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REVIEW ARTICLE

Phytoremediational approaches to combat Heavy Metal Pollution: A Brief Overview

Naina Marwa[1,2]*, Gauri Saxena[2] and Nandita Singh[1]*

[1]Plant Ecology and Climate Changes Science, National Botanical Research Institute, Rana Pratap Marg, Lucknow 226001, U.P. INDIA
[2]Department of Botany, University of Lucknow, Uttar Pradesh, INDIA

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ABSTRACT

The heavy metal pollution has caused detrimental effects on human health. Arsenic (As) being ubiquitously present as As (V) and As (III) in soil, enters the food chain through inefficient agricultural practices. Phytoremediation; an eco-friendly, solar energy driven technique has been proposed to remediate the heavy metal contaminated sites. It involves the optimum utilization of certain plants that potentially channelize the heavy metal through them, converting them into lesser toxic forms. Due to certain limitations like; slow accumulation within plants, lesser plant root biomass, etc., phytoremediation is now coupled chemically or with microbes for enhanced remediational results. However, nowadays research is emphasised on developing metal tolerant transgenic plants, which could survive under extreme conditions and yield better plant productivity.

1) INTRODUCTION

Heavy metal poisoning: a global concern

The detrimental effects caused by heavy metal pollution has become the primary concern globally over recent years. Environmental pollution by heavy metals is prominent in areas of mining, and various anthropogenic activities and its pollution is inversely proportional to the distance away from such events [1]. The term "heavy metals" is referred for any metallic element that has a relatively high density [2] compared to water and high atomic weight. The bioavailability of heavy metals to the environment has resulted in biotoxic effects when consumed above the permissible limits. World Health Organization's list of 10 globally concerned chemicals includes four major heavy metals, viz, cadmium, lead, mercury and arsenic.

Arsenic chemistry

Arsenic lies in Group V in the periodic table with atomic number 33 and electronic configuration [As] 3d104s2p3. Electron removal from the last orbital produces two stable valence states: (i) As (III) or arsenite having an electronic configuration [As] 3d104s2 (ii) As(V) or arsenate having an electronic configuration [As] 3d10 [3]. Arsenic shares structural similarities in soil with phosphorus as both belong to Group V.

Sources of arsenic

Mandal and Suzuki [4] suggested that arsenic befalls as a component in nature of over 245 minerals, generally ores comprising sulfide, along with trace metals. The weathering of such rocks and minerals seems to be the foremost source of arsenic in the soils, natural waters and organisms. It is further mobilized through a combination of natural processes such as weathering reactions, organic activity, transportation, precipitation, volcanic emissions as well as concluded by a number of other anthropogenic activities [5]. The floodplain of the rivers originating from the Himalayan Foothills and Tibetan Plateau region also contribute to the groundwater arsenic pollution issues scenario in Asia; the having arsenic contamination [6]. Based on this, arsenic pollution has been evidently detected in West Bengal, Bihar, Jharkhand, Uttar Pradesh in the Gangetic plain, Manipur in the north eastern Hill states, Brahmaputra plain in Assam and PMB (Padma-Meghna-Brahmaputra) plain in Bangladesh [7]. Islam et al. [8], reported the essential role metal-reducing bacteria in arsenic release from sediments. A similar report from Bangladesh stated that the microbial or geochemical activity facilitated reductive termination of arsenic associated with Fe oxyhydroxides to be the prime reason for arsenic release, these reducing conditions are initiated by decomposition of organic matter [9].

Effect of arsenic on human health

The dietary sources of arsenic are the intake of drinking water and arsenic accumulated food grains. The lethal effects caused by it is primarily due to its interference with the biochemistry and metabolic processes within the body. Once As(V) enters the cell it gets reduced to As (III) by glutathione (GSH). As (III) has excessive affinity for the thiol (-SH) group; thus, As(III) neutralises enzymes, other functional proteins, and low

* Corresponding Author: **Naina Marwa and Nandita Singh**
Email address: naina.marwa@gmail.com
nanditasingh8@yahoo.co.in

molecular weight compounds such as GSH and cysteine hindering the active -SH group [7]. The metal applies its harmful effects through damage of cellular respiration by hampering of numerous mitochondrial enzymes and uncoupling of oxidative phosphorylation [10]. Ingestion of inorganic arsenic causes haemolysis, melanosis, polyneuropathy, encephalopathy etc. Long-lasting human contact to arsenic can unfavourably distress reproduction besides other health hazards [11].

To combat the issue, various conventional strategies have been adopted. Strategies involve the removal of toxic metals from the contaminated soils by transportation to laboratories, soil washing with chemicals to remove metals, and finally replacing the soil at its original location or disposing of it as hazardous waste [12]. This strategy is an ex-situ approach and can be very expensive and damaging to the soil structure and ecology [13]. Immobilisation of heavy metals through the addition of lime [14] and calcium carbonate ($CaCO_3$) [15] have been suggested as other remediation techniques. These remediation technologies have the immediate results, but the problem persists as the metals are not permanently removed from the soil environment.

