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REMOVING HEAVY METALS FROM THE SOIL WITH PHYTOREMEDIATION

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Abstract

In recent years, urbanization, industrialization, population, domestic and industrial productions are increasing. However, organic and inorganic wastes are released into the ecosystem. Mining, urban or industrial solid, gas and liquid waste, pesticide and artificial fertilizer use, paint industry and car exhaust gases cause excessive release of heavy metals in nature. Some activities of heavy metals accumulate in there sulting soil. This accumulation is not just about soil and ecosystem. At the same time affects the food chain also human and animal health. These polluted soils are the most difficult work in terms of environmental engineering. The high costs of clean-up activities of contaminated soil have limited the use of classical disposal technologies limited.
Environmental engineers have also developed phytoremediation and bioremediation techniques to remove these toxic elements. The phytoremediation technique is more preferrable in this field, because of its environmental friendly properties and cost.The ability of hyperacumulator plants to absorb large amounts of toxic elements in their bodies mad ethese plant spreferrable in clean up activities. One of the most important advantages of the phytoremedical technique is that it provides in-situtreatment and it requires very few extra efforts to remove the pollution. In addition, phytoremediation does not harm natural resources. However, the phytoremediation technique can only be use in shallow regions in water, soil and sediment. Another short coming of their technique is that plants can not show their efficacy in very short time in highly polluted areas. For this reason, the phytoremediation technique can only be used at low levels of contaminated sites. In this review, the effects of heavy metals in the soil, the applications of the phytoremediation technique to remove heavy metals from the soil and the prosandcons of these methods have been studied.

Key words: *heavy metals, soil, hyperacumulator, phytoremediation.*

INTRODUCTION

As a result of industrial activities, large amounts of organic and inorganic compounds permeate the environment every year. Soil pollution is a typical side effect of industrial activity (Sabateet al. 2004). Contaminants among organic anthropogenic compounds: Polycyclic aromatic hydrocarbons (PAH), chlorinated volatile organic compounds (VOC) and alkyl benzene (benzene, toluene, ethyl benzene and xylenes, BTEX) hydrocarbons, polychlorinated biphenyls (PCB) and trichlorethylene (TCE) are common pollutants in the soil (Reible and Demnerova, 2002). Besides, with the expansion of the petroleum industry and its market; Leakage from the tanks during filling, bursting oil spillage and the formation of waste petroleum products cause environmental pollution (Adeniyive Afolabi 2002). In recent years, the method of bioremediation in hazardous waste management has become very important. Some chemicals thought to be degradation resistant, including chlorinated species such as trichloroethane and some polychlorinated biphenyls (PCBs), were found to be biodegradable in laboratory conditions (Mohn 2004; Dindar, 2010).

Conventional engineering methods used in heavily contaminated areas are expensive (Salt et al. 1995). For this reason, instead of existing remediation techniques, the focus is on low cost and environmentally friendly phytoremediation techniques (Arshad et al. 2008). Plants that accumulate 50 to 500 times more metal in the organs of the earth than the concentration of metal in the ground are called as hyperaccumulators (Clemens 2006). Approximately 450 plant species have been identified as hyperaccumulators (Baker and Brooks 1989). However, the phytoremediation potential slow growth rate of many hyperacumer plants is limited by a low biomass and a tight 2 relationship, usually with a specific habitat (Chaney et al. 2005). There is a need to develop genetically modified plant species that have the desired properties to come from above these limitations. For this reason, the physiological and molecular regulation of the mechanism of heavy metal accumulation in hypercapacitor plants needs to be well understood (Terzi, 2014).

MATERIALS AND METHODS

This work has benefited from many local and foreign sources. As a result of these evaluated resources, a literature study on the phytoremediation was made. While researching the articles, Google Scholar (https://scholar.google.com) and Prof. Dr. Özer Çınar's book "Çevre Kirliliğive Kontrolü", Bulent Ecevit University Environmental Engineering Soil Pollution and Hazardous Waste Management lesson notes were used in this study.

