INTERACTION TO THEIR PHYSIOLOGICAL, BIOCHEMICAL AND FUNCTIONAL ALTERATIONS IN PHOTOSYNTHETIC APPARATUS OF PLANTS UNDER CADMIUM STRESS: A CRITICAL REVIEW

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ABSTRACT

Cadmium is a toxic heavy metal that effect plant productivity by interfering with their photochemistry. Cadmium self-conscious the biosynthesis of chlorophyll by interfering with activity of d-aminolevulinic acid dehydratase in the rice seedlings. For the photochemical activities analyses, the extent of the decrease in photosystem II activity was much greater than that in the PS I activity. The variations occur in the chlorophyll a fluorescence parameters also indicated that cadmium toxicity drastically affected the photochemistry of PS II. Cadmium causes disturbances in a range of physiological processes of plants such as photosynthesis, water relations, ion metabolism and mineral uptake. Cadmium decrease, the level of chlorophyll, vitamin C, and the increase activities of antioxidant enzymes, Cadmium distinct affects photosynthesis by alteration of its vital machinery in all aspects. Photosynthesis is a well organised and sequential process indispensable to all green plants and microorganisms which involves various components, including photosynthetic pigments and photosystems, the electron transport system and CO_2 reduction pathways. Any damage at any level caused by Cadmium, critically affects overall photosynthetic capacity. This review focuses on the effects of Cadmium on photosynthetic apparatus including chloroplast structure, photosynthetic pigments, Chl-protein complexes and photosystems resulting in overall decrease in efficiency of carbon assimilation pathway and the effect of intensity on antioxidant enzymes gene.

Keywords: Photosynthesis, Chlorophyll, Chloroplast, Superoxidase, Catalase, Peroxidase Gene

I. INTRODUCTION

Cadmium (Cd) is a toxic element which causes serious pollution in both aquatic and terrestrial environments. The accumulation of Cd in soils and their subsequent transfer through the food chain is extremely dangerous to human health. Cd is not a nutrient element for animals and plants with no biological function, but known tocause a range of negative effects on plants (Zhang et al. 2013). At the leaf level, Cd stress causes the chlorosis, inhibits photosynthesis, and damages the structure and function of photosystem II (Zhang et al. 2013). Cd also changes hormonal status, disturbs mineral nutrition and water balance, and affects membrane structure and permeability (Xu et al. 2013). At the cellular level, Cd stress can cause the dislocation of nutrients resulting in deficiency effects in plant cell. Within the cell, Cd stress may generate oxidative stress (Belkadhi et al. 2013) and triggers indirectly the production of reactive oxygen species (ROS) including the hydrogen peroxide (H_2O_2) (Mittler et al. 2004). Cd has also been proven to induce oxidative stress by causing an overproduction of

