Int. J. Environ. Sci. Technol. (2017) 14:2023–2038
DOI 10.1007/s13762-017-1348-5

REVIEW

Metallophilic fungi research: an alternative for its use in the bioremediation of hexavalent chromium

M. A. García-Hernández[1] · J. F. Villarreal-Chiu[1] · M. T. Garza-González[1]

Received: 24 June 2016 / Revised: 21 February 2017 / Accepted: 27 April 2017 / Published online: 10 May 2017

Abstract Contamination by hexavalent chromium has had a large impact on modern society and human health. This problem is a consequence of its great industrial applicability to several products and processes. Short-term exposure to hexavalent chromium can cause irritation, ulceration in skin and stomach and in addition to cancer, dermatitis, and damage to liver, renal circulation and nervous tissues, with even death being observed in response to long-term exposures. Many techniques have been used for the remediation of this pollutant, including physical and chemical approaches and, in more recent years, biological methods. Filamentous fungi isolated from contaminated sites exhibit a significant tolerance to heavy metal; hence, they are an important source of microbiota capable of eliminating hexavalent chromium from the environment. However, these microorganisms can do so in different ways, including biosorption, bioreduction, and bioaccumulation, among others. In this review, we explore several of the most documented mechanisms that have been described for fungi/hexavalent chromium interactions and their potential use in bioremediation.

Keywords Bioremediation · Hexavalent chromium · Interaction mechanisms · Metallophilic fungi

Editorial responsibility: Hari Pant.

✉ M. T. Garza-González
maria.garzagzz@uanl.edu.mx

[1] Laboratorio de Biotecnología I, Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Av. Universidad s/n, Cd. Universitaria, 66451 San Nicolás de los Garza, NL, Mexico

Introduction

Throughout time, contamination by hexavalent chromium (Cr(VI)) has had a large impact on modern society at different levels, such as social, economic, environmental and public health. This problem is a consequence of the great industrial applicability of Cr(VI) to several products and processes (Nriagu and Pacyna 1988). Primarily, Cr(VI) has been widely used as a pigment for the production of textile dyes (such as ammonium dichromate, potassium chromate and sodium chromate), paints, inks and plastics (chromium trioxide, zinc chromate, barium chromate, calcium chromate and strontium chromate); wood conservation (chromium trioxide); chrome-plating and steel industry (chromium trioxide, strontium chromate) and the tanning process (ammonium dichromate) (Zhang et al. 2011).

Nevertheless, chromium has been considered to be one of the worst anthropogenic polluters, historically. In 1987, groundwater wells from the company Pacific Gas and Electric Company (PG&E), which is located in Hinckley, MN, were severely contaminated with Cr(VI). This pollutant concentration reached up to 580 µg/L of Cr(VI), which is 10 times higher than the maximum permitted limit (50 µg/L) established by the US Environmental Protection Agency (U.S. EPA 2006). Further, it has been reported that short-term exposure to this heavy metal above the maximum permissible limit could provoke irritation and ulceration in the skin and stomach. Additionally, it can cause cancer, dermatitis, damage to the liver, renal circulation and nervous tissues, and even death from long-term exposure (Katz 1991; Kotaś and Stasicka 2000). Smith (2008) presented a chronological tracing of the events that were generated by the contamination of wells by Cr(VI), which damaged the Chinese population in the province of Liaoning. This researcher provided several reports about

the mortality by cancer in the exposed populations in the province. First, the drinking water acquired a yellowish colour as reported by the local population, which was indicative of ferrochrome production (1959–1964). In 1965, high concentrations of Cr(VI) were detected by the local authorities in the underground waters, which caused an increase in the stomach and pulmonary cancer mortality, as published by (Beaumont et al. 2008).

However, the tannery process represents the major cause of chromium release to the environment, which is mostly in the form of chromium sulphate. This form is especially difficult to treat due its composition, which is characterised by a strong colour and a high chemical oxygen demand (COD) and biochemical oxygen demand (BOD), in addition to the suspended solids and the dissolved chromium (Sharma and Malaviya 2016; Srivastava and Thakur 2006a).

In consequence, the environmental regulations have prioritised hexavalent chromium removal from wastewater and industrial sludge before their liberation to the environment (Fu and Wang 2011). The susceptibility of chromium to redox reactions, adsorption, precipitation or complex formation can influence its speciation and mobility (Hashim et al. 2011).

Many of the techniques that are used for the remediation of Cr(VI) include physical, chemical and biological methods, and the biological methods are a very important area of research and application (Gunatilake 2015).

Biological methods have been widely studied by Mexican investigators, especially for the use of native microorganisms exposed to heavy metals. In Mexico, several Cr(VI)-resistant fungi strains, such as *Peacilomyces* sp., (Cárdenas and Acosta 2010), *Trichoderma inhamatum* (Morales and Cristiani 2008) and *Candida maltosa* (Ramírez et al. 2004), have been isolated from tannery effluents (principally).

Fungi are a very versatile group of microorganisms, and they can grow under extreme conditions of pH, temperature, and a shortage of nutrients. However, the mechanisms developed by fungi to grow and survive under hostile environments of high metal concentrations make them a focal point to be applied in the elimination of these pollutants. Additionally, filamentous fungi have been poorly studied, but some reports have indicated that they have a high tolerance to Cr(VI) and can colonise sites that are contaminated with this pollutant (Anand et al. 2006).

The aim of this review is to provide an overview of recent advancements on metallophilic fungi research to the bioremediation of hexavalent chromium, which is mainly isolated from sites that are contaminated with this metal. Further, it is a summary of the interaction mechanisms between fungi and Cr(VI) and the level of Cr(VI) tolerance that has been reported for these microorganisms.

Chemistry and toxicity of Cr(VI)

Chromium can exist in different chemical forms with oxidation states of (−2) to (+6), although the oxidation states of (+3) and (+6) are the most distributed forms in nature (Sims et al. 1992; Kotaś and Stasicka 2000). Cr(III) occurs naturally in the environment and is considered to be a trace nutrient that is essential for the proper functioning of living organisms. Cr(VI) is generally produced by industrial processes and exerts toxic effects on biological systems. Additionally, they are many different charges and physicochemical properties as well as chemical and biochemical reactivities (Kotaś and Stasicka 2000; Owlad et al. 2009).

The relationship between the hexavalent and trivalent states of chromium is described by the following equation:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr[III] + 7H_2O$$

The difference in the electrical potential of Cr(VI) and Cr(III) reflects the strong oxidation potential of hexavalent chromium and the substantial energy (+1.33 eV) that is required to reduce hexavalent chromium to the form of trivalent chromium in an acidic solution (Dayan and Paine 2001). The hydrolysis of Cr(VI) produces neutral and anionic species, the chromate ion (CrO_4^{2-}), hydrogen chromate ion ($HCrO_4^{2-}$) and dichromate ion ($Cr_2O_7^{2-}$), predominantly (Mohan et al. 2005). The predominant Cr(VI) species are dependent on the pH, and at a pH of less than 1, it is present as chromic acid (H_2CrO_4), $HCrO_4^{2-}$ between 1 and 6, CrO_4^{2-} at a pH of above 6.0 (approximately), while $Cr_2O_7^{2-}$ forms when the concentration of chromium exceeds approximately 1 g/L at the same pH as $HCrO_4^{2-}$ (Mohan and Pittman 2006).

The Cr(VI) toxicity, mobility and reactivity depend of their speciation (Tessier et al. 1979); specifically, the compounds of Cr(VI) as sodium chromate (Na_2CrO_4) and potassium chromate (K_2CrO_4) are usually classified as highly soluble in water of 873 and 629 g/L at 30 °C, respectively (Rankin 2009). On the other hand, the reduced species of Cr(III) are in the form of stable hydroxides, oxides and sulphates, which are less soluble in water and less mobile, and they have been reported to be less toxic and even 1000 times less mutagenic than Cr(VI) (Corona and Saldana 2010).

The toxicity of Cr(VI) in eukaryotic and prokaryotic organisms is related to its easy diffusion through cell membranes (Arslan et al. 1987; Liu et al. 1995; Liu and Shi 2001), and in addition, the biotransformation of Cr(III) by biological fluids has the ability to donate electrons to Cr(VI) into the cell (O'Brien and Kortenkamp 1994; Stearns et al. 1995). This process generates free radicals that are associated with direct damage of DNA (Arslan et al. 1987; Liu et al. 1995; Liu and Shi 2001). In contrast,

the Cr(III) oxidation to Cr(VI) never occurs in biological systems, but the reduction of Cr(VI) into a less soluble form of Cr(III) is produced spontaneously in organisms (Dayan and Paine 2001). The Cr(III) form is less active in cells due to its poor ability to be absorbed (Alexander and Aaseth 1995), and it can also form complexes with nucleotides and amino acids, but its mutagenic potential remains unknown (Roundhill and Koch 2002).

At physiological pH, Cr(VI) exists in the form of the oxyanion (CrO_4^{2-}) with sulphates (SO_4^{2-}), which is an essential nutrient. Therefore, the cell responds to the transport system for sulphates, allowing Cr(VI) to cross the cell membranes of living organisms (Costa 2003). Biochemical, molecular and cellular damage caused by Cr(VI) (through the peroxidation of lipids, the oxidation of proteins and nucleic acid damage) forms reactive oxygen species (ROS) as a result of the oxidative stress that is generated by these chemical species (Ercal et al. 2001; Liu and Shi 2001).

Removal techniques for Cr(VI)

Several technologies have been used to decrease Cr(VI) concentrations up to the maximum permitted levels, to respect the environmental regulations for Cr(VI) (Cheung and Gu 2007) established by the US Environmental Protection Agency (EPA) and World Health Organization (WHO), which are 0.05 mg/L for drinking water (Costa 2003; Gordon et al. 2008). In general, such technologies have the following objectives: (1) the complete or substantial destruction/degradation of the contaminants, (2) the extraction of the contaminant for its subsequent treatment or elimination, (3) stabilisation of the contaminants into less mobile toxic chemical species, (4) the separation of non-contaminated materials and their recycling and (5) the contention of contaminated materials as a measure to restrict their exposure to the environment (Fu and Wang 2011).

The most important methods reported for Cr(VI) removal are the following: adsorption, reverse osmosis filtration, ionic exchange, electrolysis, chemical precipitation and biosorption (Owlad et al. 2009). Adsorption is a very versatile and efficient method that can eliminate heavy metal pollutants, with activated carbon the adsorbent that is most commonly used (Bailey et al. 1999; Babu and Gupta 2008). However, this material is expensive and can remove only a few milligrams of metallic ions per gram of activated carbon. It is also complicated to regenerate the material for reutilisation (Jusoh et al. 2007; Kang et al. 2007). Membrane filtration is a promising technique for heavy metal removal, due to its high efficiency, easy operation and space saving aspects. Ultrafiltration, reverse osmosis and nanofiltration are mainly used for the elimination of heavy metals in water (Barakat and Schmidt 2010). The Cr(VI) removal by these techniques is conducted by electrostatic interactions between the contaminant and the membrane surface or by the molecular size. Therefore, the porous size of the membranes is an important factor in preventing the dissolved metallic ions or the low molecular weight complexes from passing through the membrane (Landaburu-Aguirre et al. 2009). The ionic exchange process uses natural or synthetic resins that have the specific capacity to exchange their ions with the heavy metals that are present in the wastewater (Kang et al. 2007), but the last ones are commonly preferred due to their ability to eliminate almost all of the metallic ions (Alyüz and Veli 2009). Usually, this technique could be affected by the pH, temperature, initial concentration of the heavy metal and contact time between the substrate and the resin.

