A REVIEW OF PHYTOREMEDIATION STRATEGIES FOR SOILS POLLUTED WITH HEAVY METALS

GEORGIANA PLOPEANU, MARIANA MARINESCU, EUGENIA GAMENT, NICOLETA VRINCEANU, VERA CARABULEA

Keywords: phytoremediation, heavy metals, polluted soils.

ABSTRACT

Mining operations, industrial production and domestic and agricultural use of metal and metal containing compound have resulted in the release of toxic metals into the environment. Heavy metal pollution has serious implications for the human health and the environment. Since heavy metals are nonbiodegradable, they accumulate in the environment and subsequently contaminate the food chain. Few heavy metals are toxic and lethal in trace concentrations and can be teratogenic, mutagenic, endocrine disruptors while others can cause behavioral and neurological disorders among infants and children. Therefore, remediation of heavy metals contaminated soil could be the only effective option to reduce the negative effects on ecosystem health. Different physical and chemical methods used for this purpose suffer from serious limitations like high cost, intensive labor, alteration of soil properties and disturbance of soil native microorganisms. Phytoremediation is the use of plants and associated soil microbes to reduce the concentrations or toxic effects of contaminants in the environments. In this article are reviewed the stratagies in the phytoremediation for remediating heavy metals from polluted soils. Phytoextraction and phytostabilization are the most promising and alternative methods for soil reclamation.

INTRODUCTION

Environmental protection implies the qualitative and quantitative protection of the environment elements: water, air and soil. It aims to protect people and the natural environment against harmful and stressful influences.

In terms of soil pollution, it consists in those actions that can cause the disruption of the normal functioning of the soil as a living environment (especially for higher plants) within different natural or anthropogenic ecosystems, causing the occurrence of harmful phenomena in the soil, which negatively affects the maintenance or stability of soil bioproductive capacity, the synthetic expression of the resulting effect of these negative characteristics being the qualitative and / or quantitative decrease of the vegetal production or the increase of the expenditures necessary to maintain the vegetal production at the quantitative or qualitative parameters prior to the soil pollution (Răuţă and Cârstea , 1983).

Heavy metal polluted soil is a serious concern in most countries. Ecological rehabilitation of the polluted soils in the industrial, agricultural, and urban territories is a great challenge in recent decades due to anthropogenic activities (Mahar et al., 2016).

Regarding their role in biological systems, heavy metals are classified as essential and non-essential. Essential heavy metals are those, which are needed by living organisms in minute quantities for vital physiological and biochemical functions. Examples of essential heavy metals are Fe, Mn, Cu, Zn, and Ni. Non-essential heavy metals are those, which are not needed by living organisms for any physiological and biochemical functions. Examples of nonessential heavy metals are Cd, Pb, As, Hg, and Cr. Heavy metal concentrations beyond threshold limits have adverse health effects because they interfere with the normal functioning of living systems.

MATERIAL AND METHOD. RESULTS.

Remediation of soils polluted with heavy metals in high concentrations often requires excavation and removal of soil, expensive site restoration (Glick, 2003). Two distinct soil remediation classes can be clearly defined: in-situ and ex-situ, the latter also having two options: spot intervention (but collecting and treating polluted soil) or out of site.

The in-situ cleaning method does not require excavation of contaminated soil and is often preferred because it is less expensive. But it generally takes more time for the effect of treatment to reach the desired limits and is less certain about the uniformity of treatment due to the inherent variability of soil characteristics and the difficulty of monitoring the progress. On the other hand, the excavation of the contaminated sites, required in the ex situ approach, and the treatment of the material on site (ex-situ, spot intervention) or its transport to a treatment site (ex situ, out of site) may become more complicated more expensive especially when large areas are affected (Fuentes et al., 2002).

