Chapter 16
Phytoremediation of Electronic Waste: A Mechanistic Overview and Role of Plant Secondary Metabolites

Mubarak Ali Khan, Nazif Ullah, Tariq Khan, Muhsin Jamal, Naseer Ali Shah, and Huma Ali

Abstract The escalating economic growth, urbanization and globalization over the last three decades have resulted in the huge production and consumption of electronic devices and appliances all over the world. This has caused an alarming situation of the disposition of electronic waste (e-waste) from the used and discarded electronic products to the environment, which can adversely affect the ecosystem and health of the humans. Management, treatment and recycling of e-waste become crucial to prevent the serious environmental complications and diseases. Among the several methods for treatment of e-waste, phytoremediation is of vital importance, which involves the application of plants and vegetation for the remediation of e-waste contaminants. Phytoremediation technology is a cost-effective green technology known for its optimal results on-site and is considered as environment-friendly and generally socially acceptable. The success of phytoremediation technology is by virtue of some unique plants which possess selective capabilities such as uptake of the metals by roots, translocation through stem and bioaccumulation in the leaves.

In this chapter, we have described in detail the process of phytoremediation as a suitable and sustainable method for remediation of e-waste contaminants including

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M. A. Khan (✉) · N. Ullah
Department of Biotechnology, Faculty of Chemical and Life Sciences, Abdul Wali Khan University Mardan (AWKUM), Mardan, Pakistan
e-mail: makhan@awkum.edu.pk

T. Khan
Department of Biotechnology, University of Malakand, Chakdara Dir Lower, Pakistan

M. Jamal
Department of Microbiology, Abdul Wali Khan University Mardan (AWKUM), Mardan, Pakistan

N. A. Shah
Department of Biosciences, COMSATS Institute of Information Technology, Islamabad, Pakistan

H. Ali
Department of Biotechnology, Bacha Khan University, Charsadda, KP, Pakistan

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heavy metals and other hazardous substances. Further, a mechanistic overview of the process of phytoremediation technology for treatment of e-waste has been elucidated to highlight the functional role of phytochemicals of plants in contaminants removal through phytoremediation.

Keywords Phytoremediation · Electronic waste · Mechanistic overview · Plant secondary metabolites

16.1 Introduction

Electronic waste (e-waste) refers to the used and unwanted material left from the different electronic devices; those have completed their normal shelf life in many household applications. E-waste is mainly composed of the metals used in the manufacturing of electronic appliances. For instance, gold, silver, copper, nickel, mercury and other hazardous metals can be extracted from the discarded materials of various electronic devices (Robinson 2009; Tsydenova and Bengtsson 2011). The primary sources of e-waste are the discarded household electronic products such as radios, TVs, photocopier, printers, CD players, batteries, calculators, tonners, cell phones, etc. However, the industrial, military and laboratory electronic machineries such as fans, washing machines, air conditioners, fridge, oven, heater, iron, grinder, keyboards, etc. also contribute in the major production of e-waste to the environment (Heacock et al. 2016). These electronic products produce large quantities of different types of e-waste. Recent analytical technologies have shown that e-waste from many electronic products is composed of hazardous substances such as polyvinyl chlorides (PVCs and PCBs), epoxy resins, thermosetting plastics, fibreglass, cadmium, germanium, lead, mercury, carbon and iron and the elements such as tin, gallium, thallium, copper, gold, beryllium, silicon, silver, vanadium, aluminium, selenium and indium (Muszyńska et al. 2015).

The escalating economic growth in the last 30 years has substantially increased the consumption and production of electronic products and equipment worldwide (Babu et al. 2007). In fact, the new electric appliances have drastically influenced every aspect of the modern-day life by providing more comfort, health and ease in acquisition and exchange of information (Sinha 2007). Further, the urbanization and globalization have forcefully uplifted the economic and technological growth through digital revolution worldwide. People all over the world are now using more electronic products than their forefathers. This has caused an alarming situation of the disposition of a variety of e-waste to the environment, which can adversely affect the ecosystem and of course the health of the humans. It is harder and challenging to dismantle and recycle e-waste due to the complex nature of its composition. Since a lot of the electronic products are made up of different materials, such as glass, plastics and some coating or colouring chemicals, this mixed composition of e-waste is the major bottleneck in its effective treatment, management and low-cost recycling (Yu et al. 2010). The mixed composition also makes e-waste to cause negative impacts on human health. The hazardous materials present in e-waste are reported to cause many serious ailments including bronchitis, skin disease, reproductive complaints and cancer (Yu et al. 2010; Robinson 2009; Li et al. 2009). Many lethal and poisonous substances from e-waste enter the human food chain through the soil-crop-food pathway and cause severe health complications. According to a recent survey, the annual global production of e-waste is estimated at approximately 40 million metric tons, and 13% of that is reported to be recycled mostly in the developing world (Laurent et al. 2014). Further, the combustion and burning of e-waste on the site results in the production of fine particulate matter that is the main pollutant responsible for cardiac and pulmonary diseases. The largest e-waste recycling unit in the world is located in Guiyu city of China. People of this city are suffering from many diseases including digestive complaints, respiratory and neurological disorders. For instance, 80% of the infants and children in Guiyu city are at risk of respiratory diseases and poisoning due to lead (Leung et al. 2008). Combustion from burning e-waste creates fine particulate matter, which is linked to the pulmonary and cardiovascular disease. While the health implications of e-waste are difficult to isolate due to the informal working conditions, poverty and poor sanitation. The worrisome thing is that majority of the chemicals from e-waste are not biodegradable and they persist in the environment for long periods of time, increasing exposure risk (Ogunseitan et al. 2009). Several methods including physical, thermal and chemical are currently employed for the treatments, management and recycling of e-waste. However, these methods have some limitations. Most of these methods are costly and do not provide optimal performance on-site (Kofoworola 2007). One of the several biological methods for remediation of e-waste metals is phytoremediation, which involves the application of plants and vegetation for the treatment of contaminated soil. Phytoremediation technology is economically justified and is considered as least environmentally invasive and generally socially acceptable. The extensive and deep root system of the hyperaccumulator plants enables purification of groundwater environment from the pollution caused by disposition of e-waste into the environment. That is why this technology of remediation of chemical contaminants is also called as green technology (Tangahu et al. 2011).

