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Selected techniques of soil contaminated phytoremediation with the use of hyperaccumulative plants and trees

MATEUSZ NIEDBAŁA[1]

[1] Department of Technology and Entrepreneurship in Wood Industry, Faculty of Wood Technology/Institute of Wood Sciences and Furniture, Warsaw University of Life Sciences - SGGW, Poland

Abstract: *Selected techniques of soil phytoremediation with the use of hyperaccumulative plants and trees* are intended to outline the possibilities of using various hyperaccumulative plants, including trees, in the phytoremediation process of contaminated soil matrix. The potential of plants that belong to the group of hyperaccumulators is huge, especially in the case of pollution of large areas of agricultural, forest and urban soil. They can be used in the process of cleaning contaminated, industrially degraded areas and supplement the physical and physicochemical methods of remediation of contaminated areas.

Keywords: hyperaccumulative plants, photoremediation, trace elements, heavy metals

INTORDUCTION

Over the last half-century, there has been an increase in the concentration of trace elements in air, water and soil ecosystems. It is one of the most burdensome elements of pollutants in the natural environment, as it also applies to heavy metals and their penetration from the air into the soil, and from the soil matrix into plants and groundwater, which enables the incorporation of trace elements and heavy metals into the food chain. Contaminated areas of air, water and, above all, soil are a threat to the health and life of plants, animals and humans. It is becoming more and more important to improve the methods and techniques of soil remediation used for agricultural crops, forests or anthropogenic soils. For this purpose, research is underway on the use of hyperaccumulative plants in these processes. The permanent nature of heavy metal contamination, the effects of which are often noticed only after several years, is very dangerous. The main anthropogenic sources of heavy metals in the environment are mining and metallurgical, petrochemical and chemical industries, industrial and municipal waste, transport, and fertilizers and pesticides used in agriculture. Among all heavy metals, Cd, Cu, Pb, Hg, Ni and Zn are considered the most dangerous. These elements are among the priority environmental pollutants, threatening human health both due to their toxicological properties and their prevalence.

Scientific research has shown that some species of higher plants have a number of specific features which enable them to transform soil contaminants. In this case, the transformation capacity consists mainly in the uptake, degradation or stabilization of various chemical compounds. As a result of a number of biological, chemical and physical processes taking place in the environment, they influence pollution in such a way as to enable themselves to go through their own life cycle. Some of the plants (including hyperaccumulators) have defense mechanisms that prevent them from concentrating pollutants in their own tissues or immobilizing them in the soil matrix.

One of the most intensively developing remediation techniques is phytoredmediation. Its origins date back to the 1820s. However, its use on an industrial scale began only in the 1980s. Thanks to the first successful attempts to use this method, the foundations for the development of the foundations of environmental biotechnology were laid, which used plants and hyperaccumulative plants in the process of removing trace elements and heavy metals from the soil matrix.

Due to the way plants influence the purification of contaminated soil ecosystems, the following types of activities are distinguished:

phytoextraction, consisting in the use of plants to remove metallic or organic pollutants accumulated in the soil and their accumulation in collectible parts,

phytodegradation, using plants and related microorganisms to decompose organic substances, phytostabilization, using plants to reduce the bioavailability of pollutants present in the environment,

METHODS AND MATERIALS

This study is an overview of the state of the art on test and field research with the use of hyperaccumulative plants and the possibility of their use in phytoremediation techniques. This study focuses mainly on the Polish experience.

RESULTS AND DISCUSSION

The possibility of soil purification is seen in the translocation of heavy metals in the environment, which is based on one of the phytoremediation techniques, i.e. phytoextraction. It is a method used in cleaning the contaminated environment, based on the use of processes developed by higher plants for the uptake of various types of substances through the root system, and then their subsequent transport to the above-ground parts. It is most often expressed by the Ti [%] translocation index, which is calculated from the formula:

$$\mathbf{Ti = Cb / Ck \cdot 100}$$

where:

Cb - metal concentration in the tissues of the aerial organs of the plant, [mg / kg],

Ck - metal concentration in plant root tissues, [mg / kg].

