Chapter 5
Phytoremediation of Cadmium and Copper: Contaminated Soils

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Abstract With the development of modern industry and agriculture, the Cadium (Cd) and Copper (Cu) contents in soil have significantly increased. Pollution of Cd and Cu is more serious in a soil–plant environment, so that the remediation of the contaminated environment has been paid more attention. Phytoremediation is to use living green plants to reduce, remove, degrade, or immobilize toxins from contaminated soil, which is an emerging cost-competitive environmental-friendly technology. Recent researches on Cd and Cu hyperaccumulators will be reviewed in this chapter. Future research on the screening Cd and Cu hyperaccumulators, and their molecular mechanisms are necessary for developing phytoremediation.

Keywords Cadmium · Copper · Phytoremediation · Hyperaccumulator

5.1 Introduction

Phytoremediation is an emerging cost-competitive environmental-friendly technology that cleans up polluted environments through the use of living green plants to reduce, remove, degrade, or immobilize toxins from contaminated soil, water, sediments, or air (Salt et al. 1995). At present, efforts have been focused on using

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X. Yin and L. Yuan (eds.), *Phytoremediation and Biofortification*,
SpringerBriefs in Green Chemistry for Sustainability,
DOI: 10.1007/978-94-007-1439-7_5,

plants and rhizosphere microorganisms to degrade organic pollutants and/or remove toxic heavy metals from contaminated sites. Phytoremediation of contaminated sites has strong public appeal being cost-competitive and environmentally sustainable, compared with other traditional remediation technologies involving excavation or chemical stabilization/conversion in situ. Moreover, phytoremediation could be esthetically pleasing to the public (Wendy et al. 2005).

Phytoremediation includes a set of processes, including phytoextraction, phytostabilization, phytovolatilization, phytofiltration, and phytodegradation. The use of plants to remove contaminants from the environment and accumulate them in above-ground plant tissues is known as phytoextraction. Pollutants can be removed from the contaminated site by harvesting pollutant-accumulated plants (Salt et al. 1998). Metals enter into the xylem through two pathways: one is the apoplastic pathway that soluble metals do not enter through the plasma membrane of epidermis and endodermis cell, but through the cribrate cell wall and the space between cells, and then cross the Casparian strip in endodermis cell; the Casparian strip is a waxy coating which is impermeable to solutes. So, soluble metals need to cross the plasma membrane and then enter into the endodermis cell to the xylem. The other is the symplastic pathway in which soluble metals cross the plasma membrane of epidermis cell and then enter into endodermis cell to the xylem. Once into the xylem, the flow of the xylem sap will transport the metal to shoot or leaf tissues. Once in the shoot or leaf tissues, metals can be stored in various cell types, depending on the species and form of the metal, it can be converted into less toxic forms (to the plant) through chemical and biological transformation or complexation. In leaves or shoots, metals can also be stored in several cellular organelles, such as cell wall, cytosol, and vacuole. Mercury, Se, and As can also be volatilized from leaves (Lombi et al. 2001a).

5.2 Cadmium Contamination

Cadmium (Cd) is a heavy metal that is of great concern to the environment. With the development of modern industry and agriculture, the Cd content in soil has significantly increased. Pollution of Cd is more serious in a soil–plant environment, so that the safety of agricultural products has become a serious matter of concern (Davis 1984). In regard to its toxic effects on humans, Cd can cause kidney damage, renal dysfunction, pulmonary emphysema, and osteoporosis (Albert and Hsu 2005). Therefore, soil Cd pollution is one of the most important environmental problems worldwide. The main sources of Cd in soil are from industrial waste discharge, Cd-containing wastewater irrigation and pesticides, herbicides and phosphate fertilizers utilization. In China, Cd contaminated land in 11 provinces and annual production of Cd-contaminated rice (i.e., containing over 1.0 mg Cd kg rice) was about 5×10^4 tons. A survey conducted in Hunan Province in the early 1990s showed that the agricultural yield was significantly reduced by 5–10 % in Cd-contaminated farmland (Wang 1997). In Japan,

