African Journal of Biotechnology Vol. 9 (37), pp. 6010-6016, 13 September, 2010
Available online at http://www.academicjournals.org/AJB
ISSN 1684–5315 © 2010 Academic Journals

Review

Trends in phytoremediation of toxic elemental and organic pollutants

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Accepted 28 December, 2009

Phytoremediation is the use of plants to extract, sequester or mineralize pollutants. This process is seen as an ecologically sound strategy for management of contaminated ecosystems. In this review, current status of several subsets of phytoremediation are discussed which includes: (a) Phytoextraction – which is a process in which high biomass pollutant accumulating plants are used to accumulate and transport pollutants from the soil to harvestable parts of plants. (b) Phytofiltration – which is a process in which plant roots are used to precipitate and concentrate pollutants from effluents. (c) Phytostabilization - here plants stabilize pollutants, thus rendering them harmless. (d) Phytovolatilization –plants absorb pollutants and convert them into gaseous components via transpiration. The advantages inherent in these technologies are also discussed. There is need for further understanding on the processes that affect pollutant availability, rhizosphere processes, pollutant uptake and sequestration.

Key words: Phytoremediation, xenobiotics, metal, pollution, decontamination.

INTRODUCTION

Phytoremediation, a novel plant-based remediation technology, is applied to inorganic and organic contaminated soils, water and sediments all over the world. Phytoremediation is defined as the use of green plants to remove pollutants from site of contamination or render them harmless. This technology makes use of naturally occurring processes by which plants and their microbial rhizosphere flora degrade and/or sequester organic and inorganic pollutants (Pradhan et al., 1998). It is more cost-effective than alternative mechanical and chemical methods of removing hazardous contaminants from soils (Bollag et al., 1994). Organic pollutants in the environment are mostly man made and xenobiotic to organisms. Many of them are toxic while some are carcinogenic. Organic pollutants are released to the environment via spills (fuel, solvents), military activity (explosives, chemical weapons), agriculture (pesticides, herbicides), industrial (chemical, petrochemical), wood treatment, etc. Depending on their properties, organic pollutants can be degraded in the root zone of plants or up-take, followed by degradation, sequestration or volatilization.The goal of phytoremediation is to completely mineralize organic pollutants into relatively non-toxic constituent, such as CO_2, nitrate, chlorine and ammonia (Cunningham et al., 1996). Organic pollutant that are potentially important targets for phytoremediation include polychlorinated biphenyls (PCBs) such as dioxins (Harms et al., 2003), polycyclic aromatics hydrocarbons (PAHs) such as benezoapyrene, nitroaromatics such as trinitro-toluene (TNT) (Hughes et al., 1997); and linear halogenated hydrocarbons such as trichloroethylene (TCE) (Burken and Schnoor, 1997; Shang et al., 2003). Many of these compounds are not only toxic and teratogenic but are also carcinogenic.

Inorganic pollutants occur as natural elements in the

Abbreviations: PCBs, Polychlorinated biphenyls; **PAHs,** polycyclic aromatics hydrocarbons; **TNT,** trinitrotoluene; **TCE,** trinichoroetoluene; **SC,** selenium; **VOC,** volatile organic compounds; **MTs,** metallothioneins; **PCs,** phytochelatins; **R-SH,** organic sulphur; **CEC,** cations-cation exchange capacity; **EDTA,** ethylene diamine tetra acetic acid; **TSCF,** transpiration stream concentration factor; **SeCys,** selenoaminoacids selencysteine; **SeMet,** selenomethionine; **DMSe,** dimethylselenide; **MerA,** mercury reductase earth's crust or atmosphere, and human activities such as mining, military, agriculture, traffic and industrial activities promote their release into the environment, thereby causing toxicity (Nriagu, 1979). Inorganics cannot be degraded but can be phytoremediated via phytostabilization, volatilization or sequestration in harvestable plant tissues. Inorganics that can be phytoremediated include macronutrients such as nitrates and phosphates (Horne, 2000; Nwoko et al., 2004) and plant trace elements such as Cr, Ni, Zn, Mn, Mo, Fe and Cu (Lytle et al., 1998), non-essential elements such as Hg, Se, Cd, Pb, V, and W (Horne, 2000; Nwoko and Egunjobi, 2002; Okeke et al., 2004), radioactive isotopes such as ^{238}U, ^{137}Cs, ^{90}Sr (Dushenkov, 2000).