The stabilization is applied to restrict the pollutants movement in the soil, and it is possible to "stabilize" them by incorporating them into a solid mass using inorganic agents such as cement, lime, gypsum, silicates or organic substances such as epoxide resins, polyesters, asphalt, polyethylene, polyethylene-butadiene and formaldehyde urea to bind contaminants in soil (Bridges, 1991). Stabilization is a technique used to immobilize soil contaminants by reducing their solubility. Also by solubilization the possibility of spreading dust contaminants is reduced. Barriers to limit the spread of soil pollutants can be built using well-known civil engineering techniques such as pillars and cement. A high-pressure water jet or high-pressure cutting technique has been developed to cut a crack into the soil where a barrier is inserted to an impermeable layer, thus sealing the polluted area. For the separation of metals from soils, physical and mechanical methods can also be used. Flotation is a physical technique used to separate metals from ores. In the treatment of polluted soils it is necessary to be suspended in water to which floating agents are added. The suspension is then aerated and the small bubbles formed take up contaminants from the foam. Contaminants should be small enough to be able to form an emulsion (Bridges, 1991).

In-situ biological methods include: bioventilation (a technology that stimulates microorganisms naturally present in soil to degrade some soil pollutants by providing the necessary oxygen), phytoremediation (a technique that uses plants to remove, transfer, stabilize, or destroy contaminants in the soil), the use of agricultural land (contaminated soils are mixed with soil amendments such as agents for reducing apparent density and nutrients, are applied to clean agricultural land and incorporated into the soil, and soil tillage are performed periodically to improve aeration and homogenization), natural attenuation (a passive bioremediation process) and improved bioremediation (also known as biostimulation involves the application of selected microorganisms, nutrients, oxygen donors, so on to accelerate natural biodegradation processes).

Ex-situ methods include: biopiles (engineering systems in which polluted soil is combined with amendments, deposited in a compost pile and closed for treatment), bioreactors (engineering systems where contaminants are degraded in a specific environment by microorganisms), composting (a biologically controlled process by which organic soil contaminants are converted by microorganisms under aerobic and anaerobic conditions into stabilized non-harmful by-products) and the use of agricultural land.

A method of great interest in the UK for the sustainable development and safe improvement of contaminated land is the uncontaminated soil cover, with very different thicknesses and types. Cultivation with perennial herbs can serve to evaluate the effectiveness of this method, following both the plant growth potential and the degree of heavy metal loading.

In accordance with the main mechanisms involved in the process, phytoremediation can be classified as follows:

- **Rhizophiltration** - the absorption, concentration and precipitation of heavy metals by the plants roots;
- **Phytoextraction** - a technique that involves the entire organism of the plant in the process of taking soil contaminants;
- **Phytotransformation** - degradation of complex organic molecules into simple molecules and incorporation of these molecules into plant tissues;
- **Phytostimulation or Plant-assisted bioremediation** - stimulates bacterial and fungi degradation by exudate / enzyme release in the root area (rhizosphere);
- **Phytostabilization** - involves the absorption and precipitation of contaminants, especially of metals, by the plants, the reduction of their mobility and the prevention of washing to ground water, or air or entering the food chain (Ali et al., 2013).

Of these methods for the soils polluted treatment with heavy metals, only phyto-extraction and phytostabilization can be applied. Phytoextraction refers to a number of technologies for water and soil decontamination based on plant use. Different phytoremediation applications can be classified based on the behavior of different types of pollutants: extraction, degradation, storage, or a combination of all three. Phytoremediation techniques based on pollutant extraction are: soil extraction and water rhizophiltration (Magistrelli et al., 2002).

Phytoremediation is the process that introduces plants into the environment and favors assimilation of contaminants into their roots and leaves. It has been recognized and demonstrated by humans for more than 300 years, but scientific studies have been undertaken only since the 1980s (Lasat, 2000).

In a 1998 EU report, it is estimated that there are 1,400,000 contaminated sites in Europe, this being the problem size. The authors of this report make a review of methods for removing metals and metalloids from soil using different plants. These methods are phytoextraction and phytoolatilization (Sarwar et al., 2017), depending on the removed element.