One of the most common treatments is to decrease the toxicity or mobility of hexavalent chromium with its transformation into less reactive species, using chemical agents (e.g., iron(II) chloride, iron sulphate and sodium sulphite) to reduce it to trivalent chromium, followed by its precipitation in the form of hydroxides (Huisman et al. 2006). The efficiency of this technique is overshadowed by the generation of toxic secondary waste, which makes it difficult to achieve its final disposal (Barrera-Díaz et al. 2012). Biological systems have been used as an alternative to chemical agents because of their capacity to biotransform or remove the heavy metals. Bioremediation is an emerging technique that uses living organisms such as bacteria, fungi, yeasts and plants for the removal of heavy metals from contaminated sites (Gadd 2000). Some in situ and ex situ examples for heavy metal bioremediations are land farming, compost, bioreactors, bioventilation by oxygen (biofilters), bioaugmentation of microbial cultures and biostimulation-supplying nutrients. Some of the other processes include bioaccumulation, biolixiviation and phytoremediation.

At the same time, the technologies of phytoremediation are potentially useful for the remediation of sites that are contaminated with metals, including phytoextraction, phytostabilisation and rhizofiltration (Vangronsveld et al. 1994).

Metallophilic fungi and their tolerance to Cr(VI)

In natural contaminated environments, microorganisms respond to Cr(VI) toxicity per concentration and the bioavailability of the metal. Each fungi mechanism depends on the fungi genetics, the type of metal and environmental factors (Hassen et al. 1998). Juvera-Espinosa et al. (2006) collected different samples from Cr(VI) contaminated sites and obtained fungal isolates that could

reduce Cr(VI) at high concentrations. Some of the samples contaminated with Cr(VI) included (1) soils (70–12,400) mg/kg; (2) mining effluents (1.7 μg/L); (3) wastewater from chrome-plating (127–3050) mg/L; (4) wastewater from textile industries (0.03–60) μg/L; and (5) tannery wastewater (2.4–16) mg/L, but only three fungi strains that were classified as LMB1, LMB2 and LMB3 could reduce Cr(VI) to Cr(III). The strains LMB1, LMB2 and LMB3 were isolated from Cr(VI) contaminated soils (251 mg/kg) chrome-plating effluents (1300 mg/L) and tannery industries (2.4 mg/L), respectively. However, only the LMB2 strain could grow and reduce the initial Cr(VI) concentration at 100% and was identified as the yeast *Candida* sp.

In addition, other autochthonous metal-resistant fungi have been isolated from sites contaminated with Cr(VI), to be applied to bioremediation; *Fusarium chlamydosporium* (Sharma and Malaviya 2014) was isolated from tannery wastewater that contained 9.86 and 12.26 mg/L of Cr(VI) and total chromium, respectively; *Aspergillus* and *Rhizopus* sp. (Ahmad et al. 2005) were obtained from crop fields watered with wastewater and industrial effluents and contained 92.5 up to 116.5 mg/g of total chromium; *Aspergillus flavus*, *Humicola grisea*, *Fusarium* sp., *Nannizzia* sp., *Helminthosporium* sp., *Curvularia* sp., *Aspergillus niger*, *Aspergillus versicolor*, and *Scopulariopsis* sp. were isolated by Iram et al. (2012) from soil watered by industrial effluents with a 76.9 mg/kg of total chromium concentration; *Penicillium* sp. was the main fungi isolated from water and sediment of industrial and tannery effluent, also municipal industrial wastewater, and contained (85.6, 369, 36.1) μg/kg in sediment and (1.06, 2.1, 0.14) mg/L in water, respectively. Other fungi strains, such as *Fusarium* sp., *Alternaria alternate* and *Geotrichum candidum*, were isolated from the same sites, but were found only in sediment (Ezzouhri et al. 2009).

The characteristic of fungi survival in Cr(VI) depends mostly on their structural and biochemical properties as well as their genetic and physiological adaptations. Such microorganisms are an extremely versatile group that can adapt and grow in extreme conditions of pH, temperature, nutrient availability and high concentrations of metals (Anand et al. 2006). Factors such as the interaction between metals and the microbial cell wall, periplasm, plasmatic membrane, cytoplasm are key for fungi adaptation in different environments (Cervantes et al. 2006). The tolerance of fungi to Cr(V) toxicity can be translated as their ability to survive in high Cr(VI) concentrations through mechanisms that they have developed in direct response to metallic species (Zafar et al. 2007). Several authors have reported filamentous fungi that exhibit a significant Cr(VI)-tolerance, especially those that live in contaminated sites (Table 1). Recently, Sharma and Malaviya (2016) reported 26 autochthonous fungi isolated from soil and sludge contaminated with Cr(VI) derived from tannery industrial wastewaters, and they are identified with the genus of *Cladosporium*, *Penicillium*, *Paecilomyces* and *Fusarium*. The maximum level of tolerance to Cr(VI) for fungi has been reported as the minimum inhibitory concentration (MIC), in liquid media and Petri plates. Fungi strains were cultivated in modified Lee's minimal medium (0.25% KH_2PO_4, 0.20% $MgSO_4$, 0.50% $(NH_4)_2SO_4$ and 0.50% NaCl and 0.25% glucose), supplied with increasing concentrations of Cr(VI): 100, 200, 300, 400, 500, 600 and 700 mg/L. The Petri plates were inoculated with 8 mm agar plugs from young fungal colonies, pre-grown on PDA and incubated at 28 °C for seven days. In the first case, the fungi growth was utilised as a viability control, and changes in the mycelium length were measured. The results showed the maximum tolerance presented by *Cladosporium* and *Fusarium* was up to 300 mg/L, and better results were presented from *Penicillium* and *Paecilomyces*, with a maximum tolerance of up to 500 mg/L for Cr(VI).

Arshad and Aishatul (2015) evaluated the Cr(VI)-tolerance of *A. niger* isolated from crop fields of Uttar Pradesh (Northern India). They defined MIC as the minimal concentration of a substance that inhibits the visible growth of a microorganism, and their results were determined by the agar diffusion method. The experiments were conducted by the addition of different Cr(VI) concentrations (25 up to 500) μg/mL on Sabouraud dextrose agar for 5 days of contact time at 25 °C. The maximum tolerance obtained for *A. niger* was 350–400 μg/mL of Cr(VI). The same technique was used by Jayanthi et al. (2014) to determinate the Cr(VI)-tolerance by *Penicillium* sp., and *A. niger* at different concentrations of hexavalent chromium (100–1500) μg/mL. The tolerance reported for these fungi corresponded to 800 and 512 μg/mL, respectively.

In general, *Aspergillus*, *Fusarium* and *Penicillium* are the most isolated fungi from sites contaminated with chromium. *Aspergillus* has been reported to have a tolerance at 200 μg/mL (Ahmad et al. 2005), 600 μg/mL (Bennett et al. 2013), 650 μg/mL (Ezzouhri et al. 2009), with 5000 μg/mL for total chromium (Ahmad et al. 2006). Others species, such as *A. flavus*, have had a Cr(VI)-tolerance of 600 μg/mL (Bennett et al. 2013), with 800 μg/mL for total chromium (Iram et al. 2012); *A. niger* had 600 μg/mL (Bennett el al. 2013) and 1000 μg/mL for total chromium (Iram et al. 2012); and *A. versicolor* reported to have a tolerance of 1000 μg/mL for Cr(VI) and total chromium (Das et al. 2008; Iram et al. 2012).

For the species with the *Fusarium* genus, the tolerance of Cr(VI) has been reported to be 1000, 1300, to 5000 μg/mL (Iram et al. 2012; Ezzouhri et al. 2009; Zafar et al. 2007), e.g., *F. solani* has a tolerance that is reported to be 1000 μg/mL (Sen and Dastidar 2011). On the other hand,

Table 1 Chromium tolerance reported by fungi isolated from contaminated sites

Fungi	Isolation site	Metal	Tolerance μg/mL	Culture condition	References
Cladosporium perangustum	Soil and sludge from tannery industries (India)	Cr^{6+}	>300	Solid and liquid	(Sharma and Malaviya 2016)
Penicillium commune			>500		
Paecilomyces lilacinus					
Fusarium equiseti			>300		
Aspergillus niger	Crop fields (India)	Cr^{6+}	350–400	Solid	(Arshad and Aishatul 2015)
Fusarium clamydosporium	Tannery industries (India)	Cr^{6+}	500	Solid	(Sharma and Malaviya 2014)
Penicillium chrysogenum	Tannery industries (India)	Cr^{6+}	800	Solid and liquid	(Jayanthi et al. 2014)
Aspergillus niger			512		
Aspergillus sp.	Soil and water (Bulacan-Filipinas)	Cr^{6+}	600	Liquid	(Bennett et al. 2013)
Aspergillus niger			600		
Aspergillus flavus			600		
Aspergillus flavus	Crop fields (Faisalabad)	Cr	800	Solid	(Iram et al. 2012)
Helminthosporium sp.			800		
Aspergillus niger			1000		
Aspergillus versicolor			1000		
Scopulariopsis sp.			1000		
Curvularia sp.			1000		
Humicola grisea sp.			400		
Nannizzia sp.			600		
Fusarium sp.			1000		
Fusarium solani	Tannery industries (India)	Cr^{6+}	1000	Liquid	(Sen and Dastidar 2011)
Penicillium sp.	Water and sediment (Moghogha river)	Cr^{6+}	1040	Solid	(Ezzouhri et al. 2009)
Aspergillus sp.			650		
Fusarium sp.			1300		
Aspergillus versicolor	Tannery effluents (India)	Cr^{6+}	1000	Solid	(Das et al. 2008)
Alternaria sp.	Crop fields (India)	Cr	900	Solid	(Zafar et al. 2007)
Aspergillus sp.			5000		
Fusarium sp.			5000		
Monilia sp.			300		
Penicillium sp.			7000		
Rhizopus sp.			7000		
Trichoderma sp.			6000		
Geotrichum sp.			600		
Aspergillus sp.	Crop fields (Aligarh)	Cr	200	Solid	(Ahmad et al. 2005)
Rhizopus sp.			400		

Penicillium species has been reported to have a tolerance of approximately 1040–7000 mg/mL of total chromium (Zafar et al. 2007). At a lower proportion, fungi such as the *Rhizopus* genus have been reported to have a tolerance to total chromium of 400 μg/mL (Ahmad et al. 2006) and up to 7000 μg/mL (Zafar et al. 2007).