SOIL POLLUTION

Soil pollution is the physical and chemical degradation of soil by solid, liquid and radioactive waste and pollutants. Important factors in the pollution of the earth; Wastes from settlements, industrial waste, exhaust gases, pesticides and chemical fertilizers.
Uncontrolled storage areas of domestic solid waste cause to soil pollution. Exhaust gases, ozone, carbon monoxide, sulfur, sulphur dioxide, cadmium etc. carry wih winds long distance transportation and pollute soil and waters with rains. It is the result of unconscious and excessive use of agricultural products and fertilizers, increasing the toxic substances to the soil and polluting the natural environment.

SOURCES OF HEAVY METALS IN THE ENVIRONMENT

Heavy metals enter the environment from natural and anthropogenic sources. The most significant natural sources are weathering of minerals, erosion and volcanic activity while anthropogenic sources include mining, smelting, electroplating, use of pesticides and (phosphate) fertilizers as well as biosolids in agriculture, sludge dumping, industrial discharge, atmospheric deposition, etc. (Modaihsh et al., 2004; Chehregani and Malayeri,2007). In below gives anthropogenic sources of selected heavy metals in the environment (Table 1) (Ali, 2013).

Table 1. Gives anthropogenic sources of selected heavy metals in the environment.

Heavy metal	Sources	Reference
As	Pesticides and wood preservatives	Thangavel and Subbhuraam (2004)
Cd	Paints and pigments, plastic stabilizers, electroplating, incineration of cadmium-containing plastics, phosphate fertilizers	Salem et al. (2000); Pulford and Watson (2003)
Cr	Tanneries, steel industries, fly ash	Khan et al. (2007)
Cu	Pesticides, fertilizers	Khan et al. (2007)
Hg	Release from Au–Ag mining and coal combustion, medical waste	Memon et al. (2001), Wuana and Okieimen (2011), Rodrigues et al. (2012)
Ni	Industrial effluents, kitchen appliances, surgical instruments, steel alloys, automobile batteries	Tariq et al. (2006)

POLLUTANTS CAUSING SOIL POLLUTION

HEAVY METALS

The definition of heavy metals and the harm that chemical substances make to the ecological system have become generalized and have begun to take place in newspaper news that heavy metals frequently cause environmental problems. This common belief is that the accumulation of heavy metals relative to other metals in a living organism over a certain period of time leads to a gradual increase with the negative effect. In fact, the definition of heavy metals is used for metals with a physical density greater than 5 g / cm^3. This group includes more than 60 metals including lead, cadmium, chromium, iron, cobalt, copper, nickel, mercury and zinc. These elements are usually present in the earth as a stabilizing compound in the form of carbonates, oxides, silicates and sulphides, or as imprisonment in silicates. Although the effects of the metals on the ecological system are tried to be defined by the action of the density values of the metals, in reality the density values of the metals are far from defining their biological effects. The most important industrial activities that cause heavy metals to be spread around are cement production, iron and steel industry, thermal power plants, glass production, waste and sludge incineration plants. Below is a list of metal species from the basic industries in general (Table 2). Heavy metals in the air eventually reach the land and animals and people through plants and food chains. They also breathe in case of aerosol by the animal and the people. Heavy metals are also active on animals and humans through the mixing of industrial wastewater into drinking water or by the pollinating of particles contaminated with heavy metals (Rether, 2007; Kahvecioğlu, 2003).

