Antioxidant Defense Systems and Remediation of Metal Toxicity in Plants

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Abstract

Over the past years, knowledge concerning bioremediation of heavy metals via fungi and bacteria has been extensively developed. Globally, there has been a notable improvement in the level of several toxic metals in different environments

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M. Hasanuzzaman (ed.), *Approaches to the Remediation of Inorganic Pollutants*,
https://doi.org/10.1007/978-981-15-6221-1_6

as well as soils due to industrial usage (anthropogenic activities) and causing a severe affair to plants and human health as well. Plants growing in such a contaminated environment show a decrease in plant growth, development, and yield; thereby, there is a high-priority to cope with the toxicity of heavy metals. Several heavy metals have been examined to give rise to oxidative injury in crops by the generation of freely available toxic O_2 radicals. In the arrangement to tackle with the toxicity of heavy metals or to keep alive the level of some vital metals inside the range of physiological processes, the plant has evolved a wide range of multiplex mechanisms for metal tolerance. Plant and microorganisms possess various mechanisms for the bioremediation of contaminated environments, including soils. Different microorganisms have been favorably employed to decrease the toxic effects of heavy metals. Nevertheless, the critical action is to sectionalize and accumulate heavy metals in plant tissues; and antioxidant defense system plus enzymatic antioxidants (SOD, CAT, APX, GR, POD, GSTs, GPx, MDHAR, and DHAR) and non-enzymatic antioxidants (ASA, GSH, carotenoids, and tocopherols) have been declared. Additionally, chelation has emerged as prospect mechanisms, which widely control the metal resistance in crops via retaining the low level of freely available metal ions in the cytoplasm. Chelation of metals can be carried out by thiol compounds (GSH, PCs, and MTs), and non-thiol compounds (organic acids, amino acids, and their derivatives). Together, GSH plays a vital role in the bioremediation process as a chelating agent, due to its high kinship of metals, and it acts as a forerunner for PCs. Under metal stress, ROS and antioxidant defense systems generate signaling, where GSH can affect the cellular pathways associated with the acclimation and repair process to tackle with oxidative damage caused by metal stress. In this chapter, we have reviewed the recent advancement in the decisive role of antioxidant defense systems in the bioremediation system along with chelation of metals in plants.

Keywords

Antioxidant defense · Bioaccumulation · Biosorption · Bioremediation · Chelation · Glutathione · Heavy metals · Metal homeostasis · Oxidative stress · ROS · Transgenic plants

1 Introduction

Environmental pollution is gradually increasing every day at a terrifying rate. Technological advancements, urbanization, and industrialization are the main contributors to pollution. Due to rapid industrializations, the level of toxic metals in the environment is exceeded and pollute not only air but also land and drinking water. Heavy metals, which are emitted from industries, are toxic, become persistent in the environment, and cause serious health problems. Enough level of metals is needed for proper biological functioning of animals and plants, but their elevated level causes metabolic interference. Cadmium (Cd), selenium (Se), lead (Pb), chromium (Cr), mercury (Hg), nickel (Ni), gold (Ag), arsenic (As), zinc (Zn), manganese (Mn), and uranium (U) act as most toxic metals, and their presence in the soil causes problems for plants. The plant growth, photosynthetic activities, and enzymatic activities become reduced (Nematian and Kazemeini 2013; Raza et al. 2019a; Salim and Raza 2020; Verma and Kuila 2019; Hasanuzzaman et al. 2020a; Raza et al. 2020a,b,c; Raza 2020). The eradication of harmful and toxic substances from the polluted environment is necessary for survival. Bioremediation is used for cleaning up the environmental site, which is contaminated due to hazardous and chemical pollutants. Living organisms like bacteria, microbes, fungi, and crops are used for degrading the hazardous compounds into less toxic compounds. Changing the pH of contaminants, redox responses, and contaminants adsorption from the adulterated site or environment are the basic principles of bioremediation (Jain and Arnepalli 2019). The process of bioremediations is redox-based, in which the microbiology and chemistry of water are modified by the addition of reagents into it, which helps in the degradation and extraction of contaminants. The harmful compounds become transferred to less toxic or inert substances through redox reactions (Tandon and Singh 2016). Through this process, few metals like Hg, Cr, Se, and As are converted into innocuous forms (Ojuederie and Babalola 2017).

The organisms used for bioremediation, environmental pressures prevailing at the origin of contamination, and the pollutants degree of that environment affect the effectiveness of the process of bioremediation (Azubuike et al. 2016). Microbes and plants are widely used for bioremediation. In microbial bioremediation, microorganisms are used to degrade the pollutants through its metabolic process into innocuous forms through the redox reactions (Jan et al. 2014). The process of remediation in which plants are used is called phytoremediation. The pollutants from the soil environment of any kind are extracted and accumulated into plants and eradicate them from the soil. The success of phytoremediation depends upon the contaminated soil, the metal concentration in it, and the metal accumulation in plants as biomass to eradicate them and make the contaminated site less toxic (Tak et al. 2013; Raza et al. 2020a).

The reactive oxygen species (ROS) and its by-products are catalytically transformed into non-toxic and stable compounds with the help of enzymes known as antioxidant enzymes. The process is an essential mechanism of defense against the cell damage induced by oxidative stress. In plants, antioxidant systems are present naturally and have a role in the removal of toxicity produced by ROS (Ojuederie and Babalola 2017; Hasanuzzaman et al. 2020b). Antioxidants have their role in the scavenging of ROS (Bulbovas et al. 2014). Superoxide dismutase (SOD) caused dismutation of superoxide ($O_2^{\bullet -}$) and in result produce oxygen and hydrogen peroxide (Gratão et al. 2012). Catalase (CAT), subsequently, causes the detoxification of hydrogen peroxide into water. This process is also carried out by several other peroxidases, which include ascorbate peroxidase (APX). Glutathione (GSH), a non-enzymatic enzyme, in reduced form is responsible for toxic metals cellular detoxification and hydrogen peroxide scavenging (Rehman and Anjum 2011). In the cell, the balance of GSH depends upon glutathione reductase (GR) enzyme, as it reduces the oxidized GSH. GSH donates thiol to

GST (glutathione *S*-transferase enzyme) which catalyzed the glutathiones conjugation with a different electrophilic substrate. The selected electrophiles are usually associated with the breakdown of secondary products and xenobiotic compounds (Ghelfi et al. 2011).

Antioxidant systems (enzymatic and non-enzymatic antioxidants) are efficient enough to play a vital role in achieving the detoxification or scavenging of excess ROS. Interior cell, SOD, GPX, CAT, and enzymes from the cycle of AsA-GSH, such as MDHAR, APX, GR, and DHAR are included in enzymatic antioxidants, while GSH, AsA, phenolics, tocopherols, and carotenoids are non-enzymatic antioxidants. Many workers report that in plants, the enzymatic activities of defense systems of antioxidants increased in order to combat oxidative stresses, which are modulated by environmental factors. Upkeep of a high ability of an antioxidant to scavenge the harmful ROS has been connected to the high resistance level of crops to metal toxicity (He et al. 2011; Islam et al. 2016; Singh et al. 2016b; Hasanuzzaman et al. 2017, 2020b).

However, against heavy metals, the plants use their physical barriers, which include all morphological structures, as their defense first line. Cuticles, trichomes, cell wall, and the mycorrhizal symbiosis, proved themselves as barriers whenever plant faces the stress of heavy metals (Emamverdian et al. 2015). If any case, pollutants cross these barriers, then the internal cellular mechanism of defense restrains the harmful effects of those pollutants or heavy metals (Silva and Matos 2016). The free radicals cause crops to lessen undesirable effects of heavy metals, the generation of enzymatic (CAT, SOD, GR) and non-enzymatic antioxidants (GSH, ascorbate, tocopherols, and alkaloids), as they remove free radicals (Ojuederie and Babalola 2017). The mechanism of defense used by plants is phytochelatin synthases synthesis, metallothioneins production, and proline production. The enzyme phytochelatin synthase binds with heavy metals when they are in excess amount (Chaudhary et al. 2018; Jadoon and Malik 2018; Raza et al. 2020a).