16.2 Available Methods for E-waste Management and Treatment

E-waste contains many hazardous substances, which are harmful not only to the environment but for humans as well. Thus, it is crucial to search out for the effective and efficient techniques for the clean-up and removal of e-waste. Several thermal and chemical methods are already being used for the management, treatment and recycling of e-waste. These methods include (1) the recycling treatment and metal recovery; (2) shredding, pulverization and crushing; (3) sustainable disposal; (4) landfilling; (5) incineration; (6) open field dumping; and (7) open burning (Kofoworola 2007). As discussed in details in other chapters of this book, each method has its own prospects and limitation. Most of these methods either are costly or do not provide optimal performance on-site. Therefore, biological methods for treatment of e-waste, for example, phytoremediation, are preferred for their potential in clean-up of the environment and recovery of valuable metals. Besides, these methods are cost-effective, eco-friendly and sustainable in optimal treatment of e-waste (Brandl et al. 2001).

16.3 Phytoremediation: An Efficient Technology for Treatment of Electronic Waste

Phytoremediation is the biological method for the remediation of e-waste through plants. This process can be used for the removal of hazardous substances from e-waste in contaminated soil, sediments and water. There are many exceptional plant species which possess the natural potential of accumulating e-waste metals and are known as hyperaccumulators (Tangahu et al. 2011). As described in Table 16.1, a substantial number of research studies are available in literatures, showing the potential of many plant species in the remediation of several types of e-waste including heavy metals and other hazardous substances. Through the distinct, unique and selective capabilities in the entire plant system such as uptake of the metals by roots, translocation through stem and bioaccumulation in the leaves, phytoremediation takes the first line in the bioremediation of e-waste. Exploitation of phytoremediation technology by using green plants and vegetation has successfully accomplished the in situ treatment of soil, sediment and water, which were highly contaminated by polychlorinated biphenyls (PCBs) and other organic hazardous substances of e-waste (Brandl et al. 2001). In Guiyu city of China, a very large portion of soil was contaminated by different types of e-waste including polycyclic aromatic hydrocarbons (PAHs), brominated diphenyl ethers (BDEs) and deca-BDE. It is worth mentioning that the area for rice fields near burning sites was less than e-waste open burning sites. Further, it was observed that e-waste open burning sites in the soil possessed fairly higher concentrations of total PCBs, polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzodioxins (PCDDs). The non-e-waste open burning sites were highly contaminated by all persistent toxic substances (PTSs), with 5–50 times more concentrations than the PTSs in the rice field. This was the very first detailed research analysis on the PTS contamination in soils which was due to open burning of e-waste. Throughout the phytoremediation technology using alfalfa plants, the soil enzyme and microbial community were enhanced for removal of polychlorinated biphenyls (PCBs) in the contaminated soil field. For remediation of polycyclic aromatic hydrocarbons (PAHs), a multi-component phytoremediation system includes PAHs degrading

Table 16.1 Application of different plant species used in the phytoremediation of e-waste metals/contaminants and their phytochemical composition