In general, the values of MIC increase considerably when they are reported as the total chromium tolerance, because the percentage of Cr(III) and Cr(VI) is not specified and can reach a tolerance of 200–7000 mg/L, higher than has been reported for Cr(VI).

Fungi/Cr(VI) interaction mechanisms

Normally, fungi interact with metals as part of their environment, or in the case of Cr(VI), by introducing it due to human activities. Fungi have a wide variety of properties that can influence their interactions with metals, due to

their requirement for trace metals and associated nutrients for their growth and metabolism, and these interactions are fundamental. Nevertheless, to survive high concentrations of Cr(VI) and other toxic metallic elements, they probably could express a variety of intrinsic properties and induce resistance to such hazardous effects (Gadd 2007).

Fungi cells can interact with chromium at different levels, from the cell wall, periplasm and plasmatic membrane to the cytoplasm and cellular organelles (Corona and Saldana 2010). Many mechanisms of interaction of fungi and Cr(VI) have been characterised as mechanisms of extracellular (chelation and linkage to the cell wall) or intracellular detoxification (linked to non-proteic thiols and transport to intracellular compartments). The extracellular mechanisms are mainly involved in preventing the entry of Cr(VI) into the cell, while the intracellular systems aim at reducing chromate in the cytosol (Bellion et al. 2006). Such mechanisms include (1) chemical transformation (intracellular or extracellular reduction) by reductive organic biomolecules (indirect mechanism); (2) biosorption (anionic coupled to the reduction and anionic/cationic); (3) transport and intracellular bioaccumulation (chelation, precipitation, compartmentalisation) (Ross 1975; Gadd 1993b, 2000; Saha and Orvig 2010).

Fungi are well known for their ability to biosorb and bioaccumulate Cr(VI) (Pillichshammer et al. 1995; Dursun et al. 2003b; Park et al. 2005). Several fungi have been studied to be applied to Cr(VI) bioremediation, such as *Aspergillus* (Dursun et al. 2003a; Park et al. 2005; Prasenjit and Sumathi 2005; Jayanthi et al. 2014), *Rhizopus* (Bai and Abraham 2001; Ahmad et al. 2005; Zafar et al. 2007), *Penicillium* (Ahmad et al. 2006; Jayanthi et al. 2014; Abigail et al. 2015), *Trichoderma* (Morales and Cristiani 2006; Morales and Cristiani 2008), *Paecilomyces* (Cárdenas and Acosta 2010; Sharma and Adholeya 2011), *Mucor* (Yan and Viraraghavan 2003; Tewari et al. 2005), and *Fusarium* (Zafar et al. 2007; Sen and Dastidar 2011). In addition, these microorganisms have also been reported by their ability to reduce Cr(VI) to Cr(III) (Gouda 2000; Pal and Paul 2004; Acevedo et al. 2006; Morales and Cristiani 2008).

Extracellular mechanisms

Through extracellular mechanisms, fungi can prevent Cr(VI) input to the cell, and these include i) uptake of reduced Cr(VI) or increasing efflux of metal; ii) immobilisation of Cr(VI) by adsorption on the cell wall, or extracellular precipitation by neoformed secondary minerals; and iii) extracellular sequestration of Cr(VI) by exopolysaccharides and other extracellular metabolites (Gadd 1993a; Macreadie et al. 1994; Blaudez et al. 2000; Perotto et al. 2002; Baldrian 2003).

In particular, the fungi cell wall excretes organic molecules to chelate Cr(VI) (Landeweert et al. 2001; van Hees et al. 2001). The extracellular and cytosolic chelation of Cr(VI) by small molecular weight metabolites, such as peptides and proteins, are an important and crucial mechanism in almost all detoxification processes in fungi; these mechanisms cannot be overestimated (Tamás et al. 2006; González et al. 2009; Wysocki and Tamás 2010; Bánfalvi 2011). For example, glutathione secretion is a very important element in yeast homeostasis under different environmental conditions (Perrone et al. 2005). In addition to the presence of pigments in their cell wall, e.g., melanin, or the production of extracellular polymeric materials (EPS) during adhesion, the formation of biofilms provides them with extra protection (Gadd 1993a; Gorbushina 2007). Additional modifications, such as the incorporation of melanin, can increase even more the capacity of the cell wall to attract Cr(VI) species (Fogarty and Tobin 1996); that process is called biosorption, and it does not depend on the metabolic activity of the fungi (Gadd 1993b).

Biosorption

The ability of fungi to act as biosorbents has been widely evaluated, and they have demonstrated the potential to incorporate Cr(VI) (Kapoor and Viraraghavan 1995). The sequestration of Cr(VI) by different components of the cell wall mainly relates to polysaccharides (galactosamine, chitin and glycan), and proteins, lipids and melanin have minor contribution. Therefore, the fungi cell wall is considered to be a mosaic of functional groups that includes carboxyl (–COOH), phosphate (PO_4^{3-}), amine ($–NH_2$), thiol (–SH) and hydroxide (–OH) groups (Bellion et al. 2006), which act as interaction sites between Cr(VI) and fungi, where ionic coordination and/or ion exchange complexes can be formed with Cr(VI) anion species.

Ramrakhiani et al. (2011) conducted cell wall surface characterisation of *Termitomyces clypeatus* to determine the biosorption mechanism by the inactive fungal biomass. The surface chemistry was characterised by FTIR and SEM-EDX analyses, and potentiometric titration to determine the pH of the zero-point charge was realised. The characteristic functional groups belong to acidic (carboxyl, imidazole, phosphate) and alkaline (amino, sulphhydryl, hydroxyl) compounds, mainly in the following order: carboxyl > phosphates > lipids > sulphhydryl > amines.

Live or dead fungal biomass can be utilised in the biosorption process for Cr(VI) removal, but it is important to consider the advantages and disadvantages that each one confers. In the first case, the use of dead biomass does not require the preparation of culture media, and they can be in contact with high concentrations of Cr(VI). In addition, Cr(VI) that is adsorbed can be easily desorbed from the

biomass, allowing its recovery for reuse once it has been regenerated (Gupta et al. 2001; Bai and Abraham 2003). For wastewater treatment, dead biomass is preferable because it is not affected by toxic chemicals and waste, but an important limitation of this technique is that biochemical reactions from the fungal metabolism can be considered to be null and do not participate in the process (Prigione et al. 2009). Different factors, such as pH, initial concentration of Cr(VI), contact time and biosorbent dose, could influence the biosorption process by the dead biomass (Religa et al. 2009; Wionczyk et al. 2011).

In the second case, when fungal biomass that is alive is used in the biosorption process, Cr(VI) removal could be conducted during its growth, allowing the omission of steps such as growth, drying and storage, first. The metabolic activity can also influence the removal process of the Cr(VI) due to changes in the pH, potential reduction (Eh), organic and inorganic nutrients and metabolites. However, the environmental Cr(VI) concentration is an important factor for this process because if it is overly high, it could be toxic for the fungus, which would cause inhibition of the functional metabolism when the growth stops. This problem can be avoided by using microorganisms that have a high tolerance to Cr(VI), as has previously been reported (Holda et al. 2011; Holda and Mlynarczykowska 2016).

The most important factors for the biosorption process are:

(a) pH

The elimination of Cr(VI) in aqueous solution that used live and dead biomass was evaluated by Holda and Mlynarczykowska (2016), which used *A. niger* biomass. The most important factor for the Cr(VI) removal was the pH, and the complete removal of Cr(VI) with dead biomass was achieved only at low pH values (1 and 2) at less contact time. However, the elimination process with living biomass was very intense during the first 5 days after the micelle formation, at pH 4 (Holda and Mlynarczykowska 2016). Several species of the genus *Aspergillus* have been studied as biosorbents for Cr(VI) removal. Sivakumar (2016) evaluated the pH effect on Cr(VI) biosorption by diverse *Aspergillus* species (*niger*, *flavus*, *fumigatus*, *nidulans*, *heteromorphus* and *viridinutans*), and they found pH 3 to have the highest percentage of biosorption. The removal percentages for each one were the following: 92.5, 86.7, 82.4, 81.6, 76.3 and 67.7, respectively, with 290 mg/L of initial Cr(VI) concentration.

These results are similar to Mungasavalli et al. (2007), Pang et al. (2011), Kavita and Keharia (2012), Abubacker and Kirthiga (2013) and Sathvika et al. (2015), where the optimal pH for the Cr(VI) biosorption was between 1 and 3. The biosorption process depends largely on the pH of the aqueous solution, because the surface charge of the biomass cell wall is modified by the pH variations. At an acidic pH, the net surface charge of the cell is mainly positive, and the chromate ions bind them easily. As the pH values increase, the net surface charge of the biomass changes to a negative form, decreasing its affinity to the chromate ions (Park et al. 2005).

(b) Biomass dose

The influence of the biomass dose represents the biosorbent/solute ratio, and it is an important factor in Cr(VI) biosorption. Shroff and Vaidya (2013) employed dead biomass of *Rhizopus arrhizus* to study its ability for Cr(VI) removal at different biomass doses (0.5–3.0 g/L). The Cr(VI) removal was dependent on the biosorbent dose, and the percentage of elimination presented was 35.9 and 79.2, respectively, both with an initial concentration of 50 mg/L.

Mungasavalli et al. (2007) worked with live, dead and pre-treated (acid, alkali, formaldehyde and detergent) *A. flavus* biomass to determine the Cr(VI) biosorption potential. The biosorption rate using dead biomass increased from 35 to 70% for 0.5 and 3.5 biomass doses (mg/L), respectively. The work presented by Tewari et al. (2005) using the fungal biomass of *Mucor hielamis* showed a similar result at 100 mg/L of concentration of Cr(VI). A higher biomass dose of 2–10 g/L increased the Cr(VI) removal to 54.6–81 mg/L, respectively. However, a biomass dose higher than 10 g/L did not show significant changes in the results.

Other studies have reported the effect of the biomass dose on the Cr(VI) biosorption process, with diverse fungal biomass, such as *A. niger* (Ren et al. 2015), *A. flavus* (Abubacker and Kirthiga 2013), *Aspergillus sojoae* and *Aspergillus oryzae* (Reya Isaac et al. 2012), *Mucor racemosus* (Liu et al. 2007) and *Pythium* sp. (Kavita et al. 2011), which showed similar behaviours. The availability of more binding sites when the biomass dose increases represents a larger adsorption area. That factor increases the efficiency of the process towards reaching an equilibrium (Kadirvelu and Cloirec 2000).