According to EPA report [16], bioremediation is the potential technique to remediated polluted soil. Bioremediation is the use of microbes to clean up contaminated soil and groundwater. It stimulates the growth of certain bacteria that use contaminants as a source of food and energy.

Although, microbes are less compliant to environmental extremes over other conventional strategies, as they are more cost effective [17]. Bioremediation has been found most suited for sites that have organic pollutants since heavy metals are not subject to degradation, several researchers have suggested that bioremediation has limited potential to remediate metal-polluted environments [18].

2) PHYTOREMEDIATION: SOLAR-ENERGY DRIVEN TECHNOLOGY

Another in-situ approach which has gained focus is the process of 'phytoremediation'. The generic term ‘phytoremediation’ consists of the Greek prefix Phyto (plant) attached to the Latin root remedium (to corrector remove an evil) [19]. It is a physio-chemical botanical in-situ remediation for contaminated sites. It is an un-destructive and eco-friendly approach to remediate pollution over the conventional approaches which require mechanical input. The potential for this technology in the tropics is high due to the prevailing climatic conditions which favour plant growth and stimulates microbial activity [20].

Mechanism of phytoremediation

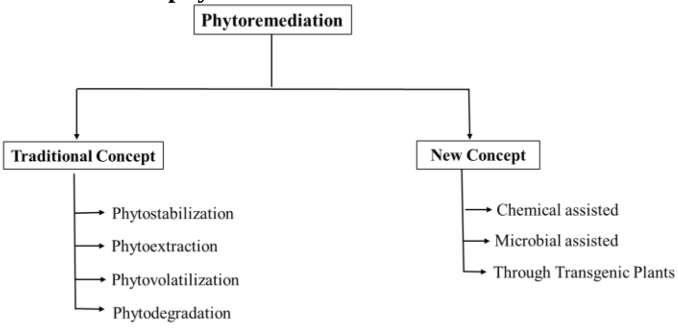

Fig 1.1 Diagrammatic representation of types of Phytoremediation

3) TRADITIONAL CONCEPT OF PHYTOREMEDIATION

Phytostabilization: in-place inactivation

This technique involves the use of plants to immobilise heavy metals, thereby reducing its phyto-availability for the plants. This technique is best suited for highly contaminated sites where phytoextraction would take a long process. Phytostabilization of heavy metals takes place as a result of precipitation, sorption, metal valence reduction, or complexation [21]. Soil amendments used in phytostabilization help to inactivate heavy metals; thus, they prevent plant metal uptake and reduce biological activity [22]. Since contaminants persist in the soil environment constant monitoring is required to combat future problems.

Phytoextraction

Phytoextraction is the most commercially applicable technique over the other phytoremediation techniques [23] due to its comprehensive approach for removal of metal/metalloids from polluted soil, water biosolids and sediments [24, 25, 26]. This is best suited to a remediated contaminated site by the use of hyperaccumulators.

Now, what are hyperaccumulators?

A hyperaccumulator is a plant species capable of accumulating 100 times more metal than a common non-accumulating plant [27].

The plants involved in phytoextraction possess following characteristics: high biomass, rapid growth rate, extensive root system, and ability to thrive in high levels of heavy metals. For example, *Pteris vitatta*, arsenic hyperaccumulator [28], *Arabidopsis halleri*, a Zn and Cd hyperaccumulator, has been studied by Sarret et al. [29]. A characteristic feature which makes phytoaccumulation feasible is the tolerance of the hyperaccumulators to the increasing concentrations of the heavy metals (hypertolerance). This could be a result of exclusion of these metals from the plants or by compartmentalization of these metal ions; that is, the metals are retained in the vacuolar compartments or cell walls and thus do not have access to cellular sites where vital functions such as respiration and cell division take place [30, 31].

Phytovolatilization

In this form of phytoremediation, plants are used to take up pollutants from the soil; these pollutants are transformed into volatile forms and are subsequently transpired into the atmosphere [16] (Fig 1.2). This is adapted to remediate the soil polluted by mercury. Examples of transgenic plants which have been used for phytovolatilization of Hg polluted soils are *Nicotiana tabacum, Arabidopsis thaliana*, and *Liriodendron tulipifera* [32, 33].

Phytodegradation

This type of phytoremediation technique is employed to remediate sites polluted with organic pollutants. Plant metabolism plays a significant role in the breakdown of the contaminant present in soil or groundwater. Intercellular plant enzymes like; laccases (degradation of anilines), nitro-reductases (degradation of nitro-aromatic compounds) and dehalogenases (degradation of chlorinated solvents and pesticides) [34, 35]. However, rhizodegradation involves the breakdown of organic pollutants in the rhizosphere through rhizospheric microbial activity.

