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Review

Chromium tolerance, bioaccumulation and localization in plants: An overview

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A B S T R A C T

In the current industrial scenario, chromium (Cr) as a metal is of great importance, but poses a major threat to the environment. Phytoremediation provides an environmentally sustainable, ecofriendly, cost effective approach for environmental cleanup of Cr. This review presents the current status of phytoremediation research with particular emphasis on cleanup of Cr contaminated soil and water systems. It gives a detailed account of the work done by different authors on the Cr bioavailability, uptake pathway, toxicity and storage in plants following the phytoextraction mechanism.

This paper also describes recent findings related to Cr localization in hyperaccumulator plants. It gives an insight into the processes and mechanisms that allow plants to remove Cr from contaminated sites under varying conditions. These detailed knowledge of changes in plant metabolic pool in response to Cr stress would immensely help understand and improve the phytoextraction process. Further, this review provides a detailed understanding of Cr uptake and detoxification mechanism by plants that can be applied in developing a suitable approach for a better applicability of the process.

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1. Introduction

Cr is a heavy metal belonging to the transition group (VI-B) of the modern periodic table with an oxidation number ranging from Cr(II) to Cr(VI). The most stable and common forms in the environment are the trivalent Cr(III) and the hexavalent Cr(VI) species, both having different physicochemical and biochemical properties (Dhal et al., 2013). The intermediate oxidation states are metastable and do not occur naturally. Cr constitutes about 0.037 percent of the crustal rock and ranks 21st in relative natural abundance. Cr(III) is the most common naturally occurring state and forms complex with organic matter present in soil and aquatic environments. It occurs as chromic oxides (Cr_2O_3), hydroxides ($Cr(OH_3)$) or sulphates ($Cr_2(SO_4)_3 \cdot 12(H_2O)$) (Gill, 2014). In contrast, Cr(VI) is considered the most noxious form of Cr with a strong oxidizing potential. It is more mobile than Cr(III) and is usually associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) ions (Sultana et al., 2014). Cr(VI) is more water soluble and, thus, more bioavailable than Cr(III). It forms stable complexes with organic matter which further increases the Cr(VI) tendency to become persistent (Langård and Costa, 2015). Cr(VI) can be transformed to Cr(III) under acidic conditions, and this reduction process is favoured in acidic soils with a high proportion of organic matter. Further, Cr(III) may also be oxidized to Cr(VI) in the oxygenated environment. Cr(VI)/Cr(III) ratio is a function of pH, dissolved oxygen concentration, presence of reducing agents and complexing factors in the environment. Under anoxic conditions, only Cr(III) is present. Cr(VI) is predominant at a pH above 7 and Cr(III) predominates at a pH less than 6. Cr(III) precipitates under neutral to basic pH and, conversely, it is soluble in acidic media. Cr(VI) salts are soluble at all pH, but may get co-precipitated with divalent cations (Stanin and Pirnie, 2004).

1.1. Chromium: health hazard/toxicity

The health hazards of exposure to Cr(VI) and Cr(III) are well documented by the World Health Organization (WHO, 1988) and the Agency for Toxic Substances and Disease Registry (ATSDR, 1991). Cr(VI) is listed by the United States Environmental Protection Agency (USEPA) among seventeen chemicals posing greatest threat to humans (Cheung and Gu, 2007). It has been classified as a Group A contaminant by the Environmental Protection Agency (EPA). Cr(VI) species namely $Cr_2O^{-}{}_2$, $Cr_2O_7^{2-}$ and CrO_4^{2-} are the most mobile and bioavailable anionic forms in the aqueous environment. These are considered as highly lethal for most organisms due to its mutagenic and carcinogenic properties (Li et al., 2013). Owing to a very high positive redox potential, Cr crosses cell membranes damaging the cellular and molecular components of the cell leading to membrane disruption, protein degradation and DNA alterations in humans, animals and plants (Oliveira, 2012). Cr(VI) induces mutation by interfering with DNA protein cross-links and causes single-strand breakage (Shanker and Venkateswarlu, 2011). Cr(VI) exposure above the permissible limit (0.05 mg/L in drinking water) is known to cause cancer in lungs. It damages kidney and liver functions and may cause epigastric pain, nausea, vomiting, allergic reactions, stomach ulcers, and hemorrhage (Fig. 1) (Gad, 2014; McCarroll et al., 2010).

In plants and many other organisms, reducing agents such as NAD(P)H, $FADH_2$, several pentoses and glutathione in the cell pool, reduce Cr(VI) to Cr(III) (Hossain et al., 2012). During this conversion, transient formation of Cr unstable states occurs leading to free radicals formation, which induces oxidative stress conditions in plants (Sharma et al., 2012). Cr is toxic for most agronomic plants at a concentration of about 0.5–5.0 mg/L in nutrient media and 5–100 mg/g under soil condition. In general concentration of Cr in plants is usually less than 1 μg/g (Oliveira, 2012).

1.2. Sources and concentration of chromium in the environment

Cr occurs naturally in the form of crustal rocks but the main source is from various industrial units. It occurs predominantly as ferrochromite ($Fe_2Cr_2O_4$) and other minerals present in the earth's crust. The main ecological toxic burden is anthropogenic source concerned with industrial operations using Cr, mainly in leather tanning, metallurgical, Cr plating, wood processing, anodizing aluminium, cleaning agents, catalytic manufacture, organic synthesis, textile dyeing and textile pigment production, Cr plating, wood preservation and alloy preparation industries (Alloway, 2013). Out of the total world production of 24,000 × 10^3 metric tons (gross weight of marketable chromite ore), about 60–70% is consumed in stainless steel and alloy preparation. Leather tanning, pigment production, electroplating and other chemical industrial processes use above 15% (Papp and Lipin, 2010). Presently more than 4000 tanneries are involved in chrome tanning processes. In India, tannery industries account for about 2000–3000 tons/year of elemental Cr discharged into the environment. Around 80–90% of leather industry uses Cr as a tanning agent. Effluents from these tanneries is loaded with about 40% of Cr used in the form of Cr(VI) and Cr(III) salts (Sundaramoorthy et al., 2010).

Cr concentration varies from 0.1 to 0.5 mg/L in fresh waters and from 0.0016 to 0.05 mg/L in sea waters (Kumar and Puri, 2012). As recommended by WHO, the maximum permissible limits for the discharge of Cr(VI) into inland surface and drinking water are 0.1 mg/L and 0.05 mg/L, respectively. Cr is ranked as the 21st most abundant element present in the earth's crust (Förstner and Wittmann, 2012). It is reported that Cr concentration in the soil ranges from 5 to 3000 μg of Cr per gram (Polti et al., 2011). Besides natural rocks, major sources of Cr are effluents from various industries, ferrochromium slag, solid wastes containing Cr as by products, leachates and dust particles where Cr concentration is found strikingly above permissible limits.

1.3. Physico-chemical methods of Cr removal

Unlike organic compounds which are mostly biodegradable, Cr cannot be degraded, and decontamination usually requires their containment. To preserve our soil, aqueous waste streams and groundwater system, different methods of removal using physico-chemical and biological processes are being studied, among which the latter has the ability to provide more efficient and affordable technological solution (Kamaludeen et al., 2003; Ranieri and Gikas, 2014). Most of the conventional, physico-chemical remediation processes include chemical precipitation (Fu and Wang, 2011), electrochemical (Heidmann and Calmano, 2008), ion exchange (de Oliveira et al., 2014), reverse osmosis (Kiril Mert and Kestioglu, 2014) and adsorption (Barrera-Díaz et al., 2012), which are either expensive or generate toxic sludge (Kurniawan et al., 2006). Moreover, these methods lead to an increase in the total dissolved solids and conductivity of treated effluents thus increasing secondary contamination. These remediation methods also exert adverse effects on soil fertility by destroying the biotic consortia causing major strain on the ecosystem. Thus, bringing the Cr(VI) concentration under maximum allowable contaminant level in Cr(VI) laden effluents is a serious task for environmental engineers.

