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Review

A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction

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ABSTRACT

Hexavalent chromium is of particular environmental concern due to its toxicity and mobility and is challenging to remove from industrial wastewater. It is a strong oxidizing agent that is carcinogenic and mutagenic and diffuses quickly through soil and aquatic environments. It does not form insoluble compounds in aqueous solutions, so separation by precipitation is not feasible. While Cr(VI) oxyanions are very mobile and toxic in the environment, Cr(III) cations are not. Like many metal cations, Cr(III) forms insoluble precipitates. Thus, reducing Cr(VI) to Cr(III) simplifies its removal from effluent and also reduces its toxicity and mobility. In this review, we describe the environmental implications of Cr(VI) presence in aqueous solutions, the chemical species that could be present and then we describe the technologies available to efficiently reduce hexavalent chromium.

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1. Environmental significance

The growth in civilization and industrial activities has caused a number of environmental problems. For decades, large quantities of pollutants have been discharged into the environment irresponsibly. In the US the superfund law was originally supposed to be used for the cleanup of abandoned hazardous waste sites and the Environmental Protection Agency (EPA) [1] began using the law to force companies to pay for contaminated sites. Nowadays, many of the sites on the current National Priority List of Superfund sites are just contaminated industrial areas. A major problem with this law has always been getting these supposedly dangerous waste sites cleaned up in a reasonable time. The Brown & Bryant case is a classic example. First investigated as a contamination problem in 1983, it was put on the Superfund list in 1989. It was not until 1996 that the lawsuit was brought. A judgment was not made on this case until 20 years after the problem was found [2].

Unlike most organic pollutants, metals are particularly problematic because they are not biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. Although at low doses some heavy metals are essential micronutrients for plants and animals, in higher doses they can detrimentally affect the health of most living organisms [3–5].

Chromium generally exists in water with two stable oxidation states: hexavalent [Cr(VI)] and trivalent [Cr(III)]. Cr(VI) species are known to be toxic and carcinogenic, causing health problems such as liver damage, pulmonary congestions, vomiting, and severe diarrhea, whereas Cr(III) is less toxic and can be readily precipitated out of solution in the form of $Cr(OH)_3$ [6,7]. Due to this, governments apply enhanced regulation for chromium species. Worldwide authorities have fixed more stringent requirements concerning their presence in drinking water (Table 1). Fortunately, the remarkable growth in economics and living standard has accelerated the development of water and wastewater purification technologies.

There is now extensive scientific literature on the treatment of highly toxic Cr(VI) species in industrial wastewater. Fig. 1 summarizes the evolution of published research concerning Cr(VI) treatment reported in the world's journal and patent literature over the latest ten years (data extracted from Sciverse).

Table 1
Revised international regulation criteria.

Country	Cr total in drinking water ($mg\,L^{-1}$)	Reference
US	0.1	U.S EPA [1]
Canada	0.05	HC [8]
International	0.05	WHO [9]
Mexico	0.05	NOM-127-SSA1-1994 [10]

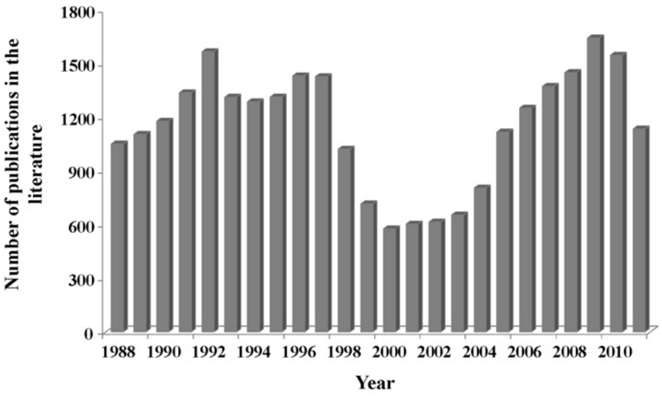

Fig. 1. Evolution of published work concerning Cr(VI) reduction since 1988. Source: Sciverse.

2. Chromium Cr(VI) and Cr(III) species in aqueous solution

The most probable Cr(VI) species in aqueous solution are $Cr_2O_7^{2-}$, CrO_4^{2-}, H_2CrO_4, and $HCrO_4^-$, the relative distribution of which depends on the solution pH, on the Cr(VI) concentration and on the redox potential [11]. However, none of these Cr(VI) species form insoluble precipitates making separation through a direct precipitation method not feasible [12]. The theoretical distribution of the predominant chemical species of Cr(VI) is presented in Fig. 2a and b; the Cr(VI) species show both pH and redox potential dependence.

It should be pointed out from the Pourbaix and predominance zone diagrams above that Cr(VI) does not exhibit any insoluble species in spite of pH variations. In this oxidation state, the metal is extremely mobile in water and soil. On the other hand, the trivalent state of Cr does form insoluble species within the pH range shown in Fig. 3.

Thus, to form a chromium solid phase, which can be easily separated from the aqueous media, it is necessary to change the oxidation state.

3. Traditional Cr(VI) reduction treatments

3.1. Sulfur compounds

For the treatment of chromate-containing rinse water the typical procedure is reduction of hexavalent chromium to the trivalent state, followed by its precipitation as Cr(III) hydroxide. The most common industrial reducing agents are sulfur dioxide gas or sodium bisulfite in an acid solution. Both of these reactants form the same active reducing agent, sulfurous acid, as shown in reactions 1 and 2.

$$SO_{2(g)} + H_2O \rightarrow H_2SO_{3(aq)} \quad (1)$$

$$NaHSO_{3(aq)} + H^+{}_{(aq)} \rightarrow H_2SO_{3(aq)} + Na^+{}_{(aq)} \quad (2)$$

The theoretical requirement is 3 kg of sodium bisulfite plus 2–3 kg of sulfuric acid, to reduce 1 kg of hexavalent chromium. Reaction (3) takes place almost instantaneously at a pH of 2.5.

$$4CrO_4{}^{2-}{}_{(aq)} + 6NaHSO_{3(aq)} + 3H_2SO_{4(aq)} + 8H^+{}_{(aq)} \rightarrow 2Cr_2(SO_4)_{3(aq)} + 3Na_2SO_{4(aq)} + 10H_2O \quad (3)$$

Subsequent treatment with sodium hydroxide precipitates the chromium(III) as indicated in reaction (4).

$$Cr_2(SO_4)_{3(aq)} + 6NaOH_{(aq)} \rightarrow 2Cr(OH)_{3(s)} + 3Na_2SO_{4(aq)} \quad (4)$$

Since chromium(III) hydroxide is precipitated, the resulting effluent will contain little or no residual chromium.

The sulfur dioxide reacts as follows:

$$2CrO_4{}^{2-}{}_{(aq)} + 3SO_{2(g)} + 4H^+{}_{(aq)} \rightarrow Cr_2(SO_4)_{3(aq)} + 2H_2O \quad (5)$$

Following reduction the effluent is treated with sodium hydroxide solution or calcium hydroxide slurry to neutralize the acidity and precipitate the chromium. Where sludge formation must be reduced to an absolute minimum, the use of sodium hydroxide solution is advised [13].

One of the main problems using this technique is that large amounts of residual sludge are generated. The sludge presents difficulties in managing, transporting and final disposal issues as well as the associated cost. Thus, new technologies are being developed to address these problems.