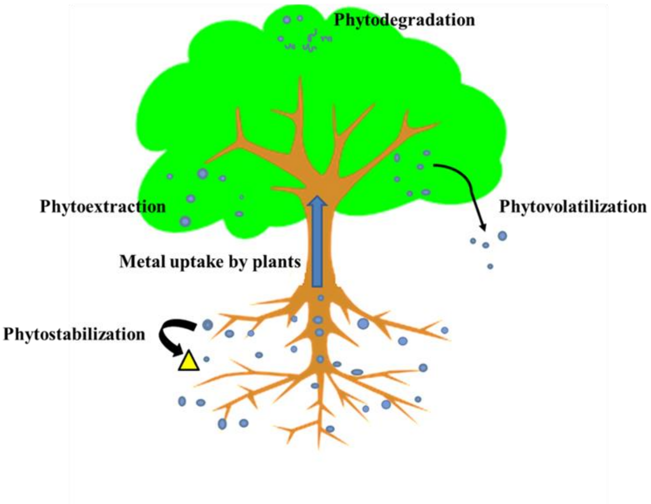

Fig. 1.2 Diagrammatic representation of different forms of Phytoremediation

4) NEW CONCEPT OF PHYTOREMEDIATION

Chemical assisted approach

Plants which potentially accumulate high concentrations of heavy metal in its aerial plant parts are designated as hyperaccumulators plants. However, Baker et al. [36] suggested the metal concentration ratio of the shoot to root as the deciding criteria to refer a plant as a hyperaccumulator plant. According to the suggestion, a ratio above 1 for plant indicates its ability to accumulate more in shoots than roots. Such plants are qualified to be referred to as hyperaccumulators and are appropriate for phytoextraction. Heavy metal concentration on aerial parts of the hyperaccumulator plants depends upon the concentration to which it is exposed. The plant growth rate and its biomass production are the limitations for phytoextraction. However, non-hyperaccumulator plants without any restrictions (as mentioned above) can be employed for phytoextraction using synthetic/artificial or organic chelating agents, hence inducing phytoextraction [13, 37]. Artificial chelating agents include ethylene diamine tetraacetic acid (EDTA), diethylene triamine penta–acetic acid (DTPA), and ethylene glycol tetra–acitic acid (AGTA) which are reported to augment metal bioavailability, facilitating plant uptake [37, 38]. Use of these synthetic chelators is questioned about its biodegradability. Organic acids such as acetic acid, citric acid, malic acid and oxalic acid having low molecular weight can be efficiently used as heavy metal chelating agents over expensive synthetic chelators. Shaheen et al. [39] suggested use of salicylic acid (SA), a phenolic compound, a signalling molecule in plants under stress (biotic or abiotic) conditions, involved in stress mitigation is also an active and evolving field of study.

Microbial assisted approach

The introduction of microbes to the plants for phytoremediation show recommendable results in remediating heavy metal polluted soil. Mycorrhizal fungi are used in various remediation studies on heavy metals, and their results prove that mycorrhizae play different mechanisms for remediating the heavy metal contaminated sites. For instance, while some studies have shown enhanced phytoextraction through the accumulation of heavy metals in plants [40, 41] , others reported enhanced phytostabilization through metal immobilization and a reduced metal concentration in plants [42, 43]. Besides mycorrhizal fungi other microorganisms are used in conjunction with plants for phytoremediation, they are plant growth-promoting rhizobacteria (PGPR); found in the rhizosphere. These PGPR stimulate plant growth via several mechanisms such as production of phytohormones and supply of nutrients [44], production of siderophores and other chelating agents [45], specific enzyme activity and N fixation [46], and reduction in ethylene production which encourages root growth [47]. For example, enhancement in phytoaccumulation of heavy metals such as Cd and Ni by its hyperaccumulators (*Brassica juncea* and *Brassica napus*) has been reported when the plants were inoculated with *Bacillus* sp. [48]. The success of the combined use of these organisms depends on the species of microbe and plants involved and to some extent on the concentration of the heavy metal in soil. [49].

Use of transgenic plants

Genetic engineering is emerging as a dynamic approach to enhance phytoremediation efficacy of the plants. The technique involves the over expression or incorporation of genes responsible for uptake, translocation, sequestration, tolerance against pollutants in genetically engineered plants [50]. Transgenic plants can be developed through direct transfer of specific genes exhibiting target feature using DNA methods or by transformation methods using *Agrobacterium tumefaciens* [25]. Assunção et al. [51] developed transgenic *Thlaspi caerulescens* using ArsC; bacterial gene responsible for As reduction from *E. Coli*. Seth et al. [25] improved Hg tolerance in transgenic plants through the introduction of bacterial gene merA and merB responsible for encoding mercuric ion reductase and organo-mercurial lyase, respectively. It can be concluded that genetically engineered plants exhibit better metal tolerance and sequestration potential and can be effectively used for phytoremediation purposes.

5) CONCLUSION

Although, the above discussed techniques reduce the heavy metal toxicity in the environment yet not much is known to completely remove them. The conversion of toxic pollutant to lesser toxic pollutant is not the permanent solution to the problem. An intensive as well as extensive study is required completely remediate the contaminant from the environment.

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