Polluted soils and sediments have been phytoremediated at military sites (TNT, metal), agricultural fields (pesticides and herbicides, selenium), industrial sites (metals etc.) and wood treatment sites (Banuelos, 2000; Ferro et al., 1999). Plants can also be used to filter air, both indoors and outdoors, from SO_2, NOx , ozone, CO_2 , dust and soot particles and halogenated volatile hydrocarbons (Jeffers and Liddy, 2003, Morikawa et al., 2003).

Pollutants can be remediated in plants via many natural biophysical and biochemical processes: adsorption, transport, hyperaccumulation and/or transformation and mineralization. For instance, elemental pollutants enter the plant through normal nutrient uptake mechanism of plants. However, the degradation of endogenous toxic organics and possible sequestration in vacuoles protect plants from toxic xenobiotics. Additional efforts in terms of over expression of plant existing genes or transgenic expression of bacterial genes are needed to enhance these natural processes. This review aims at giving an overview of the science of phytoremediation in terms of the basic mechanisms involved in toxic organic and inorganic remediation in the biota.

PHYTOREMEDIATION TECHNOLOGIES

Plants and their rhizosphere organisms are employed in phytoremediation in diverse ways. They can be used as filters in constructed wetlands and is referred to as phytofiltration (Horne, 2000; Nwoko et al., 2004). Trees can be used as hydraulic barriers to create upward water flow in the root zone, preventing contaminants leaching into the underground water or preventing contaminated water from spreading horizontally (Newman et al., 1997). Phytostabilization is a process that could involve simple erosion, leaching or runoff prevention or the conversion of pollutants to less bioavailable forms (via precipitation in rhizosphere). Plants can extract pollutants and accumulate them into their harvestable tissues. This technology is referred to as phytoextraction (Blaylock and Huang, 2000). Table 1 presents a summary of phytoremediated chemicals.

Plants can enhance biodegradation of organic pollutants by microbes in their rhizosphere (phytostimulation or rhizodegradation) (McCutcheon and Schnoor, 2003; Nwoko et al., 2007). Plants can also degrade organic pollutants directly via their own enzymatic activities (phytodegradation) (Nwoko et al., 2007). Some pollutants can also leave the plant in volatile form (phytovolatilization) (Terry et al., 1995). The above processes are not mutually exclusive. For instance, in a constructed wetland, accumulation, stabilization and volatilization can occur simultaneously.

The technologies mentioned above are compatible for a number of pollutants. Constructed wetlands have been used for many inorganics including metals, selenium (Se), nitrates, phosphates, cyanide (Horne 2000), as well as organics such as explosives and herbicides (Schnoor et al., 1995; Jacobson et al., 2003). The principle of phytostabilization is used, for example when vegetative caps are planted on sites containing organic and inorganic pollutants, or when trees are used as hydraulic barriers to prevent leaching or runoff of organic or inorganic contaminants. Trees can also be used in buffer strips to intercept horizontal migration of polluted underground water plumes and redirect water flow upwards (McCutcheon and Schnoor, 2003). Phytoextraction is mainly used for metals and toxic inorganics (Se, Pb As) (Blaylock and Huang, 2000). Plants accumulate these metals in their tissues which are subsequently harvested. The harvested parts can be used for non-food purposes (wood, cardboard) or ashed, followed by disposal in a landfill. Phytostimulation is used for hydrophobic organics that cannot be taken up by plants but can be degraded by microbes. Examples are PCBs, PAHs and other petroleum hydrocarbons (Hutchinson et al., 2003; Olson et al., 2003). Phytodegradation works well for organics that are mobile in plants such as herbicides, TNT, trichloroethylene (TCE). Phytovolatilization can be used for volatile organic compounds (VOC) (Winnike-McMillan et al., 2003) such as TCE and a few inorganics that exist in volatile form that is, Se and Hg (Hansen et al., 1998).

