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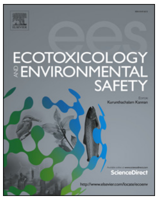

Review

Metal phytoremediation: General strategies, genetically modified plants and applications in metal nanoparticle contamination

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ABSTRACT

The accumulation of metals in different environmental compartments poses a risk to both the environment and biota health. In particular, the continuous increase of these elements in soil ecosystems is a major worldwide concern. Phytoremediation has been gaining more attention in this regard. This approach takes advantage of the unique and selective uptake capabilities of plant root systems, and applies these natural processes alongside the translocation, bioaccumulation, and contaminant degradation abilities of the entire plant and, although it is a relatively recent technology, beginning in the 90's, it is already considered a green alternative solution to the problem of metal pollution, with great potential. This review focuses on phytoremediation of metals from soil, sludge, wastewater and water, the different strategies applied, the biological and physico-chemical processes involved and the advantages and limitations of each strategy. Special note is given to the use of transgenic species and phytoremediation of metallic nanoparticles.

Contents

1. Introduction

The accumulation of metals in different environmental compartments poses a risk to both the environment and biota health,

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including humans, since these elements bioaccumulate in living organisms and also suffer biomagnification processes, in which contaminants increase in concentration in tissues of organisms at successively higher levels in a food chain (Alia et al., 2013). In particular, the continuous increase of these elements in soil ecosystems is a major worldwide concern (Pandey et al., 2015; Sharma and Pandey, 2014; Wuana and Okieimen, 2011), and, with novel technological advances and applications, novel forms of metal contamination have been noted and are of concern, such as the rising presence of metallic nanoparticles in the environment (Ebbs et al., 2016). These compounds show many positive impacts in several sectors, such as consumer products, cosmetics, pharmaceutics, energy, and agriculture, among others (Baker et al., 2014). However, the risks associated to their use are still unknown, and they may show potential adverse effects in the environment (Ruffini-Castiglione and Cremonini, 2009), making them target compounds for phytoremediation.

Many types of soil clean-up techniques have been applied over the years, categorized into physical, chemical and biological approaches (Hasegawa and Mofizur, 2015; Lim et al., 2014). Traditionally, remediation of metal-contaminated soils involves either on-site management or excavation and subsequent disposal to a landfill site. This, however, only shifts the contamination problem elsewhere and causes additional risk hazards associated with the transportation of contaminated soil and migration of the contaminants to adjacent environmental compartments (Gaur and Adholeya, 2004). An alternative to this process is soil washing, although this method is very costly, produces metal-rich residues which require further treatment, and usually renders the land unusable for plant growth, since it removes all biological activities (Gaur and Adholeya, 2004; Tangahu et al., 2011). Thus, it is recognized that physical and chemical methods suffer from severe limitations (i.e. high cost, intensive labor, irreversible changes in soil properties and disturbance of native soil microflora), while chemical methods are also problematic, since they usually create secondary pollution problems, generate large volumetric sludge and increase costs (Alia et al., 2013; Tangahu et al., 2011).

In this context, novel and better clean-up solutions for metal-contaminated soils are needed, and biological remediation techniques are considered the most adequate, since they are natural, ecological processes that do not impact the environment (Doble and Kumar, 2005). Biological remediation techniques include bioremediation, phytoremediation, bioventing, bioleaching, land forming, bioreactors, composting, bioaugmentation and biostimulation. Among these approaches, phytoremediation is the most useful (Ullah et al., 2015) and has been gaining more attention in this regard.

Phytoremediation comes from the Greek word *phyto*, meaning plant, and the word *remedium*, in Latin, meaning balance or remediation. This approach takes advantage of the unique and selective uptake capabilities of plant root systems, and applies these natural processes alongside the translocation, bioaccumulation, and contaminant degradation abilities of the entire plant (Hinchman et al., 1995). Phytoremediation can thus be applied to the environment to reduce high concentrations of several pollutants, such as organic compounds and metals (Ahmadpour et al., 2012; Pilon-Smits and Freeman, 2006), and, although it is a relatively recent technology, beginning in the 90's, it is already considered a green alternative solution to the problem of metal pollution, with great potential, since over 400 plant species have been identified as potential phytoremediators (Alia et al., 2013; Lone et al., 2008). In addition, genetically modified plants have also been gaining more attention in this regard, since they can be created to increase phytoremediation capabilities (Macek et al., 2008; Novakova et al., 2010) showing advantages against both abiotic stress and the presence of metals in the environment (Ibañez et al., 2015).

Moreover, phytoremediation allows the restoration of polluted environments with low costs and low collateral impacts (Ibañez et al., 2015), shows benefits regarding the increase of vegetation growth and can be applied in many different ecosystems (Pilon-Smits and Freeman, 2006). Some limitations to this technique do, however, exist, mainly regarding remediation time and the problems of what to do with the toxic plant waste left over after phytoremediation. In this context, the aim of the present study is to discuss and compare phytoremediation techniques in both aquatic and terrestrial ecossystems, with special regard to genetically modified plants and the increasing problem of metallic nanoparticles in the environment.

2. Phytoremediation strategies

Plants can be used for phytoremediation via different physiological processes that allow metal tolerance and absorption capacity (Peuke and Rennenberg, 2005; Pilon-Smits and Freeman, 2006). The main metal phytoremediation techniques can be categorized in: phytofiltration, phytostabilization, phytoextraction, phytovolatilization and phytotransformation (Halder and Ghosh, 2014). Fig. 1 displays a diagram of different phytoremediation technologies involving removal and containment of contaminants and the physiological processes that take place in plants during phytoremediation.

2.1. Phytofiltration

Phytofiltration can be categorized as rhizofiltration (use of plant roots), blastofiltration (use of seedlings) or caulofiltration (use of excised plant shoots; Latin *caulis*= shoot) (Sarma, 2011). In this type of process, contaminants are absorbed or adsorbed from contaminated surface waters or wastewaters, restricting their movement to underground waters. This strategy may be conducted *in situ*, where plants are grown directly in the contaminated water body, decreasing costs (Suthersan and McDonough, 1996).

Blastofiltration takes advantage of the sudden increases in surface to volume ratio that happens after germination and the fact that many seedlings are able to adsorb or absorb large amounts of metal, making them uniquely suitable for water remediation (Krishna et al., 2012). In one study reported in the literature, castor, okra, melon and moringa seeds were investigated with regard to their blastofiltration potential. In 72-h experiments with Pb- and Cd-contaminated water with 60 ppm of each, separately, metal content decreased by 96–99%. Okra and castor seeds were the most efficient, while moringa seeds removed 100% of Cd from the contaminated-water. The author in this cases postulates that plant seeds of lesser economic importance could represent the next generation green technology at bioremediation of heavy metal polluted water (Udokop, 2016). Another report, also using aqueous extracts from *Moringa oleifera* seeds reported metal uptake from contaminated water as 95% for copper, 93% for lead, 76% for cadmium and 70% for chromium (Ravikumar and Sheeja, 2013). Papaya seeds have also recently shown promise in metal removal from contaminated waters. These seeds were added to aqueous solutions contaminated with zinc, at different pH values, and results indicated that Zn uptake increased with increasing contact time and agitation rate of the solutions, while indicating the effective pH for maximum Zn uptake was pH 5.0, demonstrating that absorption efficiency is pH-dependent. In addition, decreases in sorbent particle sizes led to increases in Zn sorption due to increases in surface area and, consequently, binding sites (Ong et al., 2012). Mango seed powder has also been applied in this context, for the removal of Cu, Cd and Pb from aqueous solutions,