E-waste contaminants	Plant species used in phytoremediation	References	Bioactive metabolites in the plant
Antimony (Sb)	*Achillea wilhelmsii*	Hajiani et al. (2015)	Terpenoids, phenolics, flavonoids
	Matthiola farinosa	Hajiani et al. (2015)	Flavonoids
	Pteris fauriei	Feng et al. (2015)	Flavonoids, phenols, tannins
	Pteris vittata	Müller et al. (2013)	Flavonoids, titerpenoids, phenolics
	Pteris cretica	Feng et al. (2011)	Alkaloids, flavonoids, saponins
Arsenic (As)	*Azolla caroliniana*	Zhang et al. (2008)	Alkaloids, terpenoids, steroids
	Populus alba	Vamerali et al. (2009)	Flavonoids, polyphenols
	Daucus carota	Helgesen and Larsen (1998)	Phenolic compounds, ascorbic acid
	Oryza sativa	Heitkemper et al. (2001)	Saponins, terpenoids, tannins
	Malus domestica	Caruso et al. (2001)	Quercetin, chlorogenic acid
Barium (Ba)	*Helianthus annuus*	Sampaio Junior et al. (2015)	Tannins, saponins, flavonoids
	Brassica juncea Czern. (mustard)	Coscione and Berton (2009)	Flavonoids, n-octacosane, linolenic, oleic acid
	Lactuca sativa L.	Lamb et al. (2013)	Carotenoids, phenolic acids
	Medicago sativa L.	Gardea-Torresdey et al. (1999)	Phenols, terpenoids, flavonoids
	Calotropis procera	Gardea-Torresdey et al. (1999)	Tannins, saponins, flavonoids
Beryllium (Be)	*Brassica napus* L.	Ali et al. (2018)	Caffeic acid, chlorogenic acid, quercetin, kaempferol
Cadmium (Cd)	*Oryza sativa* L.	Liu et al. (2007)	Saponins, terpenoids, tannins
	Sorghum bicolor L.	Muranyi and Ködöböcz (2008)	Tannins, saponins, flavonoids
	Pyxine cocoes	Muranyi and Ködöböcz (2008)	Tannins, saponins, flavonoids
	Hordeum vulgare	Peralta-Videa et al. (2009)	Phenolics, flavonoids, tannins

(continued)

Table 16.1 (continued)

E-waste contaminants	Plant species used in phytoremediation	References	Bioactive metabolites in the plant
	Spinacia oleracea (spinach)	Intawongse and Dean (2006)	Rutin, quercitin, gallic acid
	Brassica juncea L.	Peralta-Videa et al. (2009)	Phytoanticipins, phytoprotectants
	Eucaliptus camaldulenses Dehnh	Pence et al. (2000)	Tannins, saponins, flavonoids
Hexavalent chromium/chromium VI (Cr VI)	*Nicotiana tabacum*	Kim et al. (2006)	Alkaloids, steroids, phenols
	Convolvulus arvensis	Montes-Holguin et al. (2006)	Phenolic compounds, ascorbic acid
	Brassica oleracea var. *botrytis (cauliflower)*	Peralta-Videa et al. (2009)	Phenolic compounds, ascorbic acid
	Lycopersicon esculentum L.	Peralta-Videa et al. (2009)	Rutin, quercitin, gallic acid
	Calotropis procera	Kim et al. (2006)	Cardenolides, flavonoids, saponins
Lead (Pb)	*Alternanthera philoxeroides*	Cho-Ruk et al. (2006)	Phenols, cardiac glycosides
	Amaranthus hybridus L.	Tangahu et al. (2011)	Flavonoids, steroids, terpenoids
	Brassica campestris L.	Tangahu et al. (2011)	Flavonoids, anthocyanins
	Brassica juncea (L.) Czern.	Van Ginneken et al. (2007)	Phytoanticipins, phytoprotectants
	Brassica nigra (L.) Koch	Cho-Ruk et al. (2006)	Phenolics, flavonoids, tannins
Mercury (Hg)	*Brassica juncea* L.	Van Ginneken et al. (2007)	Phytoanticipins, phytoprotectants
	Colocasia esculenta	Skinner et al. (2007)	Phenolics, flavonoids, tannins
	Eichornia crassipes	Skinner et al. (2007)	Phenolics, flavonoids, tannins
	Helianthus tuberosus	Sas-Nowosielska et al. (2008)	Chlorogenic acids, phenolic compounds
	Oryza sativa L.	Liu et al. (2007)	Saponins, terpenoids, tannins
Nickel (Ni)	*Salix viminalis*	Watson et al. (2003)	Phenolics, flavonoids, tannins
	Sorghum bicolor L.	Muranyi and Ködöböcz (2008)	Phenolics, flavonoids, tannins
	Hypogymnia physodes	Muranyi and Ködöböcz (2008)	Tranorin, chloroatranorin, usnic acid

(continued)

Table 16.1 (continued)

E-waste contaminants	Plant species used in phytoremediation	References	Bioactive metabolites in the plant
	Canna indica L.	Subhashini and Swamy (2014)	Phenolic compounds, tannin, saponins
	Vetiveria Zizanioides L.	Muranyi and Ködöböcz (2008)	Phenolics, flavonoids, tannins
Polychlorinated biphenyls (PCBs)	*Medicago sativa*	Petruzzelli et al. (2012)	Protchaechenic acid, caffate, kaempherol
	Lespedeza cuneata	Petruzzelli et al. (2012)	Phenolics, flavonoids, tannins
	Panicum clandestinum	Petruzzelli et al. (2012)	Alkaloids, tannins, saponins, flavonoids
	Phalaris arundinacea L.	Petruzzelli et al. (2012)	Alkaloids
	Panicum variegatum L.	Petruzzelli et al. (2012)	Alkaloids, tannins, saponins, flavonoids
Selenium (Se)	*Oryza sativa*	Dhillon and Dhillon (2009)	Saponins, terpenoids, tannins
	Brassica juncea L.	Schiavon and Pilon-Smits (2017)	Phytoanticipins, phytoprotectants
	Hibiscus cannabinus L.	Parker et al. (2003)	Phenolics, flavonoids, tannins
	Pteris vittata	Parker et al. (2003)	Phenolics, flavonoids, tannins
	Typha angustifolia L.	Srivastava et al. (2005)	Phenolics, flavonoids, tannins