Hyperaccumulation

Special category of plants is the so called 'hyperaccumulators'. The goal of most phytoremediation strategies is to efficiently hyperaccumulate immutable toxic metals in plants' above ground harvestable tissues. Hyperaccumulation is usually defined as the concentration of a metal ion to > 0.1 - 1% of the dry weight of the plant (Baker, 1999). At these concentrations, recovery of metal from plant tissues becomes very economical (Baker, 1999). Recovery of even lower hyperaccumulated concentrations of most toxic metals (for example As, Cd and Hg) and radionuclides (for example isotopes of Ce, U and Te) could be more economical compared to the alternative physical remediation methods.

Table 1. Summary of phytoremediated chemicals.

Type	Chemicals treated	References
Phytoaccumulation/extraction	Cd, Cr, Pb, Ni, Zn, radionuclides BTEX, pentachlorophenol, short chained aliphatic compounds	Horne, 2000; Blaylock and Huang, 2000
Phytodegradation/transformation	Nitrobenzene, nitroethane, nitrotoluene, atrazine, chlorinated solvent for example DDT, chloroform, etc.)	Schnoor et al, 1995; Jacobson et al, 2003
Phytostabilization	Heavymetals in ponds, phenols and chlorinated solvents	McCutcheon and Schnoor, 2003; Newman et al, 1997
Phytostimulation	Polycyclicaromatic hydrocarbon, BTEX, PCB , tetrachloroethane	Hutchinson et al, 2003; Olson et al, 2003
Phytovolatilization	Chlorinated solvent , Hg, Se	Terry et al, 1995
Phytofiltration	Heavymetals, organics and radionuclides. Plant nutrients	Horne, 2000; Nwoko et al,2004

BTEX= benzene, toluene, ethyl benzene, xylenes; PCB= Polychlorinated biphenyl.

Hyperaccumulation of metals may involve three processes viz adsorption, transport and translocation but it also requires large sinks to store pollutants. The most notable mechanisms for sequestering thio-reactive metals involve two classes of cysteine-rich peptides, the metallothioneins (MTs) and phytochelatins (PCs). Metals such as Ag (I), AsO_3 (-III), Cd (II), Co (II), Cu (II) and Hg (II) are sequestered by bonding with organic sulphur (R-SH) on cycsteine residues of these peptides. *In vitro*, MTs form metal ligands with a specificity correlating with thiolate series for cation binding (Bi > Hg > Ag > Cu > Cd > Pb > Zn) (Kagi and Schaffer, 1988), although the precise specificity of MTs and PCs are *in vivo* and are not well defined. MTs can, however, protect plants from effect of toxic metal ions and aid in their accumulation. For instance, transgenic over-expression of the 32 amino acid metal-binding α -domain of mouse MT in tobacco confers moderate levels of Cd (II) resistance and accumulation (Pan et al., 1993, 1994). Examples of hyperaccumulator species so far identified are Ni hyperaccumulator *Alyssum bertolonii* (Li et al., 2003) and As hyperacumulating fern *Pteris vittata* (Ma et al., 2001). One discouraging aspect of hyperaccumulation method is that plant species used often grow slowly and attain low biomass.

Biology of phytoremediation

The biology of phytoremediation involves plant-microbe interactions and other rhizosphere processes, plant uptake, translocation mechanisms, tolerance mechanisms (compartmentation, degradation), and plant chelators involved in storage and transport. Also, the movement of pollutants through ecosystems via the soil-water-plant system to higher trophic level needs to be studied. Table 2 shows plant species with capacity to produce enzymes that facilitate phytoremediation.

Pollutant bioavailability is very important for effective phytoremediation. Pollutant bioavailability generally depends on the chemical properties of soil, pollutant, environmental condition and biological activity. Soils with small particle size (clay) hold more water than sandy soils, and have more binding sites for ions, especially cations-cation exchange capacity (CEC) (Shang et al., 2003). The concentration of organic matter in the soil is also positively correlated with CEC, as well as with the capacity to bind hydrophobic organic pollutants.This is because humus mainly consists of dead plant materials, and plant cell walls have negatively charged groups that bind cations, as well as lignin that binds hydrophobic compounds (Winnike-McMillan et al., 2003).