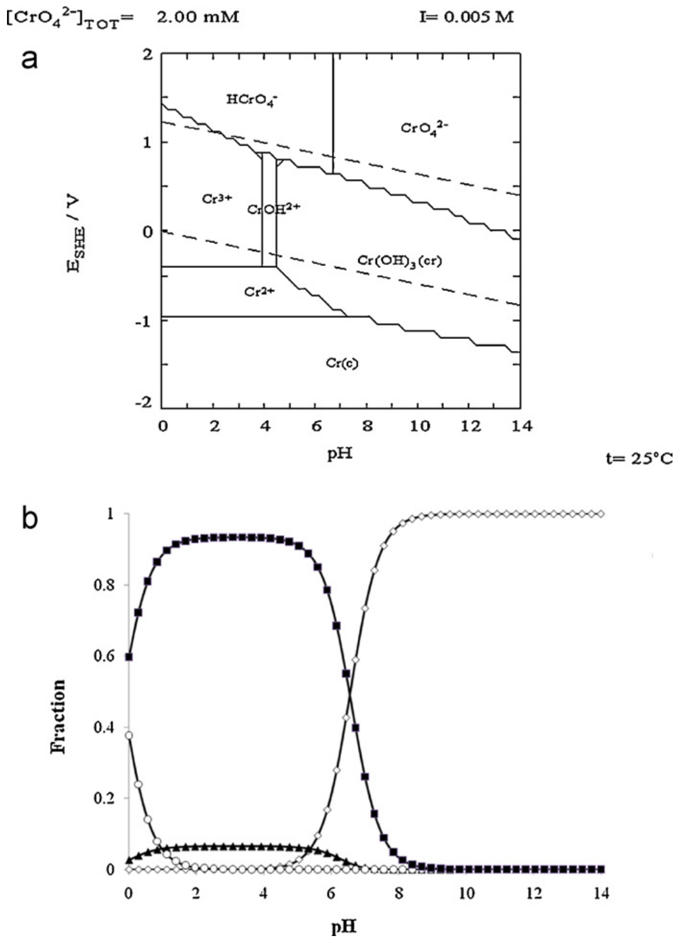

Fig. 2. (a) Pourbaix diagram for Cr chemical species in aqueous solution. $[CrO_4^{2-}] = 2.00$ mM, I = 0.005 M and $T = 25\,^{\circ}C$. (b) Predominance zone diagram for Cr(VI) chemical species in aqueous solution. (◊) CrO_4^{2-}, (▲) $Cr_2O_7^{2-}$, (○) H_2CrO_4 and (■) $HCrO_4^-$.

3.2. *Iron salts*

When iron is used as a Cr(VI) reducing agent, the reaction usually takes place under acidic conditions. At low pH values, Fe(II and III) appear as free ions in aqueous solution. Iron(II) chloride and iron(II) sulfate are commonly used for the reduction of hexavalent chromium to the trivalent state for subsequent precipitation [14].

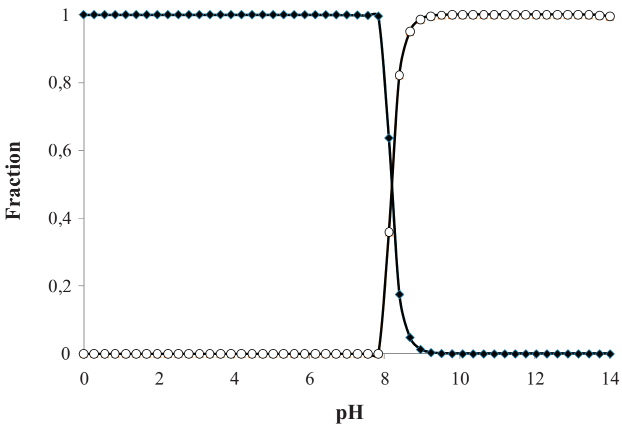

Fig. 4. Predominance zone diagram for Fe(II) chemical species in aqueous solution. (♦) Fe^{2+}, (○) $Fe(OH)_{2(s)}$.

$$6Fe^{2+}{}_{(aq)} + Cr_2O_7{}^{-2}{}_{(aq)} + 14H^+{}_{(aq)} \rightarrow\ 6Fe^{3+}{}_{(aq)} + 2Cr^{3+}{}_{(aq)} + 7H_2O \tag{6}$$

$$Cr^{3+}{}_{(aq)} + OH^-{}_{(aq)} \rightarrow\ Cr(OH)_{3(s)} \tag{7}$$

Fe(II) is present in aqueous solution as a free ion up to a pH of 4.7, as shown in Fig. 4. However, Fe(III) ions requires more acidic conditions to remain in solution, as shown in Fig. 5.

In many papers, experiments show that better the reduction rates are achieved at low pH values [15–18]. This is possibly due to charge distribution and spatial configuration changes as hydrocomplexes begin to appear in the system. This agrees with recent reports in which the reduction kinetics of Cr(VI) to Cr(III) seems to be slow at pH 3.7, in some cases remaining stable months or even years. Values of pH less than 3 are needed to accelerate the reduction reaction in aqueous solution [14].

Current methods of treating Cr(VI) are by chemical reduction to Cr(III) under acidic conditions followed by precipitation with alkali. The reducing agents are usually ferrous sulfate or sodium sulfite. However, these reduction methods have their respective shortcomings. When ferrous sulfate is used as the reducing agent, ferric hydroxide is produced as a solid waste, which requires subsequent disposal. With sodium sulfite as the reducing agent, sulfur dioxide is formed in acidic conditions, which may cause air pollution as sulfur dioxide is toxic, odorous, and volatile. Furthermore, both the sodium sulfite and ferrous sulfate are not suitable for

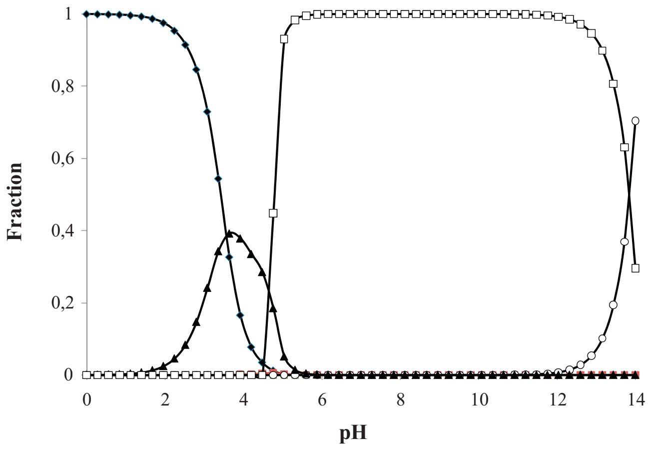

Fig. 3. Predominance zone diagram for Cr(III) chemical species in aqueous solution. (♦) Cr^{3+}, (□) $Cr(OH)_{3(s)}$, (▲) $Cr(OH)_2{}^+$, and (○) $Cr(OH)_4{}^-$.

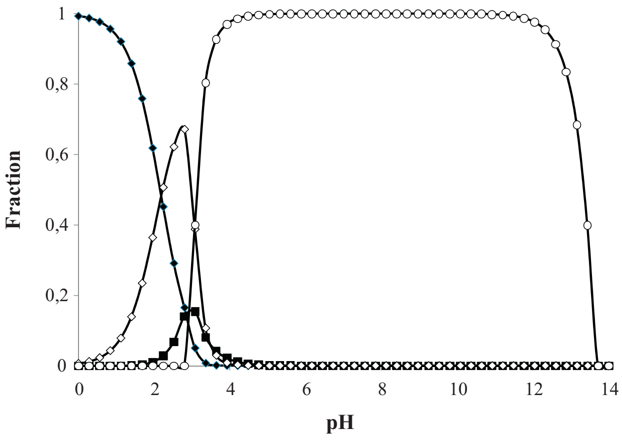

Fig. 5. Predominance zone diagram for Fe(III) chemical species in aqueous solution. (♦) Fe^{3+}, (○) $Fe(OH)_{3(s)}$, (◊) $Fe(OH)_2{}^+$ (■) $Fe(OH)^{2+}$.

treating dilute Cr(VI) solution as excessive chemicals are often required [14].

4. Electrochemical methods

The use of electrochemical methods represents an interesting option as many electrochemical and chemical reactions occur simultaneously when they are applied. Electrochemical treatment techniques have attracted a great deal of attention because of their versatility and environmental compatibility, which makes the treatments of liquids, gases, and solids possible. In fact, the main reagent is the electron, which is a "clean reagent" [19].

Electrochemical Cr(VI) reduction methods can been used in many ways, depending on the pH of the aqueous solution, the intensity of the current density, and the electrode material employed. In this sense many simultaneous processes could take place on the electrode surface or in the aqueous solution.

4.1. Electrocoagulation

Electrocoagulation is the electrochemical production of destabilization agents that neutralize the electric charge of the pollutants present in solution. An electrocoagulation reactor consists of a reservoir in which the solution is contained and two electrodes: a cathode and an anode. An external source provides the energy required for dissolution of the anode called a sacrificial electrode, which is usually aluminum or iron [20]. Hydrogen gas is released from the cathode surface and helps to float the flocculated particles to the surface in a process called electrofloculation [21].