Table 2. List of metal species from the basic industries in general

INDUSTRY	Cd	Cr	Cu	Hg	Pb	Ni	Sn	Zn
Paper Industry	-	+	+	+	+	+	-	-
Petrochemistry	+	+	-	+	+	-	+	+
Chlorine Alkali Industry	+	+	-	+	+	-	+	+
Fertilizer Industry	+	+	+	+	+	+	-	+
Iron and Steel Industry	+	+	+	+	+	+	+	+
Thermic Industry	+	+	+	+	+	+	+	+

Heavy metals may be harmful to soil as well as substances that must be found for plant growth that must be found in terms of soil. In this respect, it is materialized as follows:

- Essential elements for plant growth (Fe, Cu, Zn, Mn, Mo)
- promotive for plant growth (V, Co, Ni)
- Direct toxic effects of plant (As, Pb, Cd, Cr, Hg)

Sources that cause heavy metals to be seen are pollution caused by irregular throwing of solid wastes from mineral processes, volatile wastes from thermal power plants and factory floors, wastewater muds from fueled vehicles, tire wastes, pesticides, commercial fertilizers and industrial products.

Impact of heavy metals on agricultural health and environmental health, the plants growing here and the heavy metals found in it can enter the human and animal and cause permanent damage.

PETROLEUM HYDROCARBONS

Petroleum products are raw materials for the production of many basic materials as fuel for energy, and they have a great impact on environmental pollution because they are produced at high speed and scattered around. It is important that petroleum hydrocarbons pollute the soil and water ecosystem during transport and purification of crude oil products such as gasoline, diesel oil, kerosene, asphalt and other pollutants.

Petroleum products contain complex toxic compounds such as polycyclic aromatic hydrocarbons (PAH), BTEX compounds, benzene and its derivatives, cycloalkane chains and if it spread, it leads to the degradation of the soil resource in such a way that it can not serve the agricultural, industrial or reusable purposes and the loss of its physical-chemical-biological qualities (Şen, 2010).

DIOXINS

Dioxins are colorless, odorless, water-insoluble, non-commercially produced plastic products containing C, H, O and Cl and are side product that are unfavorably showed up during combustion. Dioxins are a common name given to a large group of substances (dioxins and furans) whose properties and toxicity are related to each other. There are 75 different dioxins and 135 different furans in the nature and 209 different PCB types, of which 29 are the most toxic compounds. Dioxins and furans are not commercially produced compounds and have no known uses. They are often exposed as undesirable byproducts in the production of chemical products (Güneş 2007). Dioxin and furan sources are as follows (Bawden 2004);

- Waste incineration
- Ferrous and non-ferrous metal production
- Electricity generation and heating
- Production of mineral (lime, cement, ceramic, glass and asphalt mixture) production
- Motor vehicles
- Uncontrolled combustion processes
- Production of chemicals and consumer foods (paper, textile, leather)
- Regular storage and accumulation (sludge treatment, composting, waste oil accumulation)
- Cigarette smoke
- Natural events such as forest fires, volcanic eruptions
- Animal feed

The toxicity of dioxins on the environment and human health Dioxins and similar compounds that are released to the soil due to various reasons remain in the soil for a very long time and do not interfere with groundwater because they are not soluble in water. The half life of dioxin in the soil is 25-100 years. Sediments under the lakes, rivers and oceans are another storage area for dioxin. Dioxins from rain, erosion and industrial aqueous systems constitute 1% of total dioxin contamination, which is extremely important for human health, because dioxin can accumulate in the food chain in the water and reach human beings and animals. They can also stay in the water for a long time because they do not evaporate easily and do not degradation (Hismioğullarıvd. 2012; Şen, 2010).

This expression we use as "Green improvement" in Turkish is the technology to improve the environment on the basis of plants. With this technology, organic and inorganic materials can be removed from the area where they are polluted by plants. The characteristics of plants used in these studies are that they can grow well in polluted areas without being harmed by existing pollutants.

The most important negative aspect of this technology is; it is not possible to display short-lived activities of plants in very dirty areas. For this reason it is only used at low levels of contaminated areas. The effectiveness of the system is limited by root depths and climatic conditions. The use of non-natural plants for this purpose can affect biological diversity negatively. Phytoremediation is the organic and inorganic pollutants of plants from the soil or water environment

- Immobilization in the root zone,
- Storage in the root and the upper organs of the plant,
- By transporting through the roots to the upper organs of the plant and metabolizing or evaporating in the body and leaves,
- Is a natural technology that cleans the soil (Vanlı, 2015).