(c) Initial Cr(VI) concentration

The availability of Cr(VI) ions increased the biomass capacity when removing this contaminant, and thus, the initial Cr(VI) concentration influences the rate of biosorption directly. Khambhaty et al. (2009) observed that increasing the initial concentration of Cr(VI) from 10 to 400 mg/L of Cr(VI), the ability of *A. niger* biosorption increased from 2.5 to 54.16 mg/g. In this case, they established that a higher concentration of metallic ions provides a higher propulsion force towards overcoming the resistance of mass transfer between the solid and aqueous phases. This circumstance resulted in an increase in the

probability of collision between the Cr(VI) ions and the biosorbent. Nevertheless, the biosorption percentage decreased when the initial Cr(VI) concentration increased from 10 to 400 g/L. This finding could be attributed to the competence between the chromate ions and the lack of free union sites available in the biomass, which could be attributed to the competence between the chromate ions and the lack of free union sites available in the biomass. Similar results were obtained using other fungi, such as *Fusarium solani*, *Pythium* sp. and *Penicillium purpurogenum*, as reported by (Say et al. 2004; Kavita et al. 2011; Sen and Dastidar 2011).

(d) Contact time

Liu et al. (2007) observed three phases in the Cr(VI) biosorption process by the *M. racemosus* biomass. The first stage was the fastest Cr(VI) removal stage, which represented almost a 50% removal approximately 100 mg/L of the initial Cr(VI) concentration in solution. Subsequently, the second stage is strongly represented by Cr(VI) reduction, because of the Cr(III) appearance in solution (1 h and 8 h), which reached equilibrium at 8 h, approximately. Last, all of the Cr(VI) ions were eliminated from the solution after 8 up to 24 h of contact. On the other hand, the critical contact time pattern in the Cr(VI) biosorption process was studied by Prakasham et al. (1999), who determined the maximum biosorption achieved by free the fungal biomass of *R. arrhizus*. In a contact time of 2 h, the Cr(VI) removal reached 50%, which increased it 10 or 15% at a longer period of contact time. They also demonstrated that the Cr(VI) biosorption by *R. arrhizus* was conducted in two phases. The first, faster phase reached nearly 50% removal in 2 h, which was followed by the slow phase, which continued until the end of the experiment. The initial phase is attributed to the surface biosorption by ion exchange action with the available functional groups of the cell wall, and the second phase is attributed to the depletion of linked sites, which decreases the removal rate.

(e) Temperature

The process of Cr(VI) biosorption conducted by *Trichoderma harzianum* mycelium (living biomass) was studied by Soumik (2013), who showed the significant role that the temperature plays in this process. The increase in the temperature from 20 to 30 °C allowed a 90% removal of the Cr(VI) ions by fungi cells. However, Cr(VI) removal decreased 20% to greater temperatures (>35 °C), because the growth, enzymatic activity and integrity of the cell wall at these temperatures could affect the living cells and the biosorption process. The temperature has a strong influence on the configuration and stability of the fungi cell wall and, therefore, in the biosorption process directly.

Tahir et al. (2014) suggested that high temperatures (>30 °C) can increase the number of active sites (Meena et al. 2005) but, in the same way, could deactivate or destroy it. They observed the rate of Cr(VI) removal by the *Gliocladium viride* biomass, and the highest removal percentage (92.84%) was obtained at 30 °C, but at higher temperatures, the biosorption rate decreased, as in previous research. In general, high temperatures are not used in the biosorption process, because the operating cost increases (Roane and Pepper 2009). In addition, the exothermic nature of some of the biosorption processes causes a diminution of the biosorption capacity in some microorganisms (Tahir et al. 2014).

The mechanisms of Cr(VI) biosorption have been described in four models: *(1) anionic biosorption*, *(2) biosorption coupled to reduction*, *(3) cationic and anionic biosorption and (4) anionic biosorption and reduction.*

1. Anionic biosorption

The anionic species of Cr(VI), such as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$), can be linked to the fungi surface through electrostatic interactions. Functional groups such as amines, which are present in chitin and chitosan, principally have positive charges. Therefore, this mechanism is strongly influenced by the pH, due to the protonation of these functional groups at low values of pH to attract anionic species of Cr(VI) (Saha and Orvig 2010).

2. Biosorption coupled to reduction

Park et al. (2005) proposed that Cr(VI) adsorption by an *A. niger* biomass occurs through two mechanisms, which are based on the reduction of Cr(VI) to Cr(III). The first mechanism (direct) occurs when Cr(VI) comes into contact with electron donors of functional groups that are present in the biomass surface at an acidic pH. Then, the Cr(III) that results from reduction is subsequently adsorbed on the biomass surface. On the other hand, the second proposed mechanism (indirect) occurs in three stages: (1) the anionic species of Cr(VI) binds to protonated functional groups of the cell surface; (2) adsorbed Cr(VI) interacts with adjacent functional groups and becomes reduced to Cr(III); and (3) Cr(III) is released to the supernatant by electrostatic repulsion. A study conducted by Das et al. (2008) demonstrated through an analysis by photoelectron X-rays (XPS) that when binding, Cr(VI) binds to the cell wall of *Aspergillus* by its components, causing a reduction of the metallic ions and metal layers accumulated on the wall.

3. Cationic and anionic biosorption

As mentioned before, part of Cr(VI) can be reduced to Cr(III), and according to the functional nature of the biomass cell wall, hexavalent (anionic) and trivalent (cationic) chromium can be adsorbed simultaneously by the biomass.

4. Anionic biosorption and reduction

According to this mechanism and as explained by Park et al. (2005), a part of Cr(VI) is reduced to Cr(III) by an interaction with the biomass, and mainly, the Cr(VI) is adsorbed while the Cr(III) remains in solution.

Intracellular mechanisms

The fungal strains required detect and regulate the intracellular levels of chromium through homeostasis systems that maintain a balance between the incorporation, expulsion and sequestration of Cr(VI) (Corona and Saldana 2010). In the intracellular mechanism, transport proteins of Cr(VI) could be involved in the tolerance or expulsion of toxic Cr(VI) from the cytosol, or they could allow Cr(VI) sequestration in the vacuolar compartment (Bellion et al. 2006). Thiol compounds, including glutathione (GSH), are often considered to be antioxidant agents (Halliwell and Gutteridge 2007); however, intracellular chelates could generate harmful free radicals for biological membranes (Pócsi et al. 2004). Pesti et al. (2002) conducted a study of Cr(VI) toxicity at a molecular level, and they characterised free radicals and glutathione from the metabolism of a sensitive mutant, *Schizosaccharomyces pombe*. They suggested that the bioaccumulation and reduction of the Cr(VI) anions were tightly coupled within the cells by the Cr(VI) gradient across the plasma membrane. The uptake of Cr(VI) is facilitated via non-specific sulphate transporters and was maintained by the fast enzymatic and non-enzymatic reduction of the entering CrO_4^{2-}. Among the non-reducing enzymes is glutathione, which plays an important role in the intracellular reduction of Cr(VI). Metallothionein is another important intracellular chelator for Cr(VI) control (Clemens 2001). These peptides are rich in cysteine and have a low molecular weight, which allows the cell to maintain the homeostasis of intracellular ions and contribute to the Cr(VI) detoxification of the cell (Zhu et al. 2009). This metallic homeostasis and detoxification process has been studied in *Pisolithus albus*, which was submitted to metallothionein. This molecule activity increased when more metal concentration was added (Reddy et al. 2015).

Cr(VI) biotransformation (reduction)

The reduction of Cr(VI) by fungi has been considered to be an additional mechanism of these microorganisms in reacting to Cr(VI) toxicity, because inside the cell, the Cr(VI) can be reduced to Cr(III) by reducing systems (Corona and Saldana 2010).

The Cr(VI) is actively transported through the biological membrane of prokaryotic and eukaryotic microorganisms (Alluri et al. 2007), and once inside the cell, Cr(VI) is reduced to Cr(III), most likely through the formation of instable intermediary forms of Cr(V) and Cr(IV) by non-enzymatic (indirect) or enzymatic reactions (direct) (Ksheminska et al. 2006); the latter is still uncertain for eukaryotic microorganisms (Gadd 2010).

Different studies conducted by bioaccumulators microorganisms (Dönmez and Aksu 2002; Baldrian 2003; Dursun et al. 2003a; Zouboulis et al. 2004; Dönmez and Koçberber 2005) have demonstrated that Cr(VI) removal includes the following phases: (1) the union of Cr(VI) to the cell surface, (2) the transport of Cr(VI) inside the cell, and (3) Cr(VI) reduction to Cr(III). Two reduction steps have been proposed for this last stage (Suzuki et al. 1992): first, Cr(VI) accepts an NADH molecule, generating Cr(V) as an intermediary (1); then, Cr(V) accepts two electrons and forms Cr(III) (2). By this process, it has been established that NADH, NADPH and electrons from the endogenous reserve are active participants in the Cr(VI) reduction process (Appenroth et al. 2000).

$$Cr(VI) + e^- \rightarrow Cr(V) \quad (1)$$

$$Cr(V) + 2e^- \rightarrow Cr(III) \quad (2)$$

Direct reduction

For eukaryotic cells, knowledge regarding enzymes for chromate reduction remains very limited (Ksheminska et al. 2006). In bacteria, the existence of ChrA proteins as part of a chromate transporter (CHR) superfamily has been informed and is related to the transport of sulphate and chromate (Nies et al. 1998). Currently, 135 homologous sequences of CHR proteins have been reported, including some of eukaryotic origin (Cervantes et al. 2001).

In addition, the enzymatic reduction of Cr(VI) by reductases in bacteria, such as membrane enzymes from *Pseudomonas putida*, oxidoreductases NADH: flavin from *Enterobacter cloacae*, nitroreductases from *Vibrio harveyi*, YieF reductase from *Escherichia coli* (Cervantes et al. 2006), suggests the possibility of enzymes that exist with the ability to reduce Cr(VI) in filamentous fungi.

Gu et al. (2014) studied Cr(VI) reduction via enzymes by intracellular components of *A. niger*. They confirmed that Cr(VI) reduction depends mainly on the cell-free extract, similar to those found in bacteria, where the activity of chromate reductase is related to the intracellular fraction (Myers and Myers 1993; Ravindranath et al. 2011). The cell-free extract was submitted at 95 °C and tested for chromate reduction, but no changes were observed, which demonstrates that one type of enzyme should be conducting the reduction process. Additional studies conducted on *C. maltosa* (Ramírez et al. 2004), *Pichia jadinii* (Ksheminska et al. 2003) and *Aspergillus tubingensis* Ed8

(Coreno et al. 2009) have demonstrated the high specific activity of chromate reductase in crude extract, but not in the membrane fraction.

