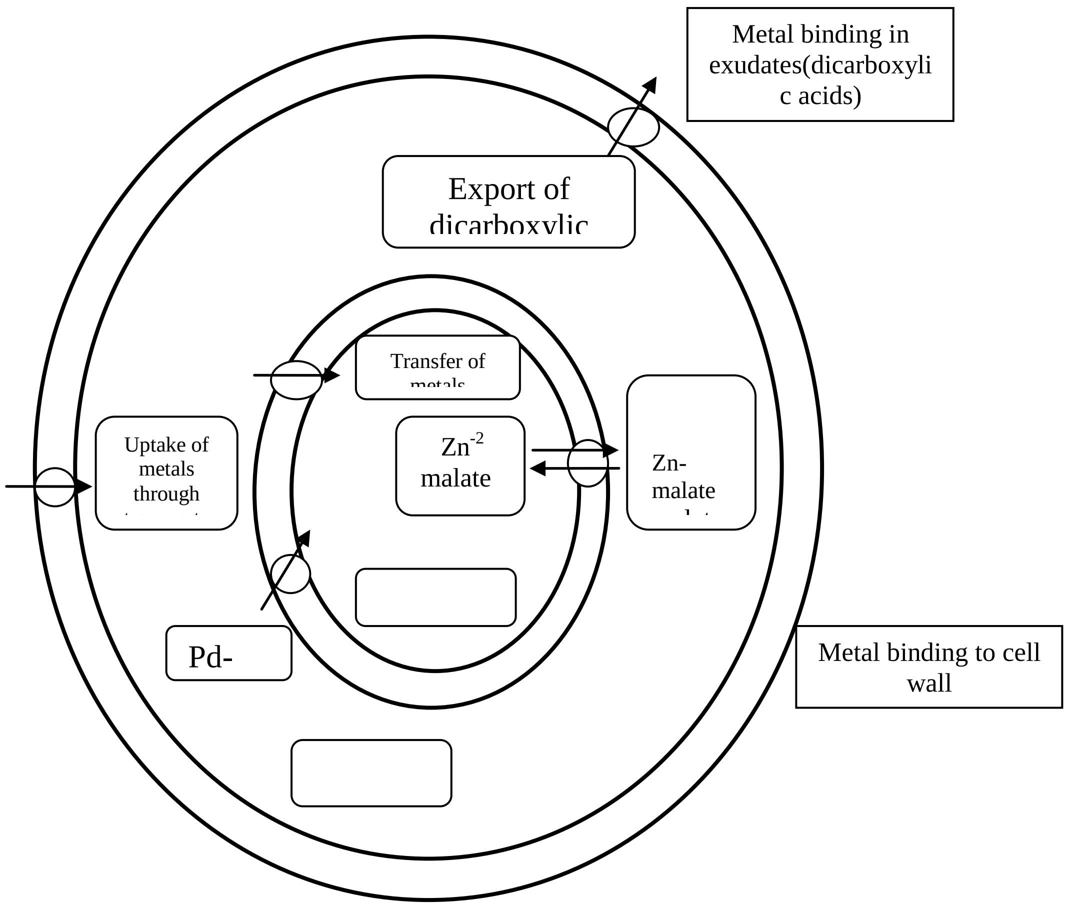


**Fig.3** Different mechanisms shown by plants for detoxification of metals (Adopted from Bothe 2011 with slight modifications)




Phytoremediation has come up as one of the best hopes for solving the problem of heavy metal stress in soil without any destruction of the environment. Inspite of vast number of studies the technology of phytoremedation remains astonishing and complex and hence more of experimental investigation is required in the concerned field. There remains a scope of exploring more hyperaccumulator species for the respective metals they can accumulate. Hyperaccumulation have been for elements such as nickel, zinc, cadmium, manganese, arsenic and selenium have been experimentally established while hyperaccumulators of lead, copper, cobalt, chromium and thallium remain are still not confirmed.

From research point of view there remains a wide spectrum of aspects due to its drawbacks that pulls it back from becoming a great success. The low biomass of crops opens opportunity for biotechnology to utilize the technique of gene manipulation in overcoming the drawback. Use of biotechnology to transfer specific genes to high-biomass promising species requires special attention to optimize the process of phytoremediation. There is a rich plant genetic resource which can be utilized as such or may be genetically engineered for more output. The strategy of phytoremediation is still in infancy. As it leaves a scope of solving the problem of deficiency of essential elements hence more of research could be done on phytoremediation of these elements which can further be utilized for biofortification.

It also add up in making the contaminated site pleasing to the eyes since it involves the growing of living green plants. The technique is relatively less costly and energy efficient. It is better suited for sites containing low to moderate contamination and can be used as a finishing step with other kind of remediation approaches.

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