4.1.1. Iron electrodes

The electrocoagulation process using iron electrodes involves the liberation of Fe(II) ions into the solution due to the anodic polarization of a plain carbon steel electrode [22]. When the pH of the solution is between 6 and 8 Fe(II) ions form insoluble species onto which Cr(VI) ions are adsorbed and removed from the solution. The reactions involved during the electrocoagulation using Fe electrode are [23]:

Anodic reaction:

$$Fe_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + 2e^- \tag{8}$$

Cathodic reaction:

$$2H_2O + 2e^- \rightarrow 2OH^-{}_{(aq)} + H_{2(g)} \tag{9}$$

Overall reactions in bulk solution

$$Cr_2O_7{}^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6Fe^{2+}{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 6Fe^{3+}{}_{(aq)} + 7H_2O \tag{10}$$

$$Cr^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Cr(OH)_{3(s)} \tag{11}$$

Iron systems show a high efficiency (>90%) and studies evaluate mainly the interactions of pH, applied electric current, and application time on the Cr(VI) removal. The removal of hexavalent chromium by electrocoagulation involves two stages: the reduction of Cr(VI) to Cr(III) at the cathode or by the Fe^{2+} ions generated from the oxidation of the iron anode and the subsequent co-precipitation of the Fe^{3+}/Cr^{3+} hydroxides. At low pH values, the reduction of Cr(VI) to Cr(III) by Fe^{2+} ions is favored, but under these pH conditions there is no precipitation of Fe(III)/Cr(III) hydroxides. The precipitation of Fe^{3+}/Cr^{3+} hydroxides takes place at pH higher than 3 due the solubility of metal hydroxide species (both chromic and iron hydroxides) at the low pH [24].

Two different removal mechanisms of Cr(VI) with iron electrodes at high and low currents are proposed. At high currents Cr(VI) is reduced directly at the cathode and precipitated afterwards as $Cr(OH)_3$. At low currents the Cr(VI) removal works by reduction by Fe^{2+} from the electrodes according to Faraday's law and the dissolved amount is two orders of magnitude higher than that at high currents [25]. The amount of sludge produced under the optimized conditions is lower than the amount generated by chemical treatment with $FeSO_4 \cdot 7H_2O$ [26].

4.1.2. Aluminum electrodes

Aluminum anodes are used to produce aluminum cations which form hydroxylated species. The pollutants present in aqueous solution are destabilized and then adsorbed on the $Al(OH)_{3(s)}$ produced. Reactions involved during the electrocoagulation using Al electrode are shown in reactions 12 and 13 [14,27].

Anodic reaction:

$$Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^- \tag{12}$$

Cathodic reaction:

$$3H_2O + 3e^- \rightarrow 3OH^-{}_{(aq)} + 3/2H_{2(g)} \tag{13}$$

Overall reaction in bulk solution:

$$Al^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Al(OH)_{3(s)} + 3/2H_{2(g)} \tag{14}$$

The electrocoagulation process using Al electrodes does not seem to be very attractive for the removal of Cr(VI) from wastewater. Although one study reported that a maximum of 91.5% Cr(VI) was removed [28], there are still disadvantages compared to iron electrodes, only about 11.5% Cr(VI) is removed. Higher aluminum coagulant dosing leads to higher Cr(VI) removal but it adversely affects the treatment efficiency as more aluminum coagulant is required per unit of pollutant removal [29]. A comparison of aluminum electrodes with the popular iron electrodes for Cr(VI) electrocoagulation, indicate that iron electrodes are better than aluminum ones [30,31]. Mouedhen et al. [32] found that unlike iron, aluminum electrodes were unsatisfactory for Cr(VI) removal and proposed that at nearly neutral pH both electrochemical reduction (Cr(VI) to Cr(III)) at the cathode surface and adsorption on $Al(OH)_3$ floc mechanisms were responsible for Cr(VI) exhaustion. The authors explain that the electrodissolution of the Al anode and the "chemical" attack on the Al cathode generate a great amount of amphoteric $Al(OH)_3$. The hydrogen evolution at the cathode induces a significant increase of the local pH at the cathode vicinity (see reaction 13), so the cationic hydrolysis products of Al (produced by chemical attack of the material) may react with OH^- ions and transform in the bulk solution into amphoteric $[Al(OH)_4]^-$ as is shown by reactions 15 and 16.

$$2Al_{(s)} + 6H_2O + 2OH^-{}_{(aq)} \rightarrow 2[Al(OH)_4]^-{}_{(aq)} + 3H_{2(g)} \tag{15}$$

$$[Al(OH)_4]^-{}_{(aq)} \rightarrow Al(OH)_{3(aq)} + OH^-{}_{(aq)} \tag{16}$$

Then, the negatively charged chromate ions should adsorb on the positively charged aluminum hydroxide precipitates minimizing the electrical repulsion between the colloidal hydroxide particles favoring large aggregate formation (charge neutralization).

Moreover, chromate ions might be somehow incorporated into the growing $Al(OH)_3$ precipitates (sweep flocculation) and thereby removed from the solution. In this study, qualitative chemical analysis conducted on the pre-washed precipitation sludge obtained with Al/Al electrodes revealed the presence of a significant amount of Cr(VI). Hence, it is more likely that adsorption process had a crucial role on chromium removal when using aluminum electrodes [32]. A summary of the efficiencies of Cr(VI) removal is presented in Table 2.

Table 2
Electrocoagulation for Cr(VI) reduction.

Electrode materials	Current/voltage/current density	Flow rates/reactor capacity	Treatment efficiency	Reactor type and connection	Reference
Iron electrodes					
Iron-stainless steel (316)	0.5 A	1000 mL	100%	Batch monopolar	[24]
Iron steel	0.5–0.2 A and 1–3 A	1200 mL	100%	Batch bipolar	[25]
Stainless steel (316)	3.5–6.5 A	1800 mL	>90%	Batch connection unspecified	[26]
Steel rods	10–62 A cm^{-2}	2000 mL	≈100%	Batch monopolar	[33]
Aluminum electrodes					
Aluminium plates	0–10 A, 10–24 V	540 mL	91.5%	Batch monopolar	[28]
Fe–Al	50–200 A m^{-2}	200 mL	100%	Semibatch monopolar	[30]
Fe/Al Stainless steel (304)	50 A m^{-2}	500 mL	39–99%	Batch monopolar	[31]
Fe–Fe, Al–Al, Pt/Ti/Fe, Pt/Ti/Al	1 A m^{-2}	900 mL	<0.5 mg L^{-1}	Batch monopolar	[32]

4.2. Electrodissolution of iron at low pH values

The main difference between electrocoagulation and electrodissolution is the pH of the solution. In mildly acidic conditions, electrocoagulation destabilizes electrical charged particles in the aqueous solution to simulate coagulation and sedimentation. Under strongly acidic conditions, electrodissolution involves ionization of iron which reacts directly with the Cr(VI) in the solution reducing it from Cr(VI) to Cr(III) [34,35].

The electrochemical reduction of Cr(VI) by electrodissolution of iron electrodes involves the liberation of Fe(II) ions into the solution by oxidation of a plain carbon steel electrode (reaction 17). These Fe(II) ions act as reducing agents on the Cr(VI) in the bulk solution. This reaction is more favourable at low pH values in the bulk solution (reaction 22). At the cathode, the polarization of the electrode involves simultaneously hydrogen evolution (reaction 18) and reduction of water (reaction 19). Additional cathodic reactions have being postulated, among these, iron reduction (reaction 20) and direct Cr(VI) electrochemical reduction (reaction 21) are indeed relevant as both bear the potential for exerting further reduction, thus aiding the overall process. However, it is important to draw attention to reaction 21, as it focuses predominantly on the ancillary reduction contribution to remove the pollutant singled out for elimination. The Cr(VI) removal process involves reactions (17–22).

Anodic reaction:

$$\mathrm{Fe_{(s)}} \rightarrow \mathrm{Fe^{2+}{}_{(aq)}} + 2e^- \tag{17}$$

Cathodic reactions:

$$2\mathrm{H^+{}_{(aq)}} + 2e^- \rightarrow \mathrm{H_{2(g)}} \tag{18}$$

$$2\mathrm{H_2O} + 2e^- \rightarrow \mathrm{H_{2(g)}} + 2\mathrm{OH^-{}_{(aq)}} \tag{19}$$

$$\mathrm{Fe^{3+}{}_{(aq)}} + e^- \rightarrow \mathrm{Fe^{2+}{}_{(aq)}} \tag{20}$$

$$\mathrm{HCrO_4{}^-{}_{(aq)}} + 7\mathrm{H^+{}_{(aq)}} + 3e^- \rightarrow \mathrm{Cr^{3+}{}_{(aq)}} + 4\mathrm{H_2O} \tag{21}$$

Bulk solution:

$$3\mathrm{Fe^{2+}{}_{(aq)}} + \mathrm{HCrO_4{}^-{}_{(aq)}} + 7\mathrm{H^+{}_{(aq)}} \leftrightarrow 3\mathrm{Fe^{3+}{}_{(aq)}} + \mathrm{Cr^{3+}{}_{(aq)}} + 4\mathrm{H_2O} \tag{22}$$

When iron electrodes are used to remove Cr(VI) from wastewater, pH is a very important parameter which affects the solubility of the Fe(III) [36]. Table 3 shows the results of the electrodissolution process.

