Review Article

Silicon Mechanisms to Ameliorate Heavy Metal Stress in Plants

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The increased contaminants caused by anthropogenic activities in the environment and the importance of finding pathways to reduce pollution caused the silicon application to be considered an important detoxification agent. Silicon, as a beneficial element, plays an important role in amelioration of abiotic stress, such as an extreme dose of heavy metal in plants. There are several mechanisms involved in silicon mediation in plants, including the reduction of heavy metal uptake by plants, changing pH value, formation of Si heavy metals, and stimulation of enzyme activity, which can work by chemical and physical pathways. The aim of this paper is to investigate the major silicon-related mechanisms that reduce the toxicity of heavy metals in plants and then to assess the role of silicon in increasing the antioxidant enzyme and nonenzyme activities to protect the plant cell.

1. Introduction

Silicon is a beneficial mineral element commonly found in soil. It is the second most abundant element after oxygen [1, 2] in soil. Since silicon is an essential element and a plant nutrient [3, 4], it has an important role in plant growth, yield [3, 5, 6], photosynthetic properties, chlorophyll contents, and enzyme activity [7–9], especially under stressful conditions [1, 10]. Currently, there is no evidence showing the direct role of silicon in plant metabolism. However, silicon can still be assumed to be essential in the process because it belongs to a molecular compound which is involved in plant metabolism. Because plants require silicon, it helps with plant growth and development. Consequently, silicon reduction can adversely affect plant growth and produce abnormal characters in plants [11, 12]. Many researchers confirmed that silicon has the ability to ameliorate the abiotic stresses such as an excess dose of heavy metal and increase the tolerance of plants against heavy metals [7, 13–15]. The mechanism by which silicon alleviates stress from heavy metals can be categorized into internal and external mechanisms [16, 17]. In the external mechanism, silicon ameliorates the heavy

metals' toxicity through various methods, such as reducing the absorption and activity of the metal or changing the metal's formation by adding a silicon compound. However, in the internal mechanisms, silicon reduces the adverse effects of heavy metal toxicity through different mechanisms, such as stimulation of antioxidant enzyme activity, complexation and compartmentalization of silicon with metal ions, and changing the cell wall by transportation control [17]. In addition, silicon can protect plants exposed to biotic and abiotic stresses [18, 19]. The protective role of silicon revealed in plants can be attributed to an accumulation of polysialic acid in plant cells. Thus, with an enhancement in polysialic acid concentration in the cell wall, plant tolerance increases and indirectly interferes with stress factors [20]. The application of silicon on tissue cultures can protect the cell wall by decreasing oxidative stress, ameliorating the plant growth cycles, including embryogenesis, organogenesis, and inducing growth in traits and leaves in vitro [21]. Moreover, the protective role of silicon in reactive oxygen species (ROS) scavenging is bold. Silicon can scavenge ROS indirectly. A previously conducted experiment shows that Si can decrease OH hydroxyl radical accumulation in cucumber leaves by

reducing the free apoplastic Mn^{+2} [19]. One of the other protective roles of silicon is regulating internal water in plants [22] so that the accumulation of silicon in epidermal tissue preserves water in the transpiration process [23]. Generally, plants tend to accumulate heavy metals, such as cadmium, in the root more than shoot and stem [24]. Therefore, silicon is accumulated in plants' roots for certain mechanisms, including a physical barrier, reduction of translation, and reduction of heavy metal uptake.

