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AN OVERVIEW ON PHYTOREMEDIATION AS A PROMISING TECHNOLOGY FOR ENVIRONMENTAL DEPOLLUTION

BY

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Abstract. The paper develops a succinct analysis of the phytoremediation process of soils polluted with heavy metals. A number of basic aspects regarding the pollution of soils with heavy metals and the consequences of this phenomenon are presented. Also, the mechanisms by which some plants absorb heavy metal ions are described, a series of studies are presented in which different categories of plants were used as hyperaccumulators to remove heavy metals from the soil and possibilities to intensify phytoremediation. Based on information from the literature, the removal of heavy metal ions (or associated with this group of chemical elements) from the soil, such as cadmium, arsenic, mercury, selenium was explored. The analysis presented in the paper could support and justify the application of phytoremediation as an alternative for environmental remediation in friendly conditions, with low costs and without additional negative impacts on the environment.

Keywords: *Brassicaceae*, heavy metals, hyperaccumulator**,** rhizosphere, soil.

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1. Introduction

The effects of soil pollution can be manifested directly or indirectly and can have immediate or long-term consequences. The classification of soils from the point of view of pollution is done according to the nature and source of pollution, the degree of pollution and the activity that generates the pollution. From the point of view of the nature of soil pollution, it can be physical, chemical, biological and radioactive (Asante-Duah, 2019; Vasilachi and Gavrilescu, 2021). The vast majority of human activities, especially industrial ones, attract an increase in solid waste landfills. These can be minerals or waste, industrial waste or residues, household waste or residues. The accumulation, storage, disposal of solid waste have become, in recent years, through the quantities circulated, stringent problems in terms of environmental quality (Lombi *et al.*, 2001; McGrath and Zhao, 2003).

Soil pollution through atmospheric emissions is mainly due to natural sources (volcanoes, cosmic dust, etc.), but also to anthropogenic sources (industry, transport, human settlements, agriculture etc.). Toxic substances from the atmosphere fall on the soil and enter it directly or together with precipitation, having as effect the soil pollution, a process that is felt in the reduction of biomass production, contamination of agricultural products, general damage to ecosystems. Precipitation has an important role in the contamination of the soil with various pollutants, which by washing the atmosphere of pollutants, pass with them on the soil surface, from where they can be entrained in deeper layers or can reach through drainage systems directly into emissions (Bleam, 2012).

A particularly important case is presented, in the case of soil pollution by heavy metals. Through precipitation, they can penetrate into the depths of the soil, and through biological accumulation, they reach plants, from where they pass through human and animal consumption. Although there is a certain resistance of living organisms to the action of heavy metals, this is manifested within certain limits. Exceeding the limits leads to the installation of serious diseases in humans and animals, as well as serious compromise of vegetation.

Phytoremediation refers to using plants for environmental bioremediation and involves the use of green plants for decontamination of soils, waters and air. It is a technology that can be applied to both organic and inorganic pollutants (especially metals) present in soil, water or air. Phytoremediation techniques can provide the only efficient way to repair hundreds of thousands of square kilometres of soil and water polluted by human activities, constituting a cheap and ecological alternative to the physical methods of remediation, destructive for the environment, currently used (Yan *et al.*, 2020).

The concept of using metal-accumulating plants for the selective removal and recycling of excess metals in the environment, which was introduced in 1983, gained particular interest in the ‘90s and was increasingly examined as a practical technology, less expensive compared to classical methods, addressing replacement or washing of contaminated soils. Phytoremediation has been used quite a lot lately, especially in the USA, which is a few decades ahead of Europe in using these types of technologies, both for the treatment of heavy metal-polluted soils and in the case of pollution with pesticides, chlorides, aromatic hydrocarbons, polycyclic, oil, and others. The ideal scenario for phytoremediation of pollutants such metallic ions involves extraction, translocation of toxic cations or oxyanions in the above-ground tissues and their harvesting, conversion of elements into roots for the occurrence of percolation in the polluted area. Some authors proposed the concomitant use of chemical amendments (calcium carbonate, phosphates, iron and manganese oxides, zeolites) and plants to transform contaminants into inaccessible and stable forms (Cozma *et al.*, 2021; Gavrilescu, 2022; Wu *et al.*, 2004).

Phytoremediation usually relates to certain plants' natural capacity to bioaccumulate, decompose, or render pollutants tolerable in soil, water, or air. From the phytoremediation point of view, the plant can be considered as a pumping and treatment system that can prevent the spread of soil contamination. Metals, pesticides, solvents, crude oil have all been reduced in phytoremediation projects around the world. Plants with high phytoremediation potential can be species from spontaneous flora that grow in polluted places or cultivated plants that have specific features, determined by the polluting environment. Pollutants can be absorbed into plants by several natural biophysical and biochemical processes, namely by: absorption, transport, translocation, hyperaccumulation and transformation (Lázaro, 2009).

Phytoremediation is considered a technology that protects the disruptive environment, as opposed to mechanical cleaning methods, such as excavating soil or pumping polluted groundwater. In the last 20 years, this technology has grown in popularity and has been used for soils contaminated with lead, uranium, and arsenic. However, one negative aspect of phytoremediation would be that it requires a long-term commitment because the process is dependent on plant growth, tolerance to toxicity and bioaccumulation capacity (Greipsson, 2011).

2. Categories of phytoremediation

The general term of phytoremediation includes plant-based techniques for removing, transferring, stabilizing and destroying pollutants from contaminated soils, water or sediments. Methods of phytoremediation have tremendous potential for particular applications and allow the remediation of much larger sites than would be possible in the context of classic remedial approaches consumers. A wide range of species of plants like sunflower or cottonwood can be utilized to eliminate pollutants through several mechanisms. Intensified biodegradation in the rhizosphere, phytoextraction, phytodegradation and phytostabilization are all examples of phytoremediation mechanisms (Fig. 1) (Rigoletto *et al.*, 2020).

Rhizodegradation occurs in the portion of soil that surrounds the roots of plants. The bacteria in the rhizosphere use the natural compounds released by the root cells as a substrate, speeding up the breakdown of pollutants. Plant cells improve soil structure, allowing for water transport and oxygenation. Such a mechanism tends to drive water to the top and dry the bottom soaked sections (Chen *et al.*, 2022).

Phytoextraction often referred as phytoaccumulation, makes advantage of plants' capacity to accumulate and extract the contaminant from the soil, especially metals, and accumulate it in their stems and leaves (Rafati *et al.*, 2011; Sekara *et al.*, 2005; Yoon *et al.*, 2006).

According to Vangronsveld *et al.* (2009), ideal phytoextractors should have the following characteristics: high growth rate; high biomass production; root system widely distributed and highly branched; accumulate heavy metals from the soil; heavy metals collected in the roots must be transferred to the stems; minimizing heavy metal toxicity; present good adaptation to the environmental and climatic conditions of the area and resistance to pathogens and pests; they must be easy to grow and harvest and repel herbivores to avoid contamination of the food chain.