4.3. Other electrodes

4.3.1. Carbon and graphite

Graphite, carbon, and carbon felt have been reported for chromium treatment [38–40] as an interesting alternative for the current electrochemical techniques. The advantages of carbon are its high surface-to-volume ratio, minimal reactivity over a wide range of process conditions, low cost, and ease of handling. Reticulated vitreous carbon (RVC) electrodes for direct Cr(VI) reduction are affected by the applied potential, pH, initial Cr(VI) concentration, electrode porosity, and electrolyte flow rate. The reduction of Cr(VI) to Cr(III) in both synthetic and field samples is virtually 100% accomplished by the application of relatively small potentials to RVC electrodes in a parallel-plate flow-by reactor [41].

4.3.2. Conducting polymers

As an alternative to the classic RVC Cr(VI) reduction electrodes, conducting polymers have been exploited as a spontaneous electron donor. Polyaniline (PANI) has been studied and shown to be the one most suitable conducting polymers with the fastest reaction rate and high stability throughout the closed circuit process. Reactions 23 and 24 are involved in Cr(VI) electroreduction [42–44].

$$\mathrm{Cr_2O_7{}^{2-}{}_{(aq)}} + 14\mathrm{H^+{}_{(aq)}} + 6e^- \rightarrow 2\mathrm{Cr^{3+}{}_{(aq)}} + 7\mathrm{H_2O} \tag{23}$$

$$\mathrm{CrO_4{}^{2-}{}_{(aq)}} + 4\mathrm{H_2O} + 3e^- \rightarrow \mathrm{Cr^{3+}{}_{(aq)}} + 8\mathrm{OH^-{}_{(aq)}} \tag{24}$$

The pH critically affects the Cr(VI) reduction and the reaction rate when RVC and RVC/PANI electrodes are used. While the maximum reaction rate using the RVC was found at pH 1.5, the RVC/PANI showed no difference in reaction rates in the range of pH between 0 and 1. Practically no reaction was observed for pH greater than 3. An increase in the applied current increases the reaction rate, but as the current efficiency decreases the energy consumption increases. The best conditions for the Cr(VI) reduction were found using RVC/PANI electrodes [43].

In order to maintain high values of current efficiency and yield during the electrochemical reduction of Cr(VI) to Cr(III), a new methodology based on control of the applied current throughout the process was tested by Routolo and Gubulin [44]. The results demonstrate that optimizing the hydrodynamic conditions and current control based on the transition concentration was proven to be a feasible and simple methodology that can be used to obtain high yields and low energy consumption down to very low Cr(VI) concentrations.

4.3.3. Copper

Copper has been proposed as an alternative electrode material for the electrochemical reduction of hexavalent chromium and presents interesting properties like high current efficiency and reaction control by mass transfer.

$$2\mathrm{HCrO_4{}^-{}_{(aq)}} + 3\mathrm{Cu_{(s)}} + 14\mathrm{H^+{}_{(aq)}} \rightarrow 2\mathrm{Cr^{3+}{}_{(aq)}} + 3\mathrm{Cu^{2+}{}_{(aq)}} + 8\mathrm{H_2O} \tag{25}$$

However to determine whether the copper electroreduction of Cr(VI) is advantageous over chemical reduction, a comparative analysis of the operating cost of both processes was done. The copper electroreduction of Cr(VI) to Cr(III) was done in a parallel-plate reactor and the chemical reduction was done with $Na_2S_2O_5$. It was

Table 3
Electrodissolution methods for Cr(VI) reduction.

Electrode materials	Current/voltage/current density	Flow rates/reactor capacity	Treatment efficiency	Reactor type and connection	Reference
Iron steel rings	$190–220\,A\,m^{-2}$ $190–350\,A\,m^{-2}$	170 L $3.0\,L\,min^{-1}$	$0.5\,mg\,L^{-1}$ $R1 = 203\,mg\,L^{-1}$ $R2 = 15.24\,mg\,L^{-1}$ $R3 = < 0.5\,mg\,L^{-1}$	Batch monopolar Continuous monopolar	[36]
Carbon steel	–	2.289 L	$0.5\,mg\,L^{-1}$	Continuous monopolar	[37]
Scrap iron	No current	300 mL	Not specified	Batch	[16]
Scrap iron	No current	$0.3\,L\,h^{-1}$	Not specified	Continuous	[17]

determined that the cost of the direct electroreduction process is about 7 times higher than the chemical method, if carried out at optimum operating conditions at pH 1.5. The costs of the two processes are closer when the electrochemical method is carried out at pH 2, but operating time is increased threefold, thereby increasing the cost [45]. Table 4 indicates the conditions reported when different electrodes are used in the Cr(VI) reduction.

5. Cr(VI) photocatalytic reduction

Photocatalysis on semiconductors involves three main steps: (i) absorption of photons with higher energies than the semiconductor bandgap, leading to the generation of electron (e^-)–hole (h^+) pairs in the semiconductor; (ii) charge separation followed by migration of these photo-generated carriers in the semiconductor; (iii) surface chemical reactions between these carriers with various compounds; electrons and holes may also recombine with each other without participating in any chemical reactions. Another class of non-oxide semiconductor photocatalyst is homogeneous sensitizer molecules, such as organic dyes and metal complexes. A strategy for achieving effective visible light harvesting is spectral sensitization of wide bandgap semiconductors (e.g., TiO_2) using sensitizer molecules [46]. Great attention is paid to chromium complexes for which photoreactivity in natural systems is of crucial environmental importance. The metal center is photoreduced by organic matter under solar irradiation and then oxidized by molecular oxygen. The photoreduction is accompanied by simultaneous oxidation of organic matter, which plays the role of ligand and/or sacrificial electron donor. Under favorable conditions complete photodegradation of organic pollutants can be achieved [47].

5.1. Organic matter for Cr(VI) reduction

Environmentally ubiquitous, naturally occurring reductants (quinones, organo-sulfur compounds and amorphous dissolved organic matter (DOM)) exhibit very slow-yet-measurable Cr(VI) reduction kinetics under predominantly acidic conditions. In contrast to these organic reductants, zerovalent iron, aqueous Fe(II), Fe(II) hydroxides, adsorbed Fe(II), and Fe(II)-chelates have been shown to reduce Cr(VI) very rapidly [48]. Fe(II)–DOM complexes exhibit enhanced rates of Cr(VI) reduction due to the addition of Fe(III) to humic acid solutions. This enhanced behavior is hypothesized to be due to some unknown reductant in the humic acid phase that is able to reduce Fe(III) to Fe(II). This means that the oxidized iron produced during Cr(VI) reduction is cycled back to Fe(II) by redox-active fulvic acid moieties with the pH dependent formation of highly reactive ferrous hydroxide species that are stronger reductants than the Fe(II)–DOM complexes [48].

Coupling humic acid (HA) and iron nanoparticles for Cr(VI) reduction has both synergistic and antagonistic effects. HA can act as an adsorbent competing for reactive sites on the surface of the Fe(0) nanoparticles, leading to a decreased Cr(VI) reduction rate. However, the quinone compounds in HA act as electron shuttles promoting electron transfer, which would have a positive enhancement on the reduction of Cr(VI) by Fe(0) nanoparticles. HA also stabilizes the nanoparticles preventing agglomeration which enhances the reactivity and counteracts the inhibitory effect [49].

The inclusion of benign naturally-occurring organic molecules like α-hydroxyl carbonyl, α-hydroxyl carboxylate, α-carbonyl carboxylate, phenolate, carboxylates and/or thiol groups, siderophore, ascorbic acid or chelating agents like ethylenediaminetetraacetic acid derivates and acetylacetone in a Cr(VI)–Fe(0) remediation system accelerates the reaction rate and can provide a protective effect for the iron metal surfaces [50]. In Table 5 the Cr(VI) reduction using different organic matter is presented.

5.2. Fe(III) photocatalytic reduction of Cr(VI) by organic acids

Recent efforts have focused on the photocatalytic impact of Fe(III) on the reduction of Cr(VI) by organic acids. The rate of Cr(VI) photoreduction in sunlit natural waters is related to the amount of Fe(III) present and the nature of the dissolved organic matter substrate and the organic acid type (classified as low Fe(III) photoreductivity acetate and succinate, and high Fe(III) photoreductivity citrate and tartrate) [51].