2. Silicon Defense Mechanisms

Silicon is often absorbed in plants through monosilicic acid formation and precipitated in internal plant parts, such as cell wall and lumens. In addition, it is deposited as an amorphous silica (Opal A; $Sio_2 \cdot nH_2o$) or in intercellular sites like phytoliths [25-10]. Phytolith is a Greek word meaning "stone of plant," which is known to be the space between the plant cells [25]. Silicon's defense mechanisms appear throughout plants. In leaves silicon is used to create structures such as epidermal trichomes and hair. Silicon is also accumulated in spines as amorphous silica (SiO_2) and phytoliths [26]. In plants and soil, there are different mechanisms and pathways by which silicon scavenges ROS and ameliorates heavy metals. In growth media (i.e., tissue culture), silicon decreases the ions' activities and limits the metal uptake and metal translocation from roots to shoots. In cell structure, silicon ameliorates heavy metal stress through various mechanisms, such as regulating the gene expression involved in metal transport and metal-chelation mechanisms, participating in coprecipitation of metals, changing the plant structure, and stimulating antioxidant enzymes' activity [13, 18, 27]. Song et al. indicated that, with the combination of silicon and cadmium, cadmium tolerance increases in *B. chinensis* demonstrating the role of silicon in the reduction of heavy metal uptake, limitation of root to shoot translocation, and stimulation of antioxidant enzyme activity [28]. Many researchers reported that codeposit of metal with silicon can reduce the concentration of toxic ions in plants [13, 17, 29]. It has been reported that, using some mechanisms, such as root exudation and pH increase, silicon limits the aluminum uptake in roots; this issue can later precipitate Al concentration in the root surface [30, 31]. In a general classification, silicon detoxification mechanisms can be grouped as either chemical or physical mechanisms. Chemical mechanisms refer to the mechanisms involved in coprecipitation of heavy metals with silicon, while in physical mechanisms silicon reduces the translocation of heavy metals to shoot and aerial parts by changing the plant structure such as the apoplastic barrier [32]. Generally, Si is involved in the alleviation process in plants exposed to abiotic stresses and heavy metals in some important mechanisms, including (1) stimulation of antioxidant enzyme activity to enhance ROS scavenging, (2) complexation and immobilization of toxic metal ions in plants [18, 33], (3) deposition and accumulation in plant tissue for developing the rigidity and stability in leaves, (4) water mobility, and (5) providing plant nutrient and coprecipitation of metal toxicity [34]. In the following, we discuss some of the key mechanisms involved in silicon detoxification in plants.

2.1. Mechanism One: Reduction of Heavy Metal Uptake by Plants. Regarding the relationship between the silicon and heavy metal uptake, it can be stated that silicon can alleviate and reduce the uptake of heavy metal and its transportation in plants [13, 28, 35, 36]. Moreover, silicon can increase the chelated ions through (1) stimulation of root exudate, which can limit metal uptake by roots in plants [13] or (2) decreasing the free metals in plant organs which reduces the translocation activity in apoplasm [13]. In the cell wall, silicon can accumulate in the lignin and improve the metal binding; it can then reduce the translocation of ions from roots to aerial organs [37, 38]. Silicon creates a complex with metal ions in the cell wall and additionally precipitates metal ions as a cofactor [30]. The results revealed that enhancement of silicon could increase malic and formic acid in plants growing process and consequently reduce the uptake of Al [30]. Furthermore, it was observed that phenolic compounds in maize can decrease the Al uptake so that flavonoid-phenolics can lead to Al-chelating link and reduce the Al uptake in plants [13]. Heavy metal chelating significantly contributes to digestion of heavy metals, and it is created by chelation of heavy metal with flavonic-phenolics or other organic acids [39]. Silicon can increase heavy metal accumulation in intercellular plant parts [13]. By investigating the amelioration role of silicon in Mn, Doncheva indicated that silicon, used as a barrier, can expand the epidermal layer of maize. It can lead to an accumulation of Mn in nonphotosynthetic tissue [40]. Then, through certain mechanisms, such as coprecipitation, it prevents the heavy metals from translocating to other plant parts. It is reported by Hai-Hong Gu that the reduction in stem-to-shoot translocation in rice was the consequence of a high concentration of silicon [32].