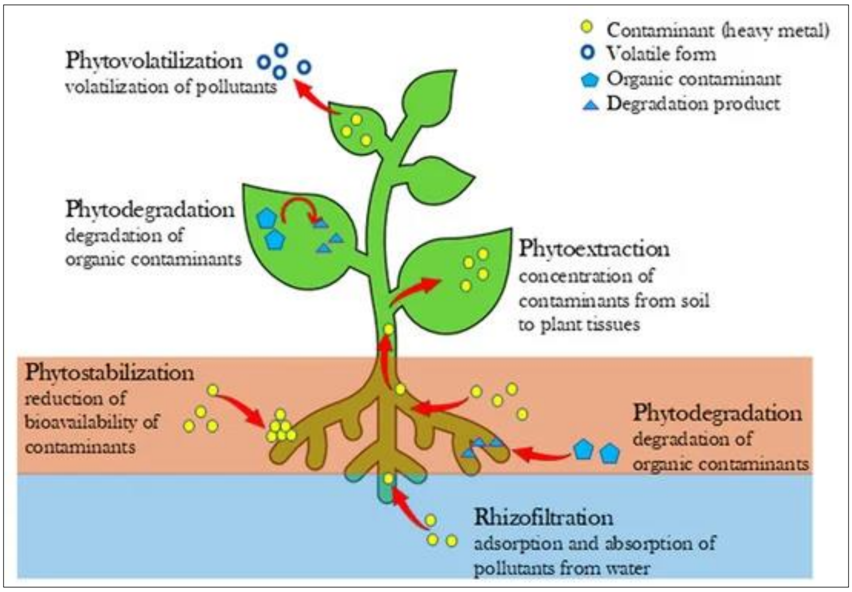

Fig. 1 – Schematic representation of different phytoremediation approaches by plants (Rigoletto *et al.*, 2020; reproduced under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

In the phytoextraction process, as indicated in Fig. 1, the appropriate species will first be chosen to be cultivated in a determined contaminated soil.

After having carried out the extraction of the pollutant by the plant, the harvest will be withdrawn, now converted into biomass enriched by the heavy metal that contaminated the soil. Subsequently, the treatment of the harvest will be carried out; by composting, compression or thermal treatments for example, to reduce the volume and / or weight of biomass. Finally, this raw material will be processed as if it were a hazardous waste, or it will be recycled to recover the elements that may have economic value (Vangronsveld *et al.*, 2009). Phytoextraction is the process by which plant roots absorb contaminants from the soil (metals, in particular), together with water and nutrients. Pollutants are not eliminated, but rather collect in root cells, branches and foliage, that can even be gathered to eliminate and neutralize the pollutants. The method of extraction is dependent on the capacity of plants to develop in soils with high metal concentrations and on their ability to extract metals from the soil under climatic conditions specific to that soil (Cunningham, 1995; Raklami *et al.*, 2022).

For phytoextraction, plant with a high natural capacity to absorb metals, known as **hyperaccumulators**, as well as species that generate a lot of biomass can both be utilized (*e.g*. indian mustard, grains, rice etc.) mechanically aided by the addition of substances that improve metal extraction capacity (Rosca *et al.*, 2021). The total of plants that can collect distinct metals is limited: some fern species have a unique propensity for accumulating arsenic (*Pteris vitata* species), buckwheat can accumulate lead, *Brassica juncea* (Indian mustard) for Cd, Cr (VI), Cs, Cu, Ni, Pb, U, Zn, *Brassica napus* (turnip) for Zn, Pb, Se etc. (Table 1).

Phytodegradation is the process of metabolizing contaminants inside leaves and stems. Some species create catalysts (dehalogenases, oxygenases) that promote the catalytic degradation of contaminants reaching the plant tissue. This approach is being investigated for the prospect of concurrent breakdown of CHAs and aromatic compounds.

Phytostabilization is the process based on the ability of certain plants to produce chemical compounds that can bind, at the root-soil interface, in an inactive form, significant amounts of toxic compounds (especially heavy metals), thus preventing their spread in groundwater or other medium (Fig. 1). Usually, the soil subject to phytostabilization is plowed, treated with various amendments for the rapid fixation of metals (lime, phosphate fertilizers, Fe or Mn oxyhydroxides, clay minerals etc.), after which it is sown with plants known as weak translocators of metals, so they should not reach the parts of the plant that can be eaten by animals. Wind grass (*Agrostis tenuis*) and red straw (*Festuca rubra*) are used in commercial applications for polluted soil phytostabilization with Pb, Zn or Cu (Bolan *et al.*, 2011; Wood *et al.*, 2016).

Rhizofiltration is similar to phytoaccumulation, with the observation that it applies only to liquid effluents. The plants are grown without soil and are transported to contaminated areas. Because the plants get contaminated, they are collected and preserved (Fig. 1). Candidate plant for rhizofiltration includes the

Indian mustard (*Brassica juncea*), sunflower (*Helianthus annuus*), corn (*Zea mays*) (Chatterjee *et al.*, 2013).

Phytovolatilization is the process by which plants absorb water contaminated with organic compounds which they then remove into the atmosphere through the leaves (Fig. 1). Some metals (Hg, As, Se) can also be removed in the form of gaseous compounds, but their toxicity calls into question the effectiveness of this method. Genetically modified tobacco plants (*Nicotiana tabacum*) have been used to absorb mercury and methylmercury from the soil, followed by their release into the atmosphere as mercury oxide (Chaterjee *et al.*, 2013).

Table 1
Heavy metal hyperaccumulator (HMH) and non-HMH plant species used in phytoextraction studies (adapted upon Wood et al., 2016)

Plant species	Family	Common name	Target metal
Heavy metal hyperaccumulator			
Alyssum murale	Brassicaceae	Yellowtuft	Ni
Alyssum serpyllifolium	Brassicaceae		Ni
Noccaea caerulescens	Brassicaceae	Alpine penny-cress	Cd, Zn
Pteris vittata	Pteridaceae	Chinese brake fern	As
Sedum alfredii	Crassulaceae		Cd, Zn
Sedum plumbizincicola	Crassulaceae		Cd, Pb, Zn
Non-heavy metal hyperaccumulator			
Brassica juncea	Brassicaceae	Indian mustard	Ni, Cu
Brassica napus	Brassicaceae	Canola	Cd
Brassica oxyrrhina	Brassicaceae	Smooth-stemmed turnip	Ni
Glycine max	Fabaceae	Soybean	Cu
Helianthus annuus	Asteraceae	Sunflower	Cd, Zn
Hordeum vulgare	Poaceae	Barley	Cd, Pb
Lens culinaris	Fabaceae	Lentil	Ni
Luffa cylindrica	Cucurbitaceae	Sponge gourd	Ni
Lycopersicon esculentum	Solanaceae	Tomato	Cd, Pb
Ricinus communis	Euphorbiaceae	Castor oil plant	Cu, Ni, Zn
Sinapis alba	Brassicaceae	White mustard	Cd, Cu, Zn
Solanum nigrum	Solanaceae	Black nightshade	Cd
Sorghum halepense	Poaceae	Sorghum	Cd, Ni
Thlaspi arvense	Brassicaceae	Field penny cress	Zn
Vigna radiata	Fabaceae	Mung bean	Cd, Ni, Zn
Zea mays	Poaceae	Corn	Cd

In the 1990s, American researchers studied the fate of selenium over large areas of California contaminated - with significant ecological problems - following irrigation by water heavily loaded with selenium (Dhillon and

Banuelos, 2017). They showed that this element can be accumulated in a chemical form by certain plants of the *Astragalus* type: through a series of reactions, these plants convert selenium into dimethylselenide, which is a volatile compound which then passes into the atmosphere. These methylation transformations are also carried out naturally in soils by microorganisms. Overall, the presence of plants leads to the elimination of selenium from the soil but also to a displacement of pollution into the atmosphere. The fact remains that a lot of research is currently being developed on this interesting path, with a view to tackling soil pollution by heavy metals such as arsenic and mercury. Figure 2 shows the volatilization process by plants of the *Astragalus* type. Selenium (Se) is transformed into dimethylselenide (DMSe) in plant cells by microorganisms in the rhizosphere. The DMSe is then volatilized via the leaves into the atmosphere (Winkel *et al.*, 2015).