2. Cr removal by phytoremediation

Phytoremediation has proved to be an efficient process for the remediation of Cr(VI) contaminated soil and wastewater owing to its simplicity in operation and high efficiency of removal. It

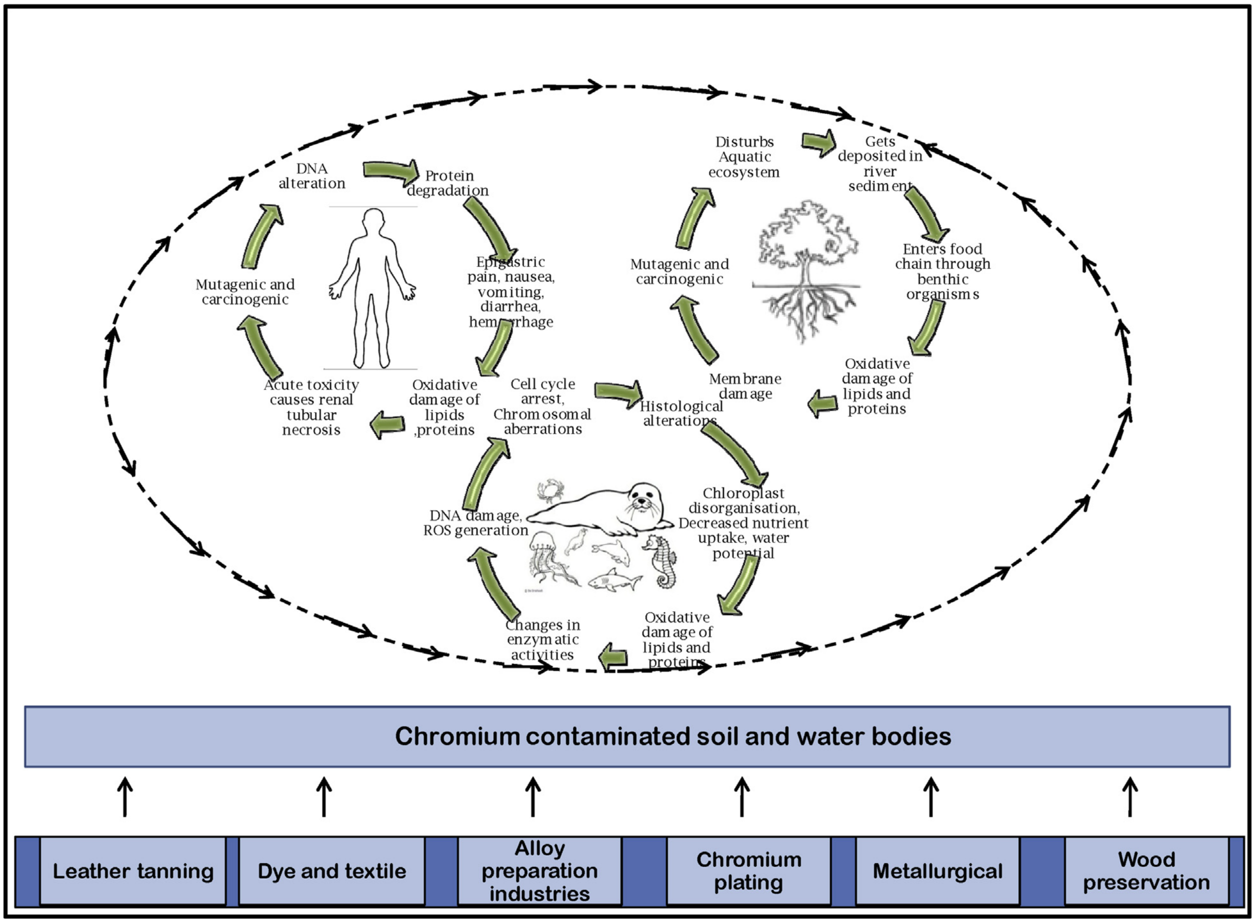

Fig. 1. Chromium toxic effects on the ecosystem.

provides a sustainable treatment method utilising solar energy. In the recent years, a lot of research investigations to understand the process mechanism has been carried out. Field applications in the form of constructed wetlands (CWs) have been established near industrial setups to process effluents loaded with toxic Cr wastes and other organics. It uses Cr hyperaccumulators with their associated microbial flora and their innate mechanisms for Cr removal. Recent research studies revealed that selected plant species bioaccumulate substantial amount of Cr through their unique metabolic and absorption pathways from soil, sediments, sludges and aquatic systems. Plants adopt various Cr-resistance mechanisms including bioaccumulation, biosorption and precipitation (Chen et al., 2010). Plants possess the potential to reduce toxic Cr(VI) into the less toxic Cr(III). Further, some plants utilize chromate efflux mechanism which can effectively serve as a method to reduce Cr pollution (Jabeen et al., 2009).

2.1. Plants with potential of Cr phytoremediation

Hyperaccumulating plants have the potential to transform contaminants, e.g. Cr, into less toxic trivalent state with reduced mobility. It utilizes the plants innate mechanism to bioaccumulate and store high levels of Cr in their roots, shoots and leaves. Cr hyperaccumulator plants can accumulate more than 1000 mg Cr/kg dry weight (DW) in their tissues (Zhang et al., 2007). Phytoremediation efficiency depends on many factors such as the soil's physical and chemical properties, Cr bioavailability, plant and microbial exudates, plant's ability to extract, accumulate, translocate, sequester and store (Hooda, 2007). Cr phytoremediation depends on five main subgroups which operate simultaneously: (i) Phytoextraction – efficient Cr accumulator plants concentrate toxic metals into their roots and translocate it to above-ground plant parts, (ii) Phytovolatilization – process of transformation of toxic compound into volatile state and evaporation from aerial parts of the plant, (iii) Phytostabilization-the use of plants to immobilize metals in soil by adsorption onto roots or precipitation in the rhizosphere, (iv) Rhizofiltration – process of absorbtion and precipitation surrounding plant root system, (v) Phytosequestration – phytochemical complexation in the root zone that can precipitate or immobilize metals in the root and such complexes are then mobilized to store in the vacuolar space of plant cells (Fig. 2). The toxic compound also gets transferred in different cells facilitated by transport proteins (Pinto et al., 2014).

Phytoremediation of Cr contaminated soil is primarily based on phytoextraction method where a specific hyperaccumulator is used to extract the pollutant through its roots which are then translocated to other plant parts (Hsiao et al., 2007). In order to make it a suitable remediation method, plants should be able to uptake significant amount of Cr, with a high translocation factor so that it gets accumulated in aerial parts and thereafter be capable of producing large biomass for an even higher Cr bioaccumulation to take place. Whereas rhizofiltration is the main process which operates in the wetlands near an industrial set up of polluted waters (Ray Chaudhuri et al., 2008). In hydroponics conditions and in constructed wetlands (CW) treating Cr laden effluents, several plant species have been studied for their Cr removal efficiency and

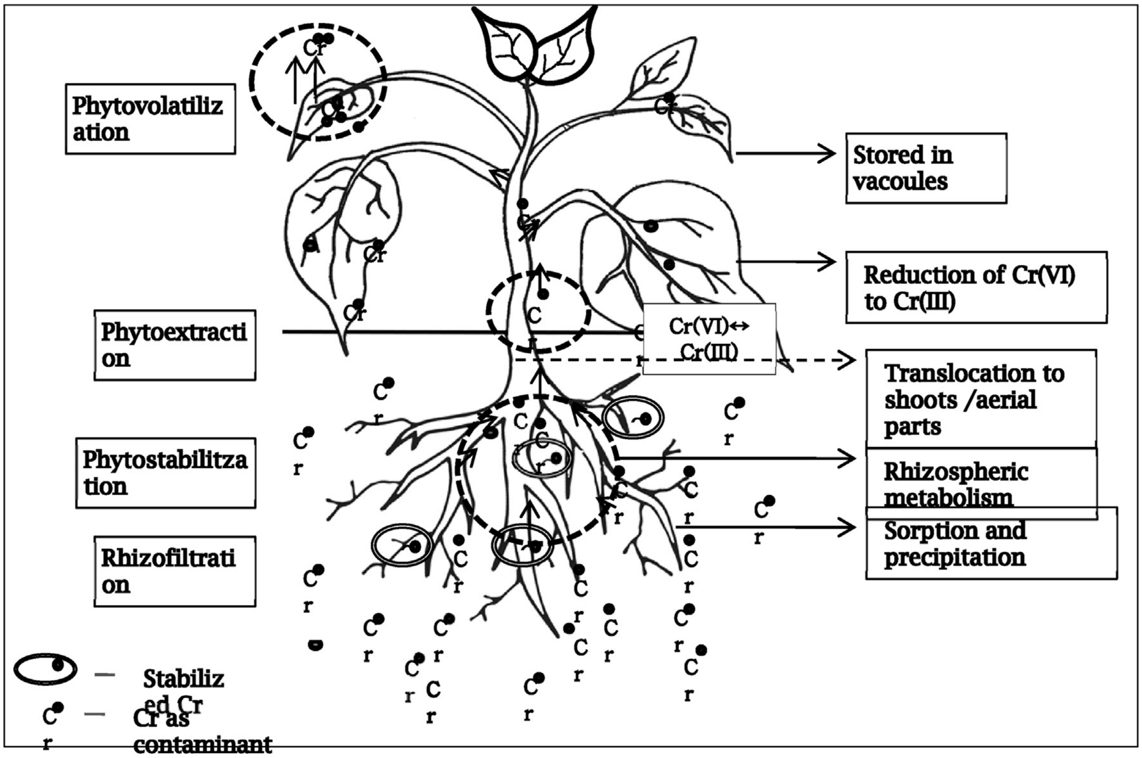

Fig. 2. Schematic showing possible fates of chromium during the phytoremediation processes.

translocation ability (Table 1).