Indirect reduction

Microbial cells can reduce Cr(VI) by non-enzymatic intracellular reduction agents. Once the metallic ion has entered the cell, it can be reduced to Cr(V), which is highly cytotoxic by its interaction with ascorbic acid, glutathione cysteine, hydrogen peroxide or riboflavin (Villegas et al. 2008). Acevedo et al. (2006) studied Cr(VI) reduction to Cr(III) by two filamentous fungi-resistant strains (*Aspergillus* sp. Ed8 and *Penicillium* sp. H13), which were isolated from contaminated industrial wastes. The ability of these strains to reduce Cr(VI) present in the growth medium without accumulating Cr(VI) in the biomass at the end of the process was determined. The reduction reaction was performed using glucose as the only carbon source; it was not observed when fungi were supplied with yeast extract as the carbon source. This result suggested that reduction by the strains Ed8 and H13 did not exhibit a direct enzymatic reaction, which occurred only by the reducing power of the carbon source outside the cell. It could be possible that the extracellular reduction of Cr(VI) in filamentous fungi was due to the production and excretion of molecules similar to those found in bacteria, or by Cr(VI)-specific reducing molecules (Coreno et al. 2009). On the other hand, the capture of chromium in fungi and yeast surfaces has been described as being a result of the union between the components of the cell wall, mostly polysaccharides. Chitin is a linear homopolymer that is linked in β-1,4-acetilglucosamina of filamentous fungi cell walls (*Aspergillus*), at 10–20%, on average (Bartnicki 1987; de Nobel et al. 1990). Glucan is the major structural polysaccharide of the fungal cell wall, and it constitutes approximately 50–60% of the wall dry weight (Nguyen et al. 1998; Kapteyn et al. 1999). Additionally, most of the proteins of the cell wall in the filamentous fungi are glycoproteins, which are estimated at 20–30% of the mass (Bowman and Free 2006).

Transport and bioaccumulation

The bioaccumulation of metals is a common mechanism that is present in living cells, which require additional energy and nutrients to fulfil this process. Elimination of Cr(VI) by this process occurs on two steps: (1) primarily, a biosorption process occurs due to a retention of metallic ions in the cell surface, (2) this step is followed by the transport of these ions inside the cell by transport proteins (Jamali et al. 2014; Murugavelh and Mohanty 2014).

Das and Guha (2009) investigated the biosorption of Cr(VI) by *T. clypeatus* and found that this metallic ion had a quick binding of the metal ion onto the cell surface, followed by a relatively slow accumulation of this metal inside the cell. Generally, the presence of toxic ions that are similar to metallic ions that are essential for fungi metabolism can be wrongly accumulated by these ions in transport systems. The elimination of Cr(VI) in the presence of sulphate ions as a competitor of chromate ions provoked a diminution in the efficiency, which demonstrates the active participation of the sulphate transport system. This arrangement was confirmed by the presence of chromium in the cell wall and cytoplasm, using TEM-XDE.

In the last decade, there have been diverse studies on the elimination of Cr(VI) through the utilisation of diverse fungi, including *Aspergillus* and *Penicillium*, which possess specific mechanisms (Table 2). In general, the active micelle can achieve bioreduction percentages of 100% at pH 4 or more (Pazouki et al. 2007; Morales et al. 2008; Morales and Cristiani 2008; Cárdenas and Acosta 2010). On the other hand, biosorption and bioreduction processes are carried out at pH values of 1 and 2, mostly by dead biomass or cellular residues (Liu et al. 2007; Gochev et al. 2010; Kavita et al. 2011; Sen and Dastidar 2011; Zheng et al. 2014).

Metallophilic fungi applications for Cr(VI) removal

The reduction/oxidation processes that are conducted by fungi have the capacity to mobilise or immobilise metals, metalloids or organometallic compounds, by increasing the solubility of some metals, or decreasing it, as in the particular case of Cr(VI) to Cr(III) reduction (Gadd 1993b; Phillips et al. 1995; Gharieb et al. 1999; Smith and Gadd 2000; Lovley et al. 2004). The microbial reduction of Cr(VI) to Cr(III) by fungi, yeast and bacteria has been one of the most studied mechanisms for the bioremediation of this metal (Lovley 1995; Wang and Shen 1995; Lonergan et al. 1996). In this way, the strategy for Cr(VI) bioremediation is to reduce it to Cr(III) not only to decrease the Cr(VI) toxicity but also to immobilise the insoluble form of Cr(III) as $Cr(OH)_3$ in soil at pH values of 6–9 (Sharma and Forster 1993; Tokunaga et al. 1999; Pellerin and Booker 2000).

The immobilisation of Cr(VI) by fungi is possible by biosorption on the compounds of the fungi cell wall (exopolysaccharides, peptides, structural biomolecules of the cell wall or metabolites), in addition to the intracellular accumulation by transport phenomena, organelle location, precipitation and other mechanisms (Gadd 2010). On the other hand, the bioremediation efficiency could be improved with the addition of organic sources (organic

Table 2 Cr(VI) elimination studies by diverse fungi mechanisms

Fungi	pH	Time (h)	$[Cr(VI)]_0$ mg/L	Inoculum	% R	% A	Mechanism	References
A. niger	4.5 ± 0.5	96	50	Active micelle	48.7		Bioreduction	(Shugaba et al. 2013)
A. parasiticus					43.6			
H. tawa	6.5			Active micelle	100		Bioreduction	(Morales et al. 2008)
Paecilomyces lilacinus	5.5	120	200	NA	100		Bioreduction	(Sharma and Adholeya 2011)
Paecilomyces sp.	4.0	168	50	Active micelle	100		Bioreduction	(Cárdenas and Acosta 2010)
A. niger var tubingensis Ed8	5.0	24	50	Active micelle	95		Bioreduction	(Coreno et al. 2009)
Aspergillus sp.	6.0	120	50	Active micelle	74		Bioreduction	(Fukuda et al. 2008)
Penicillium sp.	3.0					93	Biosorption	
T. inhamatum	6.0	192	470	Active micelle	100		Bioreduction	(Morales and Cristiani 2008)
T. viride	4.5	336	125	Active micelle		96	Biosorption	(Holda and Kisielowskam 2013)
A. awamori	1.5	48	25	Dead biomass	29	71	Biosorption/ bioreduction	(Gochev et al. 2010)
Aspergillus. sp.	1.0		360	Active micelle	68		Bioreduction	(De Sotto et al. 2015)
A. flavus	4.5	120	50	Active micelle	99.2		Bioreduction	(Sathvika et al. 2015)
A. flavus	2.0	168	150	Active micelle	99		Bioreduction	(Bennett et al. 2013)
A. niger					98			
Aspergillus sp.					98			
Auricularia polytricha	1.0	54	10	Dead biomass	97		Bioreduction	(Zheng et al. 2014)
A. niger	2.0	20	50	Dead biomass		100	Biosorption	(Holda and Mlynarczykowska 2016)
	4.0	200		Active micelle		100	Bioreduction	
Fusarium solani	2.0	24	500	Cellular debris		63.9 mg/g	Biosorption	(Sen and Dastidar 2011)
A. niger	4.0	12	50	Active micelle		98.5	Biosorption	(Holda et al. 2011)
A. niger	6.0	168	500	Active micelle		75	Biosorption	(Srivastava and Thakur 2006a)
Pythium sp.	1.0	144	100	Dead biomass		12.5 mg/g	Biosorption	(Kavita et al. 2011)
Termitomyces clypeatus	3.0	48	100	Active micelle		11.1 mg/g	Biosorption	(Das and Guha 2009)
				Dead biomass		6.75 mg/g		
Mucor racemosus	1.0	24	100	Dead biomass	50	50	Biosorption/ Bioreduction	(Liu et al. 2007)
Phanerochaete chrysosporium	5.0		10	Active micelle	98.5		Bioreduction	(Murugavelh and Mohanty 2014)
Rhizopus oryzae	7.0	72	400	Active micelle	91.15		Bioreduction	(Sukumar 2010)
A. niger	6.2	168	50	Active micelle	99.6		Bioreduction	(Rivera et al. 2015)
A. flavus	7.0	120	25	Active micelle		95.80	Bioaccumulation	(Abubacker and Kirthiga 2013)
			50		73.42		Bioreduction	
P. chrysogenum	5.0	48	50	Active micelle	100		Bioreduction	(Pazouki et al. 2007)

matter or other nutrients) in soil or water that is treated, to increase the proliferation of autochthonous fungi that can reduce Cr(VI) (Kamaludeen et al. 2003).

Sunitha and Rajkishore (2013) studied two fungi strains, *Trichoderma viride* and *A. niger*, which were isolated from Cr(VI)-contaminated soils and were exposed to different Cr(VI) concentrations, to evaluate their reduction potential in soil. The results showed a significant difference between the Cr(VI) reduction percentages in both fungi. The reduction percentages were 31 up to 58% and 50 up to 83% for *T viride* and *A. niger*, respectively. The major reduction percentage was exhibited by *A. niger*, even when both

strains could tolerate 100 mg/kg of Cr(VI) in soil. Similarly, Sivakumar (2016) isolated different fungi strains from soil contaminated by tannery wastewater in Nagalkeni, India. Such fungi strains, which belong to the genera *Aspergillus*, were employed for the reduction of Cr(VI) in tannery effluents. The reduction capacity observed for each one was *A. niger* > *A. flavus* > *A. fumigatus* > *A. nidulans* > *A. heteromorphus* > *A. foetidus* > *A. viridinutans*, listed in decreasing capacity.

Other studies were conducted on Cr(VI) bioremediation in wastewater by fungi isolated from tannery industries, including *F. chlamydosporium* (9.86 mg/L) (Sharma and Malaviya 2014), *Aspergillus sp.* (126 mg/L) (Srivastava and Thakur 2006b), *Paecilomyces lilacinus* (1.24 mg/L) (Sharma and Adholeya 2011), and consortia composed of *Cladosporeum perangustum*, *Penicillium commune*, *P. lilacinus* and *Fusarium equiseti* (10 mg/L) (Sharma and Malaviya 2016); they reached complete Cr(VI) removal at different concentrations.

Conclusion

The metallophilic fungi isolated from sites contaminated with Cr(VI) created an alternative study for Cr(VI) bioremediation. There are diverse research studies on metallophilic fungi isolated at contaminated sites, primarily tanneries and crop fields. The genuses of *Aspergillus*, *Fusarium*, *Rhizopus* and *Penicillium* are the most reported to have high Cr(VI) tolerance, ranging from 300 to 1000 ppm. Many mechanisms of interaction of fungi and Cr(VI) have been characterised as extracellular or intracellular detoxification, thus preventing the entry of Cr(VI) into the cell or reducing the chromate in the cytosol. The ability of fungi to act as biosorbents has widely been evaluated using live or dead biomass, and several species of the genus *Aspergillus* have been studied as biosorbents for Cr(VI) removal, with the sequestration of Cr(VI) by different functional groups including carboxyl (–COOH), phosphate (PO_4^{3-}), amine ($–NH_2$), thiol (–SH) and hydroxide (–OH) components of the cell wall. These have mainly been related by polysaccharides (galactosamine, chitin and glycan) in addition to proteins, lipids and melanin, which are minor in contribution. The uptake of Cr(VI) is facilitated via non-specific sulphate transporters, inside the cell, such as glutathione, which plays an important role in the intracellular reduction of Cr(VI); the enzymatic reduction (direct) by fungi is still uncertain. Studies conducted for Cr(VI) bioremediation in wastewater by fungi isolated from the tannery industries have reached complete Cr(VI) removal at different concentrations, and they provide an alternative to be applied.