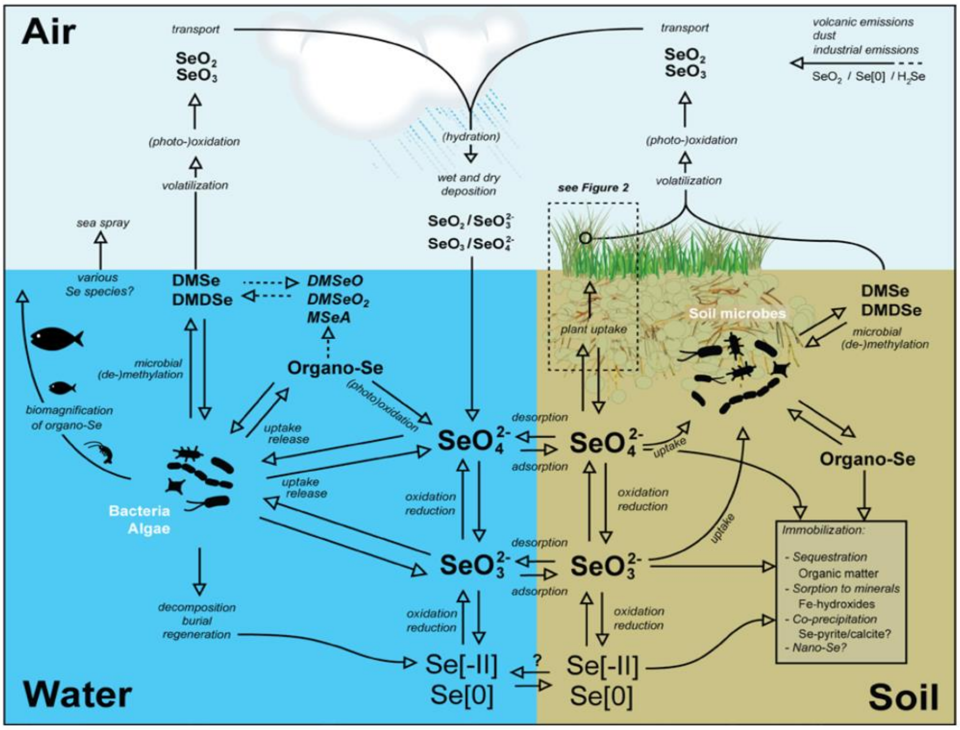

Fig. 2 – Overview of Se species, pathways and transformations in soil, water, atmosphere and their interfaces. Abiotic and biotic fluxes and transformations are indicated in italics at the corresponding arrows. Potential immobilization processes in soils are listed in the frame-inset (Winkel *et al.*, 2015; reproduced under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

3. Heavy metals removal from soils by phytoremediation

3.1. Soil pollution with heavy metals

Soil pollution with metals from various industrial activities is currently a major environmental problem worldwide. Due to the interactions between the different environmental compartments, soil contaminants are redistributed in all environmental compartments with implications on the good functionality of natural biotic systems and human health. The way in which metals are distributed and the transformations they undergo depend on the physico-chemical properties of the metals and on the environmental parameters. The chemistry of metals in the environment strongly influences their condition and the effects they have on human and ecological receptors (Harmanescu *et al.*, 2011).

The term of heavy metals refers to any metallic chemical element that has a relatively high density and is toxic or poisonous in low concentrations (https://www.lenntech.com). The danger of contamination with heavy metals is increased in the presence of complexing agents, which strongly bind these metals into soluble compounds, which cannot be removed during water treatment. Even if the toxicity of the complexes is lower than that of free metals, by their decomposition during biological processes, the harmful properties of heavy metals can manifest themselves unhindered (Diaconu *et al.*, 2021). As pollutants of the atmosphere, heavy metals through oxides and vapors (which turn into oxides in the atmosphere), pollute especially industrial regions. Heavy metals are also natural compounds in the earth's crust. They cannot be decomposed or destroyed. They reach our body in a very small amount, along with food, drinking water and air (Briffa *et al.*, 2020). In high concentrations they can be toxic. The negative effect of heavy metals can result, for example, through contaminated drinking water (eg lead pipes), high levels of air concentration around the emitting sources, or assimilation through vegetables and fruits. These toxic metals are hazardous so that they persist in the environment. This process requires an increase over time in biological organisms of the substantial concentration in an amount comparable to the concentration of the substance in the environment (Rehman *et al.*, 2017).

3.2. Plants used in the decontamination of soils polluted with heavy metals

The toxicokinetics and toxicodynamics of metals depend on the metal, the shape or compounds of the metal, and the body's ability to regulate or store the metal. In fact, heavy metals have significant toxicity to humans, animals, plants and microorganisms. Moreover, heavy metals are not subject to degradation processes and therefore remain virtually infinite in the environment, although the bioavailability of these chemicals can change considerably depending on their interactions with different soil constituents. Among the most widespread rehabilitation technologies in depollution of soil contaminated with metals is low-cost in situ phytoremediation, an impact technology that has received primary attention in the last fifteen years, due to its ecological nature (Sinha *et al.*, 2013).

Phytoremediation of soils containing heavy metals includes two main processes, presented above (Chamba *et al.*, 2017; Chatterjee *et al.*, 2013):

- phytostabilization, which consists in the immobilization of metals in the soil or roots, thus reducing their mobility and bioavailability.

- phytoextraction, which identifies the process of absorbing contaminants from the soil and translocating them from the roots into the above-ground portion of the plant.

Advantages:

The main advantage of phytoextraction is the environment. Traditional methods, which are used for cleaning soil contaminated with heavy metals disrupt soil structure and reduce soil productivity, while phytoextraction can clean the soil without causing any damage to its quality. Another advantage of phytoextraction is that it is less expensive than any other process.

Disadvantages:

Because this process is controlled by plants, it takes longer than other methods need. To achieve good phytoremediation efficiency, plants should accumulate large amounts of heavy metals, and must produce a large amount of biomass under contamination conditions.

The use of herbaceous hyperaccumulators, selected from woody species that are resistant to metal and have a rapid growth rate, a deep-rooted system, can be beneficial for soil depollution. However, only a few studies are present in the literature, most of them are on the use of poplar and willow for cadmium-contaminated soil. Many plants, such as mustard plants, alpine pennycress and goosefoot have been shown to be successful in hyperaccumulating contaminants to toxic waste sites. Alpine pennycress is a plant that has the role of tolerating and raising toxins from the soil. Alpine pennycress may extract significant amounts of zinc and cadmium from inside the soil. The rate of absorption of alpine pennycress is reduced even further when biodegradable waste is put to polluted soil where it is growing (Takahashi, 2008).

