



Bioremediation strategies for chromium removal: Current research, scale-up approach and future perspectives



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HIGHLIGHTS

- Cr(VI) of industrial effluents impact negatively in human health and environment.
- The removal of Cr(VI) from wastewater requires serious and immediate attention.
- Biological removal of Cr(VI) is a sustainable technology environmentally friendly.
- Cr(VI)-bioremediation strategies are applied in different systems and scales.
- Research is essential to solve the problems associated to the large-scale remediation.

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ABSTRACT

Industrial applications and commercial processes release a lot of chromium into the environment (soil, surface water or atmosphere) and resulting in serious human diseases because of their toxicity. Biological Cr-removal offers an alternative to traditional physic-chemical methods. This is considered as a sustainable technology of lower impact on the environment. Resistant microorganisms (e.g. bacteria, fungi, and algae) have been most extensively studied from this characteristic. Several mechanisms were developed by microorganisms to deal with chromium toxicity. These tools include biotransformation (reduction or oxidation), bioaccumulation and/or biosorption, and are considered as an alternative to remove the heavy metal. The aim of this review is summarize Cr(VI)-bioremediation technologies oriented on practical applications at larger scale technologies. In the same way, the most relevant results of several investigations focused on process feasibility and the robustness of different systems (reactors and pilot scale) designed for chromium-removal capacity are highlighted.

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1. Introduction

The population growth and different anthropogenic activities have contributed to a worsening of environmental contamination. Industrial effluents are produced by the incorporation of organic and inorganic contaminants, as well as by discharged of heavy metals such as chromium, copper, cadmium, lead, and selenium. These wastewater containing heavy metals are often discharged into the environment (water, air and soil) without appropriate treatment, resulting in a worldwide severe socio-environmental problem (Gavrilescu, 2004; Wang and Chen, 2006). They are non-degradable toxic pollutants (Modoi et al., 2014; Pavel et al., 2012), thus persistent in nature that accumulates in the food chain, which with time reach detrimental levels in living systems, resulting in several diseases such as irritation and/or cancer in lungs and digestive tract, low growth rates in plants and death of animals (Cheung and Gu, 2007; Orozco et al., 2008), and others health alterations.

Chromium is a geochemical element widely distributed in rocks, minerals soils, and fresh water. The metal present several oxidation states but the more stable forms in the environment are the trivalent [Cr(III)] and hexavalent [Cr(VI)]. Due to their oxidizing nature, Cr(VI) (mainly CrO_4^{2-} at neutral pH or alkaline conditions) is a known mutagen and carcinogen compound to living organisms, including humans (Fernández et al., 2010; Costa, 2003). This heavy metal has been designated a priority pollutant in many countries and by the United States Environmental Protection Agency-USEPA (Fernández et al., 2009; Juvera-Espinosa et al., 2006; Ksheminska et al., 2003). Studies have provided evidence that Cr(VI) toxicity is due to the fact that metal complexes can easily cross cellular membranes and trigger intracellular Reactive Oxygen Species (ROS) accumulation altering cell structures (Fernández et al., 2009; Morales-Barrera and Cristiani-Urbina, 2006). It has been estimated that Cr(VI) is 100 times more toxic and 1000 times more mutagenic than Cr(III) (Chojnacka, 2010). Instead, Cr(III) is essential to human metabolism, related to maintenance of glucose, cholesterol and triglyceride levels, cellular membrane stability, synthesis and stability of nucleic acids and proteins (Fernández et al., 2014; Frois et al., 2011; Poljsak et al., 2010). Di Bona et al. (2011) recently reported that Cr(III) can no longer be considered as a dietary supplement because rats subjected to a diet with low content of trivalent chromium suffered no adverse consequences when they are compared with rats subjected to a diet with a sufficient dose of Cr(III). However, at high concentrations Cr(III) can complex with organic compounds interfering with metalloenzyme systems (Poljsak et al., 2010; Fernández et al., 2009; Krishna and Philip, 2005), may also cause health problems e.g. lung cancer (Costa, 2003), birth deficiency and the decrease of reproductive health (Marsh and McInerney, 2001).

This heavy metal is frequently discharge into the soil and water from various polluting sources, such as electroplating, wood

preservation, leather, mining industries, and others industrial activities (Tekerekopoulou et al., 2013). The maximum permitted tolerance limits for total Cr into inland surface water is 0.5 mg/L, according to the Environmental Protection Agency (USA) (Tekerekopoulou et al., 2013; Baral and Engelken, 2002). For that reason, the removal of the metal must be applied effectively and without causing impact on the environment. The most widely used methods are the conventional physicochemical processes such as reverse osmosis, electrochemical process, ion exchange, adsorption on activated carbon, excavation and solidification/stabilization, etc. (Witek-Krowiak, 2013). These technologies reduce the negative metal effect but they present major disadvantages such as generation of toxic waste sludge, high energy requirements or incomplete removal (Bahi et al., 2012). Consequently, the search for cheaper and more effective technologies has become necessary to develop of more economical, safe, and environmentally friendly methods to remove Cr(VI) ions from industrial wastewaters. The potential of adaptation and growth of Cr-resistant microorganisms (e.g. bacteria, fungi, and yeasts) led to hypothesize that biological removal methods would be a sustainable alternative technology of lower impact on the environment. Different microorganisms have been isolated and identified as having the capacity to remove Cr(VI) contamination by different biological methods (biosorption, bioaccumulation, bioreduction). Nowadays, biological treatment of heavy metal containing wastewater by using microorganisms is one of the most active research fields (Fernández et al., 2014).