Under greenhouse conditions, plants such as *Phragmites australis* and *Ailanthus altissima* (Ranieri et al., 2016), *Cajanus cajan* (Jerez and Romero, 2016), *Helianthus annuus* L. (Bahadur et al., 2017), *Alnus acuminata* (Escobar and Dussán, 2016) were found to effectively remove Cr(VI) from contaminated soil under different conditions.

Most of these plants do not meet the hyperaccumulator criteria, as their translocation efficiency to above ground parts does not meet the requirement. However, at present these plants are reported to accumulate substantial amount of Cr and classified as significant Cr phytoremediators.

In the recent years, several studies on genetically transformed plants and microbes have provided detailed information at the genetic level in understanding Cr resistance and accumulation mechanism. Zheng et al. (2015) reported an aerobic Cr(VI)-reducing bacterium BYCr-1 where nfrA gene was found to be upregulated and played role in chromate reduction. In another study, Del et al. (2013) reported a high resistance to Cr(VI) by the insertion of GR and rolC genes in genetically modified *Nicotiana langsdorffii*. They further detailed that GR transformed lines showed high Cr accumulation where phenolics played an important function in imparting resistance to Cr(VI). Zeng et al. (2008) reported role of organic acids viz. oxalic, malic and citric acid in Cr resistance and accumulation in transformed rice lines as compared to wild species. Several similar studies have reported that genetic insertions caused a modification in the metabolism of sugars, acids and phenolic compounds that played significant role in Cr tolerance and uptake.

Plants in association with the microbes were found to have a high potential in rhizofiltrating Cr(VI). Recently, a variety of Cr-reducing bacterial strains in association with specific plants have been reported to enhance Cr remediation along with plant growth. *Pseudomonas* sp. strain R16 in association with halophyte *Juncus acutus* (Dimitroula et al., 2015), *Pseudomonas aeruginosa* strain OSG41in chickpea (Oves et al., 2013), *Microbacterium* sp. strain SUCR140 with *Zea mays* (Soni et al., 2014), *Staphylococcus sciuri* in rice plants (Dutta et al., 2017), Pantoea sp. strain FC 1 in association with *Brassica napus* hairy roots (HRs) (Ontañon et al., 2014) have shown significant enhancement in association with rhizosphere. In yet another study, *Cellulosimicrobium cellulans* strain, KUCr3, was found to increase Cr(VI) reduction in the rhizospheric soil of plants, also promoting plant growth, by enhancing IAA level and phosphate mineralization, where their levels correlated positively with the stress dosage of Cr, suggesting this strain as a potential Cr bioremediation agent (Chatterjee et al., 2009). These associations enhance the reduction and transformation of Cr(VI) by increasing plant growth hormones, inducing siderophores, solubilizing phosphorus, and certain classes of enzymes (quinone reductases, chromate reductases, nitroreductases, NADPH-dependent etc.). The key enzyme, chromate reductases, found in these chromium tolerant bacteria catalyze the reduction of Cr(VI) to Cr(III). Several classes of bacterial chromate reductases such as ChrR, NemA, LpDH and YieF has been reported which are either in the cytoplasm or membrane bound (Pradhan et al., 2016; Thatoi et al., 2014). Thus, rhizoremediation process and the in-depth knowledge of the interaction between the plants and its rhizospheric microbiome at the genomic level is an emerging area having potential application in bioremediating Cr(VI).

Following Cr bioaccumulation, the heavy metal loaded plant biomass needs to be suitably disposed. One of the disposal strategies could be pyrolysis of the plant biomass which is carried out under anaerobic conditions yielding pyrolytic fluid oil and coke in the product stream. Coke concentrated with the heavy metals can be further used in a smelter. A pilot scale reactor study reported 98.5% metal recovery (Ni, Zn, Cu, Co or Cr) in the char formed by pyrolysis and gasification of hyperaccumulating plant biomass (Koppolu et al., 2003). Incineration under controlled condition, in which ash with a high metal content is recovered, is another option

Table 1
Efficient chromium accumulator plants: habitat, culture conditions and removal mechanism.

Cr accumulator	Habitat	Family	Cr(VI) removal mechanism	Culture condition	Mode	Max % removal/ Bioaccumulation capacity	Experimental period	Influent conc.	References
Amaranthus viridis (Green amaranth)	Perennial broadleaf herb	Amaranthaceae	Increased activity of antioxidative enzymes	Hydroponic culture	Batch	Cr accumulation: Roots: 2624.39 µg/g Cr(VI) (dw) at 5.2 mg/L	20 days	0.052–5.2 mg/L Cr(VI)	Liu et al. (2008)
Azolla (Water fern)	Aquatic fern	Salviniaceae	NR	Hydroponic culture	Batch	Cr accumulation: 356 and 964 mg/kg dm Cr(VI) and Cr(III) at 1 mg/dm	12 days	1-20 mg/L Cr(VI)	Arora et al. (2006)
Bacopa monnieri (Smooth water hyssop)	Perennial, creeping herb	Plantaginaceae	NR	Hydroponic conditions	Batch	319.5 mg/kg DW for Cr at 10 µg/ml	8 weeks	0.01, 0.1, 1.0, 2.5, 5.0, 10 mg/L Cr	Shukla et al. (2007)
Brachiaria mutica (Paragrass)	Perennial grass	Poaceae	NR	Soil field study (mine wastewater)	Continuous	Transportation index (TI): 6.16 Total accumulation rate (TAR):8.2 mg/kg/day	100 days	0.65 mg/L and 0.74 mg/L for Cr(VI)	Mohanty and Patra (2012)
Brassica juncea (Indian mustard)	Annual growing perennial herb	Brassicaceae	NR	Soil condition	Batch	Cr accumulation: 48 and 58 µg Cr per plant from Cr (III) and Cr (VI)-treated soils	69 days	Soil amended with 100 mg/kg of Cr (III or VI)	Bluskov et al. (2005)
Callitricha cophocarpa (Water-starwort)	Aquatic macrophyte	Callitrichaceae	Cr(VI) reduction	Hydroponic culture	Batch	Cr accumulation: 1000 mg/kg (dw)	3 weeks	2.6–36.4 mg/L Cr(VI)	Augustynowicz et al. (2010)
				Wetland		Cr(VI) storage vascular bundles	7 days	5.2 mg/L Cr(III) and Cr(VI)	Augustynowicz et al. (2014)
						Cr accumulation: Cr(III) 28,385 mg/kg (dw) Cr(VI) 7315 mg/kg (dw) Cr(III); 98.8% removal	5 days	26-208 mg/L Cr(III)	
Convolvulus arvensis (Bindweed)	Herbaceous perennial plant	Convolvulaceae	NR	Tissue culture conditions	Batch	Cr accumulation: 3800 mg/kg Cr(VI) (dw)		20 mg/L Cr(VI)	Gardea-Torresdey et al. (2004)
Dicoma niccolifera	Terrestrial	Asteraceae	NR	–	–	Cr accumulation: >1000 mg/kg Cr	–	–	Banach et al. (2012)
Eichhornia crassipes (Water hyacinth)	Free-floating perennial aquatic plant	Pontederiaceae	Increased activity of antioxidative enzymes	Hydroponic culture	Batch	Maximum Cr accumulation: 2.52×10^3 µg/g of water hyacinth in 20 mg/L	42 days	3, 5, 7, 10 and 20 Cr(VI) mg/L	Zewge et al. (2011)
			Cr(VI) reduction			Cr removal efficiency: 91%			Mangabeira et al. (2004)
			Plants exposed to 520 mg/L Cr(VI) for 4 days did not survive 52 mg/L Cr(III) for 2 days stimulated growth	Hydroponic culture under greenhouse conditions	Batch	Maximum Cr accumulation: 1258 mg/kg (dw) 520 mg/L Cr(III) for 2 days	2-4 days	52 and 520 mg/L Cr (III) and Cr(VI)	Paiva et al. (2009)
Genipa americana L (Genipap)	Wood plant	Rubiaceae	NR	Hydroponic conditions	Batch	–	5 months	0, 5, 10, 15, 20, 25 and 30 mg/L Cr(III)	Barbosa et al. (2007)
				Hydroponic conditions	Batch	Reduction of 79 and 90% for 15 and 30 mg/L of Cr(VI)	15 days	15 and 30 mg/L Cr(III) and Cr(VI)	Santana et al. (2012)
Gynura pseudochina (Purple passion)	Herb	Asteraceae	Cr(VI) reduction	Hydroponic culture	Batch	Cr accumulation: Tubers: 823.1 mg/kg Cr(VI) (dw) Shoots: 787.9 mg/kg Cr(VI) (dw)	2 weeks	100 mg/L Cr(VI)	Mongkhonsin et al. (2011)
Helianthus annuus (Sunflower)	Annual forb	Asteraceae	NR	Cr contaminated soil	Continuous	70% chromium removal Cr accumulation:	90 days	10 mg/L Cr(VI)	Ranieri et al. (2013)