TYPES OF PHYTOREMEDIATION

The types of phytoremediation are classified as follows (Table 3) (Aybar, 2015).

Table 3. Types of phytoremediation

Methods used in metal pollutants	**Methods used in organic pollutants**
1.1. Phytoextraction	**1.2.** Phytodegradation
1.3. Rhizofiltration	**1.4.** Rhizodegradation
Phytostabilization	**1.5.** Phytovolatilization

PHYTOEXTRACTION

Phytoextraction is a method of picking up inorganic pollutants especially by plant roots and collecting some of them by moving them to the stem and leaf. These plants can adsorb 100 times more pollution than others. Then the collected plants can be used again as a fertilizer and the heavy metals in it can be recovered.

This method, called phytomining, which can lead to the extraction of uneconomic mineral ores. In this way, elements such as Ag and Ni are being recovered in the USA. This technology is mainly applied to contaminated soil from heavy metals (EPA, 2000).This method is shown below (Figure 1).

Phytoextension is used only in areas where metal pollution is low or moderate. Because very polluted areas are not suitable for growing plants. In this technology, natural hyperacuma plant plants are used. Plant residues harvested as a result of phytoextraction method;

- dried,
- burned to ash,
- being restricted by its decomposition for composting,
- can be isolated by recycling into a biological metal (bio-metal ore) (Memon and al., 2000).

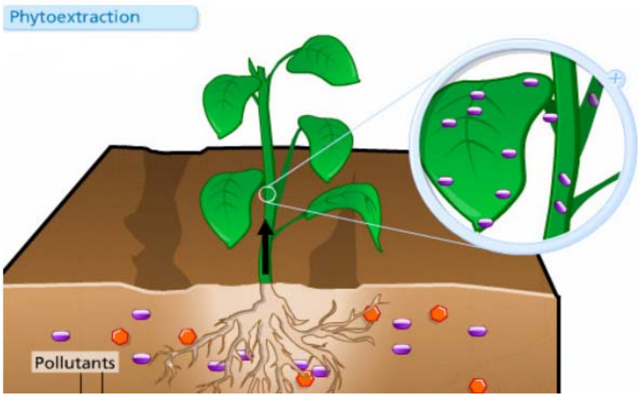

Figure 1. Phytoextraction

RHIZOFILTRATION

In the rhizofiltration method, a well-developed root system, which acts as a filter in the plants to be used, is needed compared to other methods. This method is used for the treatment of water contaminated with heavy metals rather than soil. The preferred hyperaccumulator plants for the rhizofiltration method are provided with adaptation of the pollutant in a different environment before being directly planted in the area. It is preferred that the roots of the plants are kept in clean water instead of soil until they develop at the desired level. These advanced root system plants are then transferred to a contaminated water source for adaptation purposes. Finally, after completing the adaptation problem of the plants, a rizofiltration method is applied to the contaminated area.The roots become saturated, the harvesting process is started and the destruction is carried out safely (EPA 1995; Aybar, 2015).

PHYTOSTABILIZATION

Phytostabilization is generally used to prevent the ingress of pollutants into groundwater and to prevent direct contact with the ground to prevent erosion in areas where erosion has occurred. In this technique, plant roots physically and chemically immobilize pollutants. The phytostabilization technique uses plants that are tolerant to high amounts of metals, sorption, precipitation, complexation of metals, or soil-immobilized plants by reduction of metal valences (Kocaer and Başkaya, 2003; Bert et al., 2005).

While some of the materials used in this technique are not suitable for every plant and every pollutant, some of them may cause metals to be taken, while others may cause more metal to be consumed. Root fixation is a method with the advantage of being applied in situ in soil, sediment and slurry. Planting makes the ecosystem enriched and prevents erosion and sediment movement (Anonymous, 1995). However, the pollutants are still in the environment and the risk continues (Yurdakul, 2015).