Regardless of the mechanism, the effect has been documented in a number of studies. In 1997, the study used alpine pennycress to remove zinc and cadmium from a heavily contaminated site in Pennsylvania. Lead is one of the heavy metals, around which there is much discussion and it, according to the decision of the international health care organization, is attributed to the first environmental pollution assessment indices (https://www.epa.gov/remedytech). For the decontamination of a soil contaminated with lead, a culture of Brassica juncea can be used with good results in the conditions of administration of synthetic amendments of the EDTA type. The content of lead in root cells is approximately equal to soil lead concentrations. EDTA (ethylene diamino tetraacetic acid) can also improve the accumulation of Cd, Cu, Ni and Zn. For soils contaminated with lead, crops of *Pisum sativum* (peas) and corn (*Zea mays*) can also be used. For soils contaminated with uranium can be used as remedies carboxylic acids like malic acid or citric acid. The last one mentioned is by far the most effective in extracting this metal and to determine its absorption in the tissues of *Brassica juncea* plants (Huang *et al.*, 1997).

The toxicity of these metals as well as of chromium, selenium and arsenic, manifested on plants, can be reduced by chemical reduction reactions and by incorporating elements from the structure of an organic compound. The accumulation of metals in plant leaves is not a homogeneous process. For example, the concentration of Ni in *Thlaspi montanum* plants is variable depending on the type of tissue in which it accumulates. Plants from the Arabidopsis family, *Nicotiana tabacum*, are also used to extract zinc from polluted soil (Dominguez-Solis *et al.*, 2004).

3.3. Removal of some heavy metals from soils by phytoremediation

3.3.1. Cadmium phytoremediation

Cadmium (Cd) is a very hazardous metal that is released into the atmosphere because of anthropogenic activities. Cadmium (Cd) is a trace element that may be harmful to both plants and organisms. Its presence in the food chain is a major source of worry for human health. The majority of cadmium ingestion in the human organism comes from vegetables foods (Filote *et al.*, 2021; Ryan *et al.*, 1982). A large quantity of Cd dust causes numerous organ malfunctions (Mahajan and Kaushal, 2018) (Fig. 3).

Cd accumulation in human bodies causes liver and kidney dysfunction, as well as Itai-Itai bone disease due to skeletal accumulation. As a result, it is important to find an acceptable and suitable solution for removing Cd from the environment. Cadmium-contaminated soil restoration is a serious problem all over the world, and it has grown in importance as a result of Cd transmission at higher trophic levels of the food chain. The elimination of Cd from polluted soil can be accomplished by various physical, chemical, and biological methods as shown in Fig. 4 (Mahajan and Kaushal, 2018).

Because of their capacity to withstand and absorb high quantities of heavy metal from soils, Cd hyperaccumulators are of great interest. Plants of various species have distinct capacities to hyperaccumulate Cd. Because Cd has low affinities with soil ligands due to its mobile nature, it is easily absorbed by roots and transferred to other aerial parts of the plant. Temperature, pH, Cd content in soil, and even concentration of components other than Cd are responsible for Cd remediation by plants. Figure 5 shows the phytoremediation process for Cd elimination in soil plants (Mahajan and Kaushal, 2018).

It has been reported in the literature that plant species classified as Cd hyperaccumulators may collect 100 μg g^{-1} Cd of shoot dry weight (Baker and Brooks, 1989; Mahajan and Kaushal, 2018). As shown in Table 1, a variety of plant species have been documented for Cd hyperaccumulation in soil.

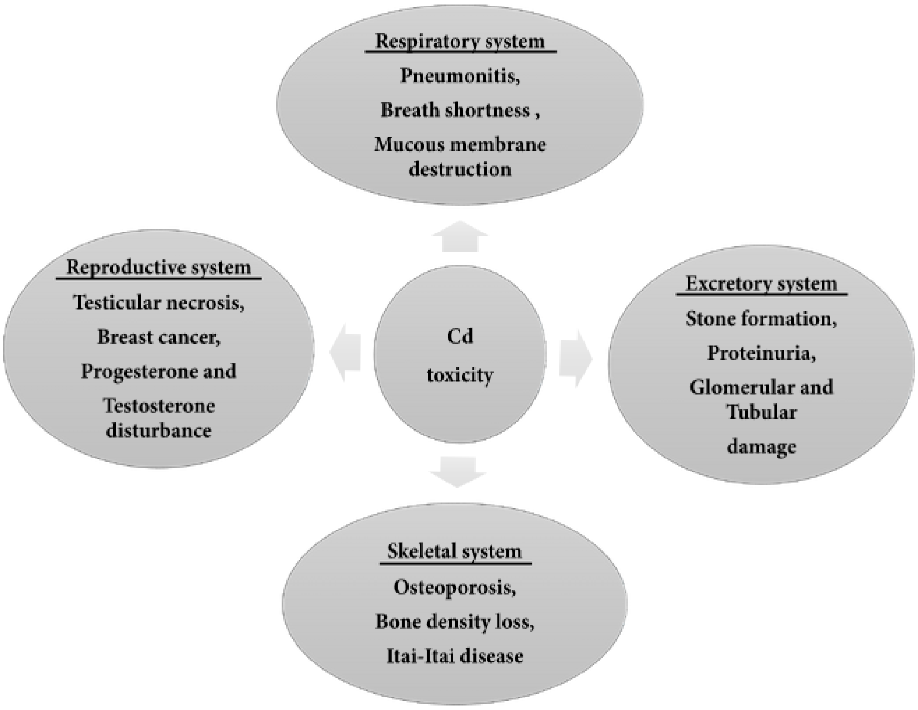

Fig. 3 – Cadmium impact on the human body's various organ systems (Mahajan and Kaushal, 2018; under the reproduced under the terms of the Creative Commons Attribution-NonCommercial-No Derivatives License (CC BY NC ND)).

- **Cd absorption and storage in** *Brassica species*

Cadmium accumulation in plants is influenced by a variety of parameters at both the soil and plant levels. These factors affect Cd mobility and bioavailability in the soil (Zaurov *et al.*, 1999). Soil factors, as well as genotypic differences, have a significant impact on Cd absorption and translocation in plants. The influence of *Brassica species* on soil pH has shown conflicting findings. Growing Brassica species in an andosol with an initial soil pH of 5.5, for example, was observed to lower rhizospheric soil pH. Growing *B. juncea* in acidic soil, on the other hand, considerably raised the rhizospheric soil-solution pH, while growing it in alkaline soil marginally increased the pH; dissolved organic carbon levels increased in the rhizosphere independent of soil type (Kim *et al.*, 2010). This change in soil pH with Brassica species might be attributable to existing heterogeneous soil characteristics, growing circumstances, or species differences.

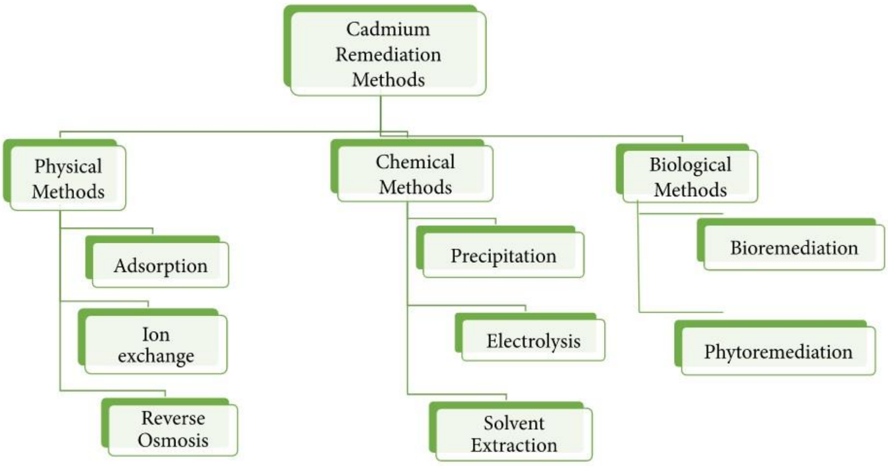

Fig. 4 – Flowchart of various methods used in Cd remediation (Mahajan and Kaushal, 2018; under the reproduced under the terms of the Creative Commons Attribution-NonCommercial-No Derivatives License (CC BY NC ND)).