Acknowledgements This work was supported by Universidad Autónoma de Nuevo León, thanks to the scholarship provided by Facultad de Ciencias Químicas, UANL. Additional financial support was obtained from PROMEP 103.5/15/6644.

References

Abigail MAE, Samuel MS, Chidambaram R (2015) Hexavalent chromium biosorption studies using *Penicillium griseofulvum* MSR1 a novel isolate from tannery effluent site: Box-Behnken optimization, equilibrium, kinetics and thermodynamic studies. J Taiwan Inst Chem Eng 49:156–164

Abubacker MN, Kirthiga B (2013) Biosorption of *Aspergillus flavus* NCBT 102 biomass in hexavalent chromium. Biosci Biotechnol Res Asia 10:767–773

Acevedo AFJ, Espino SAE, León RIL, Rivera CME, Ávila RM, Wrobel K, Wrobel K, Lappe P, Ulloa M, Gutiérrez CJF (2006) Hexavalent chromium removal in vitro and from industrial wastes, using chromate-resistant strains of filamentous fungi indigenous to contaminated wastes. Can J Microbiol 52(9):809–815

Ahmad I, Zafar S, Ahmad F (2005) Heavy metal biosorption potential of *Aspergillus* and *Rhizopus* sp. isolated from wastewater treated soil. J Appl Sci Environ Manag 9:123–126

Ahmad I, Ansari MI, Aqil F (2006) Biosorption of Ni, Cr, and Cd by metal tolerant *Aspergillus niger* and *Penicillium* sp. using single and multi-metal solution. Indian J Exp Biol 44:73–76

Alexander J, Aaseth J (1995) Uptake of chromate in human red blood cells and isolated rat liver cells: the role of the anion carrier. Analyst 129:931–933

Alluri HK, Ronda SR, Settalluri VS, Bondili SJ, Suryanarayana V, Venkateshwar P (2007) Biosorption: an eco-friendly alternative for heavy metal removal. J Biotechnol 6:2924–2931

Alyüz B, Veli S (2009) Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. J Hazard Mater 167:482–488

Anand P, Isar J, Saran S, Saxena RK (2006) Bioaccumulation of copper by *Trichoderma viride*. Bioresour Technol 97:1018–1025

Appenroth KJ, Bischoff M, Gabryś H, Stoeckel J, Swartz HM, Walczak T, Winnefeld K (2000) Kinetics of chromium(V) formation and reduction in fronds of the duckweed *Spirodela polyrhiza*-a low frequency EPR study. J Inorg Biochem 78:235–242

Arshad A, Aishatul B (2015) *Aspergillus niger*—a novel heavy metal bio-absorbent and pesticide tolerant fungus. Res J Chem Environ 19:57–66

Arslan P, Beltrame M, Tomasi A (1987) Intracellular chromium reduction. Biochim Biophys Acta 931(1):10–15

Babu BV, Gupta S (2008) Removal of Cr(VI) from wastewater using activated tamarind seeds as an adsorbent. J Environ Eng Sci 7:553–557

Bai RS, Abraham TE (2001) Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*. Bioresour Technol 79:73–81

Bai RS, Abraham TE (2003) Studies on chromium(VI) adsorption-desorption using immobilized fungal biomass. Bioresour Technol 87:17–26

Bailey SE, Olin TJ, Bricka RM, Adrian DD (1999) A review of potentially low-cost sorbents for heavy metals. Water Res 33:2469–2479

Baldrian P (2003) Interactions of heavy metals with white-rot fungi. Enzyme Microb Technol 32:78–91

Bánfalvi G (2011) Heavy metals, trace elements and their cellular effects. In: Bánfalvi G (ed) Cellular effects of heavy metals. Springer, Dordrecht, Heidelberg, London, New York, pp 3–28

Barakat MA, Schmidt E (2010) Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater. Desalination 256:90–93

Barrera-Díaz CE, Lugo LV, Bilyeu B (2012) A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction. J Hazard Mater 223–224:1–12

Bartnicki GS (1987) The cell wall: a crucial structure in fungal evolution. In: Rayner ADM, Brasier CM, Moore D (eds) Evolutionary Biology of the Fungi. Cambridge University Press, Cambridge, pp 389–403

Beaumont JJ, Sedman RM, Reynolds SD, Sherman CD, Li LH, Howd RA, Sandy MS, Zeise L, Alexeeff GV (2008) Cancer mortality in a Chinese population exposed to hexavalent chromium in drinking water. Epidemiology 19:12–23

Bellion M, Courbot M, Jacob C, Blaudez D, Chalot M (2006) Extracellular and cellular mechanisms sustaining metal tolerance in ectomycorrhizal fungi. FEMS Microbiol Lett 254:173–181

Bennett RM, Cordero PRF, Bautista GS, Dedeles GR (2013) Reduction of hexavalent chromium using fungi and bacteria isolated from contaminated soil and water samples. Chem Ecol 29:320–328

Blaudez D, Jacob C, Turnau K, Colpaert JV, Ahonen-Jonnarth U, Finlay R, Botton B, Chalot M (2000) Differential Responses of Ectomycorrhizal Fungi to Heavy Metals *in vitro*. Mycol Res 104:1366–1371

Bowman SM, Free SJ (2006) The structure and synthesis of the fungal cell wall. BioEssays 28:799–808

Cárdenas GJF, Acosta RI (2010) Hexavalent chromium removal by a *Paecilomyces sp*. fungal strain isolated from environment. Bioinorg Chem Appl 22:9–16

Cervantes C, Campos GAJ, Devars S, Gutiérrez CF, Loza TH, Torres GJC, Moreno S (2001) Interactions of chromium with microorganisms and plants. FEMS Microbiol Rev 25:335–347

Cervantes C, Espino SAE, Acevedo AF, León RIL, Rivera CME, Ávila RM, Wrobel KK, Wrobel ZK, Gutiérrez CJF, Rodríguez ZJS, Moreno SR (2006) Interacciones microbianas con metales pesados. Rev Latinoam Microbiol 48:203–210

Cheung KH, Gu JD (2007) Mechanism of hexavalent chromium detoxification by microorganisms and bioremediation application potential: a review. Int Biodeterior Biodegrad 59:8–15

Clemens S (2001) Molecular mechanisms of plant metal tolerance and homeostasis. Planta 212:475–486

Coreno AA, Acevedo AFJ, Reyna LGE, Tomasini A, Fernández FJ, Wrobel K, Wrobel K, Gutiérez CJF (2009) Cr(VI) reduction by an *Aspergillus tubingensis* strain: role of carboxylic acids and implications for natural attenuation and biotreatment of Cr(VI) contamination. Chemosphere 76:43–47

Corona J, Saldana A (2010) Mecanismos de interacción con cromo y aplicaciones biotecnológicas en hongos. Rev latinoam Biotecnol Amb Algal 1:47–63

Costa M (2003) Potential hazards of hexavalent chromate in our drinking water. Toxicol Appl Pharmacol 188:1–5

Das SK, Guha AK (2009) Biosorption of hexavalent chromium by *Termitomyces clypeatus* biomass: kinetics and transmission electron microscopic study. J Hazard Mater 167:685–691

Das SK, Mukherjee M, Guha AK (2008) Interaction of chromium with resistant strain *Aspergillus versicolor*: investigation with atomic force microscopy and other physical studies. Langmuir 24:8643–8650

Dayan AD, Paine AJ (2001) Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000. Hum Exp Toxicol 20:439–451

De Nobel JG, Klis FM, Priem J, Munnik T, van den Ende H (1990) The glucanase-soluble mannoproteins limit cell wall porosity in *Saccharomyces cerevisiae*. Yeast 6:491–499

De Sotto R, Monsanto RZ, Edora JL, Bautista RH, Bennett RM, Dedeles GR (2015) Reduction of Cr(VI)using indigenous *Aspergillus* spp. isolated from heavy metal contaminated sites. Mycosphere 6(1):53–59

Dönmez G, Aksu Z (2002) Removal of chromium(VI) from saline wastewaters by *Dunaliella species*. Process Biochem 38:751–762

Dönmez G, Koçberber N (2005) Bioaccumulation of hexavalent chromium by enriched microbial cultures obtained from molasses and NaCl containing media. Process Biochem 40:2493–2498

Dursun AY, Uslu G, Cuci Y, Aksu Z (2003a) Bioaccumulation of Cu(II), Fe(II) and Cr(VI) by growing *Aspergillus niger*. Process Biochem 38:1647–1651

Dursun AY, Uslu G, Tepe O, Cuci Y, Ekiz HI (2003b) A comparative investigation on the bioaccumulation of heavy metal ions by growing *Rhizopus arrhizus* and *Aspergillus niger*. Biochem Eng J 15:87–92

Ercal N, Gurer-Orhan H, Aykin-Burns N (2001) Toxic metals and oxidative stress part I: mechanisms involved in metal-induced oxidative damage. Curr Top Med Chem 1:529–539

Ezzouhri L, Castro E, Moya M, Espinola F, Lairini K (2009) Heavy metal tolerance of filamentous fungi isolated from polluted sites in Tangier, Morocco. J Microbiol 3:35–48

Fogarty RV, Tobin JM (1996) Fungal melanins and their interactions with metals. Enzyme Microb Technol 19:311–317

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manag 92:407–418

Fukuda T, Ishinno Y, Ogawa A, Tsutsumi K, Morita H (2008) Cr(VI) reduction from contaminated soils by *Aspergillus* sp. N2 and *Penicillium* sp. N3 isolated from chromium deposits. J Gen Appl Microbiol 54:295–303

Gadd GM (1993a) Interactions of fungi with toxic metals. New Phytol 124:25–60

Gadd GM (1993b) Microbial formation and transformation of organometallic and organometalloid compounds. FEMS Microbiol Rev 11:297–316

Gadd GM (2000) Bioremedial potential of microbial mechanisms of metal mobilization and immobilization. Curr Opin Biotechnol 11:271–279

Gadd GM (2007) Geomycology: biogeochemical transformations of rocks, minerals, metals and radionuclides by fungi, bioweathering and bioremediation. Mycol Res 111:3–49

Gadd GM (2010) Metals, minerals and microbes: geomicrobiology and bioremediation. Microbiology 156:609–643

Gharieb MM, Kierans M, Gadd GM (1999) Transformation and tolerance of tellurite by filamentous fungi: accumulation, reduction, and volatilization. Mycol Res 103:299–305

Gochev VK, Velkova ZI, Stoytcheva MS (2010) Hexavalent chromium removal by waste mycelium of *Aspergillus awamori*. J Serb Chem Soc 75:551–564

González GM, Benabdellah K, Ferrol N, Aguilar C (2009) Mechanisms underlying heavy metal tolerance in arbuscular mycorrhizas. In: Azcon AC, Barea JM, Gianinazzi S, Gianinazzi PV (eds) Mycorrhizas: functional processes and ecological impact. Springer, Berlin, pp 107–122