Considering the socio-environmental impact related to Cr in industrials effluents and the toxic effect for human and animal health, this work summarize and discuss the potentialities of bioremediation of Cr(VI) applied at different scales (bioreactors and pilot scale) to diminish the contents of Cr(VI) until acceptable levels.

2. Microbial mechanism of Cr(VI) resistant

There are a number of autochthonous microorganisms with capability to adapt to and colonize contaminated environments, which are uninhabitable for animals and plants. The isolation of Cr-tolerant strains which naturally inhabit uncontaminated or contaminated environment undergoing purification is important to conduct a future process of bioremediation.

The knowledge about the interaction between microorganisms and heavy metals has an increasing interest. Microbial remediation is defined as the process by which microorganisms are stimulated to rapidly degrade the hazardous contaminants to environmentally safe levels in soil, subsurface materials, water, sludge and residues (Asha and Sandeep, 2013). The study of microbial mechanisms interaction with Cr is of both fundamental and biotechnological interest (Gutiérrez-Corona et al., 2016). Different detoxifying mechanisms developed by these microorganisms include the metal uptake (bioaccumulation or biosorption), and/or the

biotransformation (reduction) changing the oxidative state of the metal. Among them, the bioreduction of the highly toxic, water soluble, and mobile Cr(VI) to the less toxic, insoluble, and immobile Cr(III) is an interesting option (Guillen-Jiménez et al., 2009). Many researchers reported that biosorption can be a promising and efficient method for the removal of heavy metals due to its reusability, low operating cost and the absence of associated contamination (Sepehr et al., 2012; Konczyk et al., 2010; Kumar et al., 2008; Uluozlu et al., 2008; Wu et al., 2008). Following, the Cr(VI) microbial detoxifying mechanisms are considered in more detail.

2.1. Cr(VI) biosorption

Biosorption is a passive, rapid, and reversible physico-chemical process between metal species (sorbate) and biological material (biosorbent) (Ahluwalia and Goyal, 2007). This is a passive process and independent from cell activity carried out by active or inactive microorganisms. The use of dead biomass has advantages over living cells: it is not necessary to add nutrients, it is immune to toxicity or to adverse operating conditions, the recovery of metals is easier by means of treatments that allow the regeneration of biomass and the biomass itself can be obtained more economically, as an industrial waste product. However, living cells can present a widespread variety of mechanisms for the accumulation of metals such as transport, extracellular complex formation and precipitation. These processes are not exclusive and may involve physico-chemical and metabolic uptake mechanisms may also contribute to the process (Ahluwalia and Goyal, 2007). The recovery of metals in processes that use living cells can be difficult, especially if they were compartmentalized or internally precipitated.

The importance to use microorganisms as biosorbents is due to high surface/volume ratio and low cost to produce biomass. Various microorganisms have been employed in the removal of heavy metals such as, algae, microalgae and cyanobacteria (Khoubestani et al., 2015; Kwak et al., 2015; Nemr et al., 2015), fungi (Khani et al., 2012), yeasts (Fernández et al., 2013; Mahmoud and Mohamed, 2015; Martorell et al., 2012), and bacteria (Huang et al., 2016; Wu et al., 2015). All of them showed the ability to remove Cr(VI) in biosorption processes. In the same way, sludge, aquatic macrophytes, plant, fruit and vegetable residues, and inorganic compounds should be taken in consideration (Chen et al., 2015; Khelaifia et al., 2016; Lima et al., 2011; Wang et al., 2016).

Microbial cell wall provides structural integrity and offers many functional groups (such as carboxylate, hydroxyl, amino and phosphate) that can bind heavy metal ions (Scott and Karanjkar, 1992). After that, the active sorption into the cell demand energy consumption. The presence of cytoplasmic metal-binding proteins is also associated with the second process (Doble and Kumar 2005). In fungi, carboxyl, phosphate, amine, amide and alkane groups are involved in chromium binding (Ahluwalia and Goyal, 2010). Chitin and chitosan present on the cell wall of *Rhizopus arrhizus* are also involved in Cr absorption (Ismael et al., 2004). A study carried out by Iram et al. (2013) revealed that *Aspergillus fumigatus* fungal isolated from a contaminated site has good biosorption capacity towards selected heavy metals. Mathiyazhagan and Natarajan (2011) evaluated the biological remediation using *Thiobacillus* spp and *Pseudomonas* spp. The results of biosorption process showed the *T. ferrooxidans* reduced and/or absorbed some heavy metals from mines (Cd, Ca, Zn, Cr, Mn, and Pb) while *P. aeruginosa* absorbed most of the metals than *T. ferrooxidans* could not absorb. Bahafid et al. (2013a,b) found that Cr(VI) removal by *Pichia anomala* involves adsorption on functional groups (e.g., amide I, amide II, amide III, polysaccharides, sulfonate and carboxyl) followed by accumulation inside the cell and biotransformation of Cr(VI) to Cr(III). The same authors also reported on