Nevertheless, both enzymatic and non-enzymatic antioxidants prevent the impact of ROS, and these antioxidant enzymes diffuse free radicals; hence, the oxidative stress risk becomes restricted. ROS also becomes inactivated at a cellular and molecular level. On the other hand, their low concentrations interrupt the radical chain reaction due to which the oxidative processes become delayed or inhibited (Hasanuzzaman et al. 2020b). Antioxidants can easily chelate metals ions, which generate ROS. The generation of a complex metal ion is called chelation. In the metal ion complex, the metal ions bind to uncharged or charged donor of electron known as a ligand. The ideal chelator should have the following properties: high water solubility, biotransformation resistance, the property of reaching to a metal storage site, the ability to restrict the chelation at the body fluids pH level and formation of complexes of metals less toxic to metal ions. The ideal chelator of heavy metal can quickly enter into a cell, from metal complex, with the help of metallothionein, easily chelate heavy metal. Moreover, it is noticed that chelating agent can easily bind to positively charged ions so, an effective and safe method for treatment of metal toxicity is required which can easily be fulfilled with antioxidants which exhibit all the above-mentioned chelating properties

(Flora 2009; Anjum et al. 2015; Al Mahmud et al. 2017). In this chapter, we have discussed the recent advancement in the role of antioxidant defense systems in the bioremediation system along with chelation of metals.

2 Mechanisms of Bioremediation

The bioremediation can be defined as a low-cost alternate biological process for detoxification of environmental hazards and contaminants (Wasi et al. 2011; Banerjee et al. 2015). A series of mechanisms associated with bioremediation processes have been presented in several studies (Ji and Silver 1995; Wasi et al. 2008; Dwivedi 2012). Figure 1 describes the generalized mechanisms of metal bioremediation. The detoxification and removal of metals by aids of microorganisms have been attributed to various reactions (involving siderophores and bio-emulsifiers) and processes, which include complexation, methylation, and oxidation-reduction (Wasi et al. 2008, 2013). Under high concentrations of heavy metals, the microorganism has developed numerous mechanisms to detoxify the harmful metals. These detoxifying mechanisms may be extra- or intra-cellular and highly dependent on specific metal types (Wasi et al. 2008). Nevertheless, Gadd (2010) reviewed the application of individual microbes to detoxify the toxicity of the metal in detail. The application of microorganism for the breakdown of pesticides and the process associated with this mechanism have been well investigated (Mai et al. 2001; Nawaz et al. 2011).

Under optimal availability of nutrients and favorable environmental conditions, the bacteria can incorporate the simple organic substances into their cells and able to

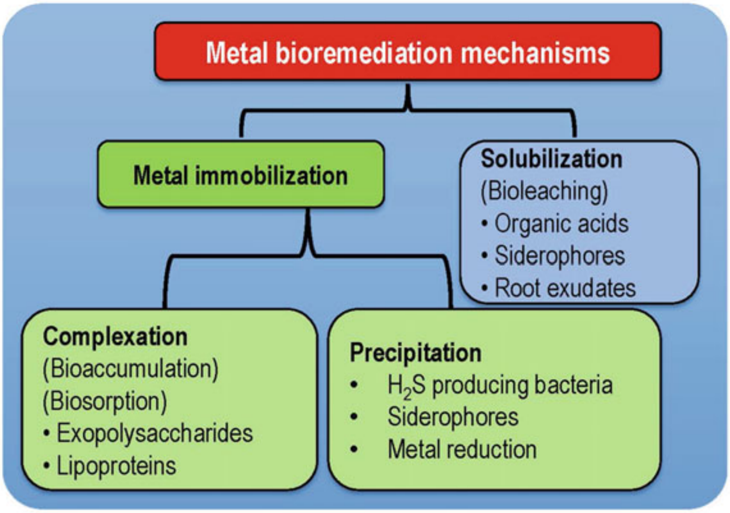

Fig. 1 Generalized mechanisms of metal bioremediation

oxidize them radially (Dwivedi 2012). Immobilization of bacterial cells under bioremediation to detoxify the pollutants from the environments is also examined in different studies (Cho et al. 2000; Das and Chandran 2011; Singh et al. 2011; Wasi et al. 2011). The connection of bacteria in the metabolism of 2,4-D is also well documented by many researchers (Fulthorpe et al. 1996; Han et al. 2015; Wasi et al. 2013). In another research, Yap et al. (1999) also reported the detoxification of phenols by *C. testosteroni* strain.

Bioremediation with algae also possessed a suitable method, since for removal of pollutants, oxygen is not required even under light conditions (Doshi et al. 2008; Dwivedi 2012; Megharaj et al. 2003). The author reported that uptake of metals under bioremediation with algae occurs through two processes, adsorption and intracellular uptake (Dwivedi 2012). During adsorption, metal ions are quickly absorbed by the surface of a cell and then transported to the cytoplasm by chemisorption process. The synthesis of phytochelatins is also reported in marine alga (Tsuji et al. 2002). Under metal toxicity, Scarano and Morelli (2002) characterize the formation of Cd and Pb phytochelatins complexes. The researchers also reported that, in green algae, some metals are sequestered in polyphosphate bodies, which provide a "storage pool" for metals, and this phenomenon is also reported for the detoxification of these metals.

3 Reactive Oxygen Species

ROS are produced due to unavoidable aerobic metabolisms consequences and play an essential part in the regulation of cell survival, cell distinction, cell death, cell signaling, and the production of inflammation-correlated factors. Free radicals and non-free radicals are included in ROS. Hydroxyl radicals and superoxide anion ($^{\bullet}OH$ and $O_2^{\bullet -}$) are free radicals, whereas singlet oxygen and hydrogen peroxide are non-free radicals. Highly reactive ROS is produced by molecular oxygen reduction in a stepwise manner either by the reaction of electron transfer or exposure of high energy. Cellular homeostasis disruption in plants due to environmental factors like salt, drought, metal toxicity, UV-radiation, and pathogen attack leads to the ROS production in enhanced ways (Abdal Dayem et al. 2017; Mishra et al. 2011; Hasanuzzaman et al. 2020b).

Moreover, a cell is in the stage of "oxidative stress" when ROS level surpasses mechanism of defense. Due to environmental stresses, the increased ROS production threatens cells and guide to cell death because of proteins oxidation, lipids peroxidation, nucleic acids damage, hampering of enzymes, and the activation of pathways leads to programmed cell death (Srivastava and Dubey 2011; Hasanuzzaman et al. 2020b). In a various cellular process, e.g., tolerance of environmental stresses, besides the destructive activities of ROS, it is also contributed as second messengers. The balance among the generation and scavenging of ROS is very delicate, and it governs the behavior of ROS either as signaling or as damaging molecules. ROS has multifunctional roles, due to which cell must manage the ROS level tightly. It will help them to bypass oxidative injury, and they will not abolish (Flora and Pachauri 2010; Hasanuzzaman et al. 2020b).

Nevertheless, against the attack of free radical antioxidant defense systems are developed in cells. GSH plays a key part in cell protection from oxidative injury, g-glutamyl-cysteinyl glycine. Firstly it targets mostly antioxidant enzymes, which are responsible for the removal of superoxide and peroxidases radical such as CAT, SOD, and GPx. Lead is involved in the inhibition of the synthesis of heme. The example of a heme-containing enzyme is CAT, and lead decreases its activity. $O_2^{\bullet-}$ is dismutase by SOD and then for its activity, it requires zinc and copper. In this reaction, copper ions played their functional by going through alternate oxidation, and zinc stabilizes the enzyme (Ercal et al. 2001). Free radicals formation, which is induced by arsenic, was mentioned first by Yamanaka et al. (1990). Superoxide anion and radical of dimethyl arsenic are formed by the reaction of molecular oxygen with dimethylarsine. The trivalent arsenic form is known as dimethylamine, and it is also an in vivo metabolite of dimethyl arsenic acid. "Dimethylarsenic peroxyl radical" is formed by the addition of one more molecular oxygen molecule onto dimethyl-arsenic radical. Due to the involvement of transition metals and cellular iron, the generation of hydroxyl radicals occurs during reactions.