The fast reaction between Cr(VI) and organic acids in the presence of Fe(III) is mainly due to the photoreaction products generated when solution is exposed to sunlight. These products like Fe(II), $HO_2/O_2^{\bullet -}$ or $CO_2^{\bullet -}$, catalyze the reduction of Cr(VI) [51]. Fe(II)/Fe(III) acts as a photocatalyst by shuttling electrons from the organic acid to Cr(VI). The photocatalytic cycle consists of (1) Fe(III)-organic acid absorbance of light to produce Fe(II) and

Table 4
Electrochemical methods for Cr(VI) reduction, other electrodes.

Electrode materials	Current/voltage/current density	Flow rates/reactor capacity	Treatment efficiency	Reactor type and connection	Reference
Carbon and graphite					
RVC and Ti/TiO_7 $Ru_{0.3}O_2$(DSA)	0.7 V	$80\,mL\,min^{-1}$	70–100%	Continuous monopolar	[41]
RVC and Ti/TiO_7 $Ru_{0.3}O_2$(DSA)	1.6–4.6 A	$0.33–0.09\,m\,s^{-1}$	>99%	Continuous connection not specified	[44]
Conducting polymers					
RVC and modified RVC/PANI	30 mA	$0.013–0.27\,m\,s^{-1}$	100%	Continuous connection no specified	[43]
Copper					
Copper mesh	2 V	$18.9\,L\,min^{-1}$	>99%	Continuous monopolar	[45]

Table 5
Organic matter for Cr(VI) reduction.

Organic acid	Catalyst	Main mechanism	Reference
Organic matter for Cr(VI) reduction			
DOM and fulvic acids (SRFA, PLFA)	Fe(II)	Oxidized iron is cycled back to Fe(II) by redox active fulvic acid	[48]
Humic acid	Fe(0) nanoparticles	HA act as adsorbent Quinone compounds of HA act as electron shutles promoting electron transfer	[49]
α-Hydroxil, carbonyl and carboxilate, phenolate, thiol groups, siderophore, ascorbic acid, EDTA derivates and acetyacetone	Fe(0)	Formation of complexes with reaction products Cr(III) and Fe(III) and $Cr_xFe_{(1-x)}(OH)_3$ which impede precipitation and Fe(0) passivation	[50]

radicals; (2) oxidation of Fe(II) to Fe(III) by Cr(VI), accompanied by the intermediate production of Cr(IV) and Cr(V); (3) reformation of Fe(III)-organic acid. In this reaction cycle, the complex formation between Fe(III) and the organic acid is a key step for the reduction of Cr(VI). This is particularly effective and determinant for organic acids having an α-OH group [51].

The reduction of Cr(VI) by organic acids in soils is coupled with apparent adsorption of Cr(III) by the soil, both of which are influenced by the types of soils, their composition, and their physical characteristics. The transition metal ions in soil particles are responsible for the catalytic reduction of Cr(VI) by organic acids. Mn(II) in soil particles is the key factor to leading fast transformation of Cr(VI) to Cr(III) in the presence of organic acids containing α-OH groups without light. However, iron ions account for the rapid removal of Cr(VI) with light. The presence of soils significantly accelerates photochemical reduction of Cr(VI) only at low soil loading. Higher soil loading is not beneficial to the improvement of Cr(VI) reduction due to the decreased light penetration into the dissolved phase [52]. Fe(III) in soil particles reacts with citric acid and tartaric acid to form a photochemically active complex, which can be transformed to stronger reductants than the organic acids through a pathway of metal–ligand–electron transfer. Consequently, the reduction of Cr(VI) is significantly accelerated. The mechanism proposes a determinant role of Fe(II)/Fe(III), which acts as a catalyst by shuttling electrons from DOM to Cr(VI) in a catalytic cycle consisting of (1) Fe(III)-DOM absorbance of light to produced Fe(II) and organic radicals; (2) oxidation of Fe(II) to Fe(III) by Cr(VI), accompanied by the intermediated production of Cr(V); (3) reformation of Fe(III)-DOM as follows (Eqs. (26)–(33)) [52,53].

$$\mathrm{Fe(III)\text{-}Cit} + \mathrm{hv} \rightarrow \mathrm{Fe(II)} + \mathrm{Cit}^{\bullet} + \mathrm{hv} + \mathrm{CO}_{2(g)} \rightarrow \mathrm{R}^{\bullet} \tag{26a}$$

$$\mathrm{Fe(III)\text{-}Tar} + \mathrm{hv} \rightarrow \mathrm{Fe(II)} + \mathrm{Tar}^{\bullet} + \mathrm{hv} + \mathrm{CO}_{2(g)} \rightarrow \mathrm{R}^{\bullet} \tag{26b}$$

$$\mathrm{R}^{\bullet} \rightarrow \mathrm{ROO}^{\bullet} \rightarrow \mathrm{O_2}^{-} \tag{27}$$

$$\mathrm{R}^{\bullet} + \mathrm{Fe(III)} \rightarrow \mathrm{Fe(II)} \tag{28}$$

$$\mathrm{H}^{+} + \mathrm{O_2}^{-} \rightarrow \mathrm{HO_2}^{\bullet} \tag{29}$$

$$\mathrm{HO_2}^{\bullet} + {}^{\bullet}\mathrm{HO_2} \rightarrow \mathrm{H_2O_2} \tag{30}$$

$$7\mathrm{H}^{+} + 3\mathrm{Fe(II)} + \mathrm{HCrO_4}^{-} \rightarrow 3\mathrm{Fe(III)} + \mathrm{Cr(III)} + 4\mathrm{H_2O} \tag{31}$$

$$\mathrm{O_2}^{-}/\mathrm{HO_2}^{\bullet} + \mathrm{Fe(II)} + \mathrm{H}^{+} \rightarrow \mathrm{Fe(III)} + \mathrm{H_2O_2} \tag{32}$$

$$\mathrm{H_2O_2} + \mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)} + {}^{\bullet}\mathrm{OH} + \mathrm{OH}^{-} \tag{33}$$

Nanoparticles as sensitizers have been investigated using iron oxides, showing that the catalytic performance increases with decreasing pH, inclusive the use of magnetic separable photocatalyst beads improve the absorption occurrence of Cr(VI) onto the catalyst surface [54]

The concomitant oxidation of organic acid contributes significantly to the photoactivity through the charge separation of electron/hole pairs [55]. One example is the following reaction of salicylic acid:

$$\mathrm{C_7H_6O_3} + 6\mathrm{O}_{2(g)} + 4\mathrm{H}^{+}_{(aq)} + 3\mathrm{H_2O} \rightarrow 7\mathrm{CO}_{2(g)} + 4\mathrm{H_3O}^{+}_{(aq)} \tag{34}$$

Metal oxides like $CuFe_2O_4$ act as electron pumps and other minerals like CdS mediate the electron transfer to chromate [55].

5.3. TiO_2 photocatalytic reduction of Cr(VI) by organic acids

The photocatalytic reduction of Cr(VI) by TiO_2 at pH 3 in both the absence and presence of organic compounds has been extensively investigated for its application to the oxidation of organic compounds and the reduction of metal ions. The mechanism involves the charge trasnsfer complex (CTC) formed between TiO_2 and small molecular weigth organic acids (SOA) [56]. The mechanism of photocatalysis on titanium dioxide particles involves generated electron/hole pairs that must be trapped in order to avoid recombination. In the absence of organic compounds hydroxyl ions (OH^-) are the likely traps for holes, leading to the formation of hydroxyl radicals which are strong oxidant agents. The traps for electrons are adsorbed oxygen species, leading to the formation of superoxide species ($O_2{}^-$) which are unstable, reactive and may evolve in several ways [57].

$$\mathrm{TiO_2} + h\nu \rightarrow \mathrm{TiO_2} + \mathrm{e}^{-}{}_{\mathrm{cb}} + \mathrm{h}^{+}{}_{\mathrm{vb}} \tag{35}$$

$$\mathrm{TiO_2{-}OH_s}^{-} + \mathrm{h}^{+} \rightarrow \mathrm{TiO_2{-}OH_s}^{\bullet} \tag{36}$$

$$\mathrm{O}_{2(ads)} + \mathrm{e}^{-} \rightarrow \mathrm{O_2}^{-} \tag{37}$$

Nanotechnology offers the potential of novel functional materials for environmental applications and many nano-based environmental technologies (e.g., sensors, sorbents, and reactants) are under very active research and development, and are expected to emerge as the next generation environmental technologies to improve or replace various conventional environmental technologies in the near future [58].