reactive oxygen species (ROS) and enhancing the level of lipid peroxidation in plant leaves and roots (J. Cherif et al. 2011). The overproduction of ROS induces protein, DNA, and lipid damage. Therefore, it is very important for plant cells to control the overproduction of ROS by correlate the action of several antioxidant enzymes, such as superoxide dismutase (SOD), peroxidase (POD), and catalase (CAT) (N. Dinakar et al. 2008). These enzymes protect against oxidation in the cell by the satisfy free radicals. For example, SOD catalyzes the dismutation of O_2 toH_2O_2 and O_2 and plays an important role in removing ROS. Subsequently, the H_2O_2 produced by SOD is broken down to H_2O and O_2 by CAT, POD, and the ascorbate glutathione cycle, another critical defense mechanism against oxidative stress by directly reducing H_2O_2, and then the oxidized form of ascorbate is, in turn, reduced by dehydroascorbate reductase using glutathione as a substrate. The oxidized glutathione can then be reduced by glutathione reductase in the presence of NADPH, allowing the cells to survive under high ROS levels. The novel increase in heavy metal pollution has become a matter of major concern over the globe (Jamali et al. 2007). Cadmium (Cd) stands 7^{th} out of the 20 toxins and has no known biological function except in marine diatoms (Morel 2008). Cd is constantly added and gets accumulated to the plough layer of soil through various natural and human activity activities such as volcanic eruptions, mining, smelting, bungle of industrial waste and use of phosphate fertilizers (Grant 2011) and its addition to the suitable land is a widely recognised problem. Cd is potentially toxic to all organisms including plants, animals and humans as well. Cd exposure, for singly produce, is acquaintance with cancers of the prostate, lungs and testes, kidney tubule damages, rhinitis, emphysema, osteomalacia and bone fractures in humans (Nawrot et al. 2006). In plants, it results in many toxic symptoms such as inhibition of growth and photosynthesis, activation or inhibition of enzymes, disturbances in plant-water relations and ion metabolism, and formation of free radicals (Valentoviova et al. 2010). Cd is taken up by roots through plasma membrane transporters such as ZIP (ZRT-IRT like protein; Zinc regulated transporter, Iron-regulated transporter) and NRAMP (natural resistance associated macrophage protein) in competition to the essential nutrients of plants (Kim et al. 2002) and congenital it is translocated to shoots thereby leading to growth repetition which in due part emanates from trouble photosynthesis (Bazzaz et al. 1974. Photosynthesis inhibition may be attributed to diminished chlorophyll biosynthesis (Shukla et al. 2008), interrupted O_2 - evolving reactions of PSII and altered electron flow around PSI and PSII (Mallick and Mohn 2003). Cd hampers Calvin cycle by slowing down activity of various enzymes hence resolve in decreased photosynthesis (Ying et al. 2010). Stomatal closure due to entry of Cd into the guard cells in competition to Ca^{+2} (Perfus-Barbeoch et al. 2002) and reduction in stomata count per unit area are also characteristic symptoms of Cd stress resulting in lesser conductance to CO_2 (Pietrini et al. 2010) which consequently leads to overall inhibition of photosynthesis. The present review is an attempt to develop an orchestrated understanding of the mechanisms involved in altering and damaging various components of photosynthetic machinery by Cd thereby leading to capable loss in the anabolic reactions of plants and also Moreover, we investigated the possible induction of oxidative stress by Cd and whether or not the alteration of these enzymes involved in the antioxidant defense system includes SOD, POD, and CAT.

II. PHOTOSYNTHETIC MECHANISMS UNDER CADMIUM STRESS

2.1 Chloroplast Structure

Cd convincingly resulted in marked distortion of chloroplast ultrastructure leading to disturbed shape and inflated thylakoids (Najeeb et al. 2011). Disruption in chloroplast structure is ensued due to increased

peroxidation of membrane fatty acid and lipid contents resulting from elevate lipooxygenase (LOX) activity (Remans 2010). LOX mediates polyunsaturated fatty acid. oxidation including chloroplast membrane lipids such as monogalactosyldiacyl-glycerol (MGDG), digalactosyldiacyl-glycerol (DGDG) and phosphatidyl glycerol (PG) hence resulting in production of free radicals. LOX activity has been positively correlated with increased lipid peroxidation in plants such as *Arabidopsis*, Barley, Lupine and *Phaseolus* under Cd stress (Maksymiec and Krupa 2006; Tamas et al. 2009). A significant decrease has also been reported in the content of polaracyl lipids especially MGDG, DGDG and PG in tomato chloroplasts membranes (Djebali et al. 2005) which is considered to be indispensable for maintenance of membrane probity. The mesophyll cells of cadmium treated rice seedlings showed swollen chloroplast, such chloroplasts were great distant from the cell wall, the seedlings also showed a substantial increase in the number of starch granules (SGs). Chloroplast structure disturbance has been partly conspicuous by a notable decrease in chloroplast number and size, grana stacking, starch grain content and accumulation of plastoglobuli observed in various plants such as *Picris divarticata* (75µM, 14 days after treatment (DAT)), *Hordeum vulgare* (5µM, 15 DAT) and *Brassica* (Ying et al. 2010; Wang et al. 2011; Elhiti et al. 2012). Further, plants show differential aggregation of grana in young and older leaves. For instance in willow, older leaves showed bulge but organised thylakoids whereas young leaves appear to be more dense structured accompanied by tannin precipitation. Grana disorganization can be attributed to reduced MGDG level, as well as the decrease in 16:1 trans fatty acid content in MGDG and PG. In *Brassica napus* (50µM, 15 DAT) leaves, remarkable decrease upto 80-84 % was observed in DGDG and MGDG respectively (Nouairi et al. 2005), which may possibly be a reason in decay grana. The growth of rice seedlings was markedly inhibited by cadmium (100 lM), and the inhibition was significantly alleviated by cerium (10 lM). Fresh weight, single seedling height and chlorophyll content of rice plants in cerium treated groups were increased by 24.4, 18.2 and 32.05 % compared to those of plants cultivated in only cadmium-present condition. Additionally, in cadmium treated plants, the addition of cerium significantly increased the value of the maximum quantum yield of primary photochemistry (Fv/Fm), indicator of PSII 'structure and functioning' (SFIABS) and the performance index on absorption basis (PIABS), elevated the activity of whole chain electron transport activity, increase the photophosphorylation and its coupling factor Ca2 -ATPase activities. Finding showed that the chloroplasts and thylakoid membrane of the rice seedlings leaves grown in cerium treatment developed better than that in cerium-absent group under cadmium toxicity (Min Wu et al. 2014).