Table 5.1 Hyperaccumulators of Cd and their accumulation

Scientific Name	Cd content in shoots or leaves (mg/kg dry weight)	Enrichment coefficient (EC)	Transfer Factor (TF)
Thlaspi caerulescens	164–3,000	>1	>1
Brassica juncea	>177	>1	. > 1
Sedum alfredii	>100	>1	. > 1
Solanum nigrum	104–125	2.68 (average)	1.04 < TF < 1.27
Viola baoshanensis	465–2310	2.38 (average)	1.32 (average)
Phytolacca acinosa Roxb	200–482	2.02 < EC < 5.52	1.67 < TF < 2.25

Cd-contaminated farmland was 472,125 ha, about 82 % of the total heavy metal-contaminated agricultural land (Liao 1993). Albert and Hsu (2005) reported that there were more than 8 % of uncontrolled Cd-contamination hazardous waste sites in the United States. The traditional physical and chemical remediation methods were effective in cleaning up Cd-contaminated soils, but the cost is generally high or very expensive. Therefore, cost-effective remediation technologies are desperately needed for Cd-contaminated sites. Since the late 1990s, phytoremediation has become popular and represents a novel, cost-competitive, and environmental-friendly promising remediation technology for metal-contaminated waters and soils.

5.3 Phytoremediation of Cd

Plants that can accumulate over 100 μg/g Cd dry weight (DW) in shoots or leaves can be selected as candidate species for Cd phytoremediation. At present, six kinds of Cd hyperaccumulators have been reported. The species include *Thlaspi. caerulescens* (Baker et al. 1994; Knight et al. 1997; Lombi et al. 2001a, b), *Brassica juncea* (Ebbs et al. 1997), *Sedum alfredii* (Yang et al. 2004; Lu et al. 2010), *Solanum nigrum* (Wei et al. 2010), *Viola baoshanensis* (Liu et al. 2003), and *Phytolacca acinosa Roxb* (Nie 2006) (Table 5.1).

Among the species, *T. caerulescens* accumulated the highest concentrations of Cd in leaves (>164 mg/kg DW). However, the remediation efficiency by *T. caerulescens* is limited due to its slow growth and small biomass production. Although concentrations of Cd in shoots of *B. juncea* (about 100 mg/kg DW) are lower than those of *T. caerulescens*, *B. juncea* can remove more Cd from the contaminated soil due to its larger size of biomass production (Pence et al. 2000). Zhuang et al. (2007) selected the plant species with high biomass production to phytoremediate paddy soils contaminated with Pb, Zn, and Cd. The results indicated that *Viola baoshanensis* accumulated 28 mg Cd/kg DW in shoots, with a bioconcentration factor of 4.8. The total phytoextraction was 0.17 kg Cd per ha, and about 1 % Cd could be removed from the soils, compared with another plant species, *Rumex crispus,* which extracted 0.16 kg Cd per ha (Zhuang et al. 2007). Ji et al. (2011) utilized the Cd hyperaccumulator species, *S. nigrum,* to clean up the farmland soil contaminated by 1.91 mg Cd kg^{-1} in the soil. They found that the planting density had significant effects on plant biomass and Cd accumulation, but *S. nigrum* could accumulate a significant amount of Cd from the soils where the Cd concentrations were relatively low (Ji et al. 2011). However, it should be pointed out that there are some restrictions on phytoremediation application; the stature and biomass of accumulator plants were small and their accumulation ability was limited. Moreover, the phytoremediation time by Cd hyperaccumulators would require many years or a long-term time commitment (Lombi et al. 2001b). Transgenic approaches could break through some of these restrictions to make Cd phytoremediation feasible with overexpression of Cd-accumulation-mediated gene. Bennett et al. (2003) studied that genetically modified *B. juncea* could accumulate 1.5 times more Cd and Zn, compared to wild-type *B. juncea* growing on metal-contaminated soil from a USEPA Superfund site. Overexpression of *E. coli* gene gshI (with a chloroplast targeting sequence) in *B. juncea* could increase the γ-glutamylcysteine synthetase (ECS) activity by five times compared with wild-type and ECS is important in Cd accumulation and tolerance (Tong et al. 2004). Song et al. (2003) reported that expression of the glutathione-Cd transporter YCF1 in Arabidopsis could significantly increase biomass production and therefore, two times more in Cd uptake.