Gorbushina AA (2007) Life on the rocks. Environ Microbiol 9:1613–1631

Gordon B, Callan P, Vickers C (2008) WHO guidelines for drinking-water quality. WHO Chron 38:564

Gouda MK (2000) Studies on chromate reduction by three *Aspergillus* species. Fresenius Environ Bull 9:799–808

Gu Y, Xu W, Liu Y, Zeng G, Huang J, Tan X, Jian H, Hu X, Li F, Wang D (2014) Mechanism of Cr(VI) reduction by *Aspergillus niger*: enzymatic characteristic, oxidative stress response, and reduction product. Environ Sci Pollut Res 22:6271–6279

Gunatilake SK (2015) Methods of removing heavy metals from industrial wastewater. J Multidiscip Eng Sci Stud 1:12–18

Gupta VK, Shrivastava AK, Jain N (2001) Biosorption of chromium(VI) from aqueous solutions by green algae *Spirogyra* species. Water Res 35:4079–4085

Halliwell B, Gutteridge JMC (2007) Cellular responses to oxidative stress: adaptation, damage, repair, senescence and death. In: Free Radicals in Biology and Medicine, 4th ed. Oxford University Press, New York, pp 187–267

Hashim MA, Mukhopadhyay S, Sahu JN, Sengupta B (2011) Remediation technologies for heavy metal contaminated groundwater. J Environ Manag 92:2355–2388

Hassen A, Saidi N, Cherif M, Boudabous A (1998) Resistance of environmental bacteria to heavy metals. Bioresour Technol 64:7–15

Holda A, Kisielowskam E (2013) Biological removal of Cr(VI) ions from aqueous solutions by *Trichoderma viride*. Physicochem Probl Miner Process 49(1):47–60

Holda A, Mlynarczykowska A (2016) Use of dead and living fungal biomass for the removal of hexavalent chromium. Physicochem Probl Miner Process 52:551–563

Holda A, Kisielowska E, Niedoba T (2011) Bioaccumulation of Cr(VI) ions from aqueos solutions by *Aspergillus niger*. Polish J Environ Stud 20:345–349

Huisman JL, Schouten G, Schultz C (2006) Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry. Hydrometallurgy 83:106–113

Iram S, Parveen K, Usman J, Nasir K, Akhtar N, Arouj S, Ahmad I (2012) Heavy metal tolerance of filamentous fungal strains isolated from soil irrigated with industrial wastewater. Biologija 58:107–116

Jamali N, Ghaderian SM, Karimi N (2014) Effects of cadmium and zinc on growth and metal accumulation of *Mathiola flavida* BOISS. Environ Eng Manag J 13:2937–2944

Jayanthi M, Kanchana D, Saranraj P, Sujitha D (2014) Bioadsorption of Chromium by *Penicillium chrysogenum* and *Aspergillus niger* Isolated from Tannery Effluent. Intl J 5:40–47

Jusoh A, Su Shiung L, Ali N, Noor MJMM (2007) A simulation study of the removal efficiency of granular activated carbon on cadmium and lead. Desalination 206:9–16

Juvera-Espinosa J, Morales BL, Cristiani UE (2006) Isolation and characterization of a yeast strain capable of removing Cr(VI). Enzyme Microb Technol 40:114–121

Kadirvelu K, Cloirec PL (2000) Removal of Cu(II), Pb(II), and Ni(II) by adsorption onto activated carbon cloths. Langmuir 16:8404–8409

Kamaludeen SPB, Megharaj M, Juhasz AL, Sethunathan N, Naidu R (2003) Chromium-microorganism interactions in soils: remediation implications. Rev Environ Contam Toxicol 178:93–164

Kang SY, Lee JU, Kim KW (2007) Biosorption of Cr(III) and Cr(VI) onto the cell surface of *Pseudomonas aeruginosa*. Biochem Eng J 36:54–58

Kapoor A, Viraraghavan T (1995) Fungal biosorption-an alternative treatment option for heavy metal bearing wastewaters: a review. Bioresour Technol 53:195–206

Kapteyn JC, Van Den Ende H, Klis FM (1999) The contribution of cell wall proteins to the organization of the yeast cell wall. Biochim Biophys Acta Gen Subj 1426:373–383

Katz SA (1991) The analytical biochemistry of chromium. Environ Health Perspect 92:13–16

Kavita B, Keharia H (2012) Biosorption potential of *Trichoderma gamsii* biomass for removal of Cr(VI) from electroplating industrial effluent. Int J Chem Eng Appl 2012:7

Kavita B, Limbachia J, Keharia H (2011) Hexavalent chromium sorption by biomass of chromium tolerant *Pythium* sp. J Basic Microbiol 51:173–182

Khambhaty Y, Mody K, Basha S, Jha B (2009) Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*. Chem Eng J 145:489–495

Kotaś J, Stasicka Z (2000) Chromium occurrence in the environment and methods of its speciation. Environ Pollut 107:263–283

Ksheminska H, Jaglarz A, Fedorovych D, Babyak L, Yanovych D, Kaszycki P, Koloczek H (2003) Bioremediation of chromium by the yeast *Pichia guilliermondii*: toxicity and accumulation of Cr(III) and Cr(VI) and the influence of riboflavin on Cr tolerance. Microbiol Res 158:59–67

Ksheminska HP, Honchar TM, Gayda GZ, Gonchar MV (2006) Extra-cellular chromate-reducing activity of the yeast cultures. Cent Eur J Biol 1:137–149

Landaburu-Aguirre J, García V, Pongrácz E, Keiski RL (2009) The removal of zinc from synthetic wastewaters by micellar-enhanced ultrafiltration: statistical design of experiments. Desalination 240:262–269

Landeweert R, Hoffland E, Finlay RD, Kuyper TW, Van Breemen N (2001) Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. Trends Ecol Evol 16:248–254

Liu KJ, Shi X (2001) *In vivo* reduction of chromium(VI) and its related free radical generation. Mol Cell Biochem 222:41–47

Liu KJ, Jiang JJ, Shi XL, Gabrys H, Walczak T, Swartz HM (1995) Low-frequency EPR study of chromium(V) formation from chromium(VI) in living plants. Biochem Biophys Res Commun 206:829–834

Liu T, Li H, Li Z, Xiao X, Chen L, Deng L (2007) Removal of hexavalent chromium by fungal biomass of *Mucor racemosus*: influencing factors and removal mechanism. World J Microbiol Biotechnol 23:1685–1693

Lonergan DJ, Jenter HL, Coates JD, Phillips EJP, Schmidt TM, Lovley DR (1996) Phylogenetic analysis of dissimilatory Fe(III) reducing bacteria. J Bacteriol 178:2402–2408

Lovley DR (1995) Bioremediation of organic and metal contaminants with dissimilatory metal reduction. J Ind Microbiol 14:85–93

Lovley DRD, De Holmes DE, Nevin KP (2004) Dissimilatory Fe(III) and Mn(IV) reduction. Adv Microb Physiol 55:220–286

Macreadie IG, Castelli LA, Mehra RK, Thorvaldsen J, Winge D (1994) Heterologous gene expression and protein secretion from *Candida glabrata*. Biotechnol Appl Biochem 19(Pt 3):265–269

Meena AK, Mishra GK, Rai PK, Rajagopal C, Nagar PN (2005) Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. J Hazard Mater 122:161–170

Mohan D, Pittman CU (2006) Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. J Hazard Mater 137:762–811

Mohan D, Singh KP, Singh VK (2005) Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth. Ind Eng Chem Res 44:1027–1042

Morales BL, Cristiani UE (2006) Removal of hexavalent chromium by *Trichoderma viride* in an airlift bioreactor. Enzyme Microb Technol 40:107–113

Morales BL, Cristiani UE (2008) Hexavalent chromium removal by a *Trichoderma inhamatum* fungal strain isolated from tannery effluent. Water Air Soil Pollut 187:327–336

Morales BL, Guillén JFDM, Ortiz MA, Villegas GTL, Sandoval CA, Hernández RCH, Cristiani UE (2008) Isolation, identification and characterization of a *Hypocrea tawa* strain with high Cr(VI) reduction potential. Biochem Eng J 40:284–292

Mungasavalli DP, Viraraghavan T, Jin YC (2007) Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*: batch and column studies. Colloids Surf A Physicochem Eng Asp 301:214–223

Murugavelh S, Mohanty K (2014) Mechanism of Cr(VI) bioaccumulation by *Phanerochaete chrysosporium*. Environ Eng Manag 13:281–287

Myers CR, Myers JM (1993) Ferric reductase is associated with the membranes of anaerobically grown *Shewanella putrefaciens* MR-1. FEMS Microbiol Lett 108:15–22

Nguyen TH, Fleet GH, Rogers PL (1998) Composition of the cell walls of several yeast species. Appl Microbiol Biotechnol 50:206–212

Nies DH, Koch S, Wachi S, Peitzsch N, Saier MH (1998) CHR, a novel family of prokaryotic proton motive force-driven transporters probably containing chromate/sulfate antiporters. J Bacteriol 180:5799–5802

Nriagu JO, Pacyna JM (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333:134–139

O'Brien P, Kortenkamp A (1994) Chemical models important in understanding the ways in which chromate can damage DNA. Environ Health Perspect 3:3–10

Owlad M, Aroua MK, Daud WAW, Baroutian S (2009) Removal of hexavalent chromium-contaminated water and wastewater: a review. Water Air Soil Pollut 200:59–77

Pal A, Paul AK (2004) Aerobic chromate reduction by chromium-resistant bacteria isolated from serpentine soil. Microbiol Res 159:347–354

Pang C, Liu YH, Cao XH, Li M, Huang GL, Hua R, Wang CX, Liu YT, An XF (2011) Biosorption of uranium(VI) from aqueous solution by dead fungal biomass of *Penicillium citrinum*. Chem Eng J 170:1–6

Park D, Yun YS, Jo JH, Park JM (2005) Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*. Water Res 39:533–540

Pazouki M, Keyanpour-Rad M, Shafie S, Shahhoseini S (2007) Efficiency of *Penicillium chrysogenum* PTCC 5037 in reducing low concentration of chromium hexavalent in a chromium electroplating plant wastewater. Bioresour Technol 98:2116–2122

Pellerin C, Booker SM (2000) Reflections on hexavalent chromium: health hazards of an industrial heavyweight. Environ Health Perspect 108:402–407

Perotto S, Girlanda M, Martino E (2002) Ericoid mycorrhizal fungi: some new perspectives on old acquaintances. Plant Soil 244:41–53

Perrone GG, Grant CM, Dawes IW (2005) Genetic and environmental factors influencing glutathione homeostasis in Saccharomyces cerevisiae. Mol Biol Cell 16:218–230

Pesti M, Gazdag Z, Emri T, Farkas N, Koósz Z, Belágyi J, Pócsi I (2002) Chromate sensitivity in fission yeast is caused by increased glutathione reductase activity and peroxide overproduction. J Basic Microbiol 42:408–419