The efficiency of phytoextraction is the product of the equation:

Biomass × element concentration in biomass.

As in any equation, both factors are important; the element's concentration in biomass is obviously decisive. Thus, it has been found that even if the annual biomass of a plant increases from 2 to 20 t/ha, the efficiency of removing an element having a concentration of less than 1000 mg/kg of dry plant is practically not high. It therefore appears that the efficiency-enhancing strategy consists in increasing the element concentration in plant, a process that can be achieved by agronomic measures.

In general, there are two ways to obtain a high-strength biomass, namely:

- increase of biomass of natural hyperaccumulators;
- increasing the yield of metal retention on non-accumulating plant species under normal conditions, by chemicals addition.

As any new approach, phytoremediation advocates the implementation of phytoextraction as a polluting soil polluting technology, with the benefit of low cost (compared to classical remediation) and aesthetic aspects that allow application of phytoremediation.

Wan et al., 2016 conducted a study on phytoremediation costs through a two-year project on a soil contaminated with arsenic, cadmium and lead. The results showed a significant decrease in heavy metals in the soil. The costs and benefits of this project have been calculated. The total cost of phytoremediation was 75,375.2 USD/hm^2 or 37.7 USD/m^3, the initial capital and operating costs accounting for 46.02% and 53.98%, respectively. Infrastructure costs (ie roads, bridges and drainage) and fertilizers were highest, mainly due to low economic development and serious contamination. The phytoremediation cost was lower than the reported values of other remediation technologies. Methods have been suggested to improve the level of phytoremediation mechanization and prevent unforeseen situations to reduce subsequent costs. According to the calculations and taking into account the environmental pollution losses, the benefits of phytoremediation will reimburse the project costs in less than seven years.

Among the potential barriers to widespread application of phytoremediation technologies, we mention:

- ♣ the necessary time for phytoremediation;
- ♣ the level of heavy metals tolerated by the plants used;
- ♣ through these technologies only the bio-available fractions of metals in the soil are treated.

In contrast to methods of immobilizing heavy metals in soil by treating different materials, phytoextraction is based on the availability of plant metals. The economic aspect of phytoremediation is generally favorable, but it can be improved.

One way to improve the economy of the process is to cultivate plants that induce value by using biomass (eg, use of coriander, lavender and other plants that can bring income from their use after harvesting). Alternatively, combustion reduces the volume of contaminated biomass, from the resulting ash being able to recover the metals retained by the plants.

In the phytoremediation strategy there are a number of factors that need to be taken into consideration: soil type and degree of soil pollution, plant selection, treatment mode, agronomic techniques used, metal retention rate, sweating speed, soil clearance time, harvesting plant, residues, how to treat the contaminated plant. So, the success of phytoremediation depends on many biological, physical and chemical factors. Hence, the need for collaboration between many categories of specialists: biologists, agronomists, soil science specialists, chemists, physicists. The creation of interdisciplinary projects and their financing is a necessity in the development of phytoremediation projects, this being the difference between phytoremediation research conducted in the USA and those conducted in Europe. Unlike the US, where phytoremediation research has been generally applicable, studies in Europe have generally been fundamental exploratory studies. In Europe, concerns about soil phytoremediation are found in the COST Action 837 actions, which is the only European initiative in the field at the end of 1998. It should be noted that this is the only program that has brought together specialty researchers. What is important to note is that a number of phytoremediation projects have been carried out for a period of 10 years, during which funding has been provided for the 14-15 units involved in these projects. Phytoremediation of soil contaminated with heavy metals involves either the extraction or inactivation of these metals in the soil. In the case of metals such as lead, which has a high immobility in soil, its extraction is limited by solubility and diffusion to the root surface (Lombi et al., 2001).

The first experiences in the field began with the study of metal and selenium phytoremediation (Banuelos et al., 1993; McGrath et al., 1993).