PHYTOVOLATILIZATION

In this method, heavy metals adsorbed by plants are transformed into less toxic volatile forms and given atmospheres by transpiration. Metals such as As, Hg and Se can be seen in the natural gas form. This method is shown below (Figure 2). It has been reported that some plants, such as naturally occurring or genetically modified Brassica Juncea and Arabidopsis Thaliana, adsorb heavy metals and convert them into gas form to give atmospheres (Ghosh and Singh, 2005). In addition, tree species such as Populus and Salix are frequently used in this technique due to their effective phytoremediation properties (Pulfordand Watson, 2003). It has been shown that Arabidopsis Thaliana and Brassica Juncea, which grew in the medium containing celentium, could produce volatile Se in the form of dimethylselenide and dimethyldiselenide.Nicotianatabacum and Arabidopsis thaliana plants containing the mercury reductase gene which transforms the ionic form of the helix (Hg^{+2}) into a less toxic form (Hg^0) have been genetically modified.

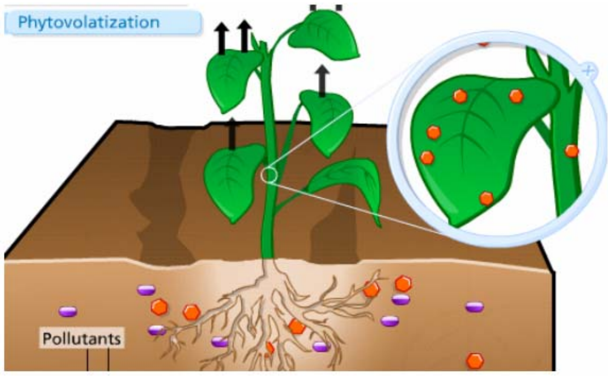

Figure 2. Phytovolatilization

PHYTODEGRADATION

Phytodegradation is the adsorption of pollutants in plant tissues. Contaminants that can be removed by the method of phytodegradation; Chlorinated compounds, pesticides, military chemicals and phenols. As an example of the removal of organic compounds, a myquatic plant Myriophyllumaquaticum (parrot feather) plant is used for the degradation of TNT. This method is shown below (Figure 3).
Using this method, many different pollutants such as solvents in groundwaters, petroleum and aromatic compounds in the soil and volatile compounds in the air can be treated (Newman and Reynolds 2004). However, plant enzymes, ammunition waste, as well as other harmful substances, such as organic herbicides, are used for the treatment of this harmful substance (Mirsal 2004; Kalkan, 2011).

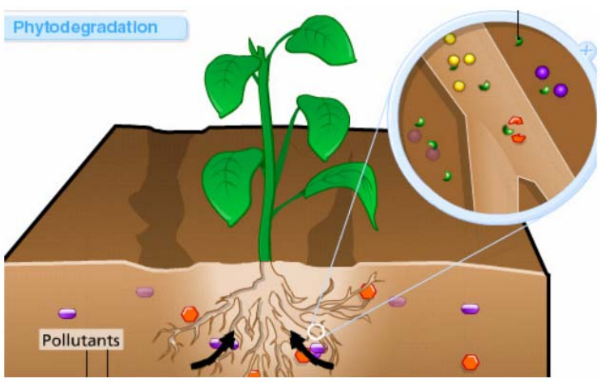

Figure 3. Phytodegradation

RHIZODEGRADATION

The working mechanism of this method is to work with soil microorganisms of plants to neutralize organic pollutants. The microorganisms that produce the nutrients needed to meet the energy needs of organisms bring about a change in the chemical structures of the pollution materials with the help of the root system. This association keeps microorganisms at an optimal level in order to sustain their vital activities and ensures a continuous breakdown of toxic pollutants.In this way, organic pollutants such as microorganisms, fuels and solvents found in the soil degrade and accumulate in their own bodies.
Among the plants used for rhizodegradation, red mulberry (Morusrubra L.), mint (Menthaspicata), alfalfa (Medicago sativa) and watercane (Typhalatifolia) plants can be counted (EPA, 2000; Vanlı, 2015). Schematic representation of the types of phytoremediation (Table 4).