Data of the bioactive compounds present in the respective plant species was obtained from the plant metabolites database (http://pmn.plantcyc.org/)

bacteria (*Acinetobacter* sp.), carbuncular mycorrhizal fungus (AMF; *Glomus mosseae*) and ryegrass (*Lolium multiflorum*). The application of AMF considerably ($p < 0.05$) enhanced the growth of ryegrass. The cultivation of ryegrass subsequently improved the growth of PAH-degrading bacteria and which consequently enhanced the peroxidase activities in soil. Similarly, the interactions of ryegrass with PAH-degrading bacteria or AMF considerably ($p < 0.05$) enhanced the dissipation of phenanthrene (PHE) and PYR (pyrene) from the soil. Using rhizobox experimentation system, a decreasing dissipation gradient of PHE and PYR was revealed along the radial direction of maize (*Zea mays* L.) root, in which the highest dissipation rates were observed in rhizosphere zone followed by near rhizosphere zone and bulk soil zone in outer sections. The results revealed that there is a great potential for the development of a multi-component phytoremediation system for PAH-contaminated soil such as PAH-degrading bacteria, plants and AMF (Xiezhi 2008). In another study, Lin et al. (2003) described the importance of phytoremediation phenomenon for treatment of PCB-contaminated soils from e-waste recycling zone. The study was targeted to compare the capabilities of four different plants including alfalfa, rice, tall fescue and ryegrass for phytoremediation of PCBs. The plants were applied to remediate PCB-contaminated soil of Taizhou city, which is one of the largest e-waste recycling centres in China. They recorded optimal results of PCBs remediation by the cultivated plants in the soil after 120 days, as compared with the unplanted soil.

16.3.1 Phytoextraction

Phytoextraction also called as phytoaccumulation is the process of removal or movement of e-waste metals from the contaminated soil through plant roots into stem and leaves (Jutsz and Gnida 2015). The plants which exhibit the natural potential of accumulating higher levels of metals are called hyperaccumulators. Thus through the phenomenon of hyperaccumulation during phytoextraction, some plants can take up a variety of e-waste metals in enormous concentration from the contaminated soil. These hyperaccumulators can carry and accumulate the obnoxious metals in different above-the-ground organs such as stem, branches and leaves in concentrations from 100 to 1000 times higher than the normal plants without being affected by any visible phytotoxic effects (Figs. 16.1 and 16.2). Further, these plants are generally observed to grow abundantly in the areas contaminated with the continuous disposition of e-waste and produce greater biomass that can be easily handled for harvesting and recovery of different valuable metals. Therefore, such plants are suitable for the process of phytoremediation (Rascio and Navari-Izzo 2011). On the basis of the quantity of metals in dried foliage such as Cd 100; Co, Cu, and Cr 300; Pb and Ni 1000; and Zn 3000 μg/g, respectively, a large number of plants (about 500 taxa) have been recognized as hyperaccumulators of important metals (Van der Ent et al. 2013). A list of such is given in Table 16.1. These plants belong to different diverse families such as *Brassicaceae*, *Violaceae*, *Cunouniaceae,* *Lamiaceae*, *Asteraceae*, *Poaceae*, *Euphorbiaceae*, *Caryophyllaceae,* *Cyperaceae*, *Fabaceae*, *Caryophyllaceae* and *Flacourtiaceae* (Muszynska and Hanus-Fajerska 2015). These plants are exclusively different from other plants due to the following characteristics: (1) a higher capability to sequester heavy metals from the contaminated soils, (2) better root to shoot transportation of metal ions, (3) a superior capability to detoxify and collect/bin tremendously huge quantity of heavy metals in the shoots, (4) fast-growing ability and accumulation capability of heavy metals anions in the shoots, and (5) a well-developed and plentiful root system (Jabeen et al. 2009; Rascio and Navari-Izzo 2011).