Worldwide, heavy metals cause stress in terrestrial ecosystems, and it increases due to extensive industrialization. Heavy metals impart deleterious effects on soil due to which it becomes accumulated in the crops and affect their productions (Shahid et al. 2015; Hasanuzzaman et al. 2020a; Raza et al. 2020a,c). Heavy metals influence the molecular and physiological activities of plants, and their growth becomes retarded (Hassan et al. 2017; Raza et al. 2019b). The essential metals which play essential role in biological processes are Zn, Mo, Ni, Cu, Mn, and Cu (Shahid et al. 2015), whereas the existence of toxic metals like Pb, As, Cr, Hg, and Cd with them causes the reduction of crops productivity (Pierart et al. 2015). They cause metabolic disorders and morphological abnormalities due to plants yields become reduced. Due to these abnormalities, ROS are produced, which in turn disrupts the cell redox homeostasis. Heavy metals by dislodging the amino acids obstruct the normal functioning of plants. In this case, the bonds are formed, which connect sulfhydryl groups and heavy metals (Krumova et al. 2016). The proper functioning of molecules of cells becomes hindered by heavy metals and the functioning of enzymes, respiration, and photosynthesis processes become suppressed (Hossain et al. 2012). The metal that is redox-active (Fe, Mn, Cu, and Cr) due to direct generation of oxidative stress in crops affect the structure of DNA, damage chloroplast and also the accessory pigments due to which ROS is produced and destroyed the cell (Martins et al. 2016). Moreover, non-redox metals also produce oxidative stress, which eventually causes the production of ROS. In plants, this imbalance becomes the primary source of toxicity of heavy metals. To cope with all these problems, defense mechanisms such as binding of metals to phytochelatins, antioxidants activation, and metals sequestration into vacuoles have evolved (Shahid et al. 2015).

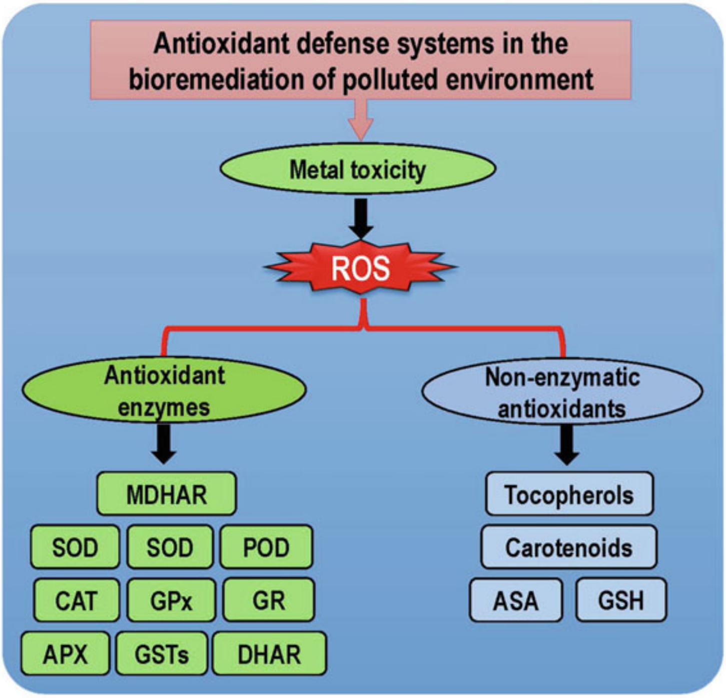

Fig. 2 Antioxidant defense systems involved in the bioremediation. Abbreviations have been described in the text

4 Role of Antioxidant Defense Systems in the Bioremediation

Environmental contaminants including metals toxicity promote the adverse effects on seed germination, photosynthetic production, and thus leading to reduce the biomass production in higher plants (Gill and Tuteja 2010b; Liu et al. 2012a; Hasanuzzaman et al. 2012, 2020a; Raza et al. 2020a,b,c). Furthermore, environment contaminants caused oxidative stress that results in enhancing the generation of ROS in plant cells. Below such circumstances, plants activate antioxidant defense systems, comprising enzymatic compounds, like CAT, APx, GR, MDHAR, DHAR, and GSTs (Fig. 2; Hasanuzzaman et al. 2012; Rahman et al. 2016; Hasanuzzaman et al. 2020b). Recently, bioremediation by the aid of plants, micro-organism, and algae can restore the contaminated environment. The available data indicate that bioremediation can regulate the antioxidant defense mechanism in plants and thus contributing to plant defense under stressed environmental condition (Creus et al. 1998; Mulligan et al. 2001; Pandey et al. 2017; Wu et al. 2010). However, Table 1 shows the information about antioxidant enzymes and their

Table 1 Information about antioxidant enzymes and their catalyzed reactions

Enzyme	EC number	KO definition	Reaction (IUBMB)
Superoxide dismutase (SOD)	1.15.1.1	K04564	$2O_2^{\bullet -} + 2H^+ < => 2H_2O_2 + O_2$
Catalase (CAT)	1.11.1.6	K03781	$2H_2O_2 < => O_2 + 2H_2O$
Ascorbate peroxidase (APX)	1.11.1.11	K00434	1. Ascorbate + H_2O_2 < => DHA + $2H_2O$ 2. 2Ascorbate + H_2O_2 < => 2MDA + $2H_2O$ 3. 2MDA < => DHA + Ascorbate
Glutathione reductase (GR/NADPH)	1.6.4.2 (changed to 1.8.1.7)	K00383	2GSH + $NADP^+$ < => GSSG + NADPH + H^+
Peroxidase (POD)	1.11.1.7	K19511	Reduced acceptor + H_2O_2 < => acceptor + $2H_2O$
Glutathione S-transferases (GSTs)	2.5.1.18	K00799	1. XR + GSH < => HX + R-S-GSH 2. RCN + GSH < => HCN + R-S-GSH 3. HSO4R + GSH < => O_4S^{-2} + R-S-GSH
Glutathione peroxidase (GPx)	1.11.1.9	K00432	H_2O_2 + 2GSH < => GSSG + $2H_2O$
Monodehydroascorbate reductase (MDHAR/NADH)	1.6.5.4	K08232	2Ascorbate + NAD^+ < => NADH + 2MDA + H^+
Dehydroascorbate reductase (DHAR)	1.8.5.1	K21888	DHA + 2GSH < => GSSG + Ascorbate

Source: https://www.brenda-enzymes.org/index.php; https://www.kegg.jp/kegg/kegg2.html
EC number enzyme commission number, KO KEGG Orthology, IUBMB International Union of Biochemistry and Molecular Biology, DHA dehydroascorbate, MDA monodehydroascorbate, GSSG glutathione disulfide, GSH glutathione, NADP nicotinamide adenine dinucleotide phosphate, HX halide, RX organic halide, RCN nitrile, HCN hydrogen cyanide, HSO_4R sulfuric monoester

catalyzed reactions; and Table 2 indicates a summary of some recent activities of antioxidant enzymes and non-enzymatic antioxidants under different bioremediation techniques.

4.1 Antioxidant Enzymes

4.1.1 Superoxide Dismutase

Under stress conditions, field-grown crops, surrounded by various types of microorganism, showed improved development and yield (Creus et al. 1998). Under high concentrations of salt, application of arbuscular mycorrhizal fungi (AMF)

Table 2 Examples of some recent studies about the activities of enzymatic and non-enzymatic antioxidants under different bioremediation techniques