(*continued on next page*)

Table 1 (*continued*)

Cr accumulator	Habitat	Family	Cr(VI) removal mechanism	Culture condition	Mode	Max % removal/ Bioaccumulation capacity	Experimental period	Influent conc.	References
						Roots (2730 mg Cr/kg dry tissue)			
Hydroctyle umbellata (Marshpennywort)	Anchored hydrophyte	Araliaceae	NR	Hydroponic culture	Batch	Cr accumulation: 18,200 mg/kg	90 days	Semi-solid tannery (wet) sludge at 0, 20, 40, and 60% total Cr concentrations.	Khilji (2008)
Jatropha curcas (Barbados nut)	Perennial plant	Euphorbiaceae	NR	Greenhouse experiment (Soil and compost based media)	Batch	50% removal	30 days	10, 30, 50, 70 and 90 mg Cr(VI)	Mangkoedihardjo et al. (2008)
Leersia hexandra (Southern cutgrass)	Perennial herb (grow in swamps)	Poaceae	Facilitates microbial growth	CWs (Lab-scale)	Continuous	99.7%	120 days	5 mg/L Cr(VI)	Liu et al. (2015)
			Cr(VI) reduction and sequestration	Hydroponic culture	Batch	Highest bioaccumulation coefficients for leaves: 486.8 for Cr(III) and 72.1 for Cr(VI) Chromium accumulated in leaves was 4868 µg Cr(III)/g and 597 µg Cr(VI)/g	45 days	10 mg/L Cr(VI) and 60 mg/L Cr(III)	Zhang et al. (2007)
Lemna sp. (Duckweed)	Free-floating aquatic plants	Araceae	NR	Hydroponic culture	Continuous	4.423 mg Cr(VI)/g	7 days	5.0 mg/L Cr(VI) pH 4.0	Uysal (2013)
Medicago sativa (Alfalfa)	Perennial flowering plant	Fabaceae	NR	Soil pot conditions	Batch	60-74%	50 days	0, 4, 8,10 mg Cr(VI) /kg soil	Karimi (2013)
Miscanthus sinensis (Chinese silver grass)	Herbaceous perennial plant	Poaceae	Altered vacuole sequestration, nitrogen metabolism and lipid peroxidation	Hydroponic culture	Batch	–	3 days	0, 2.6, 5.2, 10.4, 15.6, 26, 39 or 52 mg/L Cr(VI)	Sharmin et al. (2012)
Nymphaea spontanea (Water lilies)	Aquatic rhizomatous perennial herbs	Nymphaeaceae	NR	Hydroponic conditions	Batch	Cr accumulation: 2.119 mg/g from a 10 mg/L	9 weeks	1, 2.5, 5 and 10 mg/L Cr(VI)	Choo et al. (2006)
Penisetum purpureum (Napier grass)	Perennial tropical grass	Poaceae	NR	Hydroponis in gravel bed constructed wetland system	Continuous	78.1% removal	8 weeks	10 and 20 mg Cr/dm^3	Mant et al. (2005)
Phalaris arundinacea (Reed canarygrass)	Perennial grass	Poaceae	NR	Horizontal subsurface flow CW	Continuous	Cr accumulation: 14.7 mg/kg dry mass Roots: 18.5 mg/kg Cr.	4 years	Municipal sewage with 0.5–4 mg/L Cr	Vymazal et al. (2007)
Polygonum hydropiperoids (Swamp smartweed)	Rhizomatous perennial aquatic herb	Polygonaceae	NR	Hydroponis	Batch	Cr accumulation: Shoots: 44 mg/kg (dw)	10 days	1 mg/L Cr(VI)	Qian et al. (1999) Mei et al. (2002)
Phragmites australis (Common reed)	Perennial grass	Poaceae	Cr(VI) reduction	Soil pot conditions	Continuous	54% removal	90 days	10 mg/L Cr(VI)	Ranieri et al. (2013)
			Cr(III) precipitation	Horizontal subsurface flow CW	Continuous	Cr(VI) respectively	2 years	5.5 µg/L Cr(VI) and Cr(III)	Fibbi et al. (2012)
Pteris vittata (Chinese brake)	Fern species	Pteridaceae	NR	Hydroponic system	Batch	Cr accumulation: Fronds 234 mg/kg (dw) Roots 12,630 mg/kg (dw) at 2.6 mg/L Cr(VI)	14 days	0, 2.6, 13 and 65 mg/L	de Oliveira et al. (2014)
				Sand pot culture		65 mg/L for 2-wk in hydroponic system.	2 weeks		Sridhar et al. (2011)
Prosopis laevigata (Smooth Mesquite)	Flowering tree	Fabaceae	NR	Tissue culture conditions	Batch	Cr accumulation: Roots: 8090 mg/kg Cr(VI) (dw)	50 days	0–176.8 mg/L Cr(VI)	Buendía-González et al. (2010)

						Shoots: 5461 mg/kg Cr(VI) (dw)			
Salsola kali (Russian thistle)	Annual saltwart	Chenopodiaceae	NR	Agar based media	Batch	Maximum Cr accumulation at 20 mg/L Cr(VI): Roots: 2900 mg/kg Cr(VI) (dw) Stems: 790 mg/kg Cr(VI) (dw) Leaves:600 mg/kg Cr(VI) (dw)	15 days	0, 5, 10, and 20 mg/L Cr(VI)	Gardea-Torresdey et al. (2005)
						Maximum Cr accumulation at 20 mg/L Cr(III): Roots: 116 mg/kg Cr(III) (dw) Stems: 62 mg/kg Cr(III) (dw) Leaves: 33 mg/kg Cr(III) (dw)	15 days	0, 5, 10, and 20 mg/L Cr(III)	
Spartina argentinensis (Cordgrass)	Perennial grass	Poaceae	NR	Glasshouse experiment	Batch	Cr accumulation: 15.1 mg/g Cr(VI) (dw) at 1040 mg/L	15 days	0-1040 mg/L Cr(VI)	Redondo-Gómez et al. (2011)
Spirodela polyrrhiza (Giant duckweed)	Perennial aquatic plant	Lemnaceae	NR	Continuous flow pond system	Continuous	Maximum Cr accumulation: 4.423 mg Cr/g was found in plants grown in the first chamber of pond operated at pH 4.0 at 5.0 mg Cr/L	21 days	0.25–5.0 mg/L Cr(VI)	Mishra and Tripathi (2008)
Salvinia minima (Water spangles)	Aquatic macrophyte (Free floating fern)	Salviniaceae	Increased activity of antioxidative enzymes	Outdoor condition	Continuous	Cr accumulation: Submerged leaves 3358 µg/g Cr(VI) (dw) Floating leaves 637 µg/g Cr(VI) (dw)	7 days	26-208 mg/L Cr(III) or Cr(VI)	Prado et al. (2012)
			Cr(VI) reduction	Hydroponic culture	Batch	Maxima Cr accumulation: Submerged leaves 2210.1 µg/g Cr(VI) (dw) Floating leaves 484.5 µg/g Cr(VI) (dw) at 10 mg/L Cr concentration	6 days	2, 5, and 10 mg/L Cr(VI)	Prado et al. (2010)
Salvinia molesta (Kariba weeds)	Aquatic fern	Salviniaceae	NR	Hydroponic culture		Cr removal ranged from 40 to 99%	7 days	–	Shiny et al. (2004)
Tradescantia pallida (Wandering jew)	Succulent perennial herb	Commelinaceae	Increased activity of antioxidative enzymes	Hydroponic culture	Batch	Max Cr accumulation: 536 mg/kg dw	60 days	10 mg/L Cr(VI)	Sinha et al. (2014)
Typha latifolia (Cattails) and *Phragmites australis* *(Common reed)*	Aquatic grass Perennial grass	Typhaceae Poaceae	NR	Horizontal subsurface flow CW	Continuous	Maximum removal efficiency of 73%	17 months	Synthetic tannery waste water	Calheiros et al. (2007)
Vetiveria zizanoides (Khas-khas)	Perennial grass	Poaceae	NR	Hydroponic culture CW	Batch	77–78% for Cr uptake ability Max Cr accumulation: Stem (28.3 g/kg) 89.29% removal efficiency	–	5-20 mg/L	Singh et al. (2015)
						Cr accumulation: Roots 0.448 mg/kg (dw) Leaves 0.241 mg/kg (dw)	100 days	NR	Srisatit and Sengsai (2003)

