Removal of Heavy Metals from the Environment via Phytoremediation (Green Reclamation) Method

Fitoremediasyon (Yeşil Islah) Yöntemi ile Ortamdan Ağır Metal Uzaklaştırılması

Review Article

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ABSTRACT

New methods that are being used all over the world in order to advance technology and increase efficiency in agriculture disrupt the nature which is the main source of life while providing conveniences for people. Pollution of nature has negative effects for all living things within the ecological cycles and humans are inflicted with the most significant damage. However, since negative rebounds from the environment take a long time, the harmful effects increase irrevocably with increasing investments for future generations. In this study, phytoremediation (vegetative reclamation systems or green reclamation) methods are explained which are the means of neutralizing the harmful aspects in nature or their cleansing via hyperaccumulator plants. This method that is economical, does not disturb the aesthetic appearance and does not harm the nature is a method that can be widely used to combat soil and waters polluted with heavy metals in our country which is continuing to develop in every aspect. This study provides information about the exemplary studies in our country and in the world as well as the applicability of the method.

Key Words
Phytoremediation, hyperaccumulator, soil, water, pollution.

ÖZ

Tüm dünyada gelişen teknoloji ve tarımda verimi arttırma adına kullanılan yeni teknikler insan hayatında kolaylıklar sağlarken, yaşamın temel kaynağı olan doğayı da bozmaktadır. Doğanın kirlenmesi yani bozulması ekolojik çevrim içerisinde canlı türü ayırt etmeksizin hepsini olumsuz yönde etkilemekte, özellikle de en büyük yarayı insan almaktadır. Fakat doğadan olumsuz geri dönüşümler çok uzun zaman aldığı için gelecek nesiller adına yapılan yatırımlar kontrolsüzce büyüdükçe, zararları da geri dönüşümsüz olarak büyümektedir. Bu çalışmada doğanın kendisinin yine kendi ürünleri yani hiperakümülatör bitkiler tarafından temizlenmesi veya zararlıların etkisiz hale getirilmesi yöntemi olan fitoremediasyon (bitkisel ıslah sistemleri veya yeşil ıslah) teknikleri ve kullanım alanları anlatılmaktadır. Ekonomik, estetik görüntüyü bozmayan ve doğaya zarar vermeyen bu yöntem zengin floraya sahip, her açıdan gelişmekte olan ülkemiz için ağır metallerce kirlenmiş toprak ve sular ile mücadelede yaygın olarak kulanılabilecek bir yöntemdir. Bu yöntemin ülkemizde ve dünyadaki çalışma örnekleri ve uygulanabilirliği hakkında bilgiler bu çalışma ile anlatılmaktadır.

Anahtar Kelimeler
Fitoremediasyon, hiperakümülatör, toprak, su, kirlilik.

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INTRODUCTION

Heavy metals spread to the environment via means of refinery, industry, natural sources and agricultural means [1] and anthropogenic effects also play an important role in the spreading of heavy metals [2]. Whereas some metals are vital for life, accumulation of others cause harmful effects. The quality of soils polluted with heavy metals decreases, efficiency drops [3] while various other dangers for humans and other living beings also arise [4]. Traditional engineering methods used for the remediation of areas polluted with heavy metals are quite expensive [5-6]. Hence, focus is placed more on environmental friendly and low cost phytoremediation method instead of current remediation techniques [7-8]. Plants that can accumulate metals 50 to 500 times more in their above-ground organs in comparison with the metal concentration in the soil are known as hyperaccumulators [9]. In other words, hyperaccumulator plants can accumulate heavy metals in their above-ground organs 100 to 1000 times more in comparison with other plant types without showing any symptoms of toxicity [10]. About 450 plant types (only 0.2% of angiosperms) have been defined as hyperaccumulator [11-14]. Many studies have been carried out which evaluate the phytoremediation potentials of various plants such as *Thlaspi caerulescens*, *Arabidopsis thaliana*, *Brassica juncea* (Brassicaceae), *Lycopersicon esculentum* (Solana-ceae), *Zea mays*, *Hordeum vulgare*, *Oryza sativa* (Poaceae), *Pisum sativum* (Fabaceae), *Sedum alfredii* (Crassulaceae) with regard to different heavy metals [15-22]. On the other hand, the phytoremediation potential of many hyperaccumulator species is limited with slow growth rate, low biomass and in general a close relationship with a certain tpe of habitat [23]. Hence, plants with properties required for phytoremediation such as a deep root system, fast growth rate and heavy metal tolerance should be cultivated. Genetic arrangements carried out in order to develop heavy metal intake, translocation and tolerance by combining advanced growth characteristics and high metal accumulation capacity have enabled the actualization of transgenic approaches in many plant types [24,25]. When the flora richness and the number of endemic species in our country are considered, it can be stated that studies carried out to examine plants with hyperaccumulator properties will contribute to the development and popularization of the phytoremediation method.