Bioremediation techniques	Observations	References
Activities of antioxidant enzymes		
Bacteria (*S. bovis* and *S. ruminantium*)	Significant activities of SOD, GSHPx, and GR were observed under $HgCl_2$ stressed conditions	Lenártová et al. (1998)
Bioremediation with fungus (*Mucor hiemalis*)	Significantly increased the CAT, GR, and GSTs activities were reported	Hoque (2003) and Hoque et al. (2007)
Use of macrophyte (*Potamogeton pusillus*) as bioremediation	POD, GPs, and GR activities were reported to be enhanced	Monferrán et al. (2009)
Use of Indian mustard under Hg stress	Enhanced activeness of SOD, CAT, APX, and GR were examined under Hg stress	Ansari et al. (2009)
Remediation with bacterial strains (*Ochrobactrum* and *Bacillus* sp.)	The increased activeness of SOD, CAT, and GPs enzymes have been noticed under the toxicity of various heavy metals	Pandey et al. (2013)
Fungal bioremediation (*Aspergillus foetidus*)	The activities of CAT and GR have been investigated to be enhanced under Cd stress	Chakraborty et al. (2014)
Bacterial strain (Enterobacter cloacae)	Increased CAT and SOD activeness were reported under Cd stress	Banerjee et al. (2015)
Bioremediation with filamentous fungi (*Penicillium chrysogenum* XJ-1)	Increased SOD, CAT, GR under various Cd levels	Xu et al. (2015)
Bioremediation with bacterial strains (NBRIEAG-6, NBRIEAG-8, and NBRIEAG-9)	An increase in APX and CAT activities were reported in rice under As stress	Singh et al. (2016b)
Bacterial bioremediation (*Providencia vermicola*)	The increased activities of CAT, APX, and SOD under Cu stress were noted	Islam et al. (2016)
Inoculation of *S. nigrum* L. with *M. circinelloides*	The increased SOD activity was reported under Pb-contaminated soils	Sun et al. (2017)
Bioremediation with fungal strains (*Trichoderma hamatum* and *Rhizopus arrhizus*)	The increased activities of SOD (in *T. hamatum*), CAT (in *R. arrhizus*), GST and POX activities (in both species) were reported	Russo et al. (2019b)
Bioremediation with fungal species (*T. harzianum* and *P. simplicissimum*)	Significantly increased activities of CAT and GST (in both of the tested fungi), and SOD (in *P. simplicissimum*) were reported under HCH stress	Russo et al. (2019a)
Bioremediation of endophytic fungus (*Aspergillus tubingensis*)	Activities of CAT and SOD enzymes increased significantly under antimony treatments	Meghnous et al. (2019)

(continued)

Table 2 (continued)

Bioremediation techniques	Observations	References
Bioremediation with algae (*Chlorella vulgaris*)	An increase in SOD and CAT activities was reported on exposure to produced water concentrations	Calderón-Delgado et al. (2019)
Activates of non-enzymatic antioxidants		
Application of yeast	Activities of carotenoids increased significantly under metals toxic environments	Bhosale and Gadre (2001)
Bioremediation with pseudometallophytes	The increased activities of tocopherols were reported	Epelde et al. (2010)
Fungal bioremediation (*Aspergillus foetidus*)	The activities of tocopherols have been reported to be increased	Epelde et al. (2010)
Bioremediation of *Callitriche cophocarpa Sendtn*	A decrease of carotenoids was reported under Cr stress	Augustynowicz et al. (2010)
Bioremediation with *Microbacterium* sp.	Significantly decreased activities of GSH enzyme were reported	Liu et al. (2012b)
Bioremediation with photosynthetic bacteria	Significantly recovered the carotenoids under contaminated environments	Idi et al. (2015) and Pattanamanee et al. (2012)
Bacterial bioremediation (*S. aureus*, *E. coli*, *B. subtilis*, and *P. aeruginosa*)	An increase in carotenoids content was reported	Radhika and Kannahi (2014)
Bioremediation with microalgae	An increase in carotenoids contents was reported	Raeesossadati et al. (2014)
Bioremediated with *P. chrysogenum-10*	Increased ascorbate and GSH activities were reported in plant roots	García-Sánchez et al. (2014)
Microbial bioremediation	Increased GSH activities	Xu et al. (2015)
Bacterial inoculation (*P. vermicola*)	Significant activities of ascorbate was observed under Cu stress conditions	Islam et al. (2016)
Bioremediation with bacterial strains (*Staphylococcus* sp., *Brevibacillus* sp., and *S. arlettae*)	Reduced GSH activity was recorded in rice under As stress	Singh et al. (2016b)

remarkably improves the activeness of antioxidant systems, i.e., SOD, which helps in elevating the harmful impacts of oxidative stress in *E. aphylla* and *P. trifoliate* (Alqarawi et al. 2014; Wu et al. 2010). Induction of SOD also observed in mycorrhizal (*Glomus deserticola*) colonized lettuce roots under drought condition (Ruiz-Lozano et al. 1996). Moreover, Banerjee et al. (2015) examined the increased activity of CAT enzyme under bacterial bioremediation (*Enterobacter cloacae* strain) under cadmium-toxic condition. The overexpression of SOD also is reported under bioremediation with other bacterial strains (*Streptococcus bovis* and *Selenomonas ruminantium*) upon exposure of mercury stress (Lenártová et al. 1998). Recently, it has been investigated that bioremediation with the fungal strain (*Trichoderma hamatum)* also resulted in more SOD contents, showed enhanced protection for oxidative injury (Russo et al. 2019b). Nevertheless, Russo et al. (2019a) noticed the enhanced SOD enzyme activity with other fungal strains (*P. simplicissimum*). Bioremediation with filamentous fungi *(Penicillium chrysogenum* XJ-1) also reported enhancing the SOD activities under toxic cadmium levels, indicating its vital role to mitigate the oxidative injury (Xu et al. 2015). Improved activeness of SOD enzyme was observed under the bioremediation of endophytic fungus (*Aspergillus tubingensis*) in toxic antimony conditions (Meghnous et al. 2019). Calderón-Delgado et al. (2019) also say that bioremediation with algae (*Chlorella vulgaris*) significantly increased SOD activity. Inoculation of *S. nigrum* L. with *M. circinelloides* also resulted in increased SOD activity in lead-contaminated soils (Sun et al. 2017).

4.1.2 Catalase

Bioremediation enhanced the generation of CAT that can reduce the effect of oxidative damage in plants. Bioremediation with AMF enhanced the activity of CAT under soil salinization conditions, and thus provide resistance in *Avena Nuda* (Huang et al. 2008). According to Porcel et al. (2003), more consecration of CAT is also noticed in *G. max* roots colonized through *G. mosseae*. The increased activities of CAT enzyme were also reported in *Scytosiphon lomentaria* under copper-toxic environment, indicating the protecting role of CAT under oxidative stress (Contreras et al. 2005). Moreover, increased activity of CAT was also observed under bacterial bioremediation (*Enterobacter cloacae* strain) under Cd conditions (Banerjee et al. 2015). Russo et al. (2019b) documented that bioremediation with the fungal strain (*Rhizopus arrhizus)* significantly enhanced the CAT contents, and showed advanced protection under oxidative stress. The increased activity of CAT was also reported under bioremediation with two fungal species (*T. harzianum* and *P. simplicissimum*) (Russo et al. 2019a). However, Xu et al. (2015) observed that antioxidant enzyme activities were investigated in the bioremediation with filamentous fungi (*Penicillium chrysogenum* XJ-1) under different cadmium level. These authors observed an increase in CAT activities in tested fungi bioremediation. Further, Calderón-Delgado et al. (2019) examined a similar trend, where CAT potential was increased under bioremediation with algae (*Chlorella vulgaris*). The increased activity of CAT was reported under bioremediation with Indian mustard (Ansari et al. 2009). These findings suggest that an increase in CAT activeness could result in mitigating the Hg-induced oxidative stress.

4.1.3 Ascorbate Peroxidase

Increased APX activity plays a crucial role in countering the ROS entities under a variety of environmental stresses (Pandey et al. 2017). Bioremediation technique has been recommended as an emerging approach to increase the accumulation of APX under several environmental stresses (Blilou et al. 2000; He et al. 2007). In tomato (*L. esculentum*) colonized with AMF, more APX contents were observed, indicating a defense response under high salt concentration (He et al. 2007). Another study conducted by Ansari et al. (2009) has noted the increased APX activity when the Indian mustard is used as bioremediation under mercury stress. According to Singh et al. (2016b), the bioremediation with bacterial strains (NBRIEAG-6, NBRIEAG-8, and NBRIEAG-9) has caused an increase in APX activity in *O. sativa* under As stress. The increased synthesis was observed in APX activity under bacterial bioremediation (*Providencia vermicola*) under copper-enriched conditions (Islam et al. 2016), and significantly contributed to the elimination of ROS.