Most beneficial effects of silicon can be revealed in the accumulation in the cell walls of root, stems, leaves, and hulls, which enhance the stability of plant tissue as a physical barrier [37]. In roots, silicon increases the binding of metal ions by decreasing the apoplastic bypass flow and reduces the translocation of toxic metals from roots to shoots. Moreover, accumulation of Si in the cell wall of stems, leaves, and hulls limits the transpiration of the cuticle with alternation in the efficiency and function of the cell wall and consequently increases the plant's resistance against stresses [41]. Rizwan et al. reported that silicon decreases cadmium uptake and reduces the translocation of cadmium to shoots [42]. In the case of silicon precipitation in shoots, silica precipitates in water evaporation sites of the plant's shoot as phytoliths. This can be close to the epidermis of the plant shoot [42–44]. Additionally, silicon can shift the Mn to the leaf blade causing a homogenetic mechanism against Mn and then decrease Mn uptake [45]. Thus, it can be estimated that beneficial impacts on plants can be obtained by high deposition in shoots [46]. However, most deposition in plants depends on Si uptake by roots [37]; therefore, plants with less ability to uptake silicon could be deprived of silicon benefits [45]. The roots are the first line exposed to heavy metals; this issue shows the role of root anatomy in reducing heavy metal toxicity. Apoplastic barriers in roots, including exodermis, epiblema, and endodermis, can play an important role in reducing heavy metal uptake and consequently diminishing metal

toxins in plants [47]. Furthermore, extension of apoplastic barriers, such as development of endodermis under metal stresses, are among important mechanisms to prevent the translocation of cadmium to aerial parts [48]. This matter has been reported in the rice plant [49]. Similar results obtained from Qiong Zhong's study on *Avicennia* reported that silicon with expanding and improved apoplastic barriers in roots can reduce Cd uptake in plants [47].

2.2. Mechanism Two: Changes in pH Value in Soil and Plant Culture.

The pH value plays an important role in bioavailability and mobility of heavy metals in soil and culture [50–54]. One of the main mechanisms of silicon amelioration is the role of silicon in changing soil and growth medium's pH. Silicon compounds, like biosolids, increase the pH value so that this increase can improve the absorption of silicon. On the other hand, it can lead to an immobilization and unavailability of heavy metals, such as Cd, in plants [16] and also to a reduction of heavy metal bioavailability. Organic materials and pH exist in soil, including soil sodium metasilicate or alkaline pH, playing an important role in the reduction of metal availability in soil and consequently amelioration of metal toxicity to plants [39]. The results of [55] show that reducing the toxicity of aluminum metal ions by changing the pH in a medium can be one of the external mechanisms in amelioration of Al by silicon in soybeans. This can later lead to the unavailability and precipitation of AL [30]. Moreover, silicon can facilitate metal transport in plants. As a result, silicon with the formation of hydroxy aluminum silicate complexes in shoots can increase the transportation from root to shoot. Kopittke et al. (2017) reported that detoxification of aluminum by silicon is related to the formation of hydroxy aluminum silicates in roots [56]. However, this formation depends on pH [57], so that the formation of hydroxy aluminosilicate reduces the pH value to less than 4.0 [58].

It is seen that, in exposure to metal stress, such as extreme concentration of Al, silicon accumulates in cell walls and leads to a reduction in Al toxicity in the apoplasm. The result of one experiment showed that Al with formation of hydroxyl aluminum silicates in root apoplast can convert the Al to a nontoxic form in the apoplast and ameliorate the Al toxicity in the plant root. This issue indicates the silicon mechanism to reduce metal toxicity in the apoplast. The rate of HAS (hydroxy aluminum species) efficiency depends on the enhancement of pH and high concentration of Al and Si [58]. The pH value is an important factor in the formation of HAS. Al toxicity often occurs in low pH, and HAS formation does not have enough efficiency in low pH (<5) [58].

2.3. Mechanism Three: Formation of Si Heavy Metals.

Silicon, in the first step, detoxifies the heavy metals in plants with (1) solution chemistry mechanism (i.e., making complexes with heavy metals) and (2) planta mechanism [1, 30, 59] (i.e., stimulating the organic acid exudate from plants to chelate metals ions) [1, 30, 59]. In the solution chemistry mechanism, silicon creates a compound by forming silicates and oxides with heavy metals, which is caused by the unavailability of Si in plants [59]. For instance, Si, in a complex formation of