These processes allow the removal of excess harmful substances from the matrix together with the biomass developed in the process of growth. Phytoextraction itself is most often used in the treatment of soil matrix and bottom sediments contaminated with radionuclides (Kondzielski et al., 2003), heavy metals (Kvesitadze et al., 2006) or organic compounds. The technique itself is based on three main stages:

1. Stabilization and immobilization of the harmful factor.
2. Collection of the harmful factor by the root system.
3. Transport (translocation) to above-ground parts.

The uptake process itself is most often expressed by the bioaccumulation factor (also known as the bioconcentration factor - BCF) (Ociepa et al., 2014), which is calculated from the formula:

$$\mathbf{BCF = Cb / Cg}$$

where:

Cb - metal concentration in the above / underground parts of the plant, mg/kg,

Cg - concentration of metal in the soil at the beginning of the process, mg/kg.

It determines the amount of metal that has been assimilated by the plant both in the above-ground and in the underground part. In the case of the conducted experiment, the bioaccumulation coefficient was determined for maize roots and above-ground parts of maize. The process of uptake by plant root systems depends largely on the form of the harmful factor contained in the soil matrix, while the effectiveness of the process depends on the soil pH, microbiological activity and oxidation-reduction relationships (Schnoor and McCutcheon, 2003; Dąbrowska et al., 2014; Malina, 2016). For example, it can be indicated that metals on the surface of iron oxides such as manganese (Mn) or aluminum (Al) or in organic matter, plants absorb much faster and easier (Venditti et al., 2000; Morel, 2006). On the other hand, metals present in various types of complexes are characterized by a much lower bioavailability (Starck et al., 1995)

Table 2. Coefficient of transfer of trace elements in the soil-plant system (Kloke i in., 1984)

Pierwiastek	Współczynnik przenikania
As	0,01-0,1
Be	0,01-0,1
Pb	0,01-0,1
Cd	1-10
Se	0,1-10
Co	0,01-0,1
Sn	0,01-0,1
Cr	0,01-0,1
Zn	1-10
Cu	0,01-0,1
Hg	0,1-1
Ni	0,1-1

FITOEXTRACTION

In the literature on the subject, one can find a division into two types of phytoextraction (Buczkowski et al., 2002; Kacprzak, 2013):

1. Continuous method using hyperaccumulative plants characterized by above-average accumulation of pollutants by selected plant species (*Thlaspi caerulescens, Alyssum bertolonii, Silen ecucubalus*). This method, however, can work only in the matrix of a moderately contaminated with nickel (Ni) and cadmium (Cd). This is due to the fact that the obtained biomass from hyperaccumulators is usually low and the process itself is time-consuming. However, an opportunity for the development of this method is seen in plants with high biomass, which show high tolerance to the contamination of the matrix. Unfortunately, due to the fact that these are most often different varieties of Populus spp. (Poplar), Salix spp. (Willow) or hybrids of Paulownia spp. (*Paulownia spp*.), For technical reasons they are not used on smaller areas.

2. The induced method is based on the addition of chelating compounds to the matrix, such as EDTA (ethylenediaminetetraacetic acid or edetic acid), HEDTA (versenol) or DTPA (pantethin acid), as well as many others, which are to induce an increase in the accumulation of pollutants in plant tissues. The induced method is used in corn (*Zea mays*) sunflower (*Heliantus annus* L.) (Bosiacki, 2013: Bosiacki and Szymanowska, 2013), rapeseed (*Brassica napus*) and red mustard (Brassica juncea), as well as peppercorns (*Lepidium sativa*) (Naser, 2012; Naser, 2013; Szczygłowska, 2015) and rough amaranth (*Amaranthus retroflexus*) (Vollmannova et al., 2015). During the described phytoextraction process, a fairly large waste mass, valuable due to the relatively high content of a number of industrially useful elements, i.e. copper (Cu), nickel (Ni), cobalt (Co) and zinc (Zn), is subject to management. In the process of biomass disposal, there is a preliminary stage consisting of composting, pyrolysis and pressing the biomass (Namieśnik, 2013; Pszczółkowski, 2015). However, composting is the least useful. This is due to the need to store such biomass in hazardous waste landfills, which entails huge costs. Pyrolysis, on the other hand, seems to be the best solution because its product is always valuable