Two important chemical properties of a pollutant that affect its movement in soils are: hydrophobicity and volatility. Hydrophobicity is expressed as the octanol: water partition coefficient, or log K_{ow} (Trapp and McFarlane, 1995). A high log K_{ow} (> 3) corresponds to high hydrophobicity and such pollutants are tightly bound to soil organic matter, not easily dissolved in the soil pore water, lending to being classified as recalcitrant pollutants (for example PCBs, PAHs and others). Organics with log $K_{ow} < 3$ will be able to migrate in the soil pore water to an extent that is inversely correlated with their log $K_{ow.}$

Pollutant volatility is expressed as Henry's law constant (H_i) which is the measure of a compound's tendency to partition to air relative to water (Davis et al., 2003). Pollutants with $Hi > 10^{-4}$ tend to move in the air space between soil particles, whereas pollutants with $Hi < 10^{-6}$ move predominantly in water. Both water-mobile and air mobile organic pollutants can diffuse passively through plants. Inorganics are usually present as charged cations or anions, thus are hydrophilic. The bioavailability of cations is inversely correlated with soil cation exchange capacity (CEC). At low pH, bioavailability increases due to replacement of cations on soil CEC sites by H^+. To optimize phytoremediation, soil amendment is necessary to enhance bioavailability of pollutants. For instance, adding the natural organic acids citrate and malate will lower

Table 2. Plant enzymes that play a role in organic compounds transformation.

Enzyme	Plants that produce enzyme activity	Application
Dehalogenase	Hybrid poplar (*Populus spp*, algae (various spp) parrot-feather (*Myriophyllum aquaticum*)	Dehalogenates chlorinated solvents,
Laccase	Stonewort (*Nitella spp*), parrot-feather (*Myriophyllum aquaticum)*	Cleaves aromatic ring after TNT is reduced to triaminotoluene
Nitrilase	Willow(*Salix spp*)	Cleaves cyanide groups from aromatic ring
Nitroreductase	Hybrid poplar (*Populus spp),* Stonewort (*Nitella spp*), parrot-feather (*Myriophyllum aquaticum)*	Reduces nitro groups on explosives and other aromatic compounds.
Peroxidase	Horseradish (*Armoracia rusticana*)	Degradation of phenols
Phosphatase	Giant duckweed (*Spirodela polyrhiza)*	Cleaves phosphate groups from organophosphate pesticides

Source: Susarla et al. (2002).

pH and chelate metals such as Cd and Pb from bound sites, making them more available for plant up-take. The synthetic metal chelator; ethylene diamine tetra acetic acid (EDTA) has shown good promise at releasing metals from sorbed sites.

Role of rhizosphere in phytoremediation

Rhizosphere remediation occurs completely without plant uptake of the pollutant in the area around the root.

The rhizosphere extends approximately 1 mm around the root and is under the influence of the plant. Plants release exudates in the rhizosphere likely to serve as carbon source for microbes (Bowen and Rovira, 1991). As a result, high microbial build up of 1 - 4 orders of magnitude occur in the rhizosphere compared to bulk soils (Olson et al., 2003). Consequently, rhizosphere microbes can promote plant health by stimulating root growth via production of plant growth regulators, enhance mineral and water uptake. Rhizosphere remediation may be a passive process. Pollutants can be phytostabilized simply by erosion control and hydraulic control. There is also passive adsorption of organic pollutants and inorganic cations to plant surface. Pollutant adsorbed to lignin cells is called liginification.