4.1.4 Glutathione Reductase

Bioremediation strategies have been reported to increase the activities of GR in crops exposed to environmental contaminations. The enhanced synthesis was observed in GR activity under inoculation of lettuce with *Rhizobium* spp. (Han and Lee 2005). Similarly, Lenártová et al. (1998) reported the consequences of bioremediation with bacteria (*S. bovis* and *S. ruminantium*), and reported the increased activity of GR under $HgCl_2$ stress. Xu et al. (2015) revealed that bioremediation with filamentous fungi *(Penicillium chrysogenum* XJ-1) resulting in enhance the activities of GR under cadmium stress, indicating the protective role to mitigate the cadmium-induced oxidative damage. In another study, Ansari et al. (2009) have noted the enhanced activities of GR while evaluating the Indian mustard as a bioremediation technique under mercury stress. According to Chakraborty et al. (2014), fungal bioremediation (*Aspergillus foetidus*) also resulted in enhanced the activities of GR enzymes under Cd stress. Bioremediation with fungus (*Mucor hiemalis*) has been reported for their ability to enhance GR activity (Hoque 2003; Hoque et al. 2007). Extensive induced activities of GR by macrophyte (*Potamogeton pusillus*) bioremediation have also been reported by Monferrán et al. (2009).

4.1.5 Peroxidase

Pioneer studies on bioremediation had shown that bioremediation mediated activities of POD significantly decrease the effects of oxidative injury in crops (Kohler et al. 2009; Li et al. 2019). Higher POD activity in AM tomato significantly enhanced the plant growth under high concentration of salts (He et al. 2007). Kohler et al. (2009) documented the increased activity of POD under *Pseudomonas mendocina* Palleroni inoculation in *Lactuca sativa* L., and reported a positive effect on the development of crops under salinity. Increased activity of POD under various strains of plant growth-promoting rhizobacteria, e.g., *S. proteamaculans* and *R. leguminosarum* has also been reported (Maheshwari 2012). Recently, the enhanced POD activity has also been reported under bacterial bioremediation with *B. amyloliquefaciens* RWL-1, in rice seedling under copper-induced toxicity (Shahzad et al. 2019). However, as stated by Li et al. (2019), reduced activity of POD under bioremediation with rye-grass species was reported under As stress. Enhanced activities of POD under bioremediation with the fungal strain (*Rhizopus arrhizus* and *Trichoderma hamatum)* showed increased protection under oxidative stress (Russo et al. 2019b). Likewise, Meghnous et al. (2019) examined the increased activity of POD with bioremediation of endophytic fungus (*Aspergillus tubingensis*) exposed to antimony toxic conditions and protected the cells against oxidative stress.

4.1.6 Glutathione *S*-Transferases

Enhanced activities of GSTs in crops beneath environmental contaminants alleviate the oxidative stress (Dixon et al. 2010). The overexpression of GSTs has also been reported under bioremediation with the fungal strain (*Rhizopus arrhizus* and *Trichoderma hamatum)* (Russo et al. 2019a). These authors reported that more expression of GSTs significantly enhances the protection against oxidative stress. In another report, Russo et al. (2019a) reported the increased activity of GSTs enzyme under bioremediation with two fungal species (*T. harzianum* and *P. simplicissimum*). Fungus (*Mucor hiemalis*) bioremediation has also been reported for their ability to enhance the activity of GSTs enzymes (Hoque 2003; Hoque et al. 2007).

4.1.7 Glutathione Peroxidase

The activities of glutathione peroxidase (GPs) were reported to be increased under different bioremediation techniques (Jayanthy et al. 2014; Monferrán et al. 2009). Bacterial bioremediation (*Streptococcus bovis* and *Selenomonas ruminantium*) have been reported to enhance the activities of GPs under $HgCl_2$ stress (Lenártová et al. 1998), suggesting an important role to tackle with the oxidative damage under stress environments. Different macrophytes, such as *Potamogeton pusillus*, have been reported for their ability to enhance the activity of GPs (Monferrán et al. 2009). Increased activity of GPs in green alga (*S. quadricauda*) was reported under a high level of Se (Vítová et al. 2011). Pandey et al. (2013) also reported the increased activity of GPs in bacterial strains (Bacillus sp., PbSP6 and AsSP9) under the exposure to heavy metals. The enhanced activity of GPs under *L. leucocephala* remediation as reported in the dye contaminated soil (Jayanthy et al. 2014).

4.1.8 Monodehydroascorbate Reductase

Increased MDHAR activities facilitate AsA regeneration, which helps in the detoxification of ROS under contaminant environment (Hasanuzzaman et al. 2012; Nahar et al. 2016). The bioremediation techniques have also been reported to enhance MDHAR activities under environmental stresses. Therefore, Cuypers et al. (2000) reported increased MDHAR enzyme activity in *Phaseolus vulgaris*, when used as bioremediatory, under Cr-enriched soils. Huang et al. (2016) demonstrated that bioremediation with arbuscular mycorrhizal fungi (*G. versiforme*) could increase the activity of MDHAR significantly, in *Sorghum halepense* under Cs stress.

4.1.9 Dehydroascorbate Reductase

Under toxic metal conditions, decreased activities of dehydroascorbate reductase (DHAR) were reported in *Brassica napus* plants (Hasanuzzaman et al. 2017). While Dalton (1995) reported that DHAR is involved in detoxification of H_2O_2 in cellular compartments. Bioremediation had shown the increased activity of DHAR enzyme. For example, according to Huang et al. (2016), bioremediation with arbuscular mycorrhizal fungi (*G. mosseae* and *G. versiforme*) in Johnson grass resulted in an increase in DHAR activeness under Cs stress. Higher DHAR activity was reported in

Table 3 Sub-cellular localization of non-enzymatic antioxidants

Enzyme	Location
Ascorbate (ASA)	Mitochondria, chloroplasts, peroxisomes, vacuoles, apoplast, nucleoli, plastid, cytosol, and nuclear membrane
Glutathione (GSH)	Cytoplasm, mitochondria, and plasma membranes (peroxisomes, endoplasmic reticulum, and lysosomal membranes)
Carotenoids	Plastids and cellular membranes (photoautotrophic organisms)
Tocopherols	Nuclear and cellular membranes

mycorrhizal roots under drought stress conditions, which involved in shielding mechanisms under oxidative stress (Porcel et al. 2003).

4.2 Non-enzymatic Antioxidants

Non-enzymatic antioxidants, i.e., the ascorbate (ASA), GSH, carotenoids, and tocopherols; and the sub-cellular localization of these enzymes are presented in Table 3.

4.2.1 Ascorbate

Elevated production of ASA enzyme with different bioremediation techniques is well known (Islam et al. 2016). Increased activity of ASA in plant roots was observed on exposure to olive-mill residue bioremediation with *P. chrysogenum-10* (García-Sánchez et al. 2014). The raised activity of ASH enzyme was also reported with bacterial inoculation (*P. vermicola*), determine the potential of crops to survive under Cu-induced oxidative stress (Islam et al. 2016). Enhanced activity of ASH was also reported in phytoremediation plants (weeds plants) collected from metal-induced polluted soils (Singh et al. 2016a).

4.2.2 Glutathione

The reduced activity of total GSH was reported for bioremediation with bacterial strains (*Staphylococcus* sp., *Brevibacillus* sp., and *S. arlettae*) in rice and showed a bacteria-mediated reduction of oxidative stress under arsenic stress (Singh et al. 2016b). It has been examined by Liu et al. (2012b) that reduced activities of GSH in *Microbacterium* sp. also showed the ability to detoxify the environmental contaminants. Mala et al. (2015) reported that, in *B. methylotrophicus,* the GSH-dependent chromate reductase can detoxify chromium-induced oxidative stress. Decreased activity of GSH enzyme was also reported on exposure to olive-mill residue bioremediation with *P. chrysogenum-10* and *C. rigida* (García-Sánchez et al. 2014). Nevertheless, Singh et al. (2016a) reported the higher activity of GSH enzymes in phytoremediation plants (weeds plants) collected from metal-induced polluted soils. These authors reported that enhanced activity of GSH was found to detoxify heavy metals induced oxidative stress. Increased GSH as a result of microbial bioremediation was also reported (Xu et al. 2015). These researchers suggested that increased GSH activity significantly increased antioxidant capacity under heavy metal stress. The increased level of GSH was also reported in *Heliscus lugdunensis* by different researchers under heavy metals stress (Braha et al. 2007; Jaeckel et al. 2005). Mukherjee et al. (2010) also noted increased activity of GSH in *Aspergillus niger* under arsenate stress and reported their protective role under oxidative stress.