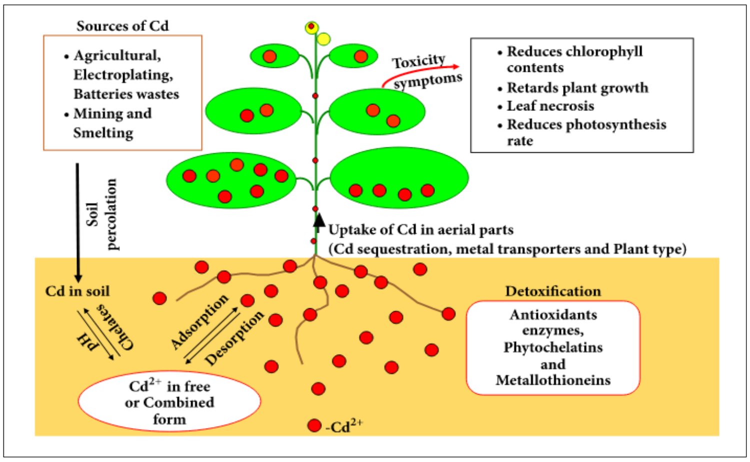

Fig. 5 – Phytoremediation mechanism of Cd adopted by soil plants (Mahajan and Kaushal, 2018; reproduced under the terms of the Creative Commons Attribution-NonCommercial-No Derivatives License (CC BY NC ND)).

Cd absorption depends on Cd speciation in the rhizospheric soil and Brassica species (*i.e.*, Cd-tolerant and Cd-sensitive species) (Ru *et al.*, 2004). Additionally, Cd absorption in Brassica plants is influenced by root morphology, which includes root length, surface area, root volume, and the quantity of fine root (Xia *et al.*, 2014). Following absorption by the roots, Cd is mostly transferred to the shoots via the xylem by combining with organic acids and amino acids. Depending on the species and cultivars of Brassica, the xylem vessels detected the long-term transport of phytochelatins (PC) in the xylem sap of *B. juncea* under Cd stress, and the PC-Cd complex increased with the rise of Cd treatments (Angelova *et al.*, 2008). The cultivation of cadmium-tolerant *Brassica* varieties has been proposed as one of the techniques for promoting more Cd phytoextraction. Cadmium absorption by Brassica differs between species and varieties of the same species. Under 100 M Cd stress, the black seeded *B. rapa* variety displayed greater growth, biomass, and Cd levels in the roots than the yellow seeded variety, which might be attributed to the higher flavonoid content in the black seeded variety. Under sensing range, cultivation of *B. juncea* ‘Zhucang Huazi' generated more biomass and accumulated more Cd than cultivation of *B. juncea* ‘Chuanyou II-93' (Liu *et al.*, 2014). When compared to sensitive varieties, *B. juncea* ‘Alankar' was more resistant to Cd stress, producing more biomass and better photosynthetic and antioxidant enzyme activities, with lower Cd in the leaves and a higher TI (Gill *et al.*, 2011). *B. juncea* ‘Varuna' is more resistant to Cd stress than *B. juncea* ‘RH30' (Mobin and Khan, 2007). Consequently, species choice is important in improving Cd phytoextraction.

It may be inferred that the Cd absorption and translocation of *Brassica* varieties widely vary, and the selection of tolerant cultivars may be useful for Cd phytoremediation of polluted soils. It has been demonstrated that the application of various low-molecular-weight organic acids improves the effectiveness of Brassica species in metal removal from metal-contaminated soils. Organic acids (*e.g.*, citric and malic acids) enhanced metal absorption by *B. napus* but decreased plant height, dry weight, and seed production relative to the control.

Because EDTA (exogenous ethylenediaminetetraacetic acid) may complex heavy metals, it has been extensively researched for the improvement of metal phytoextraction. When compared to other chelating agents, EDTA was the most efficient, using *Brassica species*, although its detrimental effects should be observed following the addition of EDTA to the soil. Exogenous application of inorganic treatments may limit Cd uptake by *B. chinensis* by altering soil Cd speciation (Feng *et al.*, 2013; Lin and Zhou, 2009; Paul and Chaney, 2017; Tan *et al.*, 2011; Yao *et al.*, 2016). The use of red mud in Cd-contaminated soil decreased Cd concentrations in *B. campestris*, perhaps due to Cd sorption and Ca release by the red mud. Cadmium absorption and translocation in *Brassica* species were similarly influenced by mineral fertilization. The dispersion of Cd and Zn in the growth medium also impacted their absorption by the plants, suggesting that the phytoremediation capacity of *B. juncea* is greater when Cd and Zn are dispersed uniformly throughout the growth medium. Exogenous selenium (Se) treatment reduced Cd concentrations in *B. juncea* tissues while increasing plant growth and antioxidant enzyme activity in Cd-stressed plants.

Chitosan foliar spray decreased Cd concentrations and MDA levels in *B. rapa* shoots while increasing plant growth, photosynthesis, and antioxidant enzyme activities (Zong *et al.*, 2017). *Brassica* species' metal tolerance ability also might be improved by genetic manipulation. For example, the incorporation of highly metal-tolerant cell lines from *B. juncea* into new *B. juncea* somaclones has improved metal tolerance. The up-regulated genes in *B. juncea* under Cd stress have been identified, and the incorporation of these genes in Cd-sensitive plants could improve Cd resistance. The phytoremediation of metals such as Cd from polluted soil is anticipated to lower metal concentrations in the soil and hence the related environmental danger.

Metals are hidden in plant biomass, resulting in a new environmental danger caused by surface biomass. As a result, proper post-processing of the biomass is required to minimize secondary contamination and environmental concerns. Some writers proposed that following pyrolysis, biomass derived from polluted areas may be used for dye adsorption. Overall, the biomass of *Brassica* produced from Cd-contaminated soil may be processed to minimize secondary contamination, and the energy and material acquired from this process might be used in other ways (Lehmann and Rebele, 2004).

- **Cd absorption and storage in other species of plants**

In the early 1990s, *Thlaspi caerulescens* was discovered to have Cd hyperaccumulation. *T. caerulescens* was considerably more tolerant to Cd, with poisoning signs occurring at concentration of 200 um. For transport of Cd from liquid mixture to higher parts, as well as its concentration in *T. caerulescens* shoots, was exceptionally high (Brown *et al.*, 1994). *T. caerulescens* plant tissue cultivation also demonstrated Cd remediation derived of its adsorption process.

Calamagrostis epigejos is a fast-growing plant who could survive inclement weather and thrives in floodplains with swampy soils. It had been chosen for its improved stability to toxic substances and investigated for Cd absorption and discovered little root to shoot transfer, implying that the plant can provide more ecological value in terms of phytostabilization than phytoextraction (Lehmann and Rebele, 2004).