Microbes and plant activities also affect pollutant bioavailability. Some bacteria release biosulfactants (rhamnolipids) that make hydrophobic pollutants more water soluble (Volkering et al., 1998). Plant exudates may also contain lipophilic compounds that increase pollutant water solubility or enhance biosulfactant-producing bacterial populations (Siciliano and Germida, 1998). Organic pollutants may be degraded in the rhizosphere by root-released plant enzymes or through phytostimulation of microbial degradation. Organics such as PAHs and PCBs and other petroleum hydrocarbons have successfully been remediated in the rhizosphere by microbial activity (Hutchinson et al., 2003, Olson et al., 2003). Plants stimulate the entire process by firstly, releasing carbon compounds to facilitate a higher microbial population around root zone. Secondly, secondary plant compounds released from the roots may specifically induce microbial genes involved in the de-gradation or act as co-metabolite to facilitate microbial degradation (Olson et al., 2003; Leigh et al., 2002). Also, roots of leguminous plants that host bacteria species with potential to convert atmospheric N_2 to inorganic N_2 in the soil can improve the C: N ratio of hydrocarbon contaminated soils, which ultimately enhance the process of rhizodegradation. Nwoko et al. (2007) reported sustained plant growth, leaf area and biomass production in *Phaseolus vulgaris* grown on spent engine oil contaminated soil. Better knowledge of these plant-microbe interactions is needed to better engineer more efficient plant-microbe consortia.

Uptake and metabolism of pollutants in plants

Uptake of pollutants by plant roots is different for organics and inorganics. Organics are man-made and thus lacks membrane transporters. Uptake is therefore driven by simple diffusion based on their chemical properties. Assimilation of organics is essential for close contact between pollutant and enzymes present in the plant cell. Absorbed pollutant could be transformed by variety of biochemical reactions in the plant system. Plants harbour versatile enzymatic machineries to attack and detoxify the contaminant (Schaffner et al., 2002). Plants normally metabolize organics by three sequential steps (Coleman et al., 1997).

Step 1 Involves all processes of hydrolysis, reduction and oxidation of the organic to facilitate its uptake and assimilation (Eapen et al., 2007; Komives and Gullner, 2005).

Step 2 Involves the conjugation or bonding between the product of step1 (organic metabolites) with endogenous hydrophilic molecules such as sugars, amino acids and glutathione (Coleman et al., 1997; Dietz and Schnoor, 2001).

Step 3 Involves the modified pollutant getting compartmentalized in the cell vacuoles or getting bound to cell wall component such as lignin and hemicellulose (Coleman et al., 1997; Dietz and Schnoor, 2001).

Step 1 generally entails hydrolytic or oxidative transformation of the organics, which involves introduction of functional groups to the organics, resulting in the formation of more polar, chemically active and water soluble compounds (Komives and Gullner, 2005).This step is very essential since it exposes the functional groups (for example hydroxyl or carboxyl), which will prepare the contaminant for step 2. Different group of enzymes are known to play important role in the oxidative metabolism of organics. In plants, oxidative metabolism of step 1 is mediated mainly by cytochrome P450 monooxygenase (Sandermann, 1994). Cytochrome P450 enzymes are very crucial during the oxidative pro-cess of bioactivation, to emulsify highly hydrophobic pollutants, and make them chemically reactive elec-trophilic compounds which form conjugates during step 2. In plants, cytochrome P450 forms the largest group of plant's protein and they play important role in deciding plant's tolerance to organics (Morant et al., 2003).

In step 2, the activated organics metabolite get activated and bound with sugar or sulfhydryl (-SH) group of glutathione resulting in hydrophilic forms. Conjugation results in less toxic and more polar compounds with higher molecular weights compared to the original compound (Edwards, 1998). Glutathione-*S*-transferases catalyse the nucleophilic attack of sulphur atom glu-tathione on electrophilic group of variety of hydro-phobic organic substrates. Conjugation of step 1 metabolites with glutathione take place in the cytosol, but it is harmful to accumulate these compounds in the cytosol (Edwards et al., 2000).

During step 3, the conjugated organic metabolites are removed from vulnerable sites. Cytosols are transported to the vacuoles or apoplast by tonoplast membrane bound transporters where they may not interfere with cellular metabolism. Vacoular compartmentalization is a major detoxification step in phytoremediation of organics (Coleman et al., 2002). ATPase is the main enzymes involved in this transport (Martinois et al., 1993).

