오염 토양의 phytoremediation

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Phytoremediation of Contaminated Soils

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ABSTRACT

Phytoremediation, using plants to remediate toxic organic and inorganic pollutants in contaminated soils, is an emerging technology for environmental cleanup. Three strategies of this technology are applicable to the remediation of toxic heavy metals, radionuclides, and toxic organic pollutants: They are (1) phytoextraction, in which plants accumulate the contaminants and are harvested for the downstream processing; (2) phytodegradation, in which plant-released enzymes or plant-associated microorganisms convert toxic pollutants into non-toxic materials; and (3) phytostabilization, in which toxic pollutants are precipitated from solution or absorbed in either the plant tissue or the soil matrix. Phytoremediation is more effective and less expensive than other current treatment technologies.

key word: Soil contamination phytoremediation, hyperaccumulators, plant enzymes, toxic pollutants.

요 약 문

식물을 이용하여 오염된 토양에 존재하는 유기 및 무기 오염 물질을 제거하는 phytoremediation은 환경 정화를 위한 새로운 기술이다. 독성 중금속, 방사성 핵종 및 독성 유기 오염 물질을 제거하는데 이용될 수 있는 phytoremediation 에는 다음의 세가지 방법이 있다. (1) phytoextraction: 독성 중금속이나 방사성 핵종과 같은 무기 오염 물질을 수확가능한 부분에 축적하는 식물체를 이용하여 정화하는 방법, (2) phytodegradation: 독성 물질을 분해하는 효소를 분비하는 식물체를 이용하거나 효소를 생산해내는 미생물과 밀접한 연관이 있는 식물체를 이용하여 독성 물질을 무독성 물질로 전환하는 방법, 그리고 (3) phytostabilization: 독성 오염 물질을 용존 상태에서 침전 혹은 식물체의 조직이나 주변 토양

matrix에 흡착시켜 안정화시키는 방법이다. 이 기술은 기존의 어떤 처리 방법보다 더 효과적이고 경제 적이다.

주제어: 토양 오염 phytoremediation, hyperaccumulators, 식물 효소, 독성 오염 물질

1. Introduction

Since the industrial revolution, mining, manufacturing, and urban activities have resulted in the significant soil contamination. Various physical, chemical, and biological treatment processes are already being used to remediate contaminated soils¹⁾²⁾³⁾. The choice of remediation technology depends mainly on the nature of the contaminants. Heavy metalcontaminated soils are usually excavated and landfilled³⁾⁴⁾. Soils contaminated with toxic organic pollutants are treated by vapor stripping, soil washing, incineration, and landfilling¹⁾²⁾³⁾. The costs associated with soil remediation depend on the contaminants, soil properties, site conditions, and the volume of pollutant to be remediated. Techniques that remediate contaminated soils in situ are generally less expensive than those that require excavation⁵⁾.

Phytoremediation, the use of plants to remediate soils contaminated with organic or inorganic pollutants in situ, is an emerging technology that promises effective and inexpensive cleanup⁶. Phytoremediation is most suited for sites with shallow contamination under 5 m depth⁷. The technology has already been shown to be effective in several pilot and full-scale studies⁸.

Because phytoremediation is still in

development, the technology is not yet used widely. Also, phytoremediation may take longer than traditional remediation technologies to reach cleanup or may be limited by soil toxicity. However, as a rule, plants will survive higher concentrations of toxic pollutants than most microorganism used for bioremediation. In addition, plants have a remarkable ability to extract and accumulate elements and compounds from air, water, and soil. A potential application of phytoremediation would be bioremediation of petrochemical spills, ammunition pollutants, chlorinated solvents, landfill leachates, agricultural pollutants (i.e., pesticides and fertilizers), non-radioactive heavy metals, and radionuclides9). Generally, phytoremediation is used in conjunction with other treatment technologies 10).

In this review paper, we concentrate on the phytoremediation of soils contaminated with heavy metals, radionuclides, and toxic organic pollutants.

2. Phytoremediation of contaminated soils

Constructed wetlands and floating-plant systems have been common for the treatment of some types of wastewater for many years ⁵⁾¹¹⁾¹²⁾. Current research efforts now focus on the phytoremediation of contaminated soils. The phytoremediation of inorganic contaminants

must either physically remove the contaminant from the system or convert it into a biologically inert form. Unlike inorganic contaminants, organic pollutants can be degraded or even mineralized by plants or their associated microorganisms. As far as soils are concerned, phytoremediation includes phytodecontamination and phytostabilization techniques.