and useful pyrolysis gas, and in turn the biomass is significantly reduced. The utilization methods also include extraction with the use of extractants. However, the cost of extraction is so high that this method seems to be economically unprofitable. It is worth mentioning, however, that of the many methods of soil matrix purification, it is phytoremediation that is the most socially acceptable method, which allows it to be constantly developed. An unquestionable advantage of this method is also a relatively low cost compared to physicochemical and engineering methods (Olszanowski et al., 2001), and additionally, this process leads to an effective cleaning of the contaminated matrix without significantly reducing its biological values. Unfortunately, this process requires a lot of time (on average it takes from 5 to 10 years) and it may take up to 20 years for the complete removal of contamination (Kondzielski et al., 2003). This method, unfortunately, does not stabilize pollutants and external factors may generate them displacing them deep into the soil profile or into the food chain. Substances used in the phytoremediation of heavy metals:

- phosphate compounds (calcium orthophosphate, $NaHPO_4$, K_2HPO_4);
- hydrated iron oxides (waste containing iron oxides);
- clay minerals (natural and artificial aluminosilicates, including zeolites);
- organic substances (slurry, compost, sewage sludge).

PHYTOSTABILIZATION

Another method is phytostabilization, which is based on the ability to retain contamination in the roots and periorospheral perimeter of highly specialized plants. The technique is based on adsorption to the surface of the roots and their subsequent precipitation in the rhizosphere. The root system of plants also prevents the movement of pollutants into the soil matrix and significantly hinders the very movement of soil aggregates. This method is based on the delivery of appropriate chemicals to the soil to reduce the solubility of harmful substances. The substrate prepared in this way is used for the cultivation of appropriate plant species, whose task is to stabilize the entire substrate. However, this method obliges us to control the rhizosphere. It should be borne in mind that root secretions must be controlled, as they may change the concentration of pollutants and lead to their penetration (washing away) into the soil profile. In the studies by Smolińska et al. (2010, 2015) it was found that although plant species belonging to the colonizing contaminated areas are not mycorrhizal species, the development of an appropriate soil structure and improvement of their physicochemical functions depends mainly on symbiotic fungi (Małachowska - Jutsz, 2008).

Table 3. Selected species used in phytostabilization

Metal lub związek	Gatunki roślin
Arsen (As)	*Populus sp.* – topola mieszańcowa (toleruje stężenie metalu do 1250 mg/kg)
Chrom (Cr)	*Brasica juncea* – gorczyca sarepska
Miedź (Cu) Cynk (Zn) Ołów (Pb)	*Festuca rubra* – kostrzewa czerwona *Agrostis sp.*- mietlica *Miscanthus giganteus* Greef et. Deu. – miskant olbrzymi

The advantage of this method is low costs and a positive impact on the area of operation due to the restoration of vegetation. Unfortunately, this method does not reduce the pollution itself in any way. Rather, it should be seen as an interim method. On the other hand, plants remaining in the contaminated area require high fertilization doses due to the high load of contamination contained in the soil matrix. The control of the contaminated object is also becoming a significant problem. The immobilization of the harmful substances themselves also requires continuous control (Singh and Ward, 2004).