4.2.3 Carotenoids

The carotenoids synthesis has been reported in a different microorganism such as yeast, bacteria, and algae (Frengova and Beshkova 2009) when they are grown under contaminated environments (Breierová et al. 2008). According to Bhosale and Gadre (2001), the increased biosynthesis of carotenoids in yeast under metals toxicity was reported. Bioremediation of shrimp bio-waste (from natural probiotic) also resulted in increased the production of carotenoids (Prameela et al. 2010). However, decreased carotenoids contents were reported under the bioremediation of *Callitriche cophocarpa Sendtn* (aquatic macrophyte) under chromium stress (Augustynowicz et al. 2010). Increased production of carotenoids content was also reported for bacterial bioremediation (*S. aureus*, *E. coli*, *B. subtilis*, and *P. aeruginosa*) (Radhika and Kannahi 2014). Bioremediation with photosynthetic bacteria also resulted in the recovery of carotenoids under contaminated environments (Idi et al. 2015; Pattanamanee et al. 2012). In another study, Azad et al. (2001), also reported the increased carotenoids contents under bioremediation techniques. Previously, Ponsano et al. (2003), showed that bioremediation with photosynthetic bacteria also generates biomass abundant in carotenoids, which can be employed as the feed of animals. Bioremediation with microalgae also can increase and/or the recovery of carotenoids contents (Raeesossadati et al. 2014). Bioremediation with manure vermicomposting showed high levels of carotenoids as compared with control (Ayyobi and Peyvast 2014). Besides, Amooaghaie and Golmohammadi (2017) reported the same results for the vermicomposting bioremediation on thyme (*Thymus vulgaris* L.) plants.

4.2.4 Tocopherols

Bioremediation strategies result in the production of non-enzymatic molecules like tocopherols, which triggered the production of ROS. Higher activities of tocopherol enzyme were reported in transgenic *Brassica* plants under abiotic stresses (Kumar et al. 2013). Higher tocopherols values were reported for bioremediation with pseudometallophytes (Epelde et al. 2010). Significant increases in tocopherols contents were also reported for bioremediation with microalgae under copper stressed conditions (Hamed et al. 2017). Increased synthesis of tocopherols was reported under bioremediation with rhizosphere associated bacteria (Salomon et al. 2016). The supplementation of 24-Epibrassinolide also increased the tocopherols contents in *R. sativus* seedlings under Cd and Hg stress (Kapoor et al. 2016).

5 Chelation of Metals and the Role of Antioxidants

In plants, the detoxification of heavy metals and their tolerance mechanisms could be separated into two unique grouped, i.e., the exterior-omission or internal-resistance. In response to the exterior detoxification, the organic acids are excreting out from plant roots, and formed a stable heavy metal-ligand bond with heavy metal ions, and thus significantly affecting their mobility and bioavailability. Thereby, in the process of internal metal-detoxification, the organic acids can chelate with heavy metals in the cytosol, and ions can be transferred into less or non-toxic forms (Clemens 2006; Hall 2002; Kushwaha et al. 2015). Below, we have briefly described the thiol and non-thiol compounds and metal chelation; while Fig. 3 shows the pivotal role and connection between these compounds and their systematization with other defense systems under metal-subjected crops.

5.1 Thiol-Compounds and Metal-Chelation

Different thiol compounds like GSH, phytochelatins (PCs), and metallothioneins (MTs) contain groups of sulfhydryl (-SH) are important for maintaining the cytosol concentration of free metal(loid) (Seth et al. 2012). In general, chelation is the inclusively spread intra-cellular process for the support of low amount and detoxification of freely available metal ions in the cytosol of plants, that could be carried out via thiol compounds like GSH, PCs, MTs, and amino acids and their derivatives (Anjum et al. 2012, 2015; Bjørklund et al. 2019; Jozefczak et al. 2012; Seth et al. 2012). Nevertheless, GSH, PCs, and MTs played a crucial part in the metal chelation in crops.

5.1.1 Glutathione-Induced Metal Chelation

GSH is widely known as a most vital metabolite associated with the defense responses under several abiotic and biotic factors; thus plants cannot live in the absence of GSH or its homologous (Kumar and Trivedi 2018; Nianiou-Obeidat et al. 2017; Noctor et al. 2012). GSH, a major -SH group present in compartments of plant cell (cytosol, endoplasmic reticulum, and mitochondria), plays an essential role in antioxidant defense mechanism and cellular redox homeostasis in plants; GSH is also associated with the detoxification and chelation of freely available metals/metalloids (Anjum et al. 2012; Nahar et al. 2015; Sabetta et al. 2017; Seth et al. 2012). Hence, Fig. 4a indicates the metabolic detoxification process of GSH under metal toxicity, and Fig. 4b shows the systematic layout for the key role of GSH in metal remediation, in which metal resistance is necessary preconditions affected by metal homeostasis. GSH plays a vital part in metal homeostasis, being a chelating agent/metabolite/substrate. However, under metal stress, ROS and antioxidant defense systems generate signaling, where GSH can affect the cellular pathways associated with the acclimation and repair process to tackle with oxidative damage caused by metal stress. Further, energy (ATP or NADPH) is required for equilibrium among antioxidant systems and ROS. Therefore, the maintenance of elevated GSH

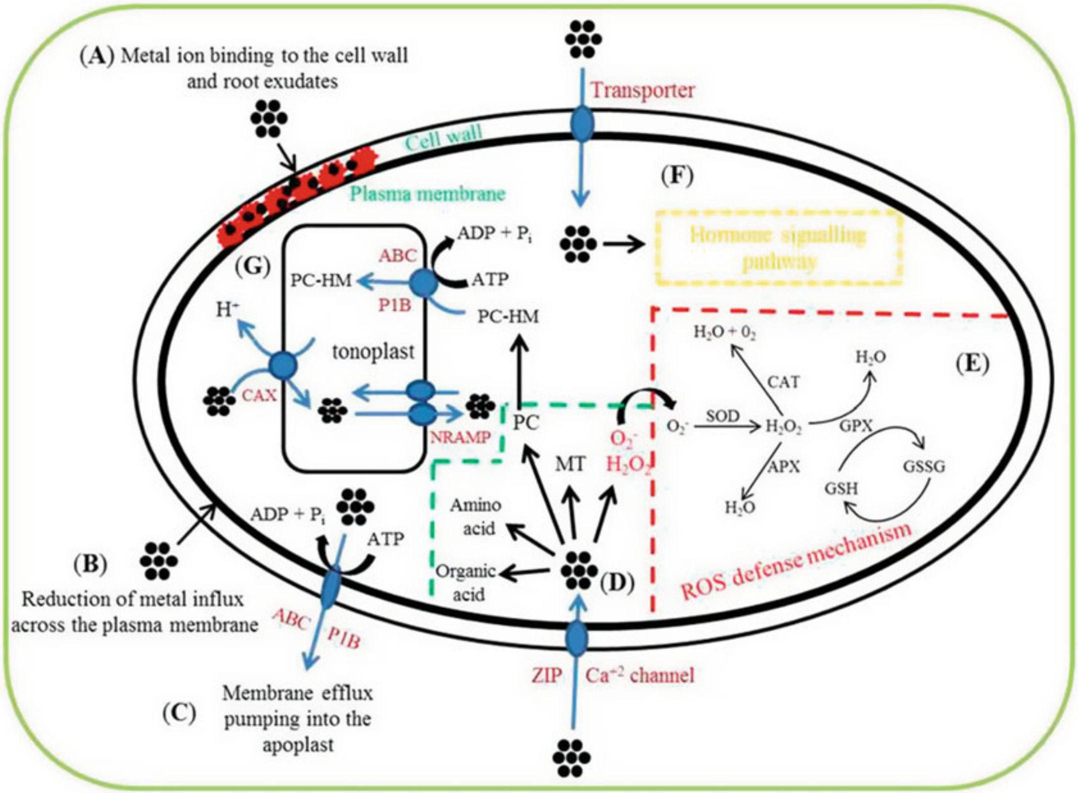

Fig. 3 Diagrammatic illustration of key role and connection between thiol and non-thiol compounds and their systematization with other defense systems under metal-subjected crops. Adapted from Anjum et al. (2015)