In the study achieved by Willscher et al., 2017 experiments were carried out to investigate phytoextraction and behavior during the development of the *Helianthus tuberosus* plant at different soil pH values and different concentrations of heavy metals. The purpose of the paper was to study the growth and accumulation of heavy metals by *H. tuberosus* under various conditions for further optimization of growth conditions and for further improvement of field production and phytoremediation.

Phytostabilization

This technique can be used to restore the vegetal mat in places where natural vegetation is lacking due to high concentrations of heavy metals in the surface horizon or due to physical degradation of surface materials. Tolerant species can be used to restore the vegetation of the site, while decreasing the potential for migrating contaminants under the influence of wind and water erosion and leaching to groundwater (erosion and leaching are frequent on non vegetation land). Plants suitable for phytostabilization in a specific place must:

- have high tolerance for the contaminant concerned;

- ensure a high production of radish biomass capable of immobilisation; - these contaminants by take-up, precipitation or reduction; - to keep the contaminants in the root against the transfer into stems and leaves. Phytostabilization ensures risk reduction by stabilizing contaminants located near the surface of the soil. This result is provided by the plant secretion of compounds that affect the pH of the soil and form metallic complexes of low solubility. Additionally, plants help reduce soil erosion and reduce leaching by increasing evapotranspiration (Ma and Kingscott, 1997; Mahar et al., 2016).

Rhizofiltration

Rhizofiltration is a method of phytoremediation that uses the plants roots together with the microorganisms in their rhizosphere to repair soils polluted with organic pollutants. It is appreciated that the method has a high potential because the root exudates support the growth and metabolic activity of microbial communities of rhizosphere, which leads to the degradation of organic pollutants. The research conducted by Hernandez et al., (2006) showed that *Lolium perenne* plants were more tolerant to the presence of diesel fuel in the soil, but *Trifolium repens* plants showed a higher degradation capacity of hydrocarbons phyitostimulation.

Phytoextraction

Phytoextraction involves the cultivation of one or more hyperaccumulative plant species to create the best conditions for development to provide as much plant mass as possible to extract, accumulate and remove as much metal as possible. The harvested vegetable mass will be subjected to other metal extraction treatments or will be dried and incinerated and the ash deposited in a controlled landfill. Phytoextraction is indicated for removing heavy metals (Pb, Cd, Ni, Cu, Cr, V), excess nutrients (ammonium nitrate) etc. of contaminated soil. Examples of plants used: *Thlaspi* sp*., Brassica* sp*., Alyzssum* sp*., Pelargonium* sp*., Zea mays, Vicia sativa* (Magistrelli et al., 2002).

CONCLUSIONS

It is obvious from the above that phytoremediation is a young process, both scientifically and technologically. In the 1990s there was a concentration of natural or chemically enhanced phytoremediation experiments. Today, it is obvious that the success of these trials has been hampered by the lack of basic knowledge on the requirements of growing hyperaccumulative plants and which chemicals and combinations are optimal to increase the concentration of metals in non-accumulating crops. Also, little is known about the basic mechanisms of plant processing, transport and seizure of the plant tissue. Especially copper and chrome appear to be difficult to fit. There is no hyperaccumulators for copper, and the only way is to use different chemicals. No chromium overcharges have been reported so far, so there was no question of the phytoextraction of this metal.

With regard to improved chemical accumulation, there is more data on the role of complexing substances for releasing lead from contaminated soil, but the exact mechanism of biomass-induced accumulation is still a mystery. Looking at the research achieved already, it can be found that the various researchers have used genuine cocktails of substances, and it is not clear which ones are responsible for the global mechanism of plant picking up and retention. Recent research has focused on how plants can achieve high levels of lead in the root and rhizosphere, as it travels in plant tissues, storage and detoxification mechanisms. Research is far from complete.

ACKNOWLEDGMENT

The financial support provided by ANCSI – project no. PN 16 07 03 06 – Studii privind utilizarea fitoextracţiei ca metodă de remediere a poluării cu metale grele.