NR: Not Reported.

available for disposal of such plant biomass (Revathi et al., 2011). Furthermore, volume reduction processes, such as composting and compaction of Cr accumulated biomass have been proposed as a post-harvest biomass treatment (Shukla et al., 2009).

In recent years, many research studies have aimed at understanding chromium tolerance, accumulation and uptake mechanism by Cr accumulator plants. Currently many phytoremediation experiments have been performed at the lab scale. So far, most of them have been carried out in hydroponic setting or in CWs fed with different concentrations of Cr, under controlled environmental conditions. These results show significant reduction and removal in Cr(VI) concentration but are constrained by the fact that laboratory conditions are quite different from those of real effluent or soil. In Cr contaminated sites, many metals are present in insoluble forms, which make Cr less available. Further, to improve the applicability of phytoremediation for real wastewater treatment, indigenous plants need to be screened which are better adapted to grow in a particular region and also survive under metal stressed condition.

2.2. Chromium transport and uptake mechanism

Very few studies have been conducted to illustrate Cr uptake pathway in plants. Cr valence state is one of the main factors affecting Cr transport inside the plant cell (Banks et al., 2006). Since Cr is a nonessential element, plants lack any specific mechanism or transporters for its uptake. It has been reported that for its entry inside the plant cell, reduction of Cr(VI) to less harmful Cr(III) takes place on plant root surface. Plant cell constituents such as NAD(P)H, glutathione, several pentoses, $FADH_2$, ascorbic acid, cyanocobalamin, cytochrome P-450, and the mitochondrial respiratory chain are involved in the reduction process (Cheung and Gu, 2007). In contrast, some authors have suggested that Cr(III) forms water insoluble compounds in non-acidic aqueous solutions and, therefore, become impermeable to biomembranes. Some research studies have further demonstrated that Cr(VI) uptake in plants occurs without undergoing reduction. Cr(VI) compounds structurally resembles SO_4^{2-} ions, and enters the cell through carriers of essential anions such as sulphate and phosphate transporters which are essential plant nutrients that easily cross the plant cell membranes (Fig. 3). Chromate transport across biological membranes is thus reported to be an active process (Schiavon et al., 2012; Marieschi et al., 2015).

Thus, it can be concluded that Cr active or passive transportation pathway depends on its oxidation state. For instance, Cr(III) uptake occurs through simple and passive diffusion through cation exchange sites of plant cell wall. In contrast, Cr(VI) is transported actively by sulphate carriers present in plants. Following uptake, Cr(VI) is reduced to Cr(III) in plant roots. The involvement of sulphate transporters in Cr(VI) uptake is evident from recent studies carried out on the inhibition of sulphate transport and assimilatory pathway using transgenic, enzymatic and metabolic inhibitors (Schiavon et al., 2012).

Following uptake and inside the cell cytoplasm, Cr(VI) detoxification pathway follows reduction of Cr(VI) to Cr(III) via intermediate formation of the unstable Cr(V) and Cr(IV) states which leads to ROS generation (Gupta and Ballal, 2015). Contrary to this no differences in the uptake of either Cr(III) or Cr(VI) were observed in *Phaseolus vulgari* (Nath et al., 2009) and *Triticum aestivum* L. (Subrahmanyam, 2008).

It has been shown that addition of multidentate chelating agents like EDTA and vermicompost enhance the Cr bioavailability and thus increases the uptake of Cr by the plants (Jean et al., 2008). This is ascertained by the fact that chelating agents possess functional groups capable of Cr absorption and conversion. Supplementation of the contaminated soil with vermicompost was reported to further enhance the plant biomass growth, thus favouring the plant bioaccumulation potential as found in *Sorghum*

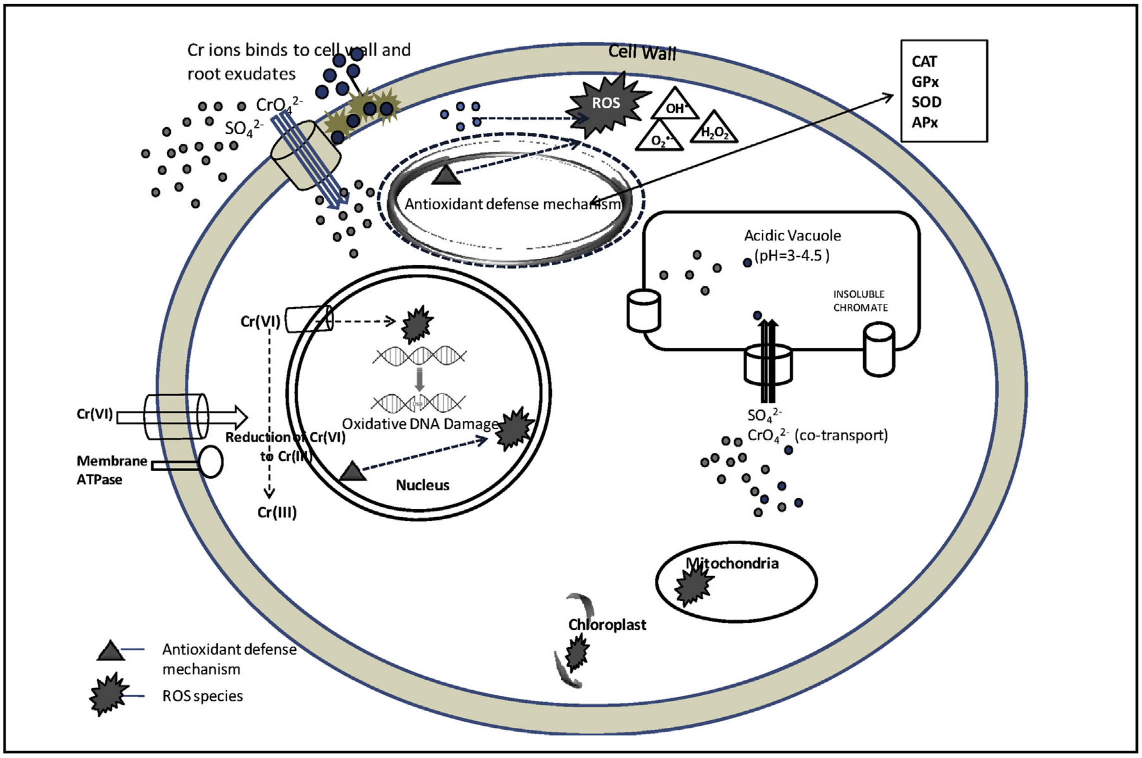

Fig. 3. Chromium uptake, transport and antioxidant defence mechanism adopted by plant cells.

(Revathi et al., 2011) and *Helianthus annus* (Jadia and Fulekar, 2009).

2.3. Chromium: phytotoxicity, accumulation and translocation

Several studies reported that chromium phytotoxicity, accumulation rate and translocation to shoots and leaves depend on different plant species, Cr speciation, bioavailability and initial media concentration (Yu et al., 2007). Soil pH, organic matter content and chelating agents are among the different parameters which play an important role in Cr absorption and translocation (Zhang et al., 2010).