Phytoremediation Introduction and Methods

Phytoremediation is defined as the use of hyperaccumulator plants for the removal of pollutants in the environment or for the neutralization of these pollutants [26]. When compared with different reclamation methods, it has many advantages such as its low cost, aesthetically satisfactory results in addition to its ease of application and its short application time [27]. Phytoremediation methods are examined in different headings according to environment properties and the pollutants in the environment.

Phytoextraction (Vegetative Assimilation)

Covers the intake of pollutants via plant roots and their accumulation in above-ground organs followed by the harvesting of these plants. This method can be used to remove actively consumed micro-nutrient elements such as Cu and Zn and heavy metals which are not nutrient elements such as Cd, Ni and Pb. Plants get these harmful metals from the soil via their roots and play an active role in their distribution to other vegetative organs. Hence, hyperaccumulator plants are used which can accumulate metals within themselves [28]. Phytoextraction technology can only be applied to areas where metal pollution is low or moderate. Because plant growth cannot be sustained in highly polluted areas [29]. The success of phytoextraction method depends on the biomass production rates of plants as well as the metal absorption ability of the plants in their trunk tissues [30].

The remains of the plants that are harvested at the end of the phytoextraction method can be isolated by;

Turning them into plant remains harvestd at the end of the phytoextraction method;
- drying,
- burning down to the askes,
- limiting them by letting them rot to make compost,
- or by retransforming them into a bio-metal ore [31].

Riso-filtration (Filtration by Roots)

Encompasses the intake and retention of excess nutrient elements or metal pollutants from fluid growth environments via plant roots. Roots of many plants which grow in hydroponic environments such as *Brassica juncea*, *Phaseolus vulgaris* and *Helianthus annuus* can be used to remove heavy metals such as Cu, Cd, Cr, Ni, Pb, Zn and U from aqueous solutions [32-34]. The ideal plant for riso-filtration should generate significant amounts of root bio-mass or surface area, should be able to accumulate and tolerate large amounts of target heavy metal, should be low cost and should produce minimum amounts of secondary waste [35].

Phytostabilization (Stabilization with Roots)

The ground surface is covered with plants in this method in order to prevent erosion, reduce the seepage of pollutants to underground waters and to prevent their direct contact with the toil [36]. The plant roots physically and chemically immobilize the pollutants in this method [37]. This method requires plants that can grow in polluted soils and that change the physiological, chemical and biological properties of the soil in order to transform toxic metals into less toxic forms. Plants that will be used for phytostabilization should have a wide root system, should be able to generate significant amounts of biomass in the presence of high concentrations of heavy metals and should translocate heavy metals to the plant stem in the minimum amount possible [38]. Indian mustard and hybrid poplars are successfully used for the remediation via phytostabilization of soils polluted with elements such as As, Cd, Cr, Cu, Hg, Pb, Zn.