BIBLIOGRAPHY

1. **Ali H., Khan E., Sajad M.A,** 2013 – *Phytoremediation of heavy metals—Concepts and applications*. Chemosphere 91 869–881.
2. **Banuelos G.S., et al.,** 1993 – *Boron and selenium removal in boron laden soils by four sprinkler irrigated plant species*, J. Envinronment Quality, 22, 786–792.
3. **Bridges E.M.,** 1991 – *Polluted and contaminated spoils,* University College of Swansen, Singleton Park, United Kingdom.
4. **Fuentes Alicia, Buitrago C., Lodolo Andrea, Miertus S.,** 2002 – *Survey of Soil Remediation Technology*. UNIDO, Trieste.
5. **Glick T., 2003 –** Phytoremediation: synergistic use of plants and bacteria to clean up the environment. Biotechnol. Adv. 21, 383–393.
6. **Hernandez-Allica J., Barrutia O., Epelde L., Blanco F., Becerril M. J., Garbisu C.,** 2006 – *Effect of diesel rhizodegradation on soil microbiological parameters*. 4th International Workshop ''Bioavailability of pollutants and soil remediation'', Sevilla, Spain.
7. **Lasat M.M., 2000** – *Phytoextraction of metals from contaminated sites – a critical review of plant/soil/metal interaction and assessment of pertinent agronomic issues*. J. Hazard Substance Res. 2, 1-25.
8. **Lombi E., Lombi E., Zhao F.J., Dunham S.J., MacGrath S.P., 2001 –** *Phytoremediation of heavy metal-contaminated soils: Natural hyperaccumulation versus chemical enhanced phytoextraction*. J. Environ.Qual. 30, 1919–1926, 2001.
9. **Ma C., Kingscott J.,** 1997 – *Recent developments for in situ treatment of metal contaminated soils,* USA-EPA, Washinton DC 20460.
10. **Magistrelli Paola, Bregante Monica, Stella de Robertis, Martella L., Paganeto Andrea, Qualich Paolo, Racah Jenny, Sora Natali Isabella, Gambale F.,** 2002 – *Decontamination of metal polluted soils by phytoextraction*, Erga edizioni, Genova.
11. **Mahar A., Wang P.,Ali A., Awasthi M.K., Lahori A.H., Wang Q, Li R., Zhang Z.,** 2016 – *Challenges and opportunities in the phytoremediation of heavy metals contaminated soils: A review*. Ecotoxicology and Environmental Safety 126, 111–121.
12. **McGrath S.P., Sidoli C.M.D., Baker A.J.M., Reeves R.D.,** 1993 – *The potential of the use of metal – accumulating plants for the in situ decontamination of metal – polluted soils*. Integrated Soil and sediment Research. A Basis for Proper Protection, Kluwer Academic, Drndrecht, 673–674.
13. **Răuţă C., Cârstea St.,** 1983 – *Prevenirea şi combaterea poluării solului*. Editura Ceres, Bucureşti.
14. **Rehman M.Z., Rizwan M., Ali S., Sik Ok Y., Ishaque W., Saifullah, Nawaz M.F., Akmal F. , Waqar M.,** 2017 – *Remediation of heavy metal contaminated soils by using Solanum nigrum: A review*. Ecotoxicology and Environmental Safety 143, 236–248.
15. **Sarwar N., Imran M., Shaheen M.R., Ishaque W., Kamran M.A., Matloob A., Rehim A., Hussain S.,** 2017 – *Phytoremediation strategies for soils contaminated with heavy metals: Modifications and future perspectives*. Chemosphere 171. 710-721.
16. **Wan X., Lei M., Chen T.,** 2016 – *Cost–benefit calculation of phytoremediation technology for heavymetal-contaminated soil*, Science of the Total Environment 563–564, 796–802.
17. **Willscher S., Jablonski L., Fona Z., Rahmi R., Wittig J.,** 2017 – *Phytoremediation experimentswith Helianthus tuberosus under different pH and heavy metal soil concentrations*, Hydrometallurgy 168, 153–158.