Solanum nigrum has been observed to accumulate significant concentrations of Cd, as well as Cu and Zn. Another plant, *Sedum alfredii* had a high potential for Cd removal. It was discovered that when exposed to Zn concentrations, the amount of Cd increases. With increasing Cd and Zn concentrations, the quantity of both metals increases in the leaves and stems. This finding demonstrated that *S. alfredii* functions as a hyperaccumulator of both Cd and Zn. Some other species, *Sedum plumbizincicola*, has been found to increase Cd and Zn concentrations with the addition of EDTA via decreasing ion mobility in polluted soil (Li *et al.*, 2018). Swinecress and edible hibiscus have been recently identified plants for Cd hyperaccumulation in hydroponics. TF was found to be greater than BCF in *C. didymus* (Sidhu *et al.*, 2017). As a result, *C.*

didymus and *A. manihot* can be utilized as Cd hyperaccumulators to remove Cd from real-world locations.

3.3.2. Arsenic phytoremediation

Because arsenic is poisonous and carcinogenic, soil pollution with this inorganic pollutant seem to be a major ecological, agronomic and safety issue. The world health organization states that, people all throughout the world may be chronically exposed to arsenic in drinking water at levels over the safety threshold. Several human activities, for example industrial processes and agricultural usage of As-based insecticides, have resulted in higher As concentrations in soil (Hughes *et al.*, 1998). The inorganic oxyanions of arsenite – As III (hazardous and mobile in polluted soils) and arsenate – As V (thought to be less harmful), both of which are extremely soluble in water, are the most common forms of arsenic in the environment.

Traditional arsenic removal procedures have low percentage removal, high - cost, and significant energy needs. Biological techniques, particularly phytoremediation, have the potential to be cost-effective in safeguarding human health and the environment, against hazardous metal pollution. The Chinese brake fern (*P. vittata*) grows in humid regions like the tropics and has an extraordinary capacity to hyperaccumulate very high amounts of As. consequently, *P. vittata* might be quite beneficial for As phytoremediation in such areas. In contrast to other land plants, *P. vittata* accumulates As in the leaf area, where it is transferred from the rhizome (Zhao *et al*., 2003). Because this species has a very distinct As hyperaccumulation mechanism, it might be an excellent source of genes for biotechnologically enhancing As hyperaccumulation in other plant species. Even though *P. vittata* has shown significant promise for As extraction from soil in field tests, there are numerous constraints to applying it for As remediation in the field. This hyperaccumulating Fern's molecular method of As detoxification is mainly unclear, and its perpetual development is limited to tropic areas. Additionally, the plant may be intrusive, and its introduction into non-native regions should be carefully considered in terms of potential ecological implications. Figure 6 displays various approaches of As phytoremediation by hyperaccumulators and accumulators/tolerators and the underlying mechanism of As uptake, transport and detoxification (Srivastava *et al.*, 2021).

The development of genetically-based, cost-effective, accessible techniques for cleaning up has been a frequently researched alternative to *P. vittata*. As contaminated area can be transferred to any species of plants that has evolved to different geoclimatic zones. Depending on the intended goal, several genetic modification techniques may be explored, such as enhanced sensitivity to polluted ecosystem, enhanced assimilation for phytoremediation, decreased absorption for improved consumer safety (Tripathi *et al.*, 2007; Zhao *et al.*, 2009).

Plants and mutated cells with high As tolerance of two bacterial genes resulted in As accumulation in the shoots. The arsenate reductase (arsC) gene from *E. coli* was produced in leaves through a synthesized soybean. Furthermore, the E. coli - glutamylcysteine synthatase, y-ECS, was generated through both the rhizomes and the stems (Dhankher *et al.*, 2002; Roy *et al.*, 2015). It has been demonstrated that plants growing in As-polluted soils are usually colonized by mycorrhizal fungi, and that the arbuscular mycorrhizal fungi (AMF) hosted by the plant improve As tolerance, primarily by restricting As accumulation: this has been noticed in several species, such as *Holcus lanatus L., Medicago truncatula Gaertn* etc.

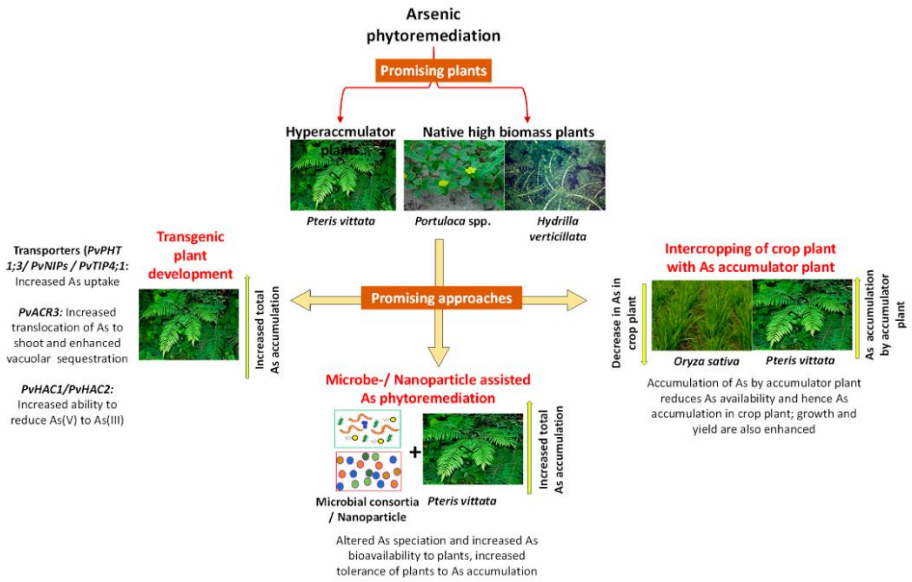

Fig. 6 – Various approaches to arsenic phytoremediation: use of hyperaccumulator plants or native high biomass and bioenergy plants; intercropping of arsenic accumulator plant with a crop plant for reduced arsenic toxicity to crop plant; microbe- or nanoparticle-assisted arsenic phytoremediation and the use of genetic engineering approaches to enhance phytoremediation potential of plants (Srivastava *et al*., 2021; reproduced under the terms of the Creative Commons Attribution-NonCommercial-No Derivatives License (CC BY NC ND)).

Rice is perhaps the most essential meal for more than half of the world's population, and it is frequently cultivated in places where As pollution is common. Between 30–50% of Bangladesh and India's rice crop fields are treated with As-contaminated groundwater. Rice fields accumulates large amounts of As III, which produce a decreasing habitat. Significantly greater levels of total As were discovered in rice cultivated in the United States. Large As levels in straw may be harmful to cattle's health and may increase As exposure in people via the plant–animal-human route (Marin *et al.*, 1993; Meharg and Hartley-Whitaker, 2002; Zhu *et al.*, 2008).

It is feasible to create crops with improved resistance and reduced absorption of Arsenic for human consumption using a biotechnological method. There are numerous choices that might be quite beneficial in this attempt. Reduced As buildup in terrestrial structures and seeds may be accomplished by increasing As V to As III reduction in roots and increasing As III enzymes in rhizome solely via root-specific promoters. Increased PC generation in roots may limit As movement to shoots via As III-PC complex formation and vacuolar sequestration in roots. Moreover, As V absorption in roots might be inhibited by altering PHTs that have a greater affinity for As V than phosphate.

Trying new phytoremediation techniques and reducing As contamination in the food chain will need a thorough knowledge of As absorption, filtration, and sequestration in plants and microorganisms, including a better understanding of the genetic variants connections associated in As metabolism (Catarecha *et al.*, 2007; Rosen, 2002).