Phytodegradation-Phytotransformation (Degradation in Plants)

In this method, organic pollutants are degraded via the rhizospheric association between the metabolic functions in plants and the soil microorganisms. The phytodegradation of organic pollutants may take place inside the plant or the rhizosphere. Many different pollutants such as the solvents in underground waters, oil in the soil and aromatic compounds along with the volatile compounds in the air can be removed using this method [39]. Plant enzymes that metabolize the pollutants such as dehalogenase, nitroreducatse, peroxidase, laccase and nitriase are released to the rizosphere where they play an acrive role in the transformation of the pollutants. Two bacterial enzymes (PETN reductase and nitroreducatase) which break down trinitrotoluene (TNT) into less harmful components have been used to increase the TNT tolerance of tobacco plants. It has been put forth that the Onr and nfs genes enable transgenic plants to show resistance against the TNT concentration that can have significant effects on the development of wild plants [40]. In addition, Banks et.al. [41] (2003) have stated that *Sorghum bicolor* plants are quite effective in the remediation of areas polluted with polycyclic aromatic hydrocarbons (PAH).

Fitovolatilization (Floral Vaporization)

In this technology, the heavy metals absorbed by the plants are transformed into less toxic and more volatile forms after which they are released to the atmosphere via transpiration. Heavy metals such as As, Hg and Se can be found in gas form in nature. It has been put forth that various plants such as *Brassica juncea* and *Arabidopsis thaliana* that are formed naturally or the genetics of which have been changed can absorb heavy metals and release them to the atmosphere after transforming them into the gas phase [42]. In addition, tree types such as Populus and Salix are frequently used in this method due to their phytoremediation properties [43]. It has been shown that *Arabidopsis thaliana* and *Brassica juncea* plants grown in selenium containing medium can generate Se in the form of dimethylselenite and dimethyldiselenite [44]. Phytovolatilization is also used in the removal of tritium (3H) which is a radioactive isotope of hydrogen that is transformed into helium [45].

Rizodegradation (Degradation with the Roots)

The operating principle of this method is based on the neutralizing of organic pollutants via cooperating with the soil microorganisms of plants. The microorganisms that generate the nutrients required to meet the energy requirements of organisms cause various changes in the chemical structure of the pollutant materials with the help of the root system. This cooperation holds the microorganisms at the optimal level in order to continue the vital activities and ensures the continuous degradation of toxic pollutants. In this way, the microorganisms in the soil break down various organic pollutants such as fuels and solvents in the soil and accumulate them within themselves. The plant root activates sugars, alcohols and organic acids as carbohydrate sources for the soil microflora while increasing microbial formation and activity. One of the most important advantages of rizodegradation is that the pollutants are removed in their own natural environments. The negative aspect is that they transform the pollutants to the plant or the atmosphere even if at a very small level [46]. TPH (total petroleum hydrocarbons), PAH (polycyclic aromatic hydrocarbons), BTEX (benzene, toluene, ethylbenzene, xylene), pesticides (herbicide, insecticide etc.), PCP (pentachlorophenol), PCB (pllychlorinatedbipheniles), surfactants LAS (linear alkylbenzenesulphonet) can be listed among the pollutants removed from the area via rizodegradation. In addition, the plant roots loosen up the soil thus increasing microbial activity [47]. Red mulberry (*Morus rubra L.*), mint (*Mentha spicata*), clover (*Medicago sativa*) and reedmace (*Typha latifolia*) plants can be listed among plants used for rizodegradation purposes.

Hydraulic Control

Phytohydraulic control or hydraulic control which is also known as hydraulic root control means the controlling or preventing of the accumulation of pollutants in underground waters via the use of plants. This process can be applied to both underground and surface waters. This system contains more than one of the aspects specified before for green remediation categories. The most important advantage is that there is no need to set up an artificial system and that the reclamation area is quite wide since roots spread out over a wider area. Whereas the most important disadvantage is the fact that the water intake of the plant varies in accordance with the season and climate. Non-evergreen trees cannot complete this task as desired [48].

Vegetative Cover Systems

Vegetative cover is the method for controlling pollutants by the use of long term and self-growing plant systems. This method can be applied in soil, sediment and mud. Poplar trees are used commercially for this purpose [42].

Buffer Strips

Buffer strips comprise the procedure of planting the suitable plants as strips along the river strips in order to remove the pollutants underground or surface waters that generally flow near the rivers. This reclamation has various responsibilities such as preventing the spreading of pollution and its mixing with ground water. It also controls system erosion and decreases sedimentation. It has been determined during studies carried out in Canada that buffer strip applications decrease soil erosion by 90%, herbicide flow by 42-70%. In addition, the system can also decrease sediments in the water by 71-91%, nitrogen by 67-96%, phosphorus by 27-97%, pesticides by %8-100 and fecal choliforms by 70-74% [49]. This method has mostly been used to remove fertilizers and pesticides. Poplar is the most frequently used plant for this purpose.