Al-Si, decreases the toxicity of Al^{3+} [30, 56]. Additionally, it decreases the Al availability [55] and reduces the free Al by the formation of the aluminum silicate compound in plant cells [60]. The plant cell wall has an important site in colocalized Al-Si in hypodermal and epidermal cells [61], which is shown to be a major site for accumulation of silicon to make wall-bound organosilicon compounds [62]. Investigating *Minuartia verna*, Neumann et al. expressed that formation of Zn-silicate precipitated in the leaf epidermis acts as an important pathway for Zn detoxification [63]. There are different ideas regarding the impact of silicon on the cell wall. In some experiments on the cell wall, the results showed that silicon could not significantly reduce the Al concentration, but they indicated an exchange enhancement in Al-cell wall binding. Therefore, it was concluded that silicon decreases the Al-cell wall binding in the apoplast [58]. There are, however, other researchers who attributed this factor to the reduction of alumina biologic activities; they believe that Si could not reduce Al concentration in the cell wall, but Si can decrease the ability of Al biologic activity in the cell wall. This is assumed as a factor in the reduction of aluminum efficiency in connection with the cell wall, which reduces the toxicity of aluminum. Prabagar et al. (2011) demonstrated that degradation of free Al by silicon in the cell wall can be an important factor to protect the plant cells in *P. abies* [60] so that the reduction of Al biological availability, hydroxy aluminum species, and silicic acid is key in the formation of HAS in low pH [30]. Silicon involved in the translocation of the cell wall is one of the crucial mechanisms in the reduction of heavy metal toxicity in plants [13, 64]. One experiment conducted by Gunes et al. (2007) showed that silicon limited baron translocation from root to shoot in spinach [65]. Formation of Si heavy metals in ultrastructures revealed the role of Si in heavy metal transport. The results of another experiment reported that, in *Cardaminopsis* sp., silicon actively contributes to the transportation of Zn to vacuoles. Through this process, Zn precipitates to the cytoplasm with silicate formation. The formation of Zn-silicate during such a fast process degrades to SiO_2 and Zn immediately. Then, Zn is transferred to the vacuole, and SiO_2 precipitates in the cytoplasm [17]. The other pathway is related to plasma member and tonoplast forming pinocytotic vesicles in which Zn is directly transferred from extracellular fractions to vacuoles [39]. This is known as a compartmentation mechanism in plants. In both cases, the formation of Si heavy metals has a vital role in the digestion and precipitation of metal ions. It can be concluded that silicon can reduce the heavy metal mobility with chemical interaction mechanisms, such as formation of Si heavy metal [39].

2.4. Mechanism Four: Stimulation of Enzyme Activities.

Metals ions, with distribution in photosynthesis electron transfer (Phet) and reduction of net photosynthesis (Pn), may lead to a severe impairment in photosynthetic metabolism [66]. Severe impairment in photosynthetic metabolism is expressed as an important factor in the generation of ROS derivatives, such as H_2O_2, O^{-2}, and OH [67] in chloroplasts, mitochondria, and plasma membranes [68], which is a primary response of plants to oxidative stress [69, 70]. An

ROS compound is divided into two categories: (1) nonradical molecules, such as singlet oxygen ($1O_2$) and hydrogen peroxide (H_2O_2), and (2) free radicals. Free radicals include hydroxyl radical (•OH), superoxide anion ($O2•-$), alkoxy radical, perhydroxyl radical (HO_2), reactive molecules, and ions. Chloroplasts and mitochondria are major colonies in generating O_2 and O^{-2} [68, 70]. The primary location in the plant for generating ROS includes the reaction center of PS1 and PS11 in chloroplast thylakoid membranes. Generation of ROS usually occurs with the excess of photons (p) in environmental changes (environmental stress) when there is an extra dose of CO_2 assimilation (A) (P > A) [71]. ROS derivatives increase oxidative stress in plants, which can lead to an increase in MDA and lipid peroxidation, disturbance in enzyme activity and amino acids in cells, and protein oxidation [68, 72, 73]. Thus, damaging impacts of ROS can be summarized as follows:

(A) Morphological impacts, including (1) decreasing of root and shoot growth and (2) leaf curling

(B) Biochemical impacts, such as (1) membrane damaging, (2) permeability, and (3) protein structure

(C) Physiological impacts, such as (1) chlorosis, (2) photosynthesis, and (3) metal uptake [74, 75].