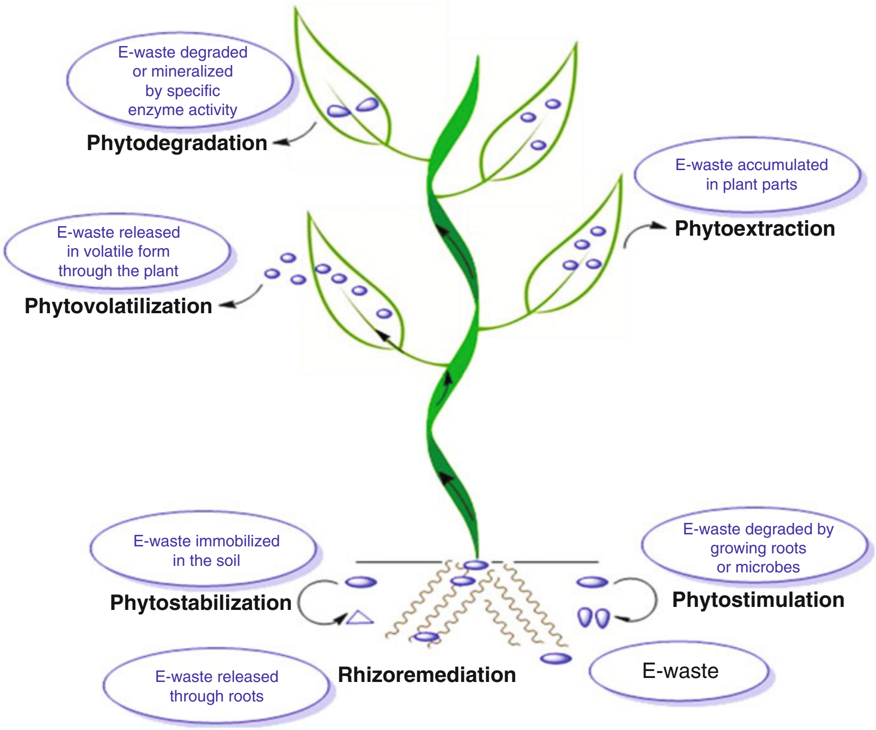

Fig. 16.1 Schematic representation of the different processes involved in the phytoremediation of e-waste in the contaminated soil

16.3.2 Phytofiltration

Phytofiltration is the use of roots, seeds and plants to adsorb or precipitate toxic metal ions from the aqueous medium (Ali et al. 2013). As illustrated in Figs. 16.1 and 16.2, phytofiltration is classified further to the following three forms, i.e. (1) rhizofiltration is the application of the plant roots for extraction of heavy metals, (2) blastofiltration is the application of the plant seedlings for extraction of heavy metals and (3) caulofiltration is the application of the cut/excised plant shoots for extraction of heavy metals. Overall, it is the remediation of heavy metals from the polluted and contaminated sites by using plant roots or seedlings (Chen et al. 2015).

16.3.3 Phytostimulation

Phytostimulation is the process of enhancing plant capability to degrade/detoxify organic wastes by stimulation of microbial enzyme activities for decontamination

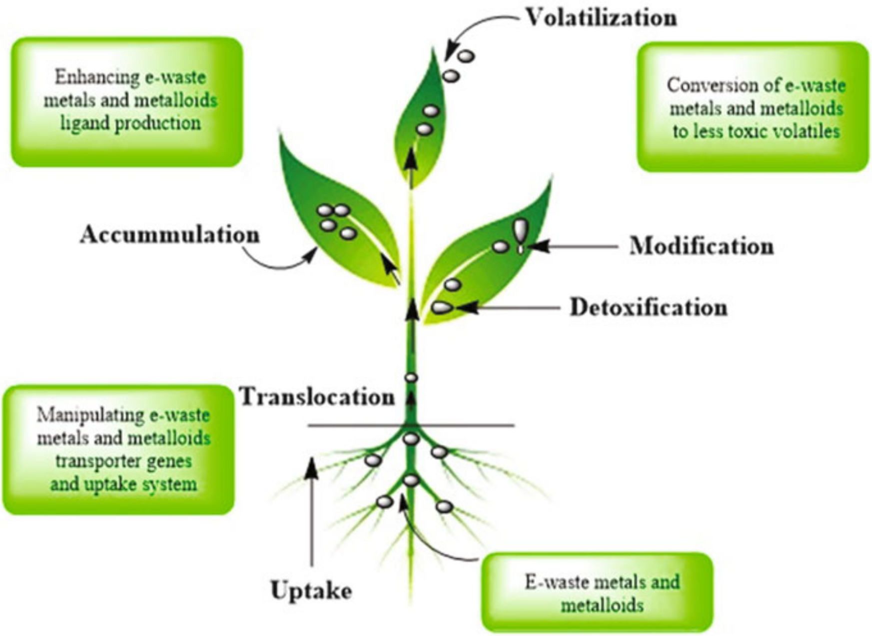

Fig. 16.2 Mechanistic overview of phytoremediation of e-waste contaminants by using hyperaccumulator plants

(Fig. 16.1). Certain plant extracts/exudates secretions from roots of the plants can be enhanced by certain microbes. For example, ethylene (a plant hormone) on one hand can stimulate elongation of roots at very low concentration and on the other hand at a higher concentration can inhibit cell division and DNA synthesis. However, this effect can be stopped by reducing ethylene concentration in plants. The reduction in ethylene can be obtained by some specific enzyme such as 1-aminocyclopropane-1-carboxylase deaminase which regulates ethylene biosynthesis by balancing ethylene-level production in plants (Donot et al. 2012; Gaiero et al. 2013). This enzyme is made by plant growth-promoting rhizobacteria (PGPR) linked with plant roots using exudates/extract released by plants as carbon and energy sources to cause degradation of e-waste metal contaminants (Tak et al. 2013).