three yeasts (*Cyberlindnera fabianii*, *Wickerhamomyces anomalus*, and *Candida tropicalis*) able to remove Cr(VI) from contaminated sites via adsorption mechanism (Bahafid et al., 2013a,b). Studies with fungal species such as *Schwanniomyces* (Mohite et al., 2015) and *Trichoderma* (Chang et al., 2016) related the exopolymeric substances (EPS) production with adsorption coupled reduction process. In the yeast *Schwanniomyces*, the exopolysaccharides generates nanoparticles that show a coupled adsorption-reduction system (Mohite et al., 2015).

2.2. Cr(VI) bioaccumulation

Different researchers summarized the results achieved using bacteria, fungi, algae, and other plant-derived biomass according to the capability of incorporating actively metals into their cells from aqueous solutions (Gavrilescu, 2004; Cheung and Gu, 2007; Wang and Chen, 2009; Chojnacka, 2010). Metal uptake by microorganisms depends on initial metal concentration and contact time. Is a metabolism-dependent mechanism which occurs only in living cells and requires energy for the transport of Cr(VI) across the membrane into the cells. However, the major limitation is the inhibition of the cell growth when the metal concentration is high (Dönmez and Aksu, 1999). The understanding of the mechanism by which some microorganisms accumulate Cr(VI) is determinant to the development of processes for concentration, removal, and recovery from contaminated solutions. Ksheminska et al. (2008) suggested that Cr(VI) compounds (analogous to anions SO_4^{2-} and PO_4^{3-}) enter cells through non-selective and oxidative state-sensitive anion channel via facilitated diffusion. Cellular membranes are often impermeable to Cr(III), possibly because they form complexes that have low solubility.

2.3. Cr(VI) biotransformation

The biotransformation of hexavalent chromium is considered as a detoxification mechanism because the trivalent form is more stable and less toxic than Cr(VI). Some recent studies reported extracellular chromate reductase activity present in the supernatant of microbial cultures (Dey and Paul, 2016; Rath et al., 2014). In bacteria (including *Pseudomonas*, *Bacillus* and *Arthrobacter*), the enzymatic Cr(VI) reduction could be related to soluble cytosolic proteins or insoluble cell membrane enzymes (Thatoi et al., 2014; Viti et al., 2014). Indeed, different chromate reductases (ChrR, YieF, Nema, and LpDH) were found in the cytoplasmic fraction (soluble) or bound to the membrane catalyzing the reaction under aerobic or anaerobic (or sometimes both) conditions.

Ksheminska et al. (2008) identified several yeasts as one of the best organisms to be used for bioremediation studies. *Pichia guilliermondii* (Ksheminska et al., 2008), *Rhodotorula mucilaginosa* (Chatterjee et al., 2012), and *Cyberlindnera jadinii* and *Wickerhamomyces anomalus* (Fernández et al., 2016, 2013) were reported by their capability to biotransform Cr(VI) to Cr(III). Ramírez-Ramírez et al. (2004) described NAD-dependent chromate-reducing activity in the soluble protein fraction of *Candida maltosa*. Cr(VI) detoxification can also occur indirectly by substances (such as sulphate and riboflavin) that are secreted by the yeast cells to the extracellular medium (Fedorovych et al., 2009; Ksheminska et al., 2006). According to this, the cell-free extracts of two yeasts (*Pichia jadinii* and *Pichia anomala*) isolated from textile-dye factory effluents present Cr(VI) reduction (Martorell et al., 2012). However, the principal reason that yeasts are resistant to chromium is related more to their limited ion uptake rather than to the biological reduction of Cr(VI) to Cr(III) (Ksheminska et al., 2005). Gu et al. (2015), described a chromate reductase of *Aspergillus niger* located in the soluble fraction and Singh and Bishnoi (2015) showed

an enzymatic Cr(VI) reduction in *Aspergillus flavus* accompanied by a biosorption process. In this context, it is important to highlight the non-enzymatic reduction by amino acids, nucleotides, sugars, vitamins, organic acids, glutathione, and anaerobic metabolic end products of iron- and sulphate-reducing bacteria (Fe(II) and H₂S) (Dhal et al., 2013; Somasundaram et al., 2009). Organic acid citrate (fungal metabolites) and oxalate, also reduce Cr(VI) through the photocatalytic effect of Fe(III) or by Mn without light (Barrera-Díaz et al., 2012; Wrobel et al., 2015).