Phytoremediation Usage Areas and Applications

Phytoremediation methods have been used against environmental problems for various different pollutants and environments and successful results have been obtained. The table below (Table 1) shows the mediums and the plant types used in pollutant containing mediums according to phytoremediation classes applied at different countries [50].

Alyüz et.al. have carried out a study in which they determined the organic compounds that can be effectively removed via phytoremediation and the plant types that can be used for this purpose. In addition, they have also examined the fundamental mechanisms in the process of phytoremediation and put forth the advantage and disadvantages of the application of this method. It was determined as a result of the study that plant types such as *Hordeum vulgare*, *Catharanthus roseus*, *Solanum nigrum* ve *Populus sp*. are used to purify organic compounds [51].

Lázaro et.al. have carried out a study in which they applied the phytoextraction method which is a form of green remediation in soil contaminated with Cr, Mn and Zn using *Cistus ladanifer*, *Lavandula stoechas*, *Plantago subulata* and *Thymus mastichina* plants. It was put forth as a result of the study that apart from P. *subulata*, the three remaining plant types specific to the Mediterranean region have remained alive as a result of their high tolerance thus putting forth a good performance for purification. In addition, it was also put forth that the three plants defined in the have a biomass that can provide economic benefits thanks to their fine scent and oils [52].

Madejon et.al. have carried out a study in which they cultivated sunflower in an old mine and compared the soil remediation with results from areas uncontaminated with heavy metals. It was put forth as a result of the study that the phytoextraction capacity of sunflower is very low, but that this plant can be used for soil conservation and that the vegetable oil obtained from the plants can be used industrially [53].

Sharma examined the green reclamation potential in soils with excessive phosphor (P) in the study he carried out. Cucumber (*Cucumis sativus*) and field pumpkin (*Cucurbita pepo var. melopepo*) were used in the study. As a result, it was put forth that these plants create a high biomass and economic value and that they are potential candidates for the phytoextraction of phosphor [54].

Vanlı carried out a study which examines the cleaning via phytoremediation method of the soils polluted with Pb, Cd and B elements. To this end, phytoremediation studies were conducted on Pb, Cd and B added soils with corn, sunflower and canola plants. In addition, complex forming chelate was added at various doses in order to increase the phytoremediation capacity of the soils and to observe the changes in the element removal performance of the plants. Sunflower, corn and canola seeds were planted to the soil within the scope of the experimental studies following the addition of $Pb(NO_3)_2$, $CdCl_2$ and H_3BO_3 after which irrigation was continued at required intervals and their developments were observed. EDTA was added to the soil seven days before the plant harvest after which the plants were harvested. Plants were solubilized in the pot after being cut one by one in order to determine the elements absorbed by the root and ground organs of the plant after which the element contents were determined via atomic absorption spectrophotometry (AAS) and inductive coupled plasma (ICP) devices. The absorbed element amounts were tried to be determined in the light of these findings [55].

Final Removal Methods of Plant Material in Phytoremediation Methods

The objective in the removal of metal in the soil via plants is to transform the metals absorbed by the soil into more controllable and transportable forms. Hence, phytoremediation is not considered as a final removal or clearing method. Final removal or cleaning can be attained by burning or storing the plants obtained as a result of phytoremediation. Since various metals such as selenium that accumulate in the plants are beneficial as nutrients for animals, it is also possible to make use of these plants as animal fodder. Table 2 shows various final removal methods of waste plant material in phytoremediation methods.

Advantages and Disadvantages of Phytoremediation Method

Even though the use of phytoremediation method for the reclamation of pollutants is not a new technology, it has many advantage and disadvantages. When it is compared with other remediation methods under the name of environmental remediation, these factors become more understandable.