Silicon accumulation in different plant tissues, such as root, stem, leaves, and hulls, can preserve the plant from abiotic and biotic stresses [76]. Plants' major defense mechanisms to adjust to heavy metal stress and to protect plant cells from oxidative stress are scavenging free radicals by ROS. ROS stimulates enzyme activities, either antioxidant enzymes or nonenzyme activities [77–80]. Antioxidant enzymes and nonenzymes include superoxide dismutase (SOD), peroxidase (POD), catalase (CAT), guaiacol peroxidase (GPX), ascorbate peroxidase (APX), glutathione reductase (GR) [65, 71, 81, 82], ascorbic acid (AA), flavonoids, reduced glutathione, α-tocopherol, carotenoids, and osmolyte proline [83, 84]. They can scavenge ROS in plants with some chemical cycles, such as ascorbate-glutathione, water-water, and peroxisomal glutathione peroxidase. And these chemical cycles are in intercell organs including cytosol, mitochondria, chloroplast, apoplast, and the peroxisomes [85–87]. They can maintain plant integrity against metal stress inside mitochondria, nuclei, and chloroplasts [28, 88]. In this case, SOD converts superoxide anion to peroxide [63]. CAT catalyzes the conversion of H_2O_2 to water and O_2 [89, 90]. Ascorbic oxidase majorly contributes to the regulation of GR and NADPH [91]. Glutathione, which shows intracellular redox potential and ascorbate, would then be involved in cytoplasmic and apoplastic signaling [92, 93]. In terms of antioxidant activity, silicon leads to stimulation of antioxidant enzyme activity in plant growth under heavy metal stress [37]. This issue has been shown in many plants under different metal stressors, including soybean [94], barley [65], rice [95], *A. thaliana* [96], cotton [7], banana [97], *Brassica chinensis* L [28], peanut [35], and ramie [98]. For instance, the results obtained from *Ajuga multiflora* indicated that the medium with extra dose of silicon to MS can increase shoot regeneration by increasing the antioxidant enzyme activities,

such as SOD, POD, APX, and CAT [99]. However, other sources indicated that silicon can impact the Mn uptake by root and reduce Mn concentration in cucumber [100]. A similar result was reported for sorghum [101]. In another experiment on rice exposed to extreme doses of Zn, it is shown that Si application increases the antioxidant activities, such as SOD, CAT, and APX, while reducing the H_2O_2 and MDA content [95]. Feng et al. indicated that an extra dose of Si applied in cucumber and exposed to manganese toxicity increases antioxidant and nonantioxidant enzyme activities, including SOD, APX, DHAR, GR, ascorbate, and GSH and decreases the lipid peroxidation [102]. Additionally, Song et al. obtained the same result in a study on cucumber exposed to Mn [95]. In general, silicon plays an important role in increasing the antioxidants in plants. However, the efficiency of this mechanism relates to the concentration of heavy metals so that in a high dose of metal toxicity antioxidant activity may not work well [13].

2.4.1. Silicon via Ascorbate. Ascorbate, as a regulator with small molecular weight, can regulate cell processes, including those through cell cycle, those during cell expansion, and senescence [103]. The main site of ascorbate is located in the mesophyll cells of leaves with 40% storage in the chloroplast, which is often decreased in stress conditions [70]. Ninety percent of AsA ascorbate is localized in cell cytoplasm, known as a frontier line in the interference with external oxidant damage [104]. It plays an important role in removing H_2O_2 from water [105]. Additionally, reduced glutathione (GSH) is an important component for the formation of ascorbate-GSH (AsA-GSH), which consists of the bench of the enzyme, including GSH sulfotransferases (GSTs), glutathione peroxidase (GPX), and glutathione reductase (GR) [106]. GSH, as a biothiol tripeptide, plays a vital role in cell tolerance to metal stresses using two pathways: (1) antioxidant and phytochelatins (PCs) regulating redox imbalance and (2) reducing the concentration of free ion cellular, respectively [107, 108], that is important to the amelioration of heavy metal stress as the antioxidant [109, 110]. Glutathione peroxidase (GPX, EC 1.11.1.9.), as one peroxidase enzyme, plays an important role in the degradation of ROS compounds in cytoplasm and apoplast area [68] and also biosynthesis of lignin [111]. GPX can scavenge ROS from intra- and extracellular media [112]. Additionally, it would scavenge H_2O_2 by reducing the glutathione and regenerating GSSG using glutathione reductase (GR) [70]. Ascorbate peroxidase (APX) (1.1.11.1) is known to be the indicator of H_2O_2 amounts in chloroplasts and cytosol, which can be used to degrade the ascorbic acid [105]. APX in the ascorbate-glutathione cycle degrades H_2O_2 to water (as a cofactor) [70, 113] which can raise its activity with some enzyme functions, such as SOD, CAT, and GSH reductase [105]. APX is the main form of AsA-GSH cycle which has the ability to scavenge H_2O_2 to H_2O and oxygen with MDHA molecular [105]. The ability to scavenge H_2O_2 in APX is much stronger than CAT [105, 114]. The role of APX in cell protection is crucial and can cover plant cells with five different isoforms, including cytosolic form (cAPX), chloroplast stromal soluble form (s APX), and thylakoid (t APX) glyoxysome membrane form (gmAPX) [105]. The role of silicon