In an effort to generate a critical review about chromate removal mechanisms, Table 1 presents the biological mechanisms of chromate resistance in different genera of bacteria, fungi, and algae from articles, reviewing the information published the last years.

3. Scale up approach

The application of microorganisms in Cr(VI) removal processes have been studied in different systems using batch, fed-batch or continuous forms. The choice of the appropriate bioreactor should be associated with the different operational conditions required for Cr(VI) removal, such as, for example, hydrodynamics, mass transfer and growth conditions. This tool is versatile in its applications since the potential for growth and adaptation of microorganisms linked to modern biotechnology. In general, a bioreactor system is more efficient (greater bioremoval rate), manageable, predictable and easy to deal with the confined environment than *in situ* or in systems developed in solid phase.

The typical categories of systems used in this scope are:

3.1. Stirred tank reactors (STRs)

The design of this reactor is equipped with a stirrer and can work in batch or continuous modes and in some cases, it is possible to work feeding the tank until reach the volume of the reaction. The advantages of STRs are related to the simplicity and ease of repetition of the experiments but the operational costs are more elevated because of the energy used for the agitation (Hlihor et al., 2014; Roman et al., 1992). Such equipment is generally used for small quantities of industrial effluents and in situations where the biosorption is seasonal (Vendruscolo et al., 2017).

In a continuous mode, the Cr(VI) solution to be treated is fed in continuously. They allow studying the variations in the Cr(VI) concentration, adjust the hydraulic retention time (as a function of microbial growth velocity) and work in series with different reactors. The disadvantages are related to the loss of cell viability and contamination (Vendruscolo et al., 2017). Chromium biosorption studies using this mode of operation are very important to evaluate the technical feasibility of a real process with respect to effluent to be treated and after Cr(VI) removal.

Additionally, performances of various bioreactors under different operating conditions with respect to Cr(VI) reduction were evaluated. *Arthrobacter rhombi*, a Cr(VI) reducing strain enriched and isolated from chromium contaminated soil, was used in a continuous reactor using three different systems designed for Cr(VI) biotransformation: (i) aerobic suspended growth, (ii) aerobic attached growth, and (iii) anoxic attached growth. Aerobic suspended and anoxic attached growth systems performed worse compared to aerobic attached growth system reaching a 98% of Cr(VI) reduction efficiency using an aerobic attached growth system (Elangovan and Philip, 2009).

3.2. Fixed-bed reactors (FXRs)

The tendency for Cr(VI) biosorption points to the need to increase the working life of the biosorbent and evaluate Cr(VI)

desorption and recovery cycles. The biosorbent is placed in a fixed bed on a column through which passes the solution contaminated with the metal. Packed bed columns (PBCs) is the most used to perform biosorption studies. The biomass can be immobilized by entrapment, encapsulation, and bonding onto polymeric materials, textile fibers and inorganic compounds. The underline advantages are the use of large particles for biosorbents immobilization and the simplicity of construction and operation (Rosca et al., 2015). Several variants of this system were developed. For example, two-stage packed bed reactor to remedy an effluent of an electroplating industry was designed in anaerobic conditions (Chang and Kim, 2007). Ajao et al. (2011) developed an immobilized microbiological preparation on agar-agar comprising a mixed culture of bacteria (*Pseudomonas aeruginosa* and *Bacillus subtilis*) capable of removing toxic component of textile industrial effluent, including Cr(VI). Krishna and Philip (2005) developed a bioreactor for the detoxification of Cr(VI) using *Ganoderma lucidum* (a wood rooting fungus) as the adsorbent. The Cr(VI) reduced effectively in. More than 80% Cr(VI) reduction was observed for 50 mg/L of Cr(VI) concentration within 8 h. Moreover, adsorption column of immobilized bioreactor showed promising Cr(III) removal capacity and removed the unspent organic matter.

3.3. Fluidized-bed bioreactors (FBRs)

FBRs are based on the development of a microbial biofilm on solid particles that support microbial growth. Counterflow system through a column maintains the particles in continuous movement (fluidized state) and constantly migrating in the entire volume of the column. When the flow rate still increases, the bed converts into a so-called fluidized state. In this type of reactor, a biosorbent is placed inside a column and a solution with metals is supplied in the counter-flow system. This allows the retention of biomass inside the reactor and, therefore, operation at short hydraulic retention time (Rosca et al., 2015).