5.4 Cu Contamination

Copper (Cu) is an essential element and enzyme co-factor for oxidases (cytochrome C oxidase, superoxide dismutase) and tyrosinases (Uauy et al. 1998). A suitable amount of Cu in human and animal body are essential for normal biological metabolisms, but excessive will be harmful.

There are two kinds of Cu contamination in soils: one is that derived from weathering and mineralizing of Cu mines and the other is anthropogenic, which is derived from mining, industrial waste, urban waste, sludge, and using of Cu pesticides (such as Bordeaux mixture) (Chen 1996). Some of soils near Cu mines had Cu contents as high as 2,000 mg kg^{-1}, which was about 10 times higher than that of non-contaminated soils/sediments (20–30 mg/kg) (Salomons and Forstner 1984). With the development of Chinese industry and modernization of agriculture, Cu and other heavy metals pollution in the environment has become more serious (Ni et al. 2003). Once the soil is contaminated with heavy metals, metal pollutants will accumulate and build up in the soil for a long time. Soil metal pollution affects the biological activity of soil microorganisms and crop growth. Toxic metals finally accumulated in the edible parts of crops will become harmful for human health (Nriagu and Pacyna 1988).

5.5 Phytoremediation of Cu

Cultivation and selection of Cu-hyperaccumulating plants is an important means for Cu-phytoremediation. Currently, 37 taxa of Cu hyperaccumulators have been reported, (Song et al. 2004), including Labiatae (5 species), Scrophulariaceae (4 species) and Asteraceae (4 species), Gramineae (3 species), Leguminosae, Cyperaceae and Amaranthaceae (2 species), Caryophyllaceae (1 specie), Convolvulaceae (1 specie), and Tiliaceae (1 specie) (Brooks et al. 1992; Tang et al. 1999). In China, Cu-accumulated plants, such as *Elsholtzia splendens*, *Dianthus superbus*, *Eriophrum comosum*, and *Polygonum microcephalum,* were found (Jiang 2003).

Cu was accumulated in the roots after absorption and avoided excess Cu to interfere with plant photosynthesis and other important physiological processes (Meharg 1993; Baker et al. 1983). However, Hogan and Rauser (1981) and McNair (1981) reported that Cu concentrations in aerial parts of Cu-tolerant plant (*Agrostis gigantea*) are higher than the non-Cu tolerant type. In fact, the cell wall and the vacuole are the most important sites for Cu accumulation, primarily in the chemical form of Cu^{2+}. Cu^{2+} is generally not toxic to plants. In a thyrium plant, about 70–90 % Cu was retained in cell wall to prevent from entering protoplast (Branquinho et al. 1997). Vacuolar accumulation of Cu was observed in Cu-tolerant plants, especially in Cu hyperaccumulators. Some lower plants, such as algae, can also accumulate Cu in vacuoles. Many substances in plants, such as enzymes, organic acids (metallothionein, plant metal chelate hormone (PC)), and sugar, can complex Cu and significantly affect the normal physiological processes of plants. Meanwhile, Cu could be detoxified by forming Cu-complexes with these compounds (Grill et al. 1985).

5.6 Summary

Phytoremediation is a cost-competitive and sustainable biotechnology for the cleanup of Cd- and Cu-contaminated soils. A few plant species have been identified with the potential for phytoremediation of Cd- and Cu-contaminated environments. Genetic engineering techniques have been applied to develop novel transgenic plants with enhanced ability of metal uptake and accumulation. However, management of Cd- and Cu-contaminated plant waste materials may become a challenging issue. Future research needs to focus on the screening Cd and Cu hyperaccumulators and mechanisms necessary for developing phytoremediation.

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