16.3.4 Phytostabilization

This process of phytoremediation refers to the application of plant roots to absorb pollutants from the soil and to retain them within the rhizosphere (Figs. 16.1 and 16.2). By this process, e-waste contaminants, especially hazardous heavy metals, are separated from the source and stabilized, limiting this contaminant from spreading to other places in the environment (Lone et al. 2008). The metals are reduced by the root system of the plants through precipitation, absorption, complication and valence reduction in the region around plant roots and thus the access and mobility of contaminant to the environment are restricted (Choudhary and Varma 2016). The quantity of heavy metals found in the rhizosphere soil around a plant indicates the efficiency and success of phytostabilization in restricting the mobility of heavy within the plant (Rajkumar et al. 2012). Plants capable of the phytostabilization process should have a broad metals recognition and the tendency for low mobilization of metals from roots to shoots (Islam et al. 2013). The phytostabilization capacity of plants can be improved by changing the physicochemical conditions such as pH and organic matter contents. These conditions can be changed by adding some substances such as biochar or compost which will increase the yield of plants and also immobilize the metals. Phytostabilization is a superior substitute to other techniques because of its higher potential of capturing hazardous metals in-situ. The contaminants are not taken up into other tissues of the plant and therefore do not disperse into the environment. It focuses primarily on heavy metal sequestration only within the rhizosphere (Tak et al. 2013).

16.3.5 Phytovolatilization

Phytovolatilization is a remediation process which uses plants for the elimination of soil contaminants which are readily changed into vapours and so are released into the environment (Ali et al. 2013). Some plants such as tobacco plants have the good capability towards the accumulation of extremely toxic methylmercury from Hg-contaminated sites and convert it to the less toxic elemental Hg in a volatile form that releases through the leaves of plants to the environment (Mukhopadhyay and Maiti 2010). This conversion of the volatile form of contaminants during phytovolatilization is due to plants' metabolic potential in combination with microbes living inside the rhizosphere (Tak et al. 2013).

16.3.6 Phytodegradation

It is the degradation of toxic organic contaminants into less or non-hazardous chemicals through plant enzymes (Ali et al. 2013). Some enzymes such as nitroreductases and dehalogenases are plant-specific enzymes which are involved in the degradation of organic contaminants (Favas et al. 2014). There should be optimum conditions such as pH and temperature for these enzymes to cause effective contaminants degradation. The process of conversion of hazards toxic organic pollutants can be improved in the soil by applying rhizospheric microbes through the process of rhizodegradation (Ogunmayowa et al. 2015). This effective conversion occurs because the rhizospheric region of the plants contains a higher amount of nutrients released from the roots. These nutrients attract more bacteria to improve the conversion of the contaminants compared to the bulk soil which has little organic compounds and would contain less population of microbes (Babalola 2010). However, phytodegradation is mainly limited to the elimination of organic pollutants since heavy metals such as Cu, Ag, Hg and Au are non-biodegradable.

16.3.7 Rhizofiltration

Rhizofiltration is the process of removing toxic substances/chemicals or pollutants from groundwater through filtration using the roots of plants. This process depends on the mechanism of rhizospheric accumulation by plants (Figs. 16.1 and 16.2). Among plants, the terrestrial plants are more proficient for the rhizofiltration of toxic chemicals compared to other aquatic plants because the former plants have special natural solar-driven pumps to sequester particular elements from the nearby environment (López-Chuken 2012). The plants that have the potential of translocation and resistance towards high amounts of toxic heavy metals such as hyperaccumulators are highly fit for the process of rhizofiltration. Addition of PGPR to an e-waste contaminated site results in the decrease of heavy metal toxicity by raising the capability of plants to become free from heavy metal contamination and safe from environmental stress (Tak et al. 2013). However, there are certain limitations of the phytoremediation technology which include: reduce the rate at which remediation take place which normally becomes inadequate when there are a large number of pollutants at the contaminated area and also low accumulation and storage of pollutants in the plant materials (Ma et al. 2011).

16.4 Silencing Mechanisms Involved in Phytoremediation of E-waste Metals

Metals at excess level hinder the metabolic processes of plant and thus stop normal plant functioning. The harm to plants is caused in various processes such as the generation of reactive oxygen species (ROS) and/or the dislocation of amino acids through the formation of bonds between these heavy metals and –SH groups of the amino acids (Emamverdian et al. 2015; Krumova et al. 2016). ROS damages the cell membrane in a way that they hinder the functional groups of important molecules in the cell which results in abnormal functioning of enzymes and pigments. In addition to these, the heavy metals suppress photosynthesis, respiration and other enzymatic activities of the plant (Emamverdian et al. 2015; Pence et al. 2000). Among the metals there are those which can undergo oxido-reduction that is redox reaction and are classified as Redox-active metals such as Chromium (Cr), Copper (Cu), Manganese (Mn), Iron (Fe), Lead (Pb) and those which are non-redox active metals such as Cadmium (Cd), Nickle (Ni), Mercury (Hg), Zinc (Zn) and Aluminium