Chirwa and Wang (2001) reported biological Cr(VI) reduction in a continuous-flow laboratory-scale biofilm reactor without the intermittent addition of fresh biomass to the system. They were the first to demonstrate the potential of a fixed-film bioreactor for reduction of Cr(VI). In these reactors, electron donors were added to the wastewater depending upon the necessity (Elangovan and Philip, 2009). At an influent Cr(VI) concentration of 5 mg/L, the Cr(VI) reduction efficiency was nearly 100%. A comparative study on adsorption of Cr(VI) ions in different types of reactors, operated under identical conditions, indicated that the maximum removal efficiency was obtained for the stirred tank reactor, followed by the fluidized reactor and packed bed reactor when a chemically modified and polysulfone-immobilized biomass of the fungus *Rhizopus nigricans* was used (Bai and Abraham, 2005).

3.4. AirLift reactors (ALRs)

Airlift and bubble columns are pneumatically shaken bioreactors that impose low shear stress. Are the best option when the microorganism selected is a fungi because permit to save the problems associated with the multicellular filaments growth and the rheology of the broth. The design reduces the formation of pellets and allows the formation of dispersing hyphae and mycelium, which increases the surface contact area. ALRs are often employed in bioprocesses where gas-liquid contact is important and are considered as practical and sustainable alternatives to the stirred tank reactors (Choi et al., 2007; Cozma and Gavrilescu, 2010). The function of the aeration is to supply the demand for dissolved oxygen, as well as promoting the pneumatic mixture and the accompanying mass transfer. If needed, additional external

Table 1
Microorganisms and biological mechanisms for Cr(VI) resistance.

Microorganisms	Mechanisms for Cr(VI) resistance	Reference
Algae		
<i>Spirulina platensis</i>	Biosorption	Magro et al. (2013)
<i>Spirulina platensis</i>	Biosorption	Kwak et al. (2015)
<i>Spirulina</i> sp.	Biosorption	Rezaei (2013)
<i>Sargassum filipendula</i>	Biosorption	Bertagnolli and Silva (2013)
<i>Pelvetia canaliculata</i>	Biosorption	Hackbarth et al. (2016)
Bacteria		
<i>Escherichia coli</i>	Biotransformation	Robins et al. (2013)
<i>Escherichia coli</i>	Biosorption	Liu et al. (2015)
<i>Acinetobacter haemolyticus</i>	Biotransformation	Ahmad et al. (2013)
<i>Acinetobacter haemolyticus</i>	Biosorption	Yahya et al. (2012)
<i>Acinetobacter junii</i>	Biosorption	Paul et al. (2012)
<i>Pseudomonas putida</i> V1	Biosorption	Cabral et al. (2014)
<i>Streptomyces violaceoruber</i> strain LZ-26-1	Biotransformation	Chen et al. (2014)
<i>Streptomyces werraensis</i> LD22	Biosorption	Latha et al. (2015)
<i>Pantoea</i> sp.	Biosorption	Ontañón et al. (2014)
<i>Leucobacter</i> sp. G161	Biotransformation	Ge et al. (2014)
<i>Bacillus amyloliquefaciens</i>	Biosorption/Bioreduction	Rath et al. (2014)
<i>Bacillus methylotrophicus</i>	Biosorption/Bioreduction	Mala et al. (2015)
<i>Serratia</i> sp.	Biotransformation	Deng et al. (2015)
<i>Pseudomonas gessardii</i>	Biotransformation	Huang et al. (2016)
<i>Methanothermobacter thermautotrophicus</i>	Biotransformation	Singh et al. (2015)
<i>Ochrobactrum</i> sp.	Biotransformation	Hora and Shetty (2015)
<i>Bacillus subtilis</i>	Biotransformation	Zheng et al. (2015)
<i>Bacillus subtilis</i> SS-1	Biosorption	Sukumar et al. (2014)
<i>Bacillus cereus</i>	Biosorption	Naik et al. (2012)
<i>Bacillus cereus</i>	Biotransformation	Zhao et al. (2012)
<i>Arthrobacter viscosus</i>	Biotransformation/Biosorption	Silva et al. (2012)
<i>Arthrobacter</i> ps-5	Biosorption	Shuhong et al. (2014)
<i>Mesorhizobium amorphae</i>	Biosorption	Xie et al. (2013)
<i>Pediococcus acidilactici</i>	Biotransformation	Lytras et al. (2017)
Yeasts		
<i>Pichia anomala</i>	Biosorption	Joutey et al. (2015)
<i>Cyberlindnera fabianii</i>	Biosorption	Joutey et al. (2015)
<i>Wickerhamomyces anomalus</i>	Biosorption	Joutey et al. (2015)
<i>Candida tropicalis</i>	Biosorption	Bahafid et al. (2013a,b)
<i>Rhodotorula mucilaginosa</i>	Biotransformation	Chatterjee et al. (2012)
<i>Cyberlindnera jadinii</i>	Biotransformation	Fernández et al. (2013)
<i>Wickerhamomyces anomalus</i>	Biotransformation	Fernández et al. (2013)
<i>Pichia jadinii</i>	Biotransformation	Martorell et al. (2012)
<i>Pichia anomala</i>	Biotransformation	Martorell et al. (2012)
Filamentous fungi		
<i>Aspergillus</i> spp.	Biosorption	Sivakumar (2016)
<i>Aspergillus flavus</i>	Biosorption	Singh et al. (2016)
<i>Aspergillus niger</i> var <i>tubingensis</i> strain Ed8	Biosorption/Bioreduction	Coreño-Alonso et al. (2014)
<i>Aspergillus niger</i>	Biosorption	Samuel et al. (2015)
<i>Aspergillus niger</i>	Biotransformation	Gu et al. (2015)
<i>Aspergillus fumigatus</i>	Biosorption	Balaji and David (2016)
<i>Penicillium</i> sp.	Bioreduction	Arévalo-Rangel et al. (2013)
<i>Penicillium</i> sp.	Biosorption	Barsainya et al. (2016)
<i>Penicillium griseofulvum</i>	Biosorption	Abigail et al. (2015)
<i>Pleurotus ostreatus</i>	Biosorption	Carol et al. (2012)
<i>Trichoderma asperellum</i>	Biosorption	Chang et al. (2016)
<i>Hypocrea tawa</i>	Biotransformation	Morales-Barrera and Cristiani-Urbina (2015)
<i>Rhizopus arrhizus</i>	Biosorption	Shroff and Vaidya (2012)