2.2 Cadmium Effect on Pigment Changes

Among the photosynthetic pigments prodigious studies have been conducted till date on reduction in chlorophyll and carotenoids in plants exposed to Cd stress. Chlorophyll destruction in older leaves and its biosynthesis inhibition in newer ones have been known to be prime cause in leaf chlorosis in plants growing in Cd treated soils (Xue et al. 2013). Inhibition of chlorophyll biosynthesis enzymes and activation of its enzymatic degradation plays crucial role in net loss in chlorophyll content (Somashekaraiah 1992). Aminolevulinate (ALA) is a essential compound in chlorophyll biosynthesis and its synthesis is the rate-limiting and regulatory step. Cd inhibits ALA synthesis at the site of availability of glutamate for ALA synthesis and intercede by interacting with SH group of enzymes, d-ALA dehydratase (Mysliwa-Kurdziel and Strzalka 2002) and porphobilinogen deaminase, (Skrebsky et al. 2008) leading to the accumulation of chlorophyll biosynthesis intermediates like ALA and porphyrins. In fact it has been reported in *Soybean* (0-100µM, 10 DAT) and *Cucumis* (0-1000µM, 10 DAT) (Noriega et al. 2007; Goncalves et al. 2009) that ALA accumulation is a reason

for generation of reactive oxygen species which alters redox status of plants thus weakening the situation. Carotenoid content in plants exposed to Cd do not exhibit a set pattern and may either increase or decrease.

The increase has been observed in many cases as in *Cucumis sativus* L. (Burzynski et al. 2007) and *Zea mays* L. (100µM, 10 DAT) (Chaneva et al. 2010). On the control decrease was also observed in a few cases e.g. *Pisum sativum* (7mg/kg, 20 DAT) (Hattab et al. 2009). Other leaf pigments including neoxanthin, lutein, violaxanthin were found to decrease in *Lycopersicon esculentum* and *Spinacea oleracea* plants (López-Millán et al. 2008; Fagioni et al. 2009). In lower organisms, Cd exposure caused a significant drop in the amounts of phycobiliprotein viz. allophycocyanin, phycocyanin, and phycoerythrin e.g. *Chlamydomonas* (50µM, for 24 hrs), *Gracilaria* (300µM, 16 DAT) and *Hypnea musciformis* (300µM, 7DAT) that led to decrease in photosynthetic efficiency (Perrault et al. 2011; Santos et al. 2012; Bouzon et al. 2012). Under cadmium stress, single plant weight and height, were sharply reduced by 41.2 and 29.8 %, respectively compared to the control seedlings. Cerium supplied can improve the growth inhibition induced by the toxicity of cadmium for rice seedlings, the single plant weight and height increased by 24.4 and 18.2 %, respectively in cadmium combined cerium treatment, followed the similar trends of chlorophyll contents in growth, but increasing the carotenoids content (Min Wu et al. 2014).

2.3 Cadmium Effect on Chlorophyll Protein Complex

Chl-proteins can be described as Chl a and Chl a/b multi cofactor proteins for both photosystems (PS) bound to chlorophylls and carotenoids (Fromme et al. 2001). Cd effects on both the PS as well as degree of damage vary in the plant species even among cultivars and populations, depending on genotypic and ecotypic differences (Prasad 1995). The inhibited effect of photosynthetic pigments including Chl a, Chl b, and carotenoid pigments content of rice seedlings unprotected to different concentrations of Cd. 100 lM Cd treatment resulted in maximum inhibition for Chl a (60.8 %) and Chl b (50.5 %) content. The data suggested chlorophyll a was found to be more sensitive to cadmium toxicity than Chl b. However, carotenoid content in terms of 38.8 % inhibition was less affected than chlorophyll at 100 lM Cd. (Yuwen et al. 2014). Apart from functioning as accessory light harvesting pigments; carotenoids play a positive role in photo protection of Chl and chloroplasts against photo oxidative damage. The expression of chlorophyll biosynthesis -related genes involving Glutamyl tRNA reductase (HEMA), Glutamate-1-semialdehyde amino transferase (GSA), ALA dehydratase (ALAD), Chlorophyll synthase (CHLG) and Chlorophyll idea oxygenase (CAO). Expression levels of most genes in the porphyrin and chlorophyll biosynthesis pathway including HEMA, ALAD CHLG and CAO were strongly down-regulated in rice seedlings leaves exposed to cadmium toxicity (Yuwen et al. 2014).