In this context TiO_2 nanoparticles and nanofibers resulted in an enhanced catalytic activity for photocatalytic Cr(VI) reduction where the hidrotermal postreatment exhibited the highest catalytic activity among TiO_2 nanoparticles. [59]. Furthermore, TiO_2 nanoparticles obtained by hydrothermal post-treatment showed the best sedimentation efficiency, highlighting its prominent potential as a readily separable and recoverable photocatalyst. Also, TiO_2 nanoparticles (Degussa P25) modified with fullerene derivative $C_{60}(CHCOOH)_2$ display a higher photocatalytic activity with 97% reduction efficiency on Cr(VI) ions. In this system the enhanced photocatalytic activity of TiO_2 nanoparticles may be ascribed to the enhancement of the photogenerated electron/hole pair separation because of the modification of the C_{60} derivative [60].

$La_2Ti_2O_7$ is a highly active photocatalyst for reduction of Cr(VI) ions in water under UV irradiation and is stable enough to be recycled multiple times. It is suitable for the elimination of Cr(VI) ions in acidic (pH 2) and dilute solutions. Under UV irradiation, electron/hole pairs are created inside $La_2Ti_2O_7$ particles. The photogenerated electrons reduce $Cr_2O_7{}^{2-}$ to Cr^{3+} on the surface of the $La_2Ti_2O_7$ particles. Meanwhile, the holes oxidize water to form O_2. The reactions occurring on the surface of the $La_2Ti_2O_7$ particles are as follows [61]:

$$\mathrm{Cr_2O_7}^{2-}{}_{(aq)} + 14\mathrm{H}^{+}{}_{(aq)} + 6\mathrm{e}^{-} \rightarrow 2\mathrm{Cr}^{3+}{}_{(aq)} + 7\mathrm{H_2O} \tag{38}$$

$$2H_2O + 4h^+ \rightarrow O_{2(g)} + 4H^+_{(aq)} \quad (39)$$

The photocatalytic reduction of Cr(VI) is dependent on both the specific surface area and crystalline structure of the photocatalyst in the absence of any organic compounds. The improved separation of electrons and holes on the modified TiO_2 surface allows more efficient channeling of the charge carriers into useful reduction and oxidation reactions rather than recombination reactions [57].

A marked synergistic effect between the photocatalytic reduction of Cr(VI) and organic compounds as sacrificial electron donors was observed over the photocatalyst with the largest specific surface area. Where the photocatalytic reduction of Cr(VI) was dominated by the specific surface area of the photocatalyst in the presence of organic compounds because of the synergistic effect between the photocatalytic reduction of Cr(IV) and the photocatalytic oxidation of organic compounds [62]. The deactivation of TiO_2 in the photocatalytic reduction of Cr(VI by Cr(III) deposits will be inhibited in the simultaneous photoreduction of Cr(VI) and photo-oxidation of organic pollutants (salycilic acid) [63].

Charge-transfer-complexes (CTC) formed between TiO_2 and small molecular weight organic acids (SOA) induce photoreduction of Cr(VI) via a CTC-mediated path governed by the chemical structure of sacrificial SOA. A higher energy of the highest occupied molecular orbital or lower ionization potential of the SOA is favorable to electron transfer within the TiO_2-SOA complex, thereby accelerating the photoreduction of Cr(VI) [63]. Surfaces of complexes of TiO_2 and electron donors (methanol, formic acid, acetic acid, triethanolamine and EDTA) can absorb visible light through a ligand-to-metal charge transfer (LMCT) mechanism. The LMCT-excited electrons in the TiO_2 conduction band are subsequently transferred to electron acceptors such as Cr(VI) and protons. The degradation of EDTA on TiO_2 under visible light was significant only in the presence of Cr(VI), so scavenge electrons with inhibiting the recombination [62]. Salicylic acid favors the charge separation in $CuAl_2O_4$ due to its stable photo corrosion by the hole consumption reaction in a Cr(VI) reduction system at pH 2 [65].

Furthermore combined nanoparticles, modified TiO_2 surfaces, and organic acids in photoreduction of Cr(VI) was successfully achieved on WO_3 doped TiO_2 nanotube (NT) arrays in the presence of citric acid, which plays an important role in the photoreduction of Cr(VI): (i) it works as a sacrificial electron donor to deplete the photogenerated holes from the excited TiO_2; and (ii) it takes part in the redox with Cr(VI) under UV illumination because of its electron-rich property. Then, an increase in probability of charge carrier separation and the extended photoresponse spectrum increases reduction rates (WO_3/TiO > TiO_2 NTs > citric acid) [66].

Other metal oxide nanoparticles (NiO and ZnO) using a novel laser-induced photocatalytic process without the use of any additive for the photocatalytic reduction of Cr(VI) show a strongly dependence on critical parameters such as calcination temperature, calcination time, laser energy, catalyst amount, chromium concentration, added electron donor and acceptor parameters [67,68]. Tables 6 and 7 shows the Cr(VI) reduction rates achieved using different kinds of catalysis.

6. Cr(VI) reducing bacteria

Microbial chromium(VI) removal from solutions typically involves the following stages: (a) the binding of chromium to the cell surface, (b) translocation of chromium into the cell, and (c) reduction of chromium(VI) to chromium(III) [69].

6.1. Aerobic Cr(VI) reducing bacteria

In the presence of oxygen, bacterial Cr(VI) reduction occurs as a two or three step process with Cr(VI) initially reduced to the short-lived intermediates Cr(V) and/or Cr(IV) before further reduction to the thermodynamically stable end product, Cr(III). Cr(V) undergoes a one-electron redox cycle to regenerate Cr(VI) by transferring the electron to oxygen. The process produces a reactive oxygen species (ROS) that easily combines with DNA–protein complexes. Nevertheless, it is presently unclear whether the reduction of Cr(V) to Cr(IV) and Cr(IV) to Cr(III) is spontaneous or enzyme mediated [70]. Chromate reductase assay from an alkaliphilic gram-positive *Bacillus subtilis* indicated that the Cr(VI) reduction was mediated by constitutive membrane bound enzymes and a decrease in pH with growth of the bacterium signified the role played by metabolites (organic acids) in chromium resistance and reduction mechanism [71]. NADH, NADPH and electrons from the endogenous reserve are implicated as electron donors in the Cr(VI) reduction process. Reductases as ChrR, YieF and Tkw3 reduce Cr(VI) species by electron shuttle to form Cr(III) [68]. Strain *Lysinibacillus fusiformis ZC1* was found to contain large numbers of metal resistance genes. Specifically, a *chrA* gene encoding a putative chromate transporter conferring chromate resistance was identified. Furthermore, a *yieF* gene and several genes encoding reductases that were possibly involved in chromate reduction were also found. Expression of adjacent putative chromate reduction related genes, *nitR* and *yieF*, was found to be constitutive. The large numbers of NADH-dependent chromate reductase genes may be responsible for the rapid chromate reduction in order to detoxify Cr(VI) and survive in the harsh wastewater environment [72].

Also, isolated bacteria putatively identified by 16S rRNA gene sequencing as *Arthrobacter aurescens* strain MM10, *Bacillus atrophaeus* strain MM20, and *Rhodococcus erythropolis* strain MM30 that present chromate reductase gene sequences found in Gram negative bacteria (*Escherichia coli* and *Shigella* spp.) have the ability to rapidly reduce highly toxic concentrations of Cr(VI) to Cr(III) when grown in minimal medium supplemented with glucose as the sole carbon source [73]. Two reaction steps have been suggested to be involved in the reduction reactions, first Cr(VI) accepts one molecule of NADH and generates Cr(V) as an intermediate (Eq. (37)), and then Cr(V) accepts two electrons to form Cr(III) (Eq. (38)) [69].

$$Cr^{6+} + e^- \rightarrow Cr^{5+} \quad (37)$$

$$Cr^{5+} + 2e^- \rightarrow Cr^{3+} \quad (38)$$

Two processes are responsible for the reduction of Cr(VI) when aerobic heterotrophic cells, non-growing cells, growing cells with chromate reductase activity, and growing cells that have lost the chromate reductase activity where used. The first one is the reduction of Cr(VI) coupled with growth and the second process is coupled with the endogenous decay of the biomass [74].