liquid circulation is added to obtain the required mixing pattern. The main advantages of ALRs are: no moving parts, low power consumption, high heat and mass transfer, maintenance of solids in suspension, homogeneous shear, rapid mixing, increased oxygen solubility, high homogenization efficiency and low shear stress to cells, easy sterilization, low contamination risk (Cozma and Gavrilescu, 2010, 2011; Luo and Dahhan, 2007; Gavrilescu and Tudose, 1998). Numerous studies on treatment technologies based on biosorption, biofilm-mediated bioremediation, suspended microorganism processes highlighted the significant advantages of ALRs to remove different pollutants from contaminated fluid (wastewater and gaseous) streams (Nikakhtari and Hill, 2008; Vergara-Fernández et al., 2008). Morales-Barrera and Cristiani-Urbina (2006, 2015), pointed out that the microorganism

Trichoderma viride and *Hypocrea tawa* showed a high biosorption capacity when cultivated in an airlift and verified that shaking using a STR caused fragmentation of the mycelium with a negative effect on biosorption.

The Table 2 present different type of bioreactors used for chromium removal using bacteria or fungal strains and a brief description of the operational mode applied in the biotechnological processes.

4. Pilot scale studies

Generally, the results of the transfer from the laboratory to the industry are a relatively slow process and do not necessarily equate to those achieved under large-scale operating conditions. For that

Table 2
Comparison of different type of bioreactors used for chromium removal.

Type of Bioreactors	Characteristics	Operational Mode	Advantages	Disadvantages	Microorganism used	Reference
Stirred Tank Bioreactors (STRs)	Reactor equipped with a stirrer that maintains the biomass in suspension	Batch and continuous	The advantages are related to the simplicity and ease of repetition of the experiments. Simple operation in comparison with other systems	Operational costs elevated for energy required for agitation	<i>Trichoderma viride</i> <i>Pediococcus acidilactici</i> <i>Aspergillus niger</i> Consortium: <i>Cladosporium perangustum</i> , <i>Penicillium commune</i> , <i>Paecilomyces lilacinus</i> , <i>Fusarium equiseti</i> <i>Escherichia coli</i>	Morales-Barrera and Cristiani-Urbina (2006) Lytras et al. (2017) Sepehr et al. (2012) Sharma and Malaviya (2016)
Fixed-Bed Reactors (FXRs)	Immobilized bioreactor and typically employed for Cr(VI) Biosorption. The biosorbent is placed in a fixed bed on a column through which passes the solution contaminated with the metal.	Batch and continuous	The underlying advantages are the use of large particles for biosorbents immobilization and the simplicity of construction and operation. The use of immobilized biosorbents increases the working life of the biosorbent, allows for the promotion of variations in the hydraulic retention time, and principally allows for the possibility of Cr(VI) desorption and recovery cycles.	The regeneration of fixed bed is necessary when the maximal sorption capacity of the biosorbent is reached. Due to this, more than one columns is required for maintaining continuous working conditions.	Consortium (<i>A. junii</i> , <i>E. coli</i> , <i>B. subtilis</i>) Mixed culture (<i>Pseudomonas aeruginosa</i> and <i>Bacillus subtilis</i>) <i>Pseudomonas aeruginosa</i> A2Chr <i>Pseudomonas mendocina</i> <i>Bacillus</i> sp. ES39	Chakraborty et al. (2013) Samuel et al. (2013) Ajao et al. (2017) Ganguli and Tripathi (2002) Konovalova et al. (2003) Camargo et al. (2004)
Fluidized-Bed Bioreactors (FBRs)	Are based on the growth of a microbial biofilm on solid particles that support microbial growth. The bed is maintained in state of suspension by liquid contaminated effluent into the reactor (fluidized state).	Continuous	Operation continuous at short hydraulic retention time. The clogging is significantly reduced respect to FRXs	Losses of cell viability and microbial contamination.	Co-culture: <i>Pseudomonas putida</i> DMP-1, <i>Escherichia coli</i> ATCC 33456	Chirwa and Wang (2001)
Air Lift Reactors (ALRs)	Are pneumatically shaken bioreactors that impose low shear stress. ALRs is often employed in bioprocesses where gas-liquid contact is important. The air bubbles forced through the sparger are responsible for the induced turbulent liquid mixing and the accompanying mass transfer. If needed, additional external liquid circulation is added to obtain the required mixing pattern.	Batch and continuous	The main advantages of ALRs are: no moving parts, low power consumption, high heat and mass transfer, homogeneous shear, rapid mixing, increased oxygen solubility, high homogenization efficiency and low shear stress to cells, easy sterilization, and low contamination risk. In the cultivation of filamentous fungi, ALRs reduce the formation of pellets and allow for the formation of disperse hyphae and mycelium, which increases the surface contact area. Of the different types of airlifts, those consisting of concentric tubes are the most used.	ALRs are not recommended when the culture medium is viscous or contains dense solid particles.	<i>Trichoderma viride</i> <i>Hypocrea tawa</i> <i>Candida</i> sp. <i>Aspergillus niger</i>	Morales-Barrera and Cristiani-Urbina (2006) Morales-Barrera and Cristiani-Urbina (2015) Guillen-Jiménez et al. (2009) Sepehr et al. (2012)