3.3.3. Mercury phytoremediation

Mercury is naturally present in the environment, but it is well fixed in minerals and does not represent a substantial concern. The issue occurs as a result of human actions that result in the release of enormous amounts of mercury into the environment, where it can then move freely for thousands of years. The major source of worry is the existence of mercury in water and soil where it is in an extroverted form. So far, human usage of mercury has resulted in the release of hundreds of thousands of tons of mercury into the environment. At the moment, quantities of the chemical in the atmosphere are up to 500% greater than normal levels. Mercury concentrations in the seas are roughly 200 percent greater than natural levels (EEA, 2018).

Because of the bioaccumulative nature of the highly hazardous methyl Hg molecule in food chains and the environment, decontamination of the soil is a global problem. At the moment, heavy metal damaged soils are largely remedied using different approaches. In comparison to conventional remediation mechanisms, phytoremediation offers the benefits of minimal investment, easy operation, in-situ remediation, and environmentally safe engineering (Lambrechts *et al.*, 2011; Sinha *et al.*, 2013).

In the case of Hg-contaminated soils, phytoextraction is a possibility, and Hg hyperaccumulators must be identified. Because of the time and economic expense of extracting Hg from polluted soils, recurrent species can be used for restoration. Despite the fact that only a few species (for example fringe centipede grass and *Erato polymnioides*) are categorized as “potential Hg hyperaccumulators,” (Chamba *et al.*, 2017; Qian *et al.*, 2018) no Hg hyperaccumulator has been identified yet. Table 2 shows some research in which mercury concentrations were higher in stems than in rhizome.

Table 2

Plants used for mercury elimination from soil by phytoremediation

<table>
<tr><th colspan="2">Plant type</th><th>Reference</th></tr>
<tr><td>A. ageratoides
B. ampestris
B. officinalis
C. acuminatus
C. barometz
C. maxim
E. ciliaris
F. multiflora</td><td>G. bicolor
H. crdata
I. sonchifolia
M. cordata
O. brachyotus
P. nummularia
P. oleracea
S. scandens</td><td>Qian et al., 2018</td></tr>
<tr><td colspan="2">A.argyi
C. macrophyllum
I. denticulate
X. sibiricum patrin ex wider</td><td>Xun et al., 2017</td></tr>
<tr><td colspan="2">A. compressus</td><td>Chamba et al., 2017</td></tr>
<tr><td colspan="2">B. juncea</td><td>Cassina et al., 2012</td></tr>
<tr><td colspan="2">C. annuum
Clidemia sp.
I. edulis
J. curcas
P. niruri</td><td>Marrugo-Negrete et al., 2016a, 2016b</td></tr>
<tr><td colspan="2">C. eragrostis
D. stromonium
P. lapathifolia
P. coloratum
P. australis</td><td>Mbaga et al., 2019</td></tr>
<tr><td colspan="2">C. glaucum</td><td>Wang et al., 2011</td></tr>
</table>

Plant shoots' high biomass is advantageous to this process, and plant stems must be eliminated on a frequent basis during the phytoremediation process. When several experimental plant species flourished in Hg-contaminated soils, the biomass of their roots and shoots reduced due to toxicity. *Jatropha curcas*, often recognized as the physic nut is a plant in the *Euphorbiaceae* family that has been identified as a fuel alternative. The species has been discovered in South America in gold mining regions where Hg is used in the amalgamation process and is present in high amounts in the soil. The *J. curcas* cultivar has been found to aid in the restoration of degraded and polluted soil.

Several researchers have conducted a study in which the biomass accumulation of *J. curcas* was used to determine its growth behavior. As the Hg content raised, the biomass accumulation dropped substantially for each exposure interval. Hazardous effects such as chlorosis and necrosis of leaves, on the other hand, were not seen; growth inhibition and loss in biomass output are common occurrences in plants exposed to toxic levels of Hg (Patra and Sharma, 2000). Despite the presence of high levels of Hg in the soil (up to 10 μg g^{-1}), *J. curcas* plants grew and developed. Even though Hg levels accumulated by the plant's aerial parts were rather modest, *J. curcas* is an excellent candidate for extraction of mercury from soil since it is simple to grow, manage and contributes to soil preservation and recovery. The forms of bioavailable Hg in soils could be changed under diverse circumstances (Fig. 7). Rhizosphere microorganisms in Hg-contaminated soils frequently had the likelihood to reduce Hg^{2+} into less toxic volatile Hg° by enzymatic reduction (Kumari *et al.*, 2020; Liu *et al.*, 2020).

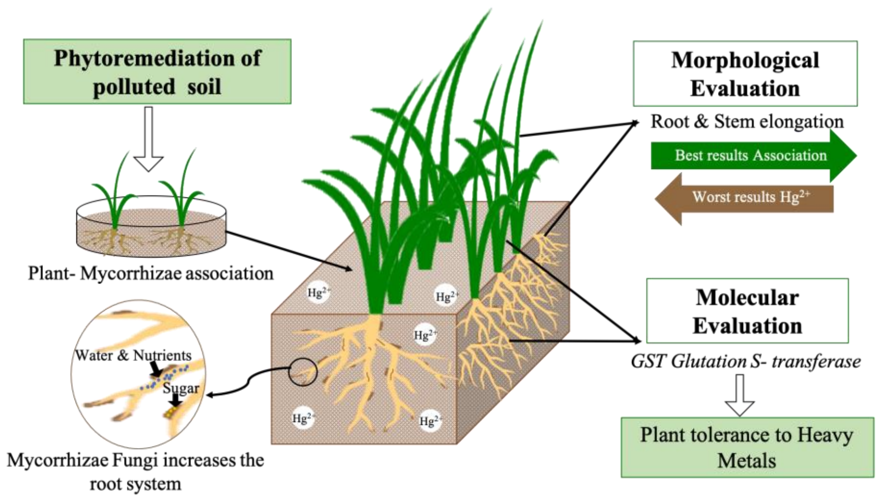

Fig. 7 – Monitoring of plants during phytoremediation of soils polluted with mercury (Leudo *et al.*, 2020; reproduced under the terms of the Creative Commons Attribution-NonCommercial-No Derivatives License (CC BY NC ND))

In certain situations, bacteria, fungus, and other microorganisms residing in the rhizosphere are closely related to plants and may help with metal ion mobilization by increasing the bioavailable percentage. Soil pH is being adjusted, chelators are being released and oxidation and reduction reactions with heavy metal ions are taking place, rhizosphere microbes might convert. Under various circumstances, the forms of bioavailable Hg in soils might be changed. Some rhizosphere bacteria may improve plant tolerance to abiotic stressors by generating solutes such soluble sugars and other suitable solutes (Yang *et al.*, 2009). The majority of prior studies were carried out on a limited scale method, and the complex dynamics of the open field, such as meteorological conditions, geographical conditions, variability of Hg contamination, and so on, could not be replicated. The quantity and frequency, chemical exposure, plant cultivation interval, and other factors must be carefully evaluated for the restoration of a large region of polluted soil. Biotechnology has been beneficial in gaining an excellent knowledge of the morphological and epigenetic processes influencing Se resistance, retention and evaporation in plants, and transgenics with higher levels of these activities show potential for application in phytoremediation and essential nutrients.

3.3.4. Selenium phytoremediation

Selenium is a necessary nutrient for many species, including humans, although it is hazardous in high concentrations. Selenium insufficiency and toxicity are issues that affect people all over the world. Although there is little evidence that Se is required for higher plants, due to its resemblance in comparison to Sulphur, selenium is absorbed rapidly and taken by vegetation through usage of sulphur carriers and metabolic processes. Plants collect Se in all cells, including seeds, and can also release Se into the environment by volatilization. Phytoremediation may take advantage of plants' capacity to collect and volatilize Se (Dhillon and Banuelos, 2017).

