Chemical and electrochemical considerations on the removal process of hexavalent chromium from aqueous media

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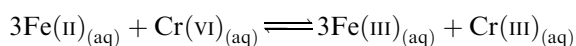(*author for correspondence, e-mail: cbarrera@uaemex.mx)

Abstract

Two methods were used to remove Cr(VI) from industrial wastewater. Although both are based in the same general reaction:

$$3Fe(\text{II})_{(aq)} + Cr(\text{VI})_{(aq)} \rightleftharpoons 3Fe(\text{III})_{(aq)} + Cr(\text{III})_{(aq)}$$

the way in which the required amount of Fe(II) is added to the wastewater is different for each method. In the chemical method, $Fe(\text{II})_{(aq)}$ is supplied by dissolving $FeSO_4 \cdot 7(H_2O)_{(s)}$ into the wastewater, while in the electrochemical process $Fe(\text{II})_{(aq)}$ ions are formed directly in solution by anodic dissolution of an steel electrode. After this reduction process, the resulting $Cr(\text{III})_{(aq)}$ and $Fe(\text{III})_{(aq)}$ ions are precipitated as insoluble hydroxide species, in both cases, changing the pH (i.e., adding $Ca(OH)_{2(s)}$). Based on the chemical and thermodynamic characteristics of the systems Cr(VI)–Cr(III)–H_2O–e⁻ and Fe(III)–Fe(II)–H_2O–e