reason, a very limited numbers of industrial processes in the heavy metal bioremediation area have been implemented. Thus, research for future technology transfer is focused on the evaluation of the feasibility of the development at higher scale and the robustness of the system (Ahluwalia, 2014).

In this perspective, treatment of Cr(VI)-containing waters using sulphate-reducing bacteria (SRB) in hydrogen-fed bioreactors at pilot scale has been reported by Battablia-Brunet et al. (2006). A 200 dm³ pilot bioreactor was designed using fixed bed column filled with pozzolana and inoculated with *Desulfomicrobium*

norvegicum (Battaglia-Brunet et al., 2006). At Cr(VI) initial concentration of 15 mg/L a 100% removal Cr(VI) was achieved during the first 18 d. Further, Barros et al. (2007) observed the average removal percentage of chromium from the reactor inoculated with municipal wastewater sludge. An average removal percentage of 99.9% was obtained, varying from 100 to 99.3% at pilot scale during the first 30 d at 10 mg/L initial concentration. Similarly, the results obtained by Quintelas et al. (2009) using biofilm of *Arthrobacter viscosus* supported on granular activated carbon (GAC) at the pilot-scale reactor were very promising for environmental applications. Data obtained showed an average of Cr(VI) removal of 99.9 and 72%, during the first 30 d, for the initial Cr(VI) concentration of 10 mg/L and 100 mg/L, respectively. Uptake values of 11.35 mg/g and 14.55 mg/g were obtained, respectively, for the initial concentration of 10 and 100 mg/L. The volume of chromium solution treated was of 8140 L for the assay with the initial concentration of 10 mg/L and 3732 L for the more concentrated solution. Rehman et al. (2009) reported the removal of chromium through biological mechanisms in dual stage process. The first stage was growth using plastic media for the formation of biofilm and the second one suspended growth process, operated under aerobic conditions. The enzymatic reduction of Cr(VI) to Cr(III) by chromium resistant bacteria, *Acinetobacter haemolyticus*, demonstrated a good decontamination system when was immobilized onto carrier material inside a bioreactor (200 L). The system constitutes the ChromeBac™ methodology. For this volume, a cheap and available industrial waste (liquid pineapple wastewater) was used as a nutrient to replace an expensive growth medium (Ahmad et al., 2010). According to this, bioremediation process at big scale must involve the study of many biochemical and physical parameters, including media formulation and culture parameters (Fernández et al., 2016).

In other publications, pilot scale studies were carried using bio-barrier employing chromium reducing bacteria (Jeyasingh et al., 2012). Results showed that a 10 cm thick bio-barrier with a concentration of 0.44 mg of initial biomass per g of soil was able to completely contain a Cr(VI) plume of 50 mg/L concentration. A mathematical model was proposed for simulating the bioremediation process and predicts the overall trends observed in the experiments, it is limited by the assumption of homogeneous conditions. Bio-barrier system was able to contain Cr(VI) plumes even for the case of high Cr(VI) concentrations, when appropriate conditions such as inoculum concentration, the thickness of barrier, injection wells number, and enough flow velocity were maintained (Jeyasingh et al., 2012).

Study presented in Williams et al. (2014) provide the basis for a low-cost, and low-maintenance strategy for the biological treatment of Cr(VI)-contaminated aquatic environment. Fixed-film pilot bioreactor was designed using a microbial community (including *Enterobacter cloacae*, *Flavobacterium* sp. and *Ralstonia* sp.) for chromium reduction. This represents the first up-scaled (24,000 L), effective demonstration an effective biological Cr(VI) bioremediation system in South Africa, resulting in maintaining the reduction of Cr(VI) (>99%).