Phytodecontamination strategies involve phytoextraction of heavy metals radionuclides⁹⁾ and phytodegradation of toxic organic pollutants. Phytoextraction is where plants accumulate the contaminants and are harvested for downstream processing. Postharvest processing of contaminants includes thermal, microbial, and chemical treatments. Phytodegradation is that plants or plantassociated microflora convert toxic pollutants into non-toxic materials. Phytostabilization is where pollutants are precipitated from solution or are absorbed or entrapped in either plant tissue or the soil matrix. The sequestration of contaminants can be enhanced by the action of plants or their microflora.

2.1 Phytoextraction of inorganic contaminants

The concept of soil remediation by phytoextraction was first proposed for cadmium (Cd) more than a decade ago¹³⁾. The processes involved in phytoextraction are shown in Figure 1. The toxic contaminant must be in a biologically accessible form and root absorption must be possible. The optimum plant for the phytoextraction process should not only be able to tolerate and accumulate high levels of heavy metals in its harvestable parts, but also have a rapid growth rate and the potential to produce a

high biomass in the field. Because most of the heavy metal-accumulating plants are relatively small and grow slowly, their potential for phytoextraction may be limited. Nevertheless, the first reported field trials of wild metal accumulators of Ni and Zn, growing on soils contaminated by long term application of heavy metal-containing sludges demonstrated the feasibility of phytoextraction¹⁴.

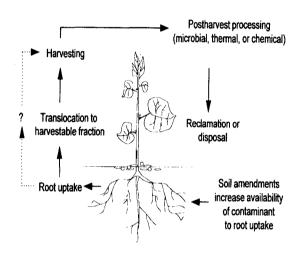


Fig. 1. Phytoextraction processes of heavy metals and radionuclides from soils.

Although plants take up and accumulate certain essential nutrients from soils to concentrations as high as $1\sim3$ % by dry weight, heavy metals are accumulated only to $0.1\sim100$ mg/kg in most plants¹³⁾¹⁵⁾. Some nonessential elements (e.g., Si and Na) that are not particularly harmful may be accumulated in large amounts. It was thought impossible to find and develop plants that hyperaccumulate normally toxic metals¹⁶⁾. However, such metal hyperaccumulators are taxonomically widespread throughout the plant kingdom. One such plant is Sebertia accuminata, a small tree

with sap that is 25 % Ni by dry weight¹⁷). Thlaspi caerulescens, a member of the Brassicaceae, can accumulate up to 4 % Zn in its tissue without apparent damage 18)19). Brassica juncea was able to grow and accumulate Pb, Cr. Cd and Ni from the soils at sites in New Jersey, in the Mariupol and Chernobyl regions of the Ukraine and in the Pennine region of England⁵⁾. juncea also demonstrated a strong accumulation of 90Sr, a radionuclide found in the soils in the Chernobyl regions of the Ukraine. Accumulation of 90Sr in B. juncea shoots is 3-fold higher than that in other plant, Zea mays, and the final concentration of 90Sr in shoots of B. juncea is 12-fold higher than in the soil⁵. Some of the hyperaccumulators and their metal accumulation capabilities are listed in Table 1. Phytoextraction of some inorganics as volatile forms may also be possible. In the case of Se, a proposed vegetation management system encouraged Se volatilization through what appears to be a plant or plant-microbe interaction²¹⁾.

Table 1. Metal concentration in known hyperaccumulators

Metal	Plant Species	Concentrations in the harvestable plant parts (dry wt. basis)
Cd	Thlaspi Caerulenscens	1,800 mg kg ⁻¹ in shoots ²⁰
Cu	Ipomoea alpina	12,300 mg kg ⁻¹ in shoots ²⁰
Co	Haumaniastrum robertii	10,200 mg kg ⁻¹ in shoots ²⁰
Рь	T. rotundifolium	8,200 mg kg ⁻¹ in shoots ²⁰
Mn	Macadamia neurophylla	51,800 mg kg ⁻¹ in shoots ²⁰
Ni	Psychotria douarrei	47,500 mg kg ⁻¹ in shoots ²⁰
	Sebertia acuminata	25% by wt. of dried sap ¹⁷
Zn	T. caerulenscens	51,600 mg kg ⁻¹ in shoots ¹⁸

The postharvest biomass processing step may be practical to recover most metal contaminants. The harvested biomass could be reduced in volume and weight by thermal, microbial, physical, or chemical techniques. Phytoextraction must have economic advantages over traditional treatment technologies, especially in cases where the extracted metals are biomining targets and have economic value (e.g., Ni, Zn and Cu)²²⁾.

2.2 Phytodegradation of organic pollutants

Successful phytodegradation requires organic contaminants to be biologically available for absorption, uptake, and metabolism by plant or plant-associated microbial systems (Fig. 2).

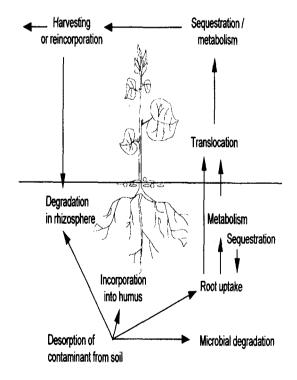


Fig. 2. Phytodegradation processes that remove toxic organic compounds from contaminated soils.