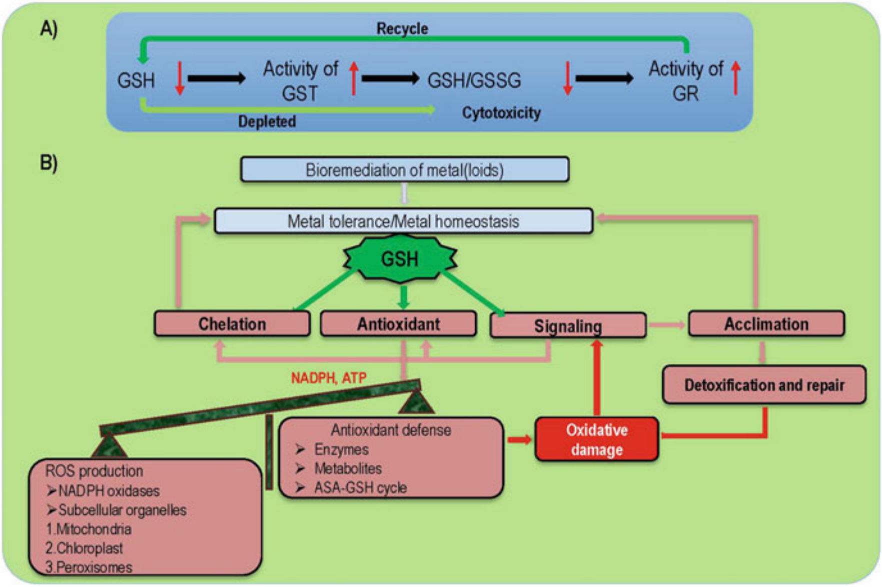

Fig. 4 Essentiality of GSH compound in the bioremediation process. (**a**) Metabolic detoxification process of GSH under metal toxicity; (**b**) Systematic layout for the key role of GSH in metals-remediation, in which metal-tolerance is a necessary precondition affected by metal homeostasis. See text for more detail

levels in plants is counted as an essential intrinsic feature, for reducing the heavy metals induced oxidative pressure in plants. The high levels of GSH in natural accruing plant species such as *T. goesingense*, *T. oxyceras*, and *H. lanatus* are well documented (Ernst et al. 2008).

Further, Hu et al. (2001) reported the higher levels of GSH in Cd-tolerant mutant of *C. reinhardtii* compared with wild-one. Therefore, Estrella-Gómez et al. (2012) described that *S. minima* plants showed glutathione synthase (GS) activity and increased GSH levels in response to Pb toxicity through a high expression level of SmGS gene. Hussain et al. (2016) documented that, the infectious disease of *A. thaliana* with a virulent pathogen *P. syringae* (*PstAvrB*) causes an improvement in the GSH level. Likewise, the increase in H_2O_2 was reported in cell subjected to stress; it also manages the GSH metabolism and protein action (Noctor et al. 2012). On the other hand, Balestrasse et al. (2001) noticed the deterioration in GSH concentration in soybean roots subjected to Cd stress; similar findings were also investigated by various researchers, e.g., in the roots of Scots pine (Schutzendubel et al. 2001), gray poplar roots (Schützendübel et al. 2002), and in *O. sativa* leaves (Hsu and Kao 2004). Piechalak et al. (2002) stated that Pb causes a reduction in the GSH level in legumes such as *V. faba*, and *P. vulgaris*. Additionally, Balestrasse et al. (2001) noticed the unchanged GSH concentration in the nodules of soybean plants under Cd stress.

5.1.2 Phytochelatins and Metal Chelation

The harmful impact of toxic metal(loids) ions in the cytoplasm can be removed with particular highly correlated ligands like PCs. Within the cytosol, firstly, PCs are generated and then moved to the vacuole in the form of a complex. However, in the existence of various metals, like Au, Zn, Mn, Mg, Se, Si, Cd, Pb, Hg, Cd, Ag, and Cu, etc. PCs can be quickly produced (Cobbett 2000; Cobbett and Goldsbrough 2002; Hasan et al. 2015). According to Volland et al. (2014), charophytic algae (*M. denticulata*) is the only one where the production of PCs has been discovered.

Hence, Zhang et al. (2010) examined the association among PCs biosynthesis and Cd amassing in *S. alfredii*, and reported that PCs are assumed as an inter-cellular Cd detoxification process in shoots instead of roots. Interestingly, Jambhulkar and Juwarkar (2009) reported that, *C. siamea* accumulated high concentrations of Pb, Ni, and Cr than other plant species cultivated on a fly ash dump having non-protein thiols; that are known for the synthesis of PCs and is accountable for the amassing of these metals. In contrast, Yadav et al. (2010) observed that, *J. curcas* accumulates an elevated concentration of Cr in roots; however, the concentration of freely available Cr ions in plant roots may last low, due to Cr ions sectionalize in the vacuole or making Cr-PCs complexes. On the other hand, knockdown of PCs genes that hold the production of PCs can enhance the susceptibility of *C. elegans* under Cd stress (Vatamaniuk et al. 2001).

An experiment performed by Mishra et al. (2006) deciphers the exposure of *B. monnieri* L. to Cd stress. The authors reported that the synthesis of PCs, along with the increased GSH levels and GR activities, plays a crucial part in the detoxification of metals and alleviation of metal-induced oxidative damage. Plants can store and resist a high level of Cd through an increased level of PCs and it is considered as a suitable antioxidant for phytoremediation. Moreover, Mukta et al. (2019) revealed that Cd-induced PCs help in reducing the Cr toxicity in rice by enhancing the GR activity and GSH level, which enhances the antioxidant defense mechanism to tackle with Cr toxicity. Under Cr stress, the enhanced PCs accumulation due to calcium treatments is also involved with vascular sequestration of Cr.

5.1.3 Metallothioneins

MTs possess a considerable affection for both vital and non-vital toxic metals, where MTs can furnish thiol compounds as a chelating agent in lessening form. Enormous affection of MTs for toxic metals such as Cd serve as a protective mechanism; on the other hand, it also plays a supporting for homeostasis of few crucial metals like Cu, Zn, Cd, etc. (Anjum et al. 2015). Previous studies show that MTs also induce or express in plants under various environmental stresses including wounding, senescence, salt, drought, high temperature, heavy metals, and cold; and these stresses can regulate MT genes expression in crops. Such as rgMT protein from rice regulated in *E. coli* and its expression were mediated by various abiotic stresses (Jin et al. 2006), *GhMT3a* from *G. hirsutum* enhanced resistance to few abiotic stresses in yeast and tobacco (Xue et al. 2008), ectopic expression of *OsMT1e-P* negotiates various abiotic stresses resistance in *Nicotiana tabacum* by ROS scavenging (Kumar et al.

2012), and functional characterization of *CsMT4* gene from cucumber increased resistance to high-salinity and osmotic stresses in *E. coli* (Zhou et al. 2019).

For heavy metals, Cu-induced H_2O_2 upregulation of *OsMT2c* gene from rice increased tolerance to Cu in *A. thaliana* (Liu et al. 2015), *CcMT1* gene from *C. cajan* regulated in *E. coli* and *Arabidopsis* improves resistance to Cd and Cu (Sekhar et al. 2011), *HbMT2a* from *H. brasiliensis* increases tolerance to Cu and Zn in *E. coli* (Li et al. 2015), *IlMT2b* from *I. lacteal* enhances tolerance to Cu in *Arabidopsis* (Gu et al. 2015), and a *PpMT2* gene from *P. patens* increased resistance to Cu and Cd in *A. thaliana* (Liu et al. 2019). In order to examine the phytoremediation availability of tobacco plants, Shestivska et al. (2011) demonstrated that the insertion of MTs in plants significantly enhanced the antioxidant properties than with non-transgenic plants. It is also reported that MTs-like proteins have also been present in *C. Vulgaris,* which can detoxify Cd and Zn toxicity (Huang et al. 2009).

5.2 Non-thiol-Compounds and Metal-Chelation

Numerous non-thiol compounds including amino acid and their derivatives (such as proline (Pro), cysteine (Cys), malate, and betaine), and organic acid (OAs; like citrate, malate, and oxalate) in isolation and coordination with different thiol compounds have been reported to be significantly contributed to the chelations of metals in plants (LaVoie et al. 2015; Pivato et al. 2014; Seth et al. 2012; Shaheen et al. 2017). Here, we discussed the recent studies on non-thiol compounds of metals in plants.