A high Cr(VI) concentration showed adverse effects in plants, causing reduction in seed germination, plant growth parameters, photosynthetic rate, nitrate reductase activity (Liu et al., 2008; Sangwan et al., 2014) and soluble protein content and damage to chlorophyll structure (Singh et al., 2013). In leaves, a high dichromate concentration caused chlorosis, a symptom often associated with detrimental effects of heavy metals in plants (Vernay et al., 2007). Seed germination may get affected due to interference of Cr on plants enzymatic activities such as amylase which affects the sugar transport (Santana et al., 2012).

Cr(VI) doses greater than 100 μM inhibited or caused a significant decrease in root growth of plant species such as *Arabidopsis thaliana* (Eleftheriou et al., 2015), *Salix viminalis* (Ranieri and Gikas, 2014), *Caesalpinia pulcherrima* (Rai et al., 2006), *Triticum aestivum* (Subrahmanyam, 2008) and *Vigna radiata* (Diwan et al., 2010). This root growth inhibition due to dichromate toxicity is attributed to decreased root cell division or due to the arrested cell cycle.

In crop species such as *Oryza sativa* (Zeng et al., 2011; Schiavon et al., 2012), *Triticum aestivum, Avena sativa* and sorghum (Lopez-Luna et al., 2009), Cr affects the biomass yield, thereby negatively affecting the crop production. Shanker and Venkateswarlu (2011) proposed that this may be due to nutrient imbalance, which resulted in stunted growth and less production. Cr shares structural and chemical similarity with some essential oxyanions including sulphate and phosphate, due to which it can affect the plant mineral nutrition through competitive uptake by common transport proteins (Martínez-Trujillo et al., 2014).

Cr(VI) adversely alters most of the plants biochemical and physiological parameters. Boonyapookana et al. (2002) reported that at a high concentration in addition to reducing the plant growth rate and crop yield production, Cr adversely affects the vital photosynthetic pigments production channel (e.g., chlorophyll, anthocyanin). In contrast, Henriques (2010) reported pigment damage due to Cr(VI) by performing a photochemical experiment with irradiated chloroplasts. It was proposed that Cr caused reduction in Ca and Mn availability, resulting in pheophytinization of the chlorophyll molecules causing disruption in its function. It is hypothesised that Cr at higher doses might even inhibit chlorophyll biosynthesis by inhibiting δ-aminolaevulinic acid dehydratase, an essential enzyme in pigment synthesis (Gill et al., 2015).

Recently, Cr effect on the Calvin cycle enzymes has been studied in detail. Dhir et al. (2009) suggested that Cr caused oxidative damage to RuBisCO (ribulose-bisphosphate carboxylase oxygenase) enzyme complex which enhanced its oxygenation activity instead of decarboxylation. This may be due to the substitution of Mg^{2+} in the active site of RuBisCO subunits by Cr ions. In some Cr tolerant species, Cr induced the expression of ATP synthase, RuBisCO small subunit and coproporphyrinogen III oxidase. Bah et al. (2010) performed proteomic analysis of *Typha angustifolia* exposed to Cr and found that exposure to Cr induced the expression of ATP synthase, RuBisCO small subunit and coproporphyrinogen III oxidase that play a protective role against Cr stress. The authors suggested that the enhanced expression of ATP synthase was due to increased energy demand under such stressed conditions. Metabolic changes in relation to energy demands as induced by Cr stress are an unfocussed area which needs to be explored. Sugars are main source of energy metabolism and it plays a key role as signaling molecules (Rosa et al., 2009). Understanding changes in the soluble sugars and starch accumulation in leaves is very crucial which will help in characterization of Cr-induced phytotoxicity. Rodriguez et al. (2012) found that in *Pisum sativum*, following exposure to Cr(VI) upto 2000 mg/L, soluble sugars and starch concentration increased, but sucrose (transport sugar) and glucose concentration decreased. Tiwari et al. (2009) reported decrease in the amount of non-reducing sugars while the reducing sugars amount increased. In contrast to these reports, Prado et al. (2010) observed an increase in sucrose levels whereas the concentration of glucose decreased in Cr treated plants. Najafian et al. (2012) found that in *Brassica napus* L. the dissolved sugar in root and aerial parts significantly raised upon Cr accumulation. This can be attributed to the plant's defence mechanism in dealing with the Cr toxicity.

High Cr(VI) concentrations lowered the uptake of essential elements, viz. Fe, K, Mg, Mn, P and Ca in *Salsola kali* (Oliveira, 2012). Tiwari et al. (2013) reported that in *Raphanus sativus*, a high concentration of Cr (20.8 mg/L) induced toxic effects on plant's metabolic activity and translocation of nutrients. As a result, iron concentration in leaves was severely affected (from 134.3 to 71.9 μg/g dw) and it negatively affected the translocation of sulphur, zinc and phosphorus.

Thus, it can be inferred from the afore-mentioned studies, that in the advent of Cr toxicity, plants respond by specific physiological and biochemical changes that render adaptation and protection against oxidative stress. Exposure to a high concentration of Cr ions exerts oxidative stress that affects basic metabolism, transport processes, membranes and cellular structure in plants. Such defence mechanisms, therefore, play a major role in protecting cellular and metabolic machinery in plants.

It is reported for most of aquatic plants that Cr concentration in the shoots is considerably lower than in the roots (Gil-Cardeza et al., 2014). Cr(VI) accumulation potential is about 10 or 100 times lower than that of Cr(III), probably owing to its high toxicity (Kováčik et al., 2014). Liu et al. (2008) performed experiments with *Amaranthus viridis* at different concentrations of Cr(VI) under hydroponic condition (Liu et al., 2008) and reported roots as the primary site for Cr accumulation. Corroborating these results are the findings of several authors (Vernay et al., 2008). Vernay et al. (2007) showed that *Lolium perenne* roots accumulated 10 times more Cr than its leaves when grown in the presence of 500 μM of Cr(VI). Further, Ghani (2011) found much lower accumulation of Cr in shoots as compared to that in roots signifying a low rate of translocation in *Brassica oleracea* grown on sand with 0.5 mM Cr(III). *Spinacia oleracea* L. cv. “Banarasi” also showed more accumulation of Cr in the roots than in the aerial parts when grown in medium supplemented with Cr(VI) (Sinha et al., 2007). *Monochoria vaginalis* accumulated the most Cr in its underground parts and *Eclipta prostrata* accumulated the most in its aboveground parts. Similar results were obtained in celery seedlings grown in the presence of Cr(III), where Cr was accumulated mainly in the roots (Scoccianti et al., 2006). In *Tradescantia pallida* plants, Cr(VI) accumulation was observed to be dose dependent with a maximum accumulation occurring in the *T. pallida* roots; a good amount was also translocated to the plant's shoots and leaves (Sinha et al., 2014). In another study performed by Lopez-Luna et al. (2009) the roots of wheat, oat, and sorghum were found to accumulate more Cr than the shoots of these crops.

Several studies have reported Cr complexation with organic compounds, thereby facilitating Cr availability to plants (Lopez-Luna et al., 2009). It has been found that exposure of *Triticum vulgare* to $CrCl_3$ supplemented with oxalic acid, malate or glycine resulted in more accumulation of Cr in roots than in plants exposed to Cr only (Cervantes et al., 2001). Furthermore, Kabata-Pendias (2010) reported 100 times more Cr accumulation in underground parts of several crops irrespective of Cr valance state with a reduced rate of translocation from roots to shoots. These reports signify that in the majority of accumulator plants, Cr is accumulated mainly in roots, followed by that in stems and leaves; however only small amounts of Cr are translocated to leaves.

Bioconcentration factors (BCF) and translocation factors (TF) are the two main parameters used to evaluate a plant's potential to remediate a particular metal. Ghafoori et al. (2013) found high amounts of Cr in the aboveground parts of *Dyera costulata* and, thus, suggested that this species has a high phytoremediation potential. *Pluchea indica* also showed a significant translocation rate and Cr concentration in leaves, thus showing good potential as a phytoremediator (Sampanpanish et al., 2006). Pandey (2012) reported a very good potential of *Azolla caroliniana* for phytoremediation of Cr with a BCF value 11 in the leaves along with uptake of multiple heavy metals. Mellem et al. (2012) reported *Amaranthus dubius* having a BCF value > 2 with a translocation factor of 1.1 at 25 mg/L of Cr(VI). Furthermore, Gardea-Torresdey et al. (2005) found that *Convolvulus arvensis* L. species in hydroponics condition (20 mg/L of Cr(VI)) accumulated around 3800 mg of Cr kg/dw tissue.