AREAS OF USE OF PHYTOREMEDIATION

The currently widely used phytoremediation studies are being tested in different countries for heavy metal and organic pollutants and successful results are obtained. The following table shows the environments in which pollutants are used and the plant species used for different countries according to their application classes (Türkoğlu, 2006).
Also the types of phytoremediation are shown on a tree as follows (Figure 4).

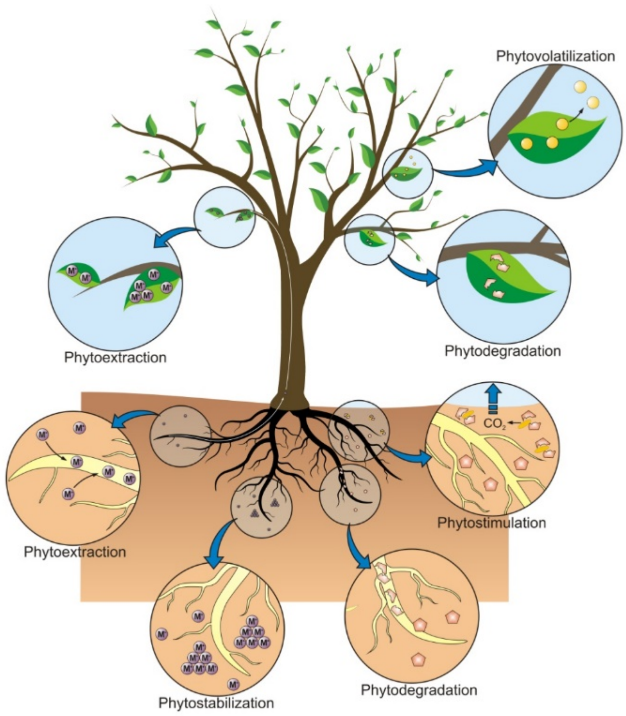

Figure 4. Types of phytoremediation

Table 4. Areas of application of the phytoremediation techniques in different polluting environments

MECHANISM	PLATFORM	OBJECTIVE	POLLUTANTS	PLANTS
Phytoextraction	soil, sediment,mud	Pollutant removal	Metals, Metalloids and Radionucleids	India mustard, Alyssum, moon flower, Hybrid poplars
Rhizofiltration	Surface and underground water	Pollutant removal	Metals, Radionucleids	Moon flower, India Mustard, water hyacinth
Phytostabilization	soil, sediment,mud	Pollutantdeactivation	As, Cd, Cr, Cu, Hs, Pb, Zn	India mustard,Hybrid poplars,Lawns
Rhizodegradation	Soil and ground water	Pollutant disperse	Organic compounds	Red mulberry, grass
1.6. Phytodegradation	Soil, sediment and mud, ground water, surface water	Pollutant disperse	Organic compounds,Chlorinate solvents,Herbicides, Phenols	Algae, Hybrid poplars,Black willow
1.7. Phytovolatilization	Soil, sediment and mud, ground water	Pollutant evaporation	Chlorinate solvents, inorganic ompounds(Se, Hg, As)	Poplars, clover, Indian mustard

HEAVY METAL REMOVAL WITH PHYTOREMEDIATION

Contaminants with potential to remove from the soil by hyperaccumulator plants; metals (Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn), metalloids (As, Se), radionuclides (90Sr, 137Cs, 239Pu, 238U, 234U), and other organic compounds (TPH, PAHs, Pesticides, PCBs).However, in order for a plant to be able to remove a pollutant from the soil, ecological conditions must first be met. The most important of these is pH.Plants with high heavy metal capacity are usually local.ButTaraxacumOfficilane (dandelion) plant has a large area (Vanlı, 2015).