The presence and influence of proteins [75] and electron donors such as glucose, fructose, sucrose and bagasse extract were found to offer great Cr(VI) reduction rates when *Bacillus* sp. and *Staphylococcus capitis* are used. Among the different electron donors, glucose provided the highest Cr(VI) reduction compared to other electron donors [76]. A new mechanism has been proposed for chromate reduction by *Brevibacterium casei*, which can reduce Cr(VI) with an azo dye Acid Orange 7 (AO7). Under nutrient-limiting conditions, AO7 was used as an e^- donor by the reduction enzyme(s) of *B. casei* for the reduction of Cr(VI). The resulted Cr(III) then complexes with the oxidized AO7 to form a purple-colored intermediate [77].

6.2. Anaerobic Cr(VI) reducing bacteria

In the absence of oxygen, Cr(VI) can serve as a terminal electron acceptor in the respiratory chain for a large array of electron donors, including carbohydrates, proteins, fats, hydrogen, NAD(P)H and endogenous electron reserves. Both soluble and

Table 6
Photocatalytic Cr(VI) reduction.

Fe photocalatytic reduction of Cr(VI) by organic acids				
Electron donor	Fe source	Reduction %, time and radiation type	Mechanism affected mainly by	Reference
Tartaric, citric, malic and n-butyric acids	Diluted and Fe(III) adsorbed onto clay	100%, 7–80 min, visible ligth	Organic acids having an α-OH group	[51]
Tartaric and citric acids	Soils	100%, 4 h, mimic solar light 300–800 nm	Transition metal ions in soil particles (Mn) and Fe(III)	[52]
Alginate	γ-Fe_2O_3 nanoparticles	≈100%, 50 min, Sunlight	Lower pH	[54]
Salicylic acid	$CuFe_2O_4$ nanoparticles	60%, 2.8 h	$CuFe_2O_4$ act as electron pumps	[55]

membrane-associated enzymes have been found to mediate the process of Cr(VI) reduction under anaerobic conditions. Unlike the Cr(VI)-reductases isolated from aerobes, the Cr(VI)-reducing activities of anaerobes are associated with their electron transfer systems ubiquitously catalyzing the electron shuttle along the respiratory chain. [70]. The overall bio-reduction of Cr(VI) and precipitation of Cr(III) is illustrated in Eqs. (42, 43). Under anaerobic conditions with glucose as an electron donor, the Cr(VI) microbial reduction is related to Eq. (44) [69].

$$CrO_4{}^{2-}{}_{(aq)} + 8H^+{}_{(aq)} + 3e^- \rightarrow Cr^{3+}{}_{(aq)} + 4H_2O \tag{42}$$

$$Cr^{3+}{}_{(aq)} + 4H_2O \rightarrow Cr(OH)_{3(s)} + 3H^+{}_{(aq)} + H_2O \tag{43}$$

$$C_6H_{12}O_6 + 8CrO_4{}^{2-}{}_{(aq)} + 14H_2O \rightarrow 8Cr(OH)_{3(s)} + 10OH^-{}_{(aq)} + 6HCO^-{}_{(aq)} \tag{44}$$

Pannonibacter phragmitetus has strong aerobic and anaerobic Cr(VI)-reduction potential under alkaline conditions but its anaerobic reduction potential is higher than aerobic, showing a potential application for Cr(VI) detoxification [78]. Compared to free cells, *P. phragmitetus* cells coated with polyethylenimine-functionalized magnetic nanoparticles, not only had the same Cr(VI)-reduction activity but could also be easily separated from reaction mixtures by magnetic force. In addition, the magnetically immobilized cells retained high specific Cr(VI)-reduction activity over six batch cycles. The results suggest that the magnetic cell separation technology has potential application for Cr(VI) detoxification in alkaline wastewater [79].

An efficient mediated microbial reduction of Cr(VI) by *E. coli* is promising for rapid anaerobic removal and the reduction of chromate by resting *E. coli* cells was significantly enhanced by the quinone redox mediators lawsone, menadione, anthraquinone-2-sulfonate, and anthraquinone-2,6-disulfonate and also by the addition of glucose as an electron donor [80]. Furthermore, *E. coli* biofilm on chitosan beads (EBCB) bioregenerated the chitosan beads after *E. coli* biofilm has grown significantly allowing Cr(VI) adsorption by chitosan beads and Cr(VI) bioreduction by *E. coli* cells [81]. Also *E. coli* cells in the presence of quinone redox mediators, have enhanced chromate reduction [82].

Sulfate and iron reducing bacteria (SRB and IRB) are important members of anaerobic microbial communities with economic, environmental and biotechnological interest. Chromium(VI) reduction by biogenic iron(II) and sulfides generated by IRB and SRB is 100 times faster than CRB alone. SRB produces H_2S, which serves as a Cr(VI) reductant and involves three stages [83]; (a) Reduction of sulfates (Eq. (45)), (b) Reduction of chromate by sulfides (Eq. (46)) and (c) Precipitation of Cr(VI) by sulfide (Eq. (47)).

$$SO_4{}^{2-}{}_{(aq)} + 2CH_2O + H^+{}_{(aq)} \rightarrow HS^-{}_{(aq)} + 2H_2O + 2CO_{2(g)} \tag{45}$$

$$8CrO_4{}^{2-}{}_{(aq)} + 3HS^-{}_{(aq)} + 17H_2O \rightarrow 8Cr(OH)_{3(s)} + 3SO_4{}^{2-}{}_{(aq)} + 13OH^-{}_{(aq)} \tag{46}$$

$$Cr^{6+}{}_{(aq)} + 3HS^-{}_{(aq)} \rightarrow CrS_{3(s)} + 3H^+{}_{(aq)} \tag{47}$$

The reduction of Cr(VI) by Fe(II) occurs when IRB reduces Fe(III) to Fe(II) which in turn reduces Cr(VI) to Cr(III) (Eq. (48–50)) [83].

$$C_6H_{12}O_6 + 24Fe^{3+} + 12H_2O \rightarrow 6HCO_3{}^- + 24Fe^{2+} + 3OH^- \tag{48}$$

$$3/4C_3H_5O_3{}^- + 3Fe(OH)_{3(s)} \rightarrow 3/4C_2H_3O_2{}^- + 3Fe^{2+} + 3/4HCO_3{}^- + 2H_2O + 1/4OH^- \tag{49}$$

Table 7
TiO_2 photocalatytic reduction of Cr(VI).

Electron donor	Type TiO_2catalyst	% Reduction, time and radiation type	Mechanism affected mainly by	Reference
SOA	TiO_2 powder	95%, 2 h, visible light	Large specific surface area	[56]
–	TiO_2 nanofiber and nanoparticles	–	Hidrotermal postreatment	[59]
–	TiO_2 nanoparticles modified with $C_{60}(CHCOOH)_2$	97%, 1.5 h, UV radiation	C_{60} modification	[60]
–	$La_2Ti_2O_7$ and salts (NaCl, KCl, $CaCl_2$, $MgCl_2$, Na_2SO_4)	98%, 3 h, UV light	Surface of the $La_2Ti_2O_7$ particles	[61]
Salycylic acid	TiO_2 powder	100%, 300–900 min, UV 253.7 nm	Oxidation of electron donor	[63]
Methanol, formic acid, acetic acid, triethanolamine, EDTA	TiO_2	550 nm, visible light	Carboxilate groups complexed with TiO_2 surface	[64]
Salicylic acid	$CuAl_2O_4/TiO_2$	95%, 3 h, visible light, 1.7–2.5 eV	Electron donor favors the charges separation	[65]
Citric acid	WO dopped TiO_2 nanotube	Increase in reduction rates $WO_3/TiO > TiO_2$ NTs > citric acid, UV light	Combined nanoparticles, modified TiO_2 surfaces, and organic acids	[66]
Other photocatalyst				
Added electron donor	NiO nanoparticles	90%, 75 min, laser radiation (Nd:YAG)(355 nm)	Critical synthesis parameters, chromium concentration and added electron donor	[67]
Added electron donor	ZnO nanoparticles	95%, 60 min, Laser radiation	Synthesis parameters, chromium concentration and added electron donor	[68]

Table 8
Bacterial Cr(VI) reduction.