3. Chromium tolerance, detoxification and avoidance mechanisms

The response to Cr stress involves a network of shared pathways that are involved in detoxification of Cr and thereby help in Cr tolerance. In Cr accumulator plant species several mechanisms have been described to account for their resistance to chromate. The significant cellular pathways which are found to get upregulated in response to Cr stress are ROS signaling, increased antioxidant system, phytochelatins production, phytosequestration and differential compartmentation which facilitate bioaccumulation ability of the cells (Fig. 4).

3.1. Tolerance mechanisms

Cr tolerant plants can be categorised on the basis of their ability to survive with Cr concentrations that are in general inhibitory or lethal to plants. These plants have developed several tolerance and detoxification mechanisms which are discussed as follows.

3.1.1. Increase in antioxidant enzyme activity

Increase in antioxidant enzyme activity is considered a vital defence mechanism against Cr stress. Cr concentration at toxic level can produce ROS via the Fenton and Haber–Weiss reactions, and indirectly by inhibiting antioxidant enzymes (Costa et al., 2010). Elevated activity of antioxidant enzymes, such as catalase, peroxidases, superoxide dismutase, ascorbate peroxidase protects the plants from reactive oxygen species (ROS) generated under Cr stress by activating scavenging machinery of the plant system (Ganesh et al., 2008; Gill and Tuteja, 2010). These enzymes inhibit or slowdown the oxidative processes by interrupting the free radical chain reaction.

3.1.2. Alteration of cellular metabolism

It has been reported that plants undergo changes at the gene expression level which alters the metabolic pool in response to oxidative stress induced by Cr (Shao et al., 2008). Glutathione reductase (GR) plays a key role in Cr tolerance. It acts as a ROS scavenger, metal chelator and as a substrate for phychelatins biosynthesis. Increase in the synthesis of GR, which is one of the main enzymes of Ascorbate–Glutathione pathway, has been reported by many authors (Anjum et al., 2012; Foyer and Noctor., 2005). GR protein (which prevents the formation of HO• radical) has been characterized and used in transgenic plants for reducing ROS load in plants (Shanker et al., 2005). In *Miscanthus sinensis*, 36 proteins including oxidative stress-related proteins, metabolism-related proteins, molecular chaperone proteins and others were found to be overexpressed in response to 50–1000 μM Cr concentration (Sharmin et al., 2012).

3.2. Detoxification mechanisms

3.2.1. Biotransformation with reductants

A key mechanism for reducing the toxicity in plants is the reduction of Cr(VI) to Cr(III) by chemical or enzymatic processes. The chemical reduction of Cr(VI) is mediated by cysteine, glutathione, sulphite and thiosulfates present in the plant cell (Whitacre,

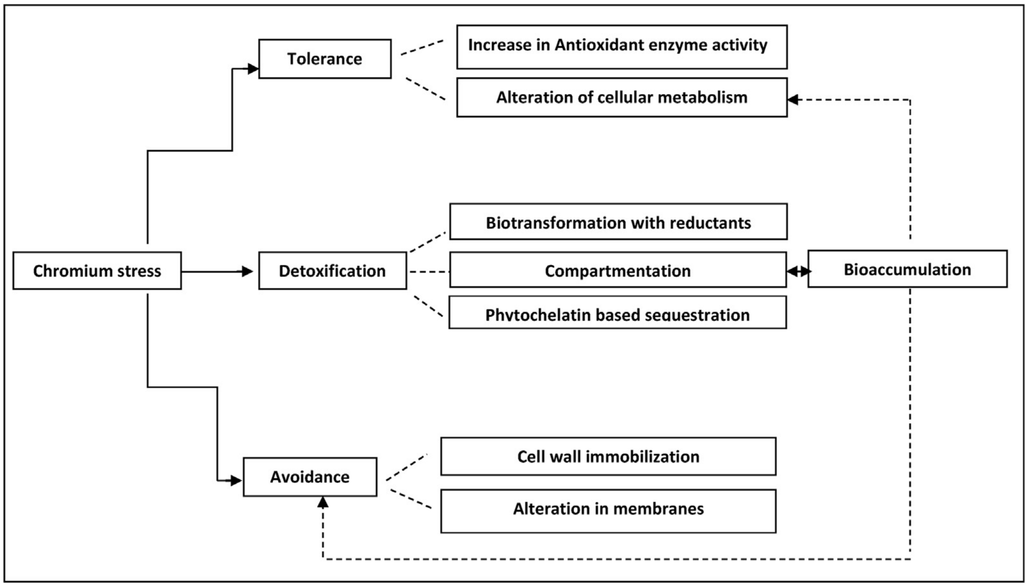

Fig. 4. Chromium tolerance and detoxification mechanisms (Arrows show interconnections of processes).

Table 2
Chromium: localization and toxicity effects based on ultra structural studies.

Plant species	Cr conc.	Main Cr accumulation sites	General effects	Toxic effects	Method used	References
Alternanthera philoxerides (Alligator-weed) Family: Amaranthaceae *Borreria scabiosoides* Family: Rubiaceae *Polygonum ferrugineum* (Knotweed) Family: Polygonaceae *Eichhornia Crassipes* (Water hyacinth) Family: Pontederiaceae	Cr(III) at 0.25, 50 mg/L	Cr accumulated principally in the roots of all the four macrophytes (8.6–30 mg/kg dw)	Cr was present mainly in the vacuoles of root parenchyma cells and cell walls of xylem and parenchyma	Alterations in the shape of the chloroplasts and nuclei in *A. philoxeroides* and *B. scabiosoides*	Inductively coupled plasma mass spectrometry (ICP-MS), Transmission Electron Microscopy (TEM) and Secondary Ion mass Spectrometry (SIMS)	Mangabeira et al. (2011)
Allium cepa (Onions) Family: Amaryllidaceae	Cr(III) at 5.2 mg/L	High amount of Cr was mainly accumulated in the cell walls and vacuoles of fourth or fifth cortical layer of root cell.	Large vacuolar precipitates surrounded by membranes inside vacuoles; increment of disintegrated organelles and high vacuolization in cytoplasm	NR	Transmission electron energy loss spectrometry	Liu and Kottke (2003)
Arabidopsis thaliana (Mouse-ear cress) Family: Brassicaceae	Cr(VI) at 5.2 mg/L	Primarily in the cell wall and secondarily in internal compartments, such as vacuoles and plastids	Severely damaged plastids, mitochondria, golgi bodies and vacuoles Endoplasmic reticulum, cytoplasm and membranes the least affected Nuclei and cell walls were intermediately affected	High ROS production. A concentration-dependent decrease of root growth and a time-dependent increase of dead cells, callose deposition, hydrogenase and peroxidase activity	Light Microscopy (LM) TEM	Eleftheriou et al. (2015)
Borreria scabiosoides Family: Rubiaceae	Cr(III) at 25, 50 mg/L	Higher number of Cr deposits in cortical parenchyma, particularly in vacuoles and cell walls, compared to stellar tissue	Cr preferentially accumulated in cell walls and in vacuoles of cortical roots cells. Plant roots exhibited higher Cr concentrations than the aerial plants parts	NR	HRI-SIMS (High-resolution imaging secondary ion mass spectrometry) ICP-MS	Mangabeira et al. (2006a,b)
Callitricha cophocarpa (Water-starwort) Family: Callitrichaceae	NR	Cr(III) accumulated solely in glands/hairs Cr(VI) accumulated mainly in vascular bundles	Cr uptake, transport and accumulation depended on the oxidative state of the element	NR	Micro X-ray fluorescence (μXRF) Electron probe X-ray microanalysis (EPXMA)	Augustynowicz et al. (2014)
Eichhornia crassipes (Water hyacinth) Family: Pontederiaceae	NR	Roots xylem cell walls	NR	NR	ICP-MS SIMS	Mangabeira et al. (2004)
Iris pseudacorus (Yellow flag) Family: Iridaceae	Cr(III) at 0.039 mg/L	Cr content was highest in cell walls of the root cortex and in the cytoplasm and intercellular spaces of the rhizome The Cr conc. in root tissues was in the order cortex > rhizodermis> Stele. Even Cr distribution in rhizome	Increased number of vacuoles and granules in rhizome cortex Cr co-occured with sulphur, indicating Cr sequestration by metal binding proteins	Ultrastructural alterations in the rhizodermis (cell wall disorganisation, thickening, plasmolysis, and electron-dense inclusions) Rhizome parenchyma showed (reduced cell size, cell wall detachment, vacuolation, and opaque granules)	TEM and Energy Dispersive X-Ray Analysis (EDX)	Caldelas et al. (2012)
Leersia hexandra Swartz (Southern cutgrass) Family: Poaceae	Cr(III) at 60 mg/L	Most of the accumulated Cr was isolated to the cell walls in roots and the vacuoles in leaves	83.2% of the root Cr was localized in the cell wall fraction, while 57.5% of leaf Cr was localized in the vacuole and cytoplasm fraction	No phototoxic symptoms No significant decrease in biomass All organelles appeared normal	Differential centrifugation, TEM and EDX	Liu et al. (2009)
Lycopersicum esculentum (Tomato) Family: Solanaceae	Cr(III) at 25, 50 mg/L	Cr accumulated mainly in the roots, and walls of xylem vessels	No Cr was detected in epidermis, palisade parenchyma and spongy parenchyma cells of the leaves Transport of Cr is restricted to the	NR	HRI-SIMS ICP-MS	Mangabeira et al. (2006a,b)