2.3.1 Phytochemistry of PS II Core Complex

Immunoblotting of Chl-protein complexes did not depict any changes in the level of polypeptides of PS II complexes comprising of CP 47, CP 43, D1 and D2 under Cd stress as demonstrated in rice (75µM Cd, 28 DAT) and spinach (100µM Cd, 30 DAT) (Pagliano et al. 2007; Fagioni et al. 2009). The same model was also observed in lower organisms i.e. *Chlamydomonas reinhardtii* (50µM, for 24 hrs) too (Perreault et al. 2011). Cd toxicity may be attributed to both acceptor and donor side of PSII thus preventing photoactivation (Sigfridsson et al. 2004). On the donor side due to high affinity, Cd exchanges with Ca^{++} in Mn^{++}/Ca^{++} cofactor present in oxygen evolving complex (Faller et al. 2005; Pagliano et al. 2007); the exchange leads to reduced kinetics of Hill reaction. On acceptor side Cd decreased the rate of electron transfer from Q_A to Q_B due to interaction with

non heme Fe and conformational modification of Q_B pocket (Geiken et al. 1998). Further decrease in lipid content in chloroplasts specifically MGDG and DGDG (Nouairi et al. 2006), considered to be indispensable for PSII activity, causes structural destroy the system of PSII beyond the limits of molecular structure (Quartacci et al. 2000).

2.3.2 Phytochemical Activities of Light Harvesting Complex (LHC) II

The most important part of chlorophyll–protein complexes was LHCII complex, while the most sensitive were PS core complexes, LHCI and Rubis CO. In addition, the enhanced fraction of the monomeric form LHCII in relation to the oligomeric form LHCII, with the main fraction of the LHCII trimers was occurred in this metal stress (data not show). LHCII monomerization suggested that cadmium toxicity led to rearrangement of the LHCII organization of the chlorophyll- protein complexes. LHCII is the principle light harvesting pigment-protein complex of PSII which absorbs light energy and transfers it to the reaction centre. The native form of LHCII is a trimer composed of three Lhcb proteins: Lhcb1, Lhcb2 and Lhcb3 (Lucinski and Jackowski 2006). These LHCII aggregates plays dynamic role in triggering the thermal dissipation of extra energy for efficient excitation quenching and display photoprotective role in case of over excitation of reaction centre and antenna (Barros et al. 2009). Cd exposure results in dissipation of total mass of Lhcb1 and Lhcb2 and accounts for disorganization of trimer-forming monomers resulting in diminished LHCII clustering of independent complexes. This was indicated by infrared studies on *Secale cereale* exposed to Cd (50µM, 7 DAT) where aggregate trimeric ratio remained 73% of the control (Janik et al. 2010). Cd toxicity resulted in constrained dissipation of excitation energy which may have been induced by alterations in the quenching centre formation or inhibition of motion transfer of thermal energy between pigments and the protein skeleton (Gruszecki et al. 2009). In *Spinacia oleracea* L. Lhcb1.1 isomers of Lhcb1 were highly affected even in small exposure to stress (75µM, 5 DAT) whereas others i.e. Lhcb2 and Lhcb3 were less affected (Fagioni et al. 2009).

Differential level of expression in Lhcb2 was observed in case of two ecotypes of *Sedum* (hyperaccumulating and non-hyperaccumulating) which suggested temporal regulation of gene expression. Upon 24 hrs of Cd (2µM) treatment non-hyperaccumulating ecotype show higher expression level than hyperaccumulating, followed by a reversal of the situation after 8 days (Zhang et al. 2011). Proteomic studies on *Oryza sativa* L. (7.5-75µM, 24 DAT) suggested contrasting results where LHCII content is not adversely affected suggesting that antenna complexes of PSII are less affected (Pagliano et al. 2006). Lipid profiling of chloroplast is conducive to suggest that decrease in 16:1 trans fatty acid content in MGDG and PG, decrease LHCII oligomerization due to its specific binding in sn-2 position in the chloroplastic PG (Vassilev et al. 2004). Cadmium due to its high affinity gets alternative in pigment protein complexes causing configuration changes (Küpper et al. 2002) leading to incorrect binding of chlorophyll molecule to the protein matrix.