Another strategy is the slurry-phase bioremediation. This *ex situ* system is a controlled treatment of soil in a bioreactor (Kulshreshtha et al., 2014).

Continuous-flow and fixed-film bioreactor offer the most reliable mode of application to be used at industrial scale due to its easiness of handling and simple operation (Ahmad et al., 2010). The technique using fixed-film bioreactors for Cr(VI) reduction was first reported by Chirwa and Wang (1997) where a laboratory-scale biofilm reactor at continuous-flow was effective to reduce Cr(VI) without the need to constantly supply fresh biomass (Ahmad et al., 2010).

5. Future perspectives with potential applications in chromium removal

The exposure to heavy metals represents a stress condition; the greater capacity of some strains towards metal tolerance may be attributed to their ability to survive under extreme environments since the expression of some genes could be involved in mechanisms battling against both stress factors (Fernández et al., 2017). Recently, bacteria and fungi have been used in transcriptomic and/or proteomic studies on their response to Cr(VI). The development of efficient biological processes (accompanied by a global analysis of macromolecules) offers numerous opportunities in the treatment of environmental heavy metal pollution. Mostly, results related to the central metabolism and energy production and conversion, as well as effects on different transporters and DNA metabolism and repair were obtained (Viti et al., 2014). In yeasts, about 22% of the genome was affected by exposure to chromium. Two arrays of metal-responsive genomic profiles were generated after exposure; one associated with metal exposure (that provides information on the transcriptional changes), and another one that offers info on the association between the expression of non-essential genes and sensitivity to metal exposure (deletome) (Jin et al., 2008).

Studies applying genetic engineering have been performed with recombinant microorganisms. Robins et al. (2013) performed a fusion of the *E. coli* *nemA* gene and the polyhydroxyalkanoate synthase gene *phaC* from *Ralstonia eutropha* to developed a system based on a stable and active chromate reductase immobilized on polyhydroxyalkanoate granules. In the same sense, was obtained a microorganism that overexpresses a mutant enzyme termed ChrR6 that showed 200-fold greater chromate-reducing activity than wild-type. Is important continue developing this technique because representing a promising approach and economic solution for *ex situ* Cr(VI) remediation.

In contrast, some recent studies have focused on the use of microbial consortia highlighting the metabolically superiority for removing metals and suitability for field applications (Joutey et al., 2015; Qian et al., 2016). A consortium of *Acinetobacter junii*, *Escherichia coli* and *Bacillus subtilis* incubated in a continuous packed bed reactor improved the removal of Cr(VI) by absorption, showing 55–65% efficiency at a Cr(VI) concentration of 100 mg/L (Samuel et al., 2013). In relation to this, bioaugmentation is one of the auspicious techniques of bioremediation; it is referring to the process of adding well-adapted microorganism strains or microbial consortia to the site to be decontaminated (Herrero and Stuckey, 2015). From an application viewpoint, the bioaugmentation using microbial consortia provides diverse metabolic pathways and robustness required for a higher-scale application (He et al., 2014); and it represents an economical and environmental friendly remediation way.

The application of immobilized microbial cells and enzymes combined with nanotechnology (e.g. carbon nanotubes impregnated into calcium alginate beads) markedly enhanced the stability of the enzyme and the reduction of Cr(VI). Another process related to remediation of sites contaminated with Cr at the nanometer scale is applying metal-reducing bacteria in combination with nano-materials (siderite) which act as electron donors in the enzymatic Cr(VI) reduction and immobilization (Cr(III)-containing precipitates) (Gutiérrez-Corona et al., 2016; Seo and Roh, 2015).

6. Concluding remarks

Diverse industrials and anthropogenic activities contaminates the environment. Cr(VI) and Cr(III) may present different behaviors; the high mobility and solubility of Cr(VI) increases the chances

for its diffusion through cell membrane which makes it a carcinogen, teratogen and mutagen. Cr(III) is no toxic and relatively insoluble in aqueous systems. The application of an eco-friendly, versatile, and low-cost tool is necessary to remove this heavy metal from water, soil and, sediments. Bioremediation offers a method based on the heavy metals removal mechanisms used by microorganisms (biosorption, bioaccumulation, and biotransformation). Among them, biosorption process has shown success in their results to the technological advances. As is clear, the biological Cr(VI) detoxification has been tested in a number of systems. It can be carried out in batch, fed-batch or continuous form according to the different operational conditions, to ensure ideal hydrodynamic, mass transfer and growing settings. So, by expanding the knowledge of genetics and dedicate experimental sites which are set aside for transfer bioremediation technology, these prospects offer potential for substantial advances; but yet a wide-ranging research have to made in this field to solve the problems associated to the large-scale remediation process.

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