Phillips EJP, Landa ER, Lovley DR (1995) Remediation of uranium contaminated soils with bicarbonate extraction and microbial U(VI) reduction. J Ind Microbiol Biotechnol 14:203–207

Pillichshammer M, Pümpel T, Pöder R, Eller K, Klima J, Schinner F (1995) Biosorption of chromium to fungi. Biometals 8:117–121

Pócsi I, Prade RA, Penninckx MJ (2004) Glutathione, altruistic metabolite in fungi. Adv Microb Physiol 49:1–76

Prakasham RS, Merrie JS, Sheela R, Saswathi N, Ramakrishna SV (1999) Biosorption of chromium VI by free and immobilized *Rhizopus arrhizus*. Environ Pollut 104:421–427

Prasenjit B, Sumathi S (2005) Uptake of chromium by *Aspergillus foetidus*. J Mater Cycles Waste Manag 7:88–92

Prigione V, Zerlottin M, Refosco D, Tigini V, Anastasi A, Varese GC (2009) Chromium removal from a real tanning effluent by autochthonous and allochthonous fungi. Bioresour Technol 100:2770–2776

Ramírez RR, Calvo MC, Ávila RM, Lappe P, Ulloa M, Vázquez JR, Gutiérrez CJF (2004) Cr(VI) reduction in a chromate-resistant strain of *Candida maltosa* isolated from the leather industry. Antonie van Leeuwenhoek, Int J Gen Mol Microbiol 85:63–68

Ramrakhiani L, Majumder R, Khowala S (2011) Removal of hexavalent chromium by heat inactivated fungal biomass of *Termitomyces clypeatus*: surface characterization and mechanism of biosorption. Chem Eng J 171:1060–1068

Rankin DWH (2009) CRC handbook of chemistry and physics. In: Lide RD (ed) Crystallogr Rev, 89th edn, vol 15, no 3. Taylor and Francis, pp 223–224

Ravindranath SP, Henne KL, Thompson DK, Irudayaraj J (2011) Surface-enhanced Raman imaging of intracellular bioreduction of chromate in *Shewanella oneidensis*. PLoS ONE 6(2):e16634

Reddy MS, Kour M, Aggarwal S, Ahuja S, Marmeisse R, Fraissinet-Tachet L (2015) Metal induction of a *Pisolithus albus* metallothionein and its potential involvement in heavy metal tolerance during mycorrhizal symbiosis. Environ Microbiol 18(8):2446–2454

Religa P, Gawronski R, Gierycz P (2009) Kinetics of chromium(III) transport through a liquid membrane containing DNNSA as a carrier. Int J Mol Sci 10:964–975

Ren B, Zhang Y, Zhao L, Zhang X (2015) Biosorption of chromium by the spores of *Aspergillus niger*. Conference: 2015 International Conference on Mechatronics, Electronic, Industrial and Control Engineering 3: 833–836.

Reya Isaac I, Rajamehala M, Lakshmi PM, Emilin RR (2012) Comparitive study on biosorption of hexavalent chromium using *Aspergillus oryzae* NCIM 637 and *Aspergillus sojae* NCIM 1198 from electroplating effluent. Int J ChemTech Res 4:1708–1719

Rivera ME, Cárdenas GJF, Martínez JVM, Acosta RI (2015) Chromium(VI) Removal by a Chromate-Resistant strain of *Aspergillus niger*. Inf Technol 26(4):13–20

Roane TM, Pepper IL (2000) Microorganisms and metal pollution. In: Maier RM, Pepper IL, Gerba CB (eds) Environmental Microbiology. Academic Press, London, p 55

Ross IS (1975) Some effects of heavy metals on fungal cells. Trans Br Mycol Soc 64:175–193

Roundhill DM, Koch HF (2002) Methods and techniques for the selective extraction and recovery of oxoanions. Chem Soc Rev 31:60–67

Saha B, Orvig C (2010) Biosorbents for hexavalent chromium elimination from industrial and municipal effluents. Coord Chem Rev 254:2959–2972

Sathvika T, Manasi M, Rajesh V, Rajesh N (2015) Prospective application of *Aspergillus* species immobilized in sodium montmorillonite to remove toxic hexavalent chromium from wastewater. RSC Adv 5:107031–107044

Say R, Yilmaz N, Denizli A (2004) Removal of chromium(VI) ions from synthetic solutions by the fungus *Penicillium purpurogenum*. Eng Life Sci 4:276–280

Sen M, Dastidar MG (2011) Biosorption of Cr(VI) by resting cells of *Fusarium solani*. Iran J Environ Health Sci Eng 8(2):153–158

Sharma S, Adholeya A (2011) Detoxification and accumulation of chromium from tannery effluent and spent chrome effluent by

Paecilomyces lilacinus fungi. Int Biodeterior Biodegrad 65:309–317
Sharma DC, Forster CF (1993) Removal of hexavalent chromium using *Sphagnum moss* peat. Water Res 27:1201–1208
Sharma S, Malaviya P (2014) Bioremediation of tannery wastewater by chromium resistant fungal isolate *Fusarium chlamydosporium* SPFS2-g. Curr World Environ 9:721–727
Sharma S, Malaviya P (2016) Bioremediation of tannery wastewater by chromium resistant novel fungal consortium. Ecol Eng 91:419–425
Shroff KA, Vaidya VK (2013) Dead fungal biomass of *Rhizopus arrhizus* for decontamination of hexavalent chromium: biosorption kinetics, equilibrium modelling and recovery. Nat Environ Pollut Technol 12:25–34
Shugaba A, Buba F, Kolo BG, Nok AG, Ameh DA, Lovi JA (2013) Uptake and reduction of hexavalent chromium by *Aspergillus niger*, and *Aspergillus parasiticus*. J Pet Environ Biotechnol 3:3
Sims JL, Suflita JM, Russell HH (1992) In-situ bioremediation of contaminated ground water. EPA: Ground Water Issue, EPA/540/S-92/003), pp 1–11
Sivakumar D (2016) Biosorption of hexavalent chromium in a tannery industry wastewater using fungi species. Glob J Environ Sci Manag 2:105–124
Smith AH (2008) Hexavalent chromium, yellow water, and cancer: a convoluted saga. Epidemiology 19:24–26
Smith WL, Gadd GM (2000) Reduction and precipitation of chromate by mixed culture sulphate-reducing bacterial biofilms. J Appl Microbiol 88:983–991
Soumik S (2013) Hexavalent Chromium (Cr(VI)) removal by live mycelium of a *Trichoderma harzianum* Strain. Mol Soil Biol 4:1–6
Srivastava S, Thakur IS (2006a) Biosorption potency of *Aspergillus niger* for removal of chromium (VI). Curr Microbiol 53:232–237
Srivastava S, Thakur IS (2006b) Evaluation of bioremediation and detoxification potentiality of *Aspergillus niger* for removal of hexavalent chromium in soil microcosm. Soil Biol Biochem 38:1904–1911
Stearns DM, Wise JP, Patierno SR, Wetterhahn KE (1995) Chromium(III) picolinate produces chromosome damage in Chinese hamster ovary cells. Fed Am Soc Exp Biol J 9:1643–1648
Sukumar M (2010) Reduction of hexavalent chromium by *Rhizopus oryzae*. Afr J Environ Sci Technol 4(7):412–418
Sunitha R, Rajkishore SK (2013) Biotransformation of hexavalent chromium as influenced by indigenous microbes in tannery effluent contaminated sites. Int J Sci Res 2:234–236
Suzuki T, Miyata N, Horitsu H et al (1992) NAD(P)H-dependent chromium(VI) reductase of *Pseudomonas ambigua* G-1: A Cr(V) intermediate is formed during the reduction of Cr(VI) to Cr(III). J Bacteriol 174:5340–5345
Tahir A, Abdel-Megeed A, Zahid S (2014) Temperature and pH kinetics for enhanced biosorption of Cr(VI) by highly chromium resistant fungi *Gliocladium* spp. SPP ZIC. Pak J Bot 46(6):2285–2292
Tamás MJ, Labarre J, Toledano MB, Wysocki R (2006) Mechanisms of toxic metal tolerance in yeast. Top Curr Genet 14:395–454
Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–851
Tewari N, Vasudevan P, Guha BK (2005) Study on biosorption of Cr(VI) by *Mucor hiemalis*. Biochem Eng J 23:185–192
Tokunaga TK, Wan J, Firestone MK, Hazen TC, Olson KR, Herman DJ, Sutton SR, Lanzirotti A (1999) In situ reduction of chromium(VI) in heavily contaminated soils through organic carbon amendment. J Environ Qual 32:1641–1649
U.S. EPA (2006) In Situ Treatment Technologies for Contaminated Soil. In Situ. EPA 542/F-06/013, pp 1–35
van Hees PA, Tipping E, Lundström US (2001) Aluminium speciation in forest soil solution—modelling the contribution of low molecular weight organic acids. Sci Total Environ 278:215–229
Vangronsveld J, Van Assche F, Clijsters H (1994) Reclamation of a bare industrial area contaminated by non-ferrous metals: in situ metal immobilization and revegetation. Environ Pollut 87:51–59
Villegas LB, Fernández PM, Amoroso MJ, De Figueroa LIC (2008) Chromate removal by yeasts isolated from sediments of a tanning factory and a mine site in Argentina. Biometals 21:591–600
Wang YT, Shen H (1995) Bacterial reduction of hexavalent chromium. J Ind Microbiol 14:159–163
Wionczyk B, Cierpiszewski R, Mól A, Prochaska K (2011) Studies on the kinetics and equilibrium of the solvent extraction of chromium(III) from alkaline aqueous solutions of different composition in the system with Aliquat 336. J Hazard Mater 198:257–268
Wysocki R, Tamás MJ (2010) How *Saccharomyces cerevisiae* copes with toxic metals and metalloids. FEMS Microbiol Rev 34:925–951
Yan G, Viraraghavan T (2003) Heavy-metal removal from aqueous solution by fungus *Mucor rouxii*. Water Res 37:4486–4496
Zafar S, Aqil F, Ahmad I (2007) Metal tolerance and biosorption potential of filamentous fungi isolated from metal contaminated agricultural soil. Bioresour Technol 98:2557–2561
Zhang X-H, Zhang X, Wang X-C, Jin L-F, Yang Z-P, Jiang C-X, Chen Q, Ren X-B, Cao J-Z, Wang Q, Zhu Y-M (2011) Chronic occupational exposure to hexavalent chromium causes DNA damage in electroplating workers. BMC Public Health 11:224
Zheng S, Huang H, Zhang R, Cao L (2014) Removal of Cr(VI) from aqueous solutions by fruiting bodies of the jelly fungus (*Auricularia polytricha*). Appl Microbiol Biotechnol 98:8729–8736
Zhu W, Zhao DX, Miao Q et al (2009) *Arabidopsis thaliana* metallothionein, AtMT2a, Mediates ROS balance during oxidative stress. J Plant Biol 52:585–592
Zouboulis AI, Loukidou MX, Matis KA (2004) Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils. Process Biochem 39:909–916