2.3.3 Phytochemistry of PS I Core Complexes

In some plants exposed to cadmium stress PSI instead of PSII is the prime site of damage. In fact, observations suggesting greater damage to PSI have been reported in *Cucumis sativus* L. (10µM, 35 DAT) (Sarvari et al. 1999) Proteomic and expression studies conducted on basal leaves of *Spinacia oleracea* L. (100µM, 0-33 DAT) revealed disappearing of PSI core proteins stating accumulation of incomplete monomeric units leading to disruption of PSI super network (Fagioni et al. 2009).

2.3.4 Composition and Structure Change in Thylakod Membrane

The changes in the protein complex of thylakoid membranes under cadmium treatment, the complexes of non-treated and cadmium-treated seedlings were gently released from thylakoids by b-DM and separated by BN-PAGE. Fig. 4a, b showed a representative scan of gel electrophoresis of thylakoid membranes without (control) and with

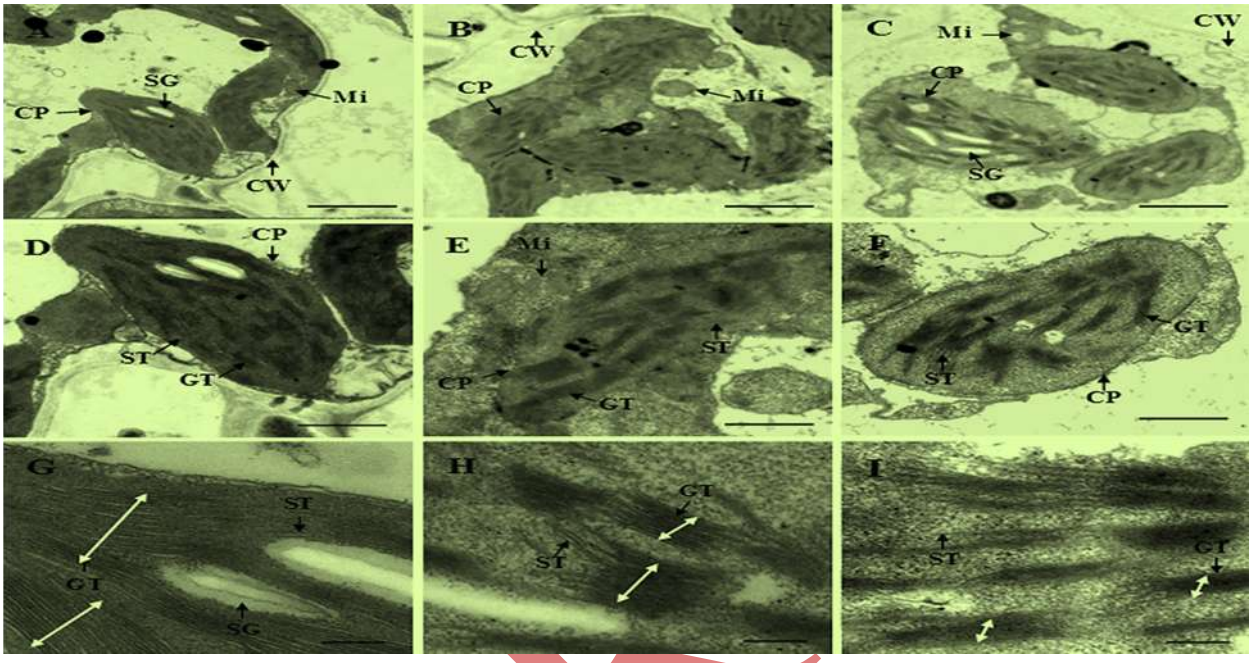

Figure 1. Transmission electron micrographs of chloroplast and thylakoid in leaf mesophyll cells of rice seedlings at low and high magnifications. a–c TEM micrographs of leaf mesophyll cells (Bar 2 lm), d–f TEM micrographs of chloroplast (Bar 1 lm), g–i TEM micrographs of thylakoid stacking (Bar 0.5 lm) in different Cd concentration, 0, 50, 100 lM respectively. Cell wall (CW), chloroplast (CP), starch grain (SG), mitochondria (Mi), grana thylakoid (GT), stroma thylakoid (ST) (Yuwen et al. 2014).

