



Review

Chromium tolerance, bioaccumulation and localization in plants: An overview

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ABSTRACT

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 ($\text{Cr}(\text{OH})_3$) or sulphates ($\text{Cr}_2(\text{SO}_4)_3 \cdot 12(\text{H}_2\text{O})$) (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 ($\text{Cr}_2\text{O}_7^{2-}$) 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 $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_2\text{O}_4^{2-}$ 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, FADH₂, 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 ($\text{Fe}_2\text{Cr}_2\text{O}_4$) 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 $24,000 \times 10^3$ 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

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