PHYTODEGRADATION

This method is often referred to as the phytotransformation process. It is based on the mechanism of decomposition of pollutants in soil due to the metabolic activity of plants. This phenomenon takes place both inside and outside the plant itself. Thanks to the enzymes secreted into the rhizospheric part, there is an increased activity of microorganisms that lead to detoxification. The plant partially absorbs some dissolved substances through its root system, which it builds into its own tissues through transformation. These compounds can also be evaporated by the stomata or broken down into simple inorganic compounds. This method has been used in the treatment of areas contaminated with petroleum derivatives, halogenated substances, explosives and herbicides. This method uses hybrid poplar species (*Populus sp*.) And hybrid willow (Salix sp.) (Chadzinikolau et al. 2011). The ability to accumulate and translocate in the soil matrix and plant system depends primarily on specific environmental factors (Gasco et al., 2004; McBride, 2003). Above all, however, the ability to uptake heavy metals and trace elements depends on the soil conditions, plant species and type of metal. The indicated factors, through interaction and physicochemical relationships, determine how much of a given metal or element will be taken and what will be temporarily deposited in the soil matrix. Immobilization of metals and trace elements occurs as a result of mechanical, physical, exchange and biological sorption (Chaney et al .; 1998; Ociepa et al., 2011). The methods and combinations of fertilization may significantly affect the pH of the soil, sorption capacity, the content of ferric or manganese oxides, the abundance of organic matter, the grain size composition, which in turn significantly affects the absorption of metals and trace elements by plants. As it is commonly known, an organic substance in combination with heavy metals and trace elements forms chelated simple or complex compounds (Terry and Banuelos, 2000). This process allows for the deposition of hazardous substances in the soil matrix and significantly prevents their movement in the soil profile. However, for the binding of heavy metals with soil organic matter, an appropriate number of active binding sites with the medium is indispensable. The proper processes responsible for the binding of metals with humus substance have not been thoroughly known and investigated, therefore the ability to dissolve metals in the soil environment with appropriate parameters can be a good indicator of the ability to uptake them by higher plants (Paul and Clark, 2000; Kabata-Pendias, 2010: Kabata-Pendias and Mukherjee, 2007; Bednarek et al., 2011; Smolińska and Rowe, 2015).

CONCLUSION

The phytoremediation techniques, apart from the obvious benefits of cleaning the environment from harmful substances, also have a number of other advantages. They can be used directly at the point of contamination, even in large areas. An undoubted advantage is also the fact that the pollutants collected by the plant are located in the produced biomass, which as an organic substance can be utilized in the combustion process, where it is completely or significantly degraded. Another very important advantage of phytoremediation is its price competitiveness in relation to industrial methods. It is estimated that the cost of cleaning one cubic meter of soil is from 700 to 960 EUR, while in the case of phytoremediation this price, depending on the metal and its concentration, ranges from 45 to 175 EUR. Moreover, due to the fact that the techniques with the use of plants do not damage the environment, and additionally improve its aesthetic values, they enjoy great social acceptance.

One of the basic limitations is the relatively long waiting time for the desired results. Usually the cleaning process takes two to five years, although in the case of heavy metals, this period can be up to thirty years. The rate of removal of pollutants is influenced, among others, by the length of the growing season, the type of soil, the appropriate amount of nutrients and water, and the resistance of plants to diseases and pests. In addition, plants can clean the substrate only to the depth of penetration through the root system, therefore the contaminants lying below do not undergo phytoremediation. Another obstacle is the unpredictable direction of degradation of the substances absorbed by plants and their too low resistance to high concentrations of toxic compounds that threaten the environment. However, intensive development in the field of environmental biotechnology allows us to hope that in the near future all barriers will be overcome and that phytoremediation will become the main method of cleaning the natural environment.

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Streszczenie: ***Wybrane techniki fitoremediacji gleb z użyciem roślin i drzew hiperakumulatorowych*** ma na celu zarysowanie możliwości wykorzystania różnych roślin hiperakumulatorowych, w tym drzew, w procesie fitoremediacji zanieczyszczonej matrycy glebowej. Potencjał roślin, które należą do grupy hiperakumulatorów jest ogromny szczególnie w przypadku zanieczyszczeń dużych areałów gleb rolniczych, leśnych i urbanoziemnych. Mogą one być wykorzystywane w procesie oczyszczania terenów skażonych, zdegradowanych przemysłowo oraz stanowić uzupełnienie metod fizycznych i fizykochemicznych remediacji skażonych terenów

Słowa kluczowe: rośliny hiperakumulacyjne, fotoremediacja, pierwiastki śladowe, metale ciężkie

Corresponding author:

Mateusz Niedbała
159 Nowourysnowska Street,
02-787 Warszawa, Poland
e-mail: mateusz_niedbala@sggw.edu.pl