Bioavailability of contaminants depends on their relative lipophilicity, the age of the spill and the soil properties, such as soil structure, organic matter content, pH, and the amount of clay present. Contaminants that are not readily mobile and resist uptake by microorganisms or plants make poor targets for phytodegradation. However, if these contaminants are tightly adsorbed to soil particles, phytodegradation should be considered. Most of compounds inside the plants are either stored unchanged, are bound to plant structural constituents, are metabolized, or are passed through the plant and volatilized. Plants have significant metabolic activities in the root and the shoot that may be exploited for phytodegradation⁷.

Plants may release enzymes that help degrade toxic organic contaminants. In studies at EPA's laboratory, five enzyme systems (dehalogenase, nitroreductase, peroxidase, laccase, and nitrilase) have been identified⁷⁾. Table 2 shows some plants and associated enzymes that degrade toxic organic pollutants. Through the use of mass balances and pathway analyses, it has been shown that nitroreductase and laccase enzymes break down ammunition wastes (e.g., TNT). Another plant-derived enzyme, dehalogenase, helps reduce chlorinated solvents such as trichloroethylene to chloride ion, carbon dioxide and water. Plant enzymes released into the environment may have significant catalytic effects and be useful for phytodegradation⁷.

The metabolic capacity of plant-associated microbial systems is under investigation. In the rhizosphere, accelerated rates of degradation for many pesticides and herbicides 11)23, as well as trichloroethylene 24) and petroleum hydrocarbons

²⁵⁾, have been observed. However, as a rule, the overall degradation rate of toxic organic compounds has been relatively slow. Soil or rhizospheric microorganisms can play a major role in the decomposition of many organic contaminants. However, because mass balance studies for a contaminant are often incomplete to understand the fate and metabolic impact of the contaminant, it is not easy to investigate the mechanisms and parameters of phytodegradation under field conditions.

Table 2. Plant-derived enzyme systems

	Half-life (h) ^b		
Plant	Nitroreductase	Dehalogenase ^d	Laccase
Algas Nitella (stonewort)	10~50	90	70
Eleocharis sp.	20~110		
Anthrocerotae sp.	10~67	120	
Algae Spirogyra	4~100	95	
Potamogeton pusillus	8~57		
Myriophyllium spicatum	20~240	120	70
Lemna minor (duckweed)	20		
Hydrilla verticillata	12		
Sagittaria sp.(arrowroot)	35		
Nostoc sp.(blue-green algae)	60		
Chara sp.	75		
Populus sp.(Hybrid poplars)	<10	50	

^aSystems have been shown to remediate nitroaromatic compounds, halogenated hydrocarbons (e.g., chlorinated solvents and pesticides), and anilines.

Just a little soil has been successfully decontaminated by either phytoextraction or phytodegradation. Pilot projects that target organic contaminants in the water phase (e.g., TNT and TCE) look promising. However, more research on less-mobile contaminants (e.g.,

bHalf-lives are dependent on the initial concentration of contaminant and the plant: water ratios.

Nitroreductase with 2,4,6-trinitrotoluene.

^dDehalogenase with hexachloroethane.

Laccase with 2,4,6-triaminotoluene.

PCBs and PAHs) is needed before they undergo large-scale field testing¹³⁾. Results from field trials involving metal phytoextraction show that metal-removal rates currently remain too low to be commercially useful. New plant and soil management practices will need to be developed before large-scale pilot trials can be planted.

2.3 Phytostabilization of contaminants

Although chemical and biological associations formed by organic and inorganic contaminants effectively decrease contaminant availability for bioremediation, they also reduce the effect of leaching. Such processes include the incorporation of organics into lignin or soil humus, and precipitation or sequestration of metals into iron hydroxide coatings that form on soil particles¹³⁾. Figure 3 shows phytostabilization processes of contaminated soils. In some cases, the reduction in bioavailability may exclude biological decontamination strategies. Phytostabilization techniques exploit these processes to decrease bioavailability and environmental harm or human health risk posed by the contaminants at the site. The practice is well advanced for decontaminating metals at mining sites, but this process is also applicable to organic contaminants¹³⁾.

The role of plants is to increase the sequestration of the contaminant by altering water flux through the soil, incorporating residual free contaminant into roots, and preventing wind and rain erosion. A good phytostabilizing plant should tolerate high levels of heavy metals and immobilize these metals in the soil via root uptake, precipitation or

reduction. Some organics can be incorporated into the plant lignin. Also, certain contaminants can be precipitated into an insoluble form (e.g., lead into lead phosphate). The roots of *B. juncea* are able to reduce available and toxic Cr (VI) to unavailable and less toxic Cr(III)⁵).