Bacterial type	% Reduction C_0, time, pH, carbon source	Main mechanisms affected by	Reference
Aerobic Cr(VI) reduction			
Bacillus subtillis (Alkaliphilic Gram-positive)	100%, pH 9	Constitutive membrane bound enzymes, decrease of pH and growth bacterium	[71]
Lysinibacillus fusiformis ZC1	≈100%, $C_0 = 1$ mM K_2CrO_4, 12 h	Large numbers of NADH-dependent chromate reductase genes: *chrA* and *yieF*	[72]
Arthrobacter aurescens MM10, *B. atrophaeus* MM20, *Rhodococcus erythropolis* MM30	Glucose	Chromate reductase genes found in Gram negative bacteria	[73]
Heterotrophic strain	$C_0 = 0–100$ mg Cr L^{-1} cheese whey and lactose	Chromate reductase activity, growth bacterium and endogenous decay of the biomass	[74]
Bacillus sp. JDM-2-1 and *Staphylococcus capitis*	86% and 89%, respectively, 144 h	Induced protein of molecular weight around 25 kDa	[75]
Bacillus sp. immobilized in calcium alginate	pH 7 and 37 °C	Electron donors such as glucose, fructose, sucrose and bagasse extract	[76]
Brevibacterium casei, azo dye Acid Orange 7 (AO7)	83.4 ± 0.6%	AO7 used as an e^- donor	[77]
Anaerobic Cr(VI) reduction			
Pannonibacter phragmitetus	100%, $C_0 = 100–1000$ mg L^{-1}, 9–24 h, 37 °C and pH 9.0	Alkaline conditions, six batch cycles	[78]
Pannonibacter phragmitetus LSSE-09 cells immobilized in Fe_3O_4 NPs	Alkaline conditions	Magnetically immobilized cells retained with high specific Cr (VI)-reduction activity	[79]
Microbial fuel cell	42.5–100%, 4–12 h, pH 2	H_2O_2 cathode electrogeneration driven by iron-reducing bacteria(IRB)	[80]
Escherichia coli	84%, $C_0 = 5$ mg L^{-1}	Adsorption by chitosan beads, bioreduction by *E. coli* cells and mass transport diffusion	[81]
Escherichia coli	97.5%, $C_0 = 50–250$ mg L^{-1}, 4 h	Glucose as electron donor to promote the reduction process	[82]
Sulfate-reducing bacteria	96%, $C_0 = 50$ mg L^{-1}, Lactate	Sulfate Cr(VI) reduction	[69]
Chromium-reducing, sulfate-reducing, iron-reducing bacteria	100%, 20 mg L^{-1} of Cr(VI), 500–648 h	Sulfate and iron Cr(VI) reduction.	[83]
Hansenula polymorpha cells	39–53%, pH 6.3, 0.5 mM chromate, 30 min	Reduction by cytochrome c-oxidoreductase (flavocytochrome b2, FC b2) in the presence of L-lactate	[84]

$$3Fe^{2+} + HCrO_4^{-} + 8H_2O \rightarrow 3Fe(OH)_{3(s)} + Cr(OH)_{3(s)} + 5H^{+} \qquad (50)$$

Efficient reduction of Cr(VI) can be achieved with an air-bubbling-cathode in an air–cathode dual-chamber microbial fuel cell (MFC). The reduction of Cr(VI) is strongly associated with electrogenerated H_2O_2 at the cathode driven by iron-reducing bacteria when Cr(VI) is reduced in situ at a carbon felt cathode [83].

The cytochrome family (e.g., cytochrome b and c) is frequently involved in enzymatic anaerobic Cr(VI) reduction [71]. *Hansenula polymorpha* over-producing flavocytochrome (FC) b2 was studied and a competitive effect of chromate on current generation during oxidation of L-lactate based on the model of bioelectrodes prepared by immobilization of FC b2 on a platinum surface was observed. This phenomenon can be used in the construction of chromate selective biosensors to reduce chromate in the presence of L-lactate as an electron donor and synthetic dyes as electron transfer mediators. Recombinant yeast cells can be readily used in chromate detoxification using dairy waste as a cheap source of L-lactate [84]. Table 8 summarizes the results of using different bacteria in the Cr(VI) reduction.

6.3. Fungi

Some species of fungus are capable of reducing Cr(VI) to Cr(III). Identification of these species involves isolating them from their native soil or aqueous environment, characterizing them, then testing their chromium reducing activity in solution under various conditions. *Aspergillus sp. N2* and *Penicillium sp. N3* are chromate-resistant filamentous fungi. When they were tested in 50 ppm Cr(VI) aqueous solutions at near neutral pH, *Aspergillus sp. N2* reduced the Cr(VI) concentration by about 75%, whereas *Penicillium sp. N3* was only able to reduce it by 35%. The mechanisms of Cr(VI) reduction in *Aspergillus sp. N2* and *Penicillium sp. N3* were enzymatic reduction and sorption to mycelia [85]. Another fungus identified as *Hypocrea tawa* by the D1/D2 domain sequence of its 26S rRNA gene, was used for Cr(VI) reduction in batch cultures conducted at initial Cr(VI) concentrations ranging from 0.59 to 4.13 mM. The fungus showed a remarkable capacity to completely reduce high concentrations of Cr(VI) (4.13 mM) under aerobic conditions [86].

The chromium-resistant fungus *Paecilomyces lilacinus* was grown and used to remove Cr(VI) from undiluted tannery industry effluents in the presence of cane sugar (carbon source). The fungus has a broad pH tolerance range and can reduce Cr(VI) both in acidic (pH 5.5) and alkaline (pH 8.0) conditions. The fungus showed the ability to remove Cr(VI) (1.24 mg/L) from tannery effluent. *Paecilomyces lilacinus* showed Cr(VI) reduction as a major mechanism of Cr(VI) detoxification. The time-course study revealed the log phase of the growth for the maximum specific reduction of Cr(VI) and stationary phase of the growth for its maximum specific accumulation of both the forms of chromium [Cr(III) and Cr(VI)] in its biomass [87].

Some studies have shown that the carbon source is a key parameter for microbial dynamics and enhanced chromium reduction so should be taken into account for efficient bioreactor design. The analysis of the microbial structure in one reactor showed that the dominant communities were bacterial species (*Acinetobacter lwoffii*, *Defluvibacter lusatiensis*, *Pseudoxanthomonas japonensis*, *Mesorhizium chacoense*, and *Flavobacterium suncheonense*) when sodium acetate was used as carbon source and fungal strains (*Trichoderma viride* and *Pichia jadinii*), when sodium acetate was replaced by sucrose [88].

Interactions of Cr(VI) with renewable biomaterials are considered an important pathway for Cr(VI) removal in ecosystems. Biomaterials are susceptible to dissolution, and their dissolved components provide a surface-involved pathway for scavenging Cr(VI). One study showed that the dissolved organic compounds (polysaccharides, peptides, and glycoproteins) derived from *Neurospora crassa* biomass contributes to a 53.8–59.5% reduction of the Cr(VI) in aqueous media [89].

Light-induced Cr(VI) reduction by fungus is less reported and needs to be explored since anthropogenic or natural activities may bring this process into a sunlit environment. The interactions of *N. crassa* with Cr(VI) indicate that 2.7 mg Cr(VI) can be reduced by 1 g biomass at pH 1–3. However, 5 mg Cr(VI) can be reduced with 1 g biomass under the same reaction time and experimental conditions when light was present. The rapid disappearance of Cr(VI) in solution was due to the reduction of Cr(VI) by the excited biomass upon light absorption, and the rates of redox reactions increased with a decrease at pH. Spectroscopic studies indicated that the amide and carboxyl groups of *N. crassa*-biomass may be responsible for initiating Cr(VI) reduction. Comparatively, the cyclo-carbons of chitin, glucan, and their derivatives were more persistent to oxidation by Cr(VI) [90].

7. Conclusions

In this review paper we describe the current technologies that are being used to effectively reduce Cr(VI) present in aqueous solutions by means of chemical, electrochemical and biological methods. In general, the chemical and electrochemical methods require that the process takes place under acidic conditions (optimally pH 2) so that the chromium and iron ions remain in the aqueous phase where the reactions take place. When the pH of the aqueous solution is raised, chromium and iron hydroxides precipitate. Both chemical and electrochemical processes precipitate chromium and iron as hydroxides (or oxides), but the electrochemical process produces less sludge and requires fewer chemical reagents. On the other hand, biological methods require even fewer reagents, mainly just a carbon source. They must initially be isolated, identified, and characterized from their native soil or aqueous environment, but can be propagated after that. Growth and activity does require a carbon source like a polysaccharide, but are relatively easy and inexpensive to operate. Although, some aquatic bacteria and fungi are relatively tolerant to high levels of Cr(VI), it is a strong oxidant and at a certain level it does attack the membrane and tissues of the microbes.

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