The resulting amino acids are not specifically incorporated into enzymes and is considered to be the cause of Se toxicity. Till now, studies on genetic engineering of Se metabolism have concentrated on selenate reduction, the inhibition of SeCys incorporation into proteins, and Se volatilization. Inactivation of ATP sulfurylase (APS1) in *B. juncea* to alter the first stage of Se metabolism was one of the earliest initiatives in genetic engineering to increase phytoremediation effectiveness, *e.g*. selenate reduction (Pilon-Smits *et al.*, 1999). APS1 amplification resulted in enhanced selenate reduction in planta and a two–threefold increase in Se accumulation in shoots and roots. APS plants were also more resistant to Se. Some other effective technique for avoiding SeCys incorporation into protein has been the inclusion of a SeCys methyltransferase (SMT). The most common type of Se collected in hyperaccumulator plants is SeMeSeCys. Rockcress and Indian mustard increased Se resistance, collection, and volatilization in both species significantly (LeDuc *et al.*, 2004).

Because elemental selenium is not mobile, it is generally safe. As a result, the overall soil selenium content is not a problem in remediation. The concentration of transportable selenium, generally selenate, determines whether or not intervention is required. The evolution of mobile plants that accumulate or volatilize selenium receive what is extractable, and Se concentration is the measure of success (Fig. 8). Chelators were not required since it is assumed that mobile, extractable selenium is what is damaging.

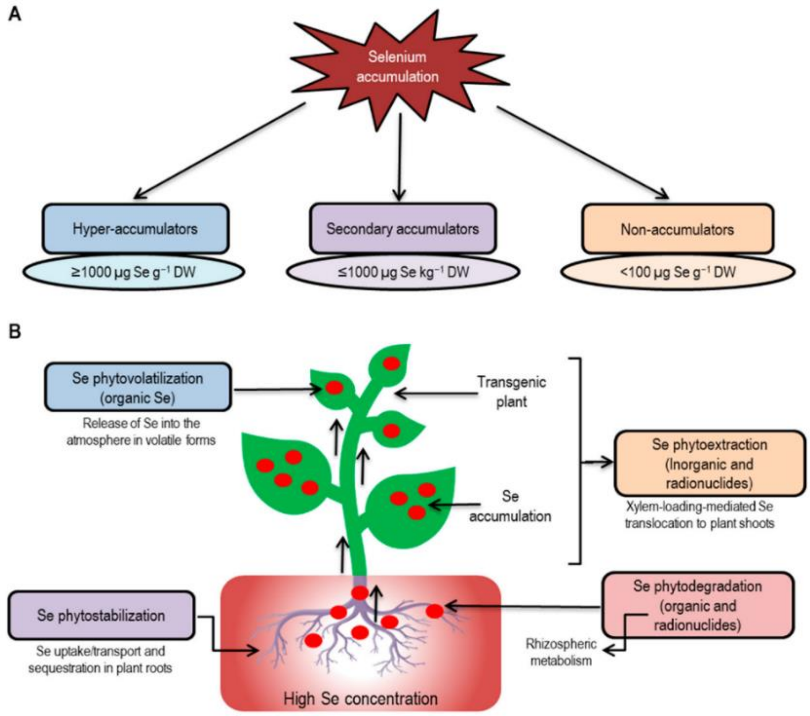

Fig. 8 – Phytoremediation of Se-polluted environments. (**A**) plants types according to Se accumulation in biomass), (**B**) phytoremediation processes of Se polluted environments. Various phytotechnologies can be used to remediate Se contaminants by accumulating them at large amounts in various parts of plants, especially transgenic plants can provide safe and quick Se phytoremediation to avoid the adverse environmental impact and toxicity to consumers. The main bioavailable form of Se in soils is SeO_4^{2-}. After uptaken up by plants, SeO_4^{2-} can be accumulated in the root and easily translocated to the shoots. Inorganic SeO_4^{2-} can be integrated into Se-Cys and other forms of organic Se. A few types of organic Se are volatile and can be released by the plants into the atmosphere as a harmless gas. Selenium accumulation and volatilization may be used to produce Se-biofortified crops and in phytoremediation, respectively (Hasanuzzaman *et al.*, 2020; reproduced under the terms of the Creative Commons Attribution-NonCommercial-No Derivatives License (CC BY NC ND)).

Early phytoaccumulation research aimed to discover high biomass-producing plants capable of selenium hyperaccumulation. Members of the *Brassicaceae* family, particularly Indian mustard and canola, have demonstrated a high capacity for selenium absorption. Exceptional terrestrial Brassicaceae plants that Se volatilize include cabbage, broccoli, cauliflower, and

Indian/Chinese mustards. Certain crops, such as rice and hybrid poplars, have been found to have significant selenium volatilization rates.

There have been few investigations on the rhizofiltration of Se by wetland plants. Duckweed (*Lemna minor* L.), a floating aquatic plant, was demonstrated in the lab to collect Se amounts equivalent to other known Se accumulating plants (Zayed *et al.*, 1998). A comparable research found *Eichhornia crassipes* to be a moderate Se accumulator. Each of these plants are frequently utilized for wastewater treatment in artificial wetlands (Zhu *et al.*, 1999).

4. Conclusions

Phytoremediation of soils polluted by heavy metals appears to be an alternative route that is less expensive, widespread, with less negative impacts on soil environment, and adequate for soil rehabilitation, compared to the physicochemical processes, which are costly and often destructive processes. Despite their definite advantages and their growing interest in the context of the protection of soil resources, current phytoremediation methods are still applied to a lesser extent, and often only in particular cases, and this especially since they do not generally allow to obtain satisfactory soil treatment in a timely manner.

Some plants have the potential to absorb toxic metals up to several percent of their biomass from dried shoots, these plants are known as hyperaccumulators. New plant species suitable for eliminating heavy metals from polluted soil should be found. Phytoextraction by hyperaccumulative plants and phytoextraction assisted by chelating agents often can enhance the soil remediation to an acceptable level.

There is therefore today a recurring need for new phytoremediation solutions, which make it possible to obtain satisfactory pollution control, for a wide range of metals, and which at the same time ensure simplified management of pollutants, in association with the costs of acceptable operation and with reasonable processing times.

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ANALIZA FITOREMEDIERII CA TEHNOLOGIE PROMIȚĂTOARE PENTRU DEPOLUAREA MEDIULUI

(Rezumat)

Lucrarea reprezintă o analiză succintă a procesului de fitoremediere a solurilor poluate cu metale grele. Sunt prezentate o serie de aspecte de bază privind poluarea solurilor cu metale grele și consecințele acestui fenomen. De asemenea, sunt descrise mecanismele prin care unele plante absorb ionii de metale grele, sunt prezentate o serie de studii în care diferite categorii de plante au fost folosite ca hiperacumulatori pentru îndepărtarea metalelor grele din sol și posibilități de intensificare a fitoremedierii. Pe baza informațiilor din literatură, a fost explorată îndepărtarea ionilor de metale grele (sau asociate cu acest grup de elemente chimice) din sol, precum cadmiul, arsenul, mercurul, seleniul. Analiza prezentată în lucrare ar putea susține și justifica aplicarea fitoremedierii ca alternativă pentru remedierea mediului în condiții prietenoase, cu costuri reduse și fără impacturi negative suplimentare asupra mediului.