In contrast, inorganics are taken up by biological processes via membrane transporter proteins. These tranporters occur naturally since inorganics pollutants are either plant nutrients (for example nitrates, phosphates, manganese and copper) or are chemically similar to nutrients and are taken up inadvertently (for example arsenate is taken up by phosphate transporters, selenate by sulphate transporters) (Abedin et al., 2002). Inorganics usually exist as ions and cannot pass membranes without the aid of membrane transporter protein. Because uptake of inorganics depends on a discrete number of membrane proteins, their uptake is saturable, following Michaelis Menten kinetics (Marschner, 1995). Individual transporter proteins have unique properties with respect to transport rate, substrate affinity and substrate specificity (Marschner, 1995). Also, the abundance of each transporter varies with tissue-type and environmental conditions, which may be regulated at the transcription level or through endocytosis.

Translocation of absorbed pollutants

Translocation from root to shoot requires a membrane transport step from root symplast into xylem apoplast.

The impermeable suberin layer in the cell wall of the root endodermis (casparian strip) prevents solutes from flowing straight from the soil solution or root apoplast into the root xylem (Taiz and Zieger, 1992).

Organic pollutants pass the membrane between root symplast and xylem apoplast via simple diffusion. Transpiration stream concentration factor (TSCF) is the ratio of the concentration of a compound in the xylem fluid relative to the external solution, and is a measure of uptake into the plant shoot. Entry of organic pollutants into the xylem depends on similar passive movement over membranes as their uptake into the plants. Mass flow in the xylem from the shoot creates negative tension in the xylem that pulls up water and solutes (Taiz and Zieger, 1992). Plant transpiration depends on plant properties and environmental conditions. Plant species differ in transpiration rate, due to metabolic differences (for example C3/C4/CAM photosynthetic pathway) and anatomical differences (for example surface to volume ratio, stomatal density, rooting depth) (Taiz and Zieger, 1992). Transpiration is maximal at high temperature, moderate wind, low relative air humidity as well as light intensity (Taiz and Zieger, 1992).

Phytovolatilization

Phytovolatilization is a mechanism by which plants convert contaminants into gaseous form, thereby removing the contaminant from soil or water (Terry et al., 1995). For example, inorganic Se can be volatilized by plants and microorganisms. Volatilization of Se involves assimilation of inorganic Se into the organic selenoaminoacids selencysteine (SeCys) and selenomethionine (SeMet). Selenomethioine is methylated to form a volatile, less toxic compound; dimethylselenide (DMSe).

Volatilization can be promoted through several ways. One of such means is the use of phreatophytes species with high transpiration rates and can prevent stomatal closure through sufficient irrigation. For Se, enzymes of the S assimilation pathway mediate Se volatilization, and overexpression of one of these, cystathionine-*y*-synthase promotes Se volalization (Van Huysen et al., 2003). Volatilization of mercury by plants was achieved by introducing a bacterial mercury reductase (MerA). *Arabidopsis thaliana* has successfully volatilized organic and inorganic mercury and significantly Hg-tolerant (Rugh et al., 1997; Watanabe, 1997).

Advantages inherent in the use of plant for phytoremediation

Plants enjoy tremendous reduction in energy cost and utilization by virtue of deriving energy from solar radiation. Plant can tolerate wide range of environmental conditions. Enzyme and protein constitution of plants are of immense benefit for phytoremediation. Sedentary nature of most plants is of advantage since they can over time develop mechanisms to acquire nutrients, detoxify pollutants and control local geochemical conditions. Infiltration is a primary pathway in contaminant migration to ground water, and plants play important role in regulating water content in soil. Root of plants supplement microbial nutrient and provide aeration to the soil, consequently increasing microbial population compared to non-vegetated area. Above all, phytoremediation gives better aesthetic appeal than other physical means of remediation.

CONCLUSION

Phytoremediation of pollutants is a growing technology. It is necessary for scientist in this field to pool resources and share knowledge gained from both laboratory and field researches. Plants and their associated microbes can remediate pollutants via stabilization, degradation in both rhizosphere and plants, extraction in harvestable plant part, or volatilization. Phytoremediation is obviously more cost-effective and environmentally friendly than other remediation alternatives. Further research is hereby recommended to improve the existing technology especially in the use of transgenic plants and fungi.

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