is to increase the APX, GSH, and AsA activity under heavy metal stress conditions. Silicon application also has a positive impact on the ascorbate-glutathione cycle and can improve it by increasing APX [28]. Thus, it can be concluded that silicon indirectly associates with the degradation of ROS compounds, such as H_2O_2 and OH to detoxify plant toxicity, and consequently can increase the plant tolerance to metal stress.

2.4.2. Silicon via Glutathione. Glutathione, as a redox buffer, plays an important role in the antioxidant mechanisms to scavenge ROS by preserving the balance of cellular redox [115]. Glutathione reductase (GR, EC, 1.6.4.2) is a compound containing disulfide groups. It is categorized as flavoenzymes, which can work with some mechanisms, including catalyzing and oxidizing flavin with NADH and disulfide. It also interchanges some reactions by GSSG degradation in disulfate [116], which has an important role in the synthesis of phytochelatins and is an essential factor in sequestering heavy metals [117]. Additionally, it has the ability to scavenge ROS by converting it to sulfhydryl form GSH through catalyzing glutathione disulfide [118], which has a major role in the control of H_2O_2 levels [119]. Glutathione reductase occurs during the photosynthetic process for scavenging and degradation of H_2O_2 [120, 121] and was often localized in chloroplasts. However, a small amount of that was also found in mitochondria and cytosol, which play the catalyst role in ASH-GSH cycle by mechanisms of degradation and regeneration of GSH [122]. GSH plays an important role in the cell system through certain mechanisms such as the regulation of the sulfhydryl (-SH) group and GSTs [123]. In addition, it is known to be one of the important antioxidant and redox buffers and has an important role in cell division [123]. GR and APX, with the ascorbate-glutathione cycle, play an important role in scavenging ROS by degrading H_2O_2, so that ascorbate converts H_2O_2 to H_2O and GR in the first line of this pathway and continues degrading H_2O_2 to reduced glutathione level in the last step [71, 124].

2.4.3. Superoxide Dismutase. The soluble enzyme dismutase has an important duty in the dismutation of O^{-2} to O_2 and H_2O_2 [125]. It also plays a vital role in cell protection. In the case of heavy metal toxicity, superoxide dismutase (SOD) with enzyme code (EC 1.15.1.1) is known to be the first line in the detoxification of ROS compound. Firstly the enzyme causes a dismutation of O^{-2} and secondly it reduces the possibility of OH formation [125]. The dismutation reaction is conducted by three types of formations to use different metals as cofactors in SOD, including manganese (Mn-SOD), iron (Fe-SOD), and copper/zinc (Cu/Zn-SOD) [126]. The SOD site, in a plant cell, can be located in the chloroplast, mitochondria, cytosol, or peroxisomes. More precisely, the sites of these three types of formations are normally in peroxisomes; however, their specific sites are manganese in mitochondria, iron in the chloroplast, and copper/zinc in glyoxysomes, chloroplast, and cytosol [127, 128].