Advantages of Phytoremediation;

- More economic in comparison with other remediation technologies,
- Does not require another plant to repopulate the field,
- Does not require an additional field for waste disposal,
- Provides an aesthetically appealing and satisfactory appearance that is also accepted by the public when compared with other methods,
- Thanks to its on-site remediation property, the spreading of pollutants is prevented without the need to transport the polluted area to somewhere else,

Table 1. Usage areas of phytoremediation methods for different pollutants and environments [48].

Mechanism	Environment	Process Goal	Pollutants	Plants
Phytoextraction	Soil, sediment and mud	Pollutant intake and removal	Metals, metalloids and radionucleids	Indian mustard, alyssum, sunflower, hybrid poplars
Risofiltration	Surface and groundwater	Pollutant intake and removal	Metals, radionucleids	Indian mustard, water orchid
Phytostabilization	Soil, sediment and mud	Pollutant neutralization	As, Cd, Cr, Cu, Hs, Pb, Zn	Indian mustard, hybrid poplars, grass
Risodegradation	Soil, groundwater	Pollutant removal	Organic compounds	Red mulberry, grass
Phytodegradation	Soil, sediment and mud, groundwater, surface water	Pollutant removal	Organic compounds, chlorinate solvents, herbicides, phenols	Alg, Hybrid poplars, Black willow, cypress
Phytovolatilization	Soil, sediment and mud, groundwater	Pollutant vaporization	Chlorinate solvents, Some inorganics (Se, Hg, As)	Poplars, clover, Indian mustard
Vegatative cover systems (prevention by the plant of the direct access of the water to the underground pollutant)	Soil, sediment and mud	Erosion control	Organic and inorganic compounds	Poplars, grass
Buffer Strips (prevention of the mixing of pollutants to the rivers etc. via water flow)	Surface and groundwater	Pollutant removal	Aqueous organic and inorganics	Poplars

Table 2. Final removal methods of waste plant material in different phytoremediation methods.

Method	Decomposition/ Destruction	Removal/ Intake	Prevention/ Limiting
Phytoextraction		*	
Phytostabilization		*	
Phytovolatilization		*	
Rizodegradation	*		
Phytodegradation	*		
Rizofiltration		*	
Hydraulic control	*		
Vegetative cover systems	*		*
Riparian buffer strips	*	*	*
(prevention of the mixing of			
pollutants with rivers via water flow)			

- The area can be remediated by struggling against many pollutants other than a single pollutant type.

Disadvantages of Phytoremediation;

- Success rate depends on the adaptation of the plant to be used to the edaphic and biotic factors of the environment as well as the resistance of the plant against the pollutant,
- The pollutants that accumulate in the leaves can mix with the soil again with defoliation in autumn,
- Pollutants may have accumulated in the textures of the plants that are used as firewood,
- Remediation can take longer when compared with other methods,
- There is an increased chance that pollutants will dissolve and mix with the soil as a result of washing [28].

CONCLUSION

The mixing with leaves of heavy metals left in the environment as technology waste result in severe and deadly diseases. Especially, the heavy metals in agricultural fields accumulate in the bodies of final consumers without exception and thus gives the maximum damage to the humans as the adaptation to the food chain. This problem that is observed in all countries of the world increases the importance of phytoremediation.

Phytoremediation technology is a method that is used to remediate soil and water sources that are polluted with heavy metals and organic pollutants. Since hyperaccumulator plants are used for the remediation of polluted areas, their use has continued to increase in recent years. Negative aspects of phytoremediation technology generally arise due to the low biomass of many of the hyperaccumulator plants as well as their difficulties in adapting to negative environmental conditions. Mechanisms in plants related with metal hyperaccumulation should thus be examined in detail in order to overcome such difficulties [25].

In addition to the medical, economic and nutrient etc. attributes of plants, they also continue to serve nature more thanks to such methods. New plants with phytoremediation potential can be obtained via cooperations between fields of science such as molecular biology, environmental sciences, bioengineering, botany etc. or via the transfer of genes from different microorganisms to plants thus providing important gains in the fight against environmental pollution. The fact that this method does not harm the nature and is economic will enhance its sustainability. The rich flora of our country is an indication of our high potential in this field.

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