PLANT-METAL UPTAKE

Plants extract and accumulate metals from soil solution. Before the metal can move from the soil solution into the plant, it must pass the surface of the root. This can either be a passive process, with metal ions moving through the porous cell wall of the root cells, or an activeprocess by which metal ions move symplastically through the cells of the root.

This latter process requires that the metal ions traverse the plasmalemma, a selectively permeable barrier that surrounds cells (Pilon-Smits, 2005). Special plant membrane proteins recognize the chemical structure of essential metals; these proteins bind the metals and are then ready for uptake and transport. Numerous protein transporters exist in plants. For example, the model plant thale cress (A. thaliana) contains 150 different cation transporters (Axelsen and Palmgren, 2001) and even more than one transporter for some metals (Hawkesford, 2003). Some of the essential, nonessential and toxic metals, however, are analogous in chemical structure so that these proteins regard them as the same. For example arsenate is taken up by P transporters(Abedin et al. 2002) studied the uptake kinetics of as species, arsenite and arsenate, in rice plants and found that arsenate uptake was strongly suppressed in the presence of arsenite. (Clarkson and Luttge, 1989) reported that Cu and Zn, Ni and Cd compete for the same membrane carriers. For root to shoot transport these elements are transported via the vascular system to the above-soil biomassshoots. The shoots are harvested, incinerated to reduce volume, disposed of as hazardous waste, or precious metals can be recycled (phytomining). Different chelators may be involved in the translocation of metal cations through the xylem, such as organic acid chelators. Since the metal is complexed within a chelate it can be translocated upwards in the xylem without being adsorbed by the high cation exchange capacity of the xylem (Von Wiren et al., 1999)

ADVANTAGES AND DISADVANTAGES OF PHYTOREMEDIATION

The advantages and disadvantages of the phytoremedia are described below (Table 5) (Ghosh, 2005).

Table 5. Advantages and disadvantages of the phytoremedia

No	Advantages	Disadvantages / Limitations
1	Amendable to a variety of organic and inorganic compounds	Restricted to sites with shallow contamination within rooting zone of remediative plants.
2	In Situ / Ex Situ Application possible with effluent/soil substrate respectively.	May take up to several years to remediate a contaminated site.
3	In Situ applications decrease the amount of soil disturbance compared to conventional methods.	Restricted to sites with low contaminant concentrations.
4	Reduces the amount of waste to be landfilled (up to 95%), can be further utilized as bio-ore of heavy metals.	Harvested plant biomass from phytoextraction may be classified as a hazardous waste hence disposal should be proper.
5	In Situ applications decrease spread of contaminant via air and water.	Climatic conditions are a limiting factor
6	Does not require expensive equipment or highly specialized personnel.	Introduction of nonnative species may affect biodiversity
7	In large scale applications the potential energy stored can be utilized to generate thermal energy.	Consumption/utilization of contaminated plant biomass is a cause of concern.

CONCLUSIONS

The technologies used to control heavy metals, which constitute a serious danger to soil pollution, are not preferred because of the high cost of the treatment, the longer duration of the treatment and the problems of destroying contaminant residues accumulating at the end of the treatment. Therefore, the green improvement (phytoremediation) using plants makes it possible to obtain more favorable economic and ecological results. Thus becoming a more widely preferred method.

The many different methods that are preferred within the scope of phytoremediation and the availability of alternative plant species to be used increase the use of phytoremediation technology. However, methods of removing polluted plants that occur as a result of phytoremediation should be evaluate well.In addition, the plants in the environment form a vegetative cover and prevent pollutants from being transported from one place to another, especially by water and wind erosion. As a result of this study the importance of the removal of heavy metals by phytoremediation and applicabilities shown.

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