2.4.4. Catalase. In peroxisomes and photorespiration, catalase acts as a dismutation factor in scavenging H_2O_2 to oxygen and H_2O through the process of β-oxidation of fatty acids. Oxidation has a vital role in the digestion of the ROS components especially for H_2O_2 [129, 130]. One molecule of CAT can catalyze two molecules of H_2O_2 to water and oxygen [131]. Additionally, CAT can degrade some hydroperoxide groups, including methyl hydrogen peroxide (MeOH). By controlling the H_2O_2 compound, CAT preserves cell walls from lipid production and membrane damage. It is also involved in photosynthesis and prevents chlorophyll degradation [132].

3. Conclusion

Silicon is the second most abundant element in soil and the earth's crust. It cannot be found as a free element in soil and always appears as a combination of oxygen and silicate and other elements, which can be used in plants as silicic acid, $Si(OH)_4$. Silicon can be considered a quasi-essential element to increase plant growth and development and to reduce the abiotic and biotic stresses in plants through different mechanisms. It also plays a positive role in increasing the plant's resistance against stress, which can be achieved by silicon accumulation in plant parts, including roots stem, leaves, and hulls.

Silicon is generally used in plant protection processes against heavy metals in two mechanisms: avoidance and tolerance. Avoidance mechanisms include silicon reducing heavy metal uptake and availability by increasing the soil pH. It can additionally chelate-heavy metal compounds with root exudates, such as phenolics and organic acids, or decrease the translocation of heavy metals in the plant. However, in tolerance mechanisms, silicon elevates heavy metal stress with various mechanisms, including compartmentalizing heavy metals into cell walls and vacuoles, increasing enzyme antioxidant and nonenzyme antioxidant activity, limiting transportation in plants, homogeneously distributing metals in the leaf surface, and chelating or making a heavy metal barrier to reduce translocation in plants. The pH value mechanism caused by silicon is one of the important mechanisms for amelioration of heavy metals. Having additional silicon in the soil causes the pH value to increase. It can be vital for the immobility of heavy metals, may decrease heavy metal uptake, and can finally reduce the precipitation of silicon and heavy metals. Reduction of heavy metal uptake can be done in two ways: chemical or physical pathways. In the first way, stimulating the root exudate, silicon leads to an increase in chelating heavy metals, which can then reduce the ion uptake by plants. In the other case, plasmids in root cells prevent the translocation of heavy metals from root to shoot with building barriers. This can be counted as a physical mechanism to reduce heavy metal uptake in plants. The terms "chemical solution" and "planta" in silicon mechanisms are very important; "planta" expresses the increase in organic acid exuded from plants for chelation purposes of metals ions, as previously discussed. However, "chemical solutions" often occur in plant cells; they have this ability to initiate a silicon-to-metals ion formation and make a new compound of the silicon-heavy metal, which can cause the precipitation of heavy metal and silicon in the space between cells and phytoliths. The impacts of silicon

on antioxidant enzymes' and nonenzymes' activities are considered one of the important mechanisms to reduce the negative effects of heavy metals in plants. This can effectively protect plant cells from oxidative stress and scavenging free radicals caused by ROS to stimulate both antioxidant enzymes' and nonenzymes' activities, such as superoxide dismutase (SOD), peroxidase (POD), catalase (CAT), guaiacol peroxidase (GPX), ascorbate peroxidase (APX), glutathione reductase (GR), ascorbic acid (AA), flavonoids, reduced glutathione, α-tocopherol, carotenoids, and osmolyte proline. Antioxidants can scavenge ROS in plants with some chemical cycles, such as ascorbate-glutathione, water-water, and peroxisomal glutathione peroxidase. And these chemical cycles are in plant intercell organs, including cytosol, mitochondria, chloroplasts, apoplast, and peroxisomes. Another mechanism related to silicon mediation under heavy metal stress is gene expression. Physiologic alteration in plants related to a change in gene expression and changes in plant structures causes amelioration of heavy metals. This topic requires more research to identify mechanisms and thus will be followed by the authors in future research.

This article attempted to highlight the major mechanisms of silicon in reducing and ameliorating heavy metals in plants. Additionally, it tried to address the role of genes and intracellular organs and nuclei in plants.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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