(*continued on next page*)

Table 2 (*continued*)

Plant species	Cr conc.	Main Cr accumulation sites	General effects	Toxic effects	Method used	References
			vascular system of roots, stems and leaves			
Pteris vittata (Chinese brake) Family: Pteridaceae	Cr(VI) at 300 mg/L (22 days)	Roots (upto 7686 mg/kg dry weight) Shoots (upto 2108 mg/kg dry weight)	Stunted growth with an increase in Cr concentration Dose-dependent inhibition	Water stress and collapse of internal structure (leaves and cellular breakdown of roots)	LM, Scanning Electron Microscopy (SEM) and TEM	de Oliveira et al. (2014) Sridhar et al. (2011)
Raphanus sativus L. (Radish) Family: Brassicaceae	Cr(III) at 0–7 mg/L	Cr accumulated in periplasmic zone (cell wall) of root cortical cells and not in the matrix	Presence of Cr deposit inclusions in root cortical cells	NR	TEM	Lahouti et al. (2008)
Taxithelium nepalense (Schwaegr.) (moss) Family: Sematophyllaceae	Cr(VI) at 0, 5.2 and 52 mg/L	NR	NR	Increase in H_2O_2 and O^{-}_2 radical. Distortion of the thylakoid, distortion of chloroplast membrane. Increase in the lipid peroxidation.	TEM	Choudhury and Panda (2005)
Transgenic cotton cultivars (J208, Z905)	Cr(VI) at 0.52, 2.6, 5.2 mg/L (7days)	Cr accumulated more in roots	Increase in number of nuclei and vacuoles Presence of Cr dense granules in dead parts of the cell (vacuoles/cell wall) Upregulation of malondialdehyde (MDA), hydrogen peroxide (H_2O_2), total soluble proteins, superoxide dismutase (SOD), peroxidase (POD), ascorbate peroxidase (APX), catalase (CAT), and glutathione reductase (GR) with elevated levels of Cr	Significant reduction in root/shoot length, number of secondary roots, and fresh root and dry biomass at 5.2 mg/L	Multiple biomarkers approach	Daud et al. (2014)
Ocimum basilicum (Basil) Family: Lamiaceae	Cr(III) at 4, 6, and 8 mg/L	Cr accumulated maximally in the roots	Dense granular metal deposits in the periplasmic zone along the cell walls in root cortex cells Cr was mainly deposited in the cytoplasm of root cortex cells and enlarged periplasmic zone along the innermost layer of the cell wall.	–	TEM, X-ray microanalysis	Bishehkolaei et al. (2011)

NR: Not Reported.

2010). Enzymatic reduction of Cr(VI) is carried out by a diverse range of rhizospheric bacteria for example, *Staphylococcusarlettae* spp. (Sagar et al., 2012), *Ochrobacterium intermedium* (Sultan and Hasnain, 2007), *Pseudomonas* sp. (Dogan et al., 2011), *Bacillus* spp. (Das et al., 2014), *Mesorhizobium* spp. (Wani et al., 2008) and *Cellulosimicrobium cellulans* $KUCr_3$ (Chatterjee et al., 2009). These have soluble and membrane-bound reductases such as flavin reductase, cytochromes and hydrogenases that can use chromate as the terminal electron acceptor in electron transport system (Soni et al., 2013). In addition to biotransformation these bacteria also releases plant growth promoting substances that further makes the process more suitable.

3.2.2. *Differential compartmentation*

To prevent toxicity upon Cr ions uptake, plant system has adopted different mechanisms to store the Cr ions in metabolically inactive organelles. Liu et al. (2009) reported that *Leersia hexandra* accumulated and preferentially stored Cr in the root cell walls and the leaf vacuoles. They reported Cr sequestration inside the cell wall as a primary site and secondarily in internal organelles, mainly inside the vacuoles and plastids. Lahouti et al. (2008) reported presence of Cr as inclusion bodies in the cell wall of root cortical cells in *Raphanus sativus*. Eleftheriou et al. (2015) reported membrane integrity, particularly of plasma membrane and tonoplast, as another cellular defence mechanism in *Arabidopsis thaliana*, to attenuate Cr toxicity.

Further compartmentalization in the cytoplasm or in the vacuole has been reported in the literature (Mangabeira et al., 2011; Volland et al., 2012; Leitenmaier and Küpper, 2013) (Table 2). This subcellular compartmentalization of Cr inside the vacuoles represents a key mechanism of Cr detoxification by hyperaccumulator plant cells (Zeng et al., 2011). In this mechanism, Cr ions entry into metabolically active compartments e.g. chloroplast, mitochondria, which are the most vital organelles for carrying out photosynthesis and respiration was prevented. Such a process helps in maintaining a low cytoplasmic Cr concentration, thereby acting as a possible detoxifying mechanism (Liu et al., 2009).

3.2.3. *Phytochelatin based sequestration*

Oliveira (2012) reported Cr tolerance in hyperaccumulator plants through chelation with suitable high-affinity ligands and biotransformation with reductants. Plants enrich their cytoplasmic pool with the increased production of phytochelatins, histidine, glutathione, ascorbic acid and other biochemically similar molecules which further help protect the plant metalloenzyme systems against Cr damage and combat the stress situation (Diwan et al., 2010; Yadav, 2010). Studies were conducted in four salix species to identify Cr-stress responsive genes involved in the regulation of Cr tolerance and accumulation (Quaggiotti et al., 2007). These strategies adopted by plants help in overcoming the Cr toxicity.

Hence, it could be concluded that plant strategies in response to Cr toxicity are genotype-specific. The underlying mechanism of plant's tolerance is a combination of processes that enables certain plants to survive Cr stress and adapt to maintain its growth and development without any toxicity symptoms.

3.3. *Avoidance mechanisms*

Avoidance mechanism helps the plants to restrict the uptake of Cr ions within root tissue itself and prevent it from entering into the active cellular pool and its further translocation.

3.3.1. *Cell wall immobilization and alterations in membrane*

The binding of Cr ions onto the cell walls is frequently reported in Cr accumulating aquatic and terrestrial plants spp. (Elangovan et al., 2008; Mangabeira et al., 2011). Cell wall provides abundant pectic sites, and secretes extra-cellular carbohydrates such as callose and mucilage that reduces Cr translocation into cytosol. Pectins are polysaccharides rich in carboxyl groups (−COOH) which enable the binding of Cr ions. Lignin, another polymer rich in hydroxyl (−OH) and phenolic groups, plays a crucial role in Cr binding onto secondary cell wall (Miretzky and Cirelli, 2010). Zeng et al. (2014) reported the up regulation of two proteins related to cell wall structure, NAD-dependent epimerase/dehydratase and reversibly glycosylated polypeptide in response to Cr stress in *Oryza sativa* L. Their enhancements along with callose accumulation under Cr stressed condition suggest that cell wall is an important barrier for rice plants to reduce its translocation as a resistance mechanism. Further, transport of Cr ions occurs using active efflux pumps present in membranes to apoplastic regions like cell wall where it binds with the cell wall components and precipitates.

4. Conclusions and future directions

Phytoremediation of Cr contaminated sites is a rapidly growing area of research. Knowledge of suitable indigenous plants, that can bioremediate Cr is particularly limited, and needs to be further explored. One of the key aspects is to develop transgenics to enhance their tolerance and accumulation rate at environmentally relevant concentrations. More research is needed to understand the interconversion of the Cr species within the plant system and its localization following uptake which would unravel the complete metabolic machinery and the gained knowledge can be utilized to develop the transgenics. By upregulation of genes responsible for Cr uptake, transport and sequestration, or antioxidant enzymes involved in the detoxification mechanism, the process can be made more commercially viable.

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