5.2.1 Organic Acids

Organic acids (OAs), low molecular weight compounds (LMWC), contain no less than one carboxyl group and are called as O_2-donor metal ligand. Among the various OA compounds, some compounds are elaborated in the oxidation of pyruvate when it existed in plant cells acting as a central point for the tricarboxylic acid cycle (TCA) cycle (Adeleke et al. 2017). OAs potentially perform various roles in the rhizospheres. OAs can carry the minus charge, therefore allowing movement of anions from soil origin and complexation of the metal cation in the solution (Jakkeral and Kajjidoni 2011). A major OA “citrate” is reported to belong to the crucial class of metabolites in plant cells. Large quantities of citrate have been reported in various plants such as in alfalfa (Lipton et al. 1987), tomato (Yilmaz et al. 2008), citrus (Sadka et al. 2001), tobacco (Lopez-Bucio et al. 2000), soybean (Yang et al. 2001), strawberry (Iannetta et al. 2004), and maize under light (Eprintsev et al. 2018).

In different cellular compartments, several metabolic pathways have been reported for the metabolism of citrate in plants. The involvement of citrate OA in carbon metabolism, and the abiotic and biotic stress resistance in plants have been reported in citrus under low temperature (Lin et al. 2016; Sheng et al. 2017), in rice under herbicide diclofop-methyl toxicity (Ding et al. 2014), soybean under Al stress (Zhou et al. 2018). Oxalate, an essential organic acid, is accumulated at a high level in plants, and plays an essential role in balancing the excess of inorganic cations over various anions (Lou et al. 2016; Ma et al. 2018; Osmolovskaya et al. 2018). The involvement oxalic acid in Al-resistance in *O. sativa* has been reported by Yokosho et al. (2011); Cu tolerance in *W. cocos* (Clausen et al. 2000); Cd elucidation in *B. nivea* (Li et al. 2014); Cu and Zn tolerance in fungi (Sazanova et al. 2015); Pb tolerance in *P. falcataria* (Setyaningsih et al. 2012), and phytoextraction of Pb, and Cd using *H. annuus* (Niu et al. 2010). Nevertheless, the role of dicarboxylic acid malate in photosynthesis process, respiration, oxidation of fatty acid, and biosynthesis of amino acids have been well documented (Casati et al. 1999; Fernie and Martinoia 2009; Musrati et al. 1998; Selinski and Scheibe 2019; Van Der Merwe et al. 2009; Zell et al. 2010).

5.2.2 Amino Acids and Their Derivatives

Under the high concentrations of metals, several amino acids like Pro, histidine, Cys, arginine, and the polyamines are synthesized in small amounts and showed their roles in stress resistance (Majumdar et al. 2019; Pivato et al. 2014). Nicotianamine is abundantly expressed in higher plants and plays a crucial part in metal chelation and homeostasis in plants (Banakar et al. 2019; Uraguchi et al. 2019). Arginine and Cys, diverse amino acids in living cells, play a significant part in the biosynthesis of other substances under higher concentrations of metals (Liu et al. 2018; Zhuang et al. 2017). The critical role of Arginine in metal chelation has been documented by various researchers (Futaki et al. 2004; Wojciechowska et al. 2015; Xu et al. 2018; Zhang et al. 2018). Polyamines are ubiquitous having differentiated properties such as acid neutralizing, antioxidant features, the stability of membrane and cell wall, and these characteristics make them effective protectants for abiotic stresses. The exogenous and endogenous applications of polyamines confer the tolerance against environmental stresses (Gill and Tuteja 2010a; Wen et al. 2008; Zhao and Yang 2008) including heavy metals, Cu tolerance in *N. peltatum* (Wang et al. 2007), Cd tolerance in wheat (Rady and Hemida 2015), Pb tolerance in wheat (Rady et al. 2016), and Cr tolerance in Kinnow mandarin (Shahid et al. 2018).

Another essential chelating agent, histidine is also present in some plants, especially in Ni-hyperaccumulators (Assunção et al. 2003). The significant roles of glycine betaine (GBs) as an osmoprotectant, ROS-scavenger, and as metal-chelators has been demonstrated in metal-subjected crops (Anjum et al. 2015; Asgher et al. 2013; Sharma and Dietz 2006; Theriappan et al. 2011). Proline plays a useful role in crops on exposure to different stress environments. Proline can act as an excellent osmolyte, and thus enhances the antioxidative defense mechanism and signaling molecules under stressed conditions. The involvement of flavonoids, phenylpropanoids, and phenolic acids in antioxidant defense mechanism is well understood (Ahmad et al. 2016; Gill and Tuteja 2010b; Rejeb et al. 2014).

6 Conclusion and Future Outlooks

Environmental pollution is enhancing gradually at a forbidding rate. Technological advancements, urbanization, and industrialization are the main contributors to pollution. Due to rapid industrializations, the increasing metals toxicity in the atmosphere is polluting the environment, not only air but also land and drinking water. Heavy metals, which are emitted from industries, are toxic, become persistent in the environment, and cause serious health problems. A sufficient concentration of heavy metal is needed for proper biological functions of animals and plants; hence, their elevated level causes metabolic interference. In the arrangement to tackle with the toxicity of heavy metals or to keep alive the level of some vital metals inside the range of physiological processes, the plant has evolved a wide range of multiplex mechanisms for metal tolerance. Plant and microorganisms possess various mechanisms for the metal-induced bioremediation of contaminated environments, including soils. Different microorganisms have been favorably employed to decrease the toxic effects of harmful metals.

Nevertheless, both enzymatic and non-enzymatic antioxidant defense systems thwart the impact of ROS. Thereby, these defense systems diffuse free radicals; hence, the oxidative stress risk becomes restricted. ROS also become inactivated at a cellular and molecular level. However, their low concentrations interrupt the radical chain reaction due to which the oxidative processes become delayed or inhibited. Antioxidants can easily chelate metal ions, which generate ROS. In coming years, it will be essential to comprehend that, how ROS modulate changes in crops function and development under the toxicity of heavy metals, consequently influence the crops, and boost their sustainable agricultural production.

Both antioxidant systems which are efficient enough play a vital role in achieving the detoxification or scavenging of excess ROS. Inside the cell, SOD, GPX, CAT, and enzymes from the cycle of AsA-GSH, such as MDHAR, APX, GR, and DHAR are included in enzymatic antioxidants, while GSH, AsA, phenolics, tocopherols, and carotenoids are non-enzymatic antioxidants. Many workers report that in plants, the enzymatic activities of defense systems of antioxidants increased in order to combat oxidative stresses, which are caused by various environmental factors. Increased antioxidant enzyme activities is linked with the scavenging of harmful ROS to enhance the high tolerance level of crops under metal stress. However, comprehensive research has been carried out on the production of ROS and response of defense systems in plants, thereby, more to the point works need to be done mainly in connection for the capabilities of antioxidant enzymes for the crop improvement under heavy metal stress.

Nevertheless, a good understanding is required on actual compounds that aid crops to manage the freely available metals in the cytoplasm. In this regard, thiol- and non-thiol compounds play a crucial part in the chelation of metals and control the low amount of freely available metals in the cytoplasm. Among these compounds, MTs and PCs are best-identified compounds due to their strong interaction with metals, metal chelation, reducing their level inside the cytosol, and ultimately reducing their toxic effect. Interestingly, GSH also plays an essential part in the bioremediation process as a chelating agent, due to its high kinship of metals, and it acts as a forerunner for PCs. Under metal stress, ROS and antioxidant defense systems generate signaling, where GSH can affect the cellular pathways associated with the acclimation and repair process to tackle with oxidative damage caused by metal toxicity. Besides this, GSH also acts as a crucial antioxidant defense agent, and redox signaling, including plant growth and development. Therefore, it is concluded that more studies are required to completely unrevealed the potential role of thiol- and non-thiol compounds for metal chelation. Transgenic plants can be introduced to boost the potential of metal bioremediation from toxic environments, and soils as well. Moreover, transgenic plants with modified GSH metabolisms have indicated encouraging outcomes; thereby, shortly, these plants should be implemented in field conditions on a large scale. Conjointly, the recommended investigations will help to generate the transgenic plants on a large scale for commercial usage, which can chelate various metals and prevent their toxicity in the environment.

Acknowledgement We are thankful to the researchers whose contributions have been cited in this study, which helped us to get more insight into the presented area and helped us to prepare this chapter. Further, we apologize to those whose contributions have not been cited in this chapter due to space limitation.

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