(Al) (Bücker-Neto et al. 2017). Redox-active metals directly produce ROS and thus generate oxidative stress in cells causing disruption to DNA structure and function, chloroplast and other pigments eventually destroying the cell (Singh et al. 2016). On the other hand, the non-redox active metals activate ROS-producing enzymes and restrain antioxidant system thus causing the damage (Emamverdian et al. 2015). In any case, ROS is generated, and the ultimate damage is caused by the excess oxidation of membranes and biomolecules. Plants protect itself from these metals by hindering the uptake through physical barriers such as thick cuticle, cell walls, and tissues such as trichomes. However, as we are studying the phytoremediation of these metals, we will discuss the system in which the plant modify/detoxify these metals for its own good and thus protect the environment too.

Plants protect itself from oxidation through its defence system primarily run by the secondary metabolites classified as phytochemicals. Once the metals surpass the barriers and enter the tissues and cells of the plant, different defence mechanisms in the cell are initiated to alleviate the damaging effects of the heavy metal (Silva and Matos 2016). One mechanism is the activation of antioxidant-generating enzymes such as superoxide dismutase, catalase and glutathione reductase and non-enzymatic antioxidants such as phenolic compounds, ascorbate, glutathione, alkaloids and tocopherols that remove the free radicals (Sharma et al. 2012). As an example, the detoxification of metals by phenolic compounds is detailed later. Apart from the role of secondary metabolites, one example of the defence process used by the plants is the production of the enzyme phytochelatin synthase that binds to heavy metals (Gupta et al. 2013). Phytochelatin synthase results in the formation of phytochelatins (PCs) which are short-chain thiol-rich repetitions of peptides of low-molecular-weight and are used as biomarkers for detecting the level of metals (Saba et al. 2013). Other than PCs, plant synthesize metallothioneins (MTs) which are also low-molecular-weight proteins rich in cysteine and having affinity for metals such as Cu, Zn, Cd and As (Guo et al. 2013). These are among the many different mechanisms used by the plants to silence heavy metals. However, our main aim is to focus on how secondary metabolites plant their role in remediation of toxic metals of e-waste.

16.5 Role of Plant Secondary Metabolites in the Phytoremediation of E-waste Metals

Controlling soil contamination such as that from e-waste through phytoremediation has been in the limelight since recent. Although there are many different schemes of the exact mechanism of contaminant removal through phytoremediation, the role of secondary metabolites in plants cannot be undermined. Secondary metabolites are phytochemicals produced as a product of secondary metabolism which is not directly involved in the growth and development of plants. Secondary metabolites generally play an important role in plant interactions and defence system. There is no sharp rule for classification of secondary metabolites; however, the phytochemicals which play a role in plant defence response are categorized into the following classes: alkaloids, flavonoids, glycosides, phenols and terpenoids broadly. Every category encompasses a variety of types of metabolites, every class playing a role in different defence processes of the plant (Bourgaud et al. 2001).

Many different studies have hinted towards the role of phytochemicals and antioxidants in the detoxification of heavy metals accumulated at the sites of e-waste disposal. For instance, results from studies by Agwaramgbo (2005) suggested that the phytoremediation capabilities of the plants tested had a direct correlation with the antioxidant potential. They further concluded that the plants having the highest amount of phytochemicals such as carotene and vitamin C were having the highest antioxidant potential and thus were able to remediate 2,4,6-trinitrotoluene effectively.

Similarly, another study has suggested that the concentration of important phytochemicals such as flavonoid, alkaloid, tannin, saponin and steroid was detected to be higher in leafy vegetables which has the high accumulation of metals such as Copper (Cu), nickel (Ni), zinc (Zn), lead (Pb), cadmium (Cd) and arsenic (As) (Ogoko 2015). In another study, Smeets et al. (2005) observed an increased accumulation of phenolic compounds in *Phaseolus vulgaris* when exposed to cadmium. This suggests the direct involvement of phenolic compounds in heavy metal detoxification. Similarly, studies on leaves of *Phyllanthus tenellus* sprayed with copper sulfate reported an elevated level of phenolic compounds compared to the control plants (Michalak 2006). Other plants such as wheat also induced an increased shift towards phenolic compound biosynthesis pathway (shikimate pathway) in response to nickel toxicity (Díaz et al. 2001).

Although the majority of the studies so far have reported the role of enzymes and other biomolecules in the process of quenching the toxic metals in the plant during phytoremediation, the role of secondary metabolites is emerging as an important area of consideration. There is a diverse variety of secondary metabolites in plants and thus there may be many different possible mechanisms for the detoxification of heavy metals in the plants. Taking the example of phenolic compounds for detoxification of lead, which is one of the harmful components accumulated via e-wastes, can be a case for the involvement of secondary metabolites in phytoremediation.