cadmium at the concentration of 50 or 100 lM. The bands obtained were identified according to Ku¨gler et al. (1997) and Shao et al. (2011). Hence, band 1 contained some super complexes. Band 2 and 5 contained the PS I core complexes with and without its light-harvesting complexes. Band 3 and 6 were calm of different part of ATPase complex. Band 4 corresponded to the RubisCO complex. Band 7 and 8 contained the Cyb6/f, PS II core complexes. Band 9, 10 and 11 represented different forms of lightharvesting complex LHCII, trimeric, dimeric and monomeric form respectively. Band 12 contained only free pigments. Differences in the intensity bands of the chlorophyll-protein complexes suggested that the composition or the content of these complexes had been altered, although some bands in this study were unknown (Yuwen et al.2014). These results partly indicated that the rate of degradation for each chlorophyll-protein complex (mainly in two photosystems) was different, and the most fixed of chlorophyll–protein complexes was LHCII complex, while the most sensitive were PS core complexes, LHCI and Rubis CO. In addition, the increased fraction of the monomeric form LHCII in relation to the oligomeric form LHCII, with the main fraction of the LHCII trimers was occurred in this metal stress (data not show). LHCII monomerization suggested that cadmium toxicity led to rearrangement of the LHCII organization of the chlorophyll- protein complexes. To determine the alteration of the major subunits inthe chlorophyll-protein of the thylakoid membranes under the cadmium toxicity, immunoblot analyses were performed using antibodies specific to PS core complexes, LHC protein and RubisCO (Yuwen et. 2014).

Yuwen et al. (2014) suggest the influence of cadmium toxicity on chloroplast structure and thylakoid stacking is important for understanding the physiological alterations. Three types of changes could be distinguished: (1) The chloroplasts from cadmium stress condition became more rounded or swollen instead of an ellipsoidal shape, such chloroplasts were great distant from the cell wall (Fig. 1b, c); (2) Loose or most unaerated grana thylakoid membrane system was obviously detected under the cadmium treatment (Fig. 1h, i); (3) The seedlings exposed to the cadmium also showed an increase in the number of starch granules (Fig. 1c) showed the compansion of the extent of thylakoid stacking in the control and Cd-treatment of rice seedling chloroplasts in leaves. The high stacking of thylakoids in control seedlings, while thylakoid stacking in cadmium toxicity was greatly decreased. Numbers of grana per chloroplast for plants decreased by 39 and 48 % at the different toxic cadmium level, respectively, compared with that of the controls. The cadmium concentration of 100 µM cadmium caused the maximum decrease in granal area per chloroplast compared with this of the control.

III. CONCLUSION

In conclusion, Cd affects either directly or indirectly decreasing the crop yield. We reviewed also its inhibitory effect on pigments, lipids, photosystems proteins and chloroplasts. All we notice that net loss in photosynthesis. It can be said that much has been known about Cd toxicity to plants but many mechanisms remains deductable about its interaction with photosynthetic proteins i.e. D1 and D2 and oxygen evolving complexes. In particular, we should increase our knowledge towards the PSI measurements to get a tangled knowledge on effect of Cd on photosynthesis. Strategies must be evolved on understanding the mechanism of Cd hyperaccumulation to uphold various phytoremediation strategies. Over-accumulation of Cd in plants shows various symptoms of toxicity, including growth inhibition, chlorotic leaves, and a decrease in biomass. The researchers discovered that N could effectively assuage Cd induced damage in plants. Adding substitute N to poplars under Cd stress can enhance plant growth, promote the synthesis of chlorophyll, and induce the activity of antioxidant enzymes and gene expression. Other findings suggested to Cd caused little reduction of the biomass and the Chl content but an increase in the activities of SOD and POD. Most of the Cd absorbed by the *A. cristatum* plants was loose in the roots and only a small amount was transported to the shoots. This review suggests that the *A. cristatum* plants are Cd tolerant and suitable for phytoremediation of contaminated soils.

Abbreviations: Cd, cadmium; ZIP, ZRT-IRT like protein; ZRT, zinc regulated transporter; IRT, iron-regulated transporter; NRAMP, natural resistance associated macrophage protein; MGDG, monogalactosyldiacyl-glycerol; LOX, lipooxygenase; DGDG, digalactosyldiacyl-glycerol; PG, phosphatidyl glycerol; DAT, days after treatment; ALA, aminolevulinate; PS, photosystems; LHC, light harvesting complex; SOD, superoxide; CAT, catalyse; APX,

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