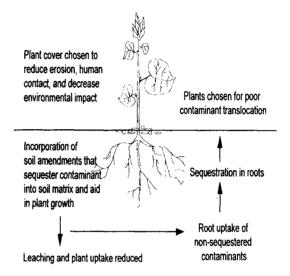


Fig. 3. Processes involved in the phytostabilization of contaminated soils.

Heavy metal-contaminated soils usually lack established vegetation cover due to the toxic effects of contaminants. A simple solution to the stabilization is re-vegetation with metal-tolerant plant. Three cultivars of different grasses were made commercially available: Agrostis tenuis cv Goginan for acid Pb/Zn wastes; Festuca rubra cv Merlin for calcareous Pb/Zn wastes; Agrostis tenuis cv Parys for Cu wastes⁵). Currently, there is an extensive effort to stabilize Cd- and Zn-contaminated soils with metal tolerant grasses.

Phytostabilization techniques are most appropriate for relatively immobile materials and large surface areas. The technique is currently acceptable for remediation at mining sites, but relatively few urban or industrially contaminated sites. Field tests and discussions of phytostabilization are ongoing in a number of countries.

3. Limitations of phytoremediation

The limitations of phytoremediation are that the plant must be able to grow in the contaminated soils. If plants can be grown and maintained, then phytoremediation may have potential. However, there are some inherent limitations in the technology. Because rooting depths are not infinite, treatment depths are generally limited to a range of 1 to 10 m depending on pollutant, crop and permeability of the matrix to roots¹³⁾. Therefore, deep contaminated sites are not good for applications of phytoremediation. The contaminant must be within the rhizosphere of plants that are actively growing. Roots are living and have significant environmental limiting factors, such as pH, soil texture, temperature, osmotic pressure, water content, and oxygen.

Phytoremediation is frequently slower than physical and chemical treatment processes. Degradation of organic pollutants by plant enzymes is so fast that desorption and transport of chemicals from the soil may become the rate-limiting step. Therefore, phytoremediation may require more time to achieve cleanup goals than traditional technologies such as excavation or ex situ treatment, especially for hydrophobic pollutants that are tightly bound to soil particles⁷⁾.

4. Future of phytoremediation

A lot of efforts are being made to overcome the inherent limitations of current plants for phytoremediation. The development of new plants with hyperaccumulator tendencies will make phytoremediation more effective and acceptable than traditional remediation technologies¹³⁾. The improvement of plant root structure and engineering of the rhizosphere will enhance the effect of phytoremediation. These include root depth, root density and the plant-microbial interaction in the rhizosphere²⁶⁾.

Metal hyperaccumulating plants often do not accumulate all elements of interest, but accumulate only a specific element. Systematic screening for mutants might yield useful hyperaccumulators. In Pisum sativum, a single gene mutation causes 10 to 100-fold higher accumulation of Fe than the wild type²⁷⁾. A mutant of Arabidopsis thaliana exhibited hypersensitivity to various combinations of Cd, Cu, Hg, or other heavy metals²⁸⁾. One widely reported strategy is the creation of heavy metalresistant plants by the incorporation of bacterial degradative genes²⁹⁾³⁰⁾. For example, a bacterial mercuric ion reductase has been engineered into Arabidopsis thaliana, and the transgenic plant is capable of tolerating and volatilizing mercuric ions²⁹⁾.

Many combinations of phytoremediation with traditional engineering remediation techniques are being tried in laboratories throughout the world. For example, the combination between the process of electroosmosis and phytoextraction can increase the rate of contaminant migration to the root and plant loading rates¹⁰.

Such hybrid technologies look as technically, economically and scientifically promising³¹⁾.

5. Conclusions

Despite a number of inherent limitations, plants have potential as agents for remediating soils contaminated with toxic heavy metals and organic pollutants¹⁰⁾. The roots of some plants have an unusually high capacity for heavy metal uptake, and the uptaken heavy metals are translocated and accumulated to the shoots. This plant biomass can be readily harvested and processed for metal recovery. In some cases, phytoremediation might be due to the activity of plant associated microorganisms. Microorganisms can contribute to remediation by catabolizing organic molecules, mobilizing soil-bounded metals, and excreting metal chelating organic molecules. Thus, the ability of plants to attract and provide nutrients for microbes may play a significant role in phytoremediation. Phytoremediation is clearly an emerging technology that holds great potential. In order to realize this promise, it is necessary to understand the many processes that are involved in phytoremediation. Also, analytical techniques are a critical factor in the development of phytoremediation. This will require multidisciplinary approaches between fields as diverse as plant biology, microbiology, agricultural engineering, soil science and genetic engineering⁵⁾³¹⁾.

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