A general sketch of the silencing of metals through phenolic compounds is given (Figs. 16.3 and 16.4). Metals accumulated in soil from e-waste are toxic to plants. These metals upon uptake by the plants generate reactive oxygen species (ROS) in the plant. ROS because of quick and high rates of oxidation is lethal for the plant as it damages the membranes. The plants cope with ROS through different defence systems, the secondary metabolite system being notable. This system employs the antioxidant action of secondary metabolites such as phenolic compounds. Through this antioxidant action, the phenolic compounds chelate metals such as lead from e-waste. Phenolics possess hydroxyl and carboxyl groups, able to bind particularly metals, and thus act as a suitable chelating agent for the intoxicating lead. This may inactivate lead and thus suppress its ROS forming capacity. For instance, direct chelation, or binding to polyphenols, was observed with methanol extracts of

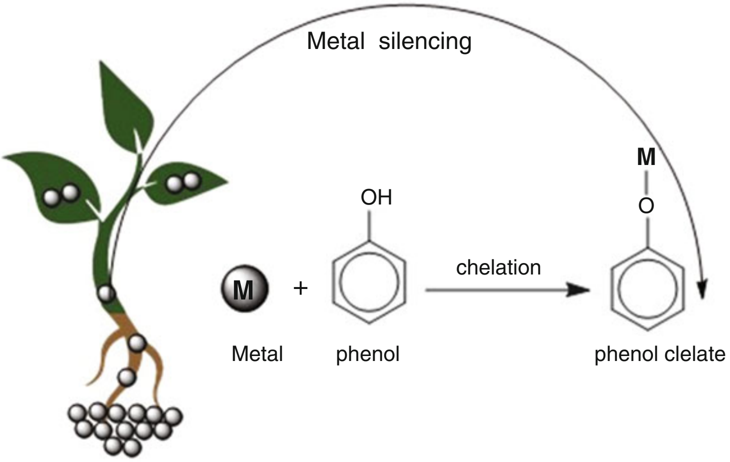

Fig. 16.3 The proposed mechanism of action of e-waste metal detoxification by plant phenolic compounds

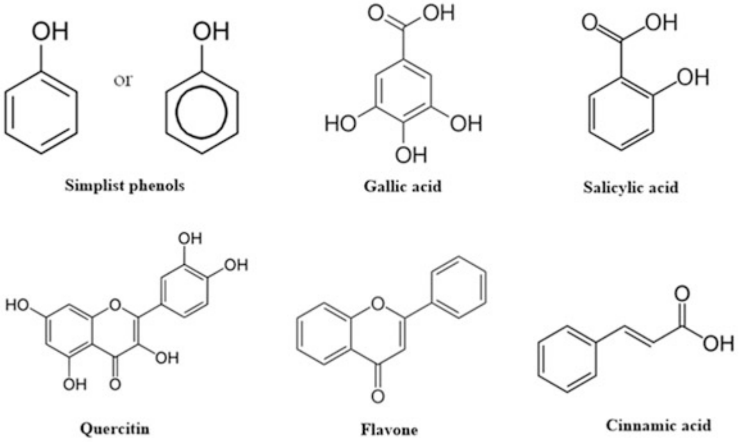

Fig. 16.4 Representative structures of important phenolic compounds found in plants. Data was taken from NCBI PubChem and structures were constructed through ChemDraw Ultra

rhizome polyphenols from *Nympheae* for Pb and other toxic metals such as chromium and mercury (Lavid et al. 2001).

Going further, other than chelation, the antioxidant ability of phenolic compounds is harnessed through another mechanism too. Metal ions decompose lipid hydroperoxide (lOOH) by the hemolytic cleavage of the O-O bond and give lipid alkoxyl radicals, which initiate free radical chain oxidation. Phenolic antioxidants inhibit lipid peroxidation by trapping the lipid alkoxyl radical and thus fight the damaging effect of the metals by unarming them (Dinis et al. 1994).

In short, the phytochemicals specifically secondary metabolites play an inevitable role in detoxifying metals accumulated via e-waste disposal. To be able to fully explore the metal remediation potential of plants, the response of secondary metabolism to metal accumulation needs to be understood. In addition to this, the transformation of plants in terms of metabolic engineering can be a nice area to enhance the generation of certain metabolites that play important role in metal detoxification in specific plants. A major benefit of this technology will be in the application of these plants to remove metals at the very entry point thus inhibiting its bioaccumulation and the chances of ultimate release in the environment through processes such as phytovolatilization.

16.6 Conclusions

Controlling and management of e-waste contamination through phytoremediation have got the global attraction in recent years. Though many different routes are involved in the mechanism of remediation of e-waste contaminants through phytoremediation, the role of secondary metabolites in plants cannot be undermined. Secondary metabolites generally play an important role in plant interactions and defence system in the overall process of phytoremediation of contaminants. To get more and more advantages from the phytoremediation technology, more research studies need to be done to explore the existing plants potential to more effectively remediate the heavy metals from the contaminated environments. Additionally, further studies are needed to find some more plants with promising characters such as plants with more aggressive nature towards metal extraction and accumulation. Besides, genetic engineering techniques can be used to engineer new plant varieties for efficient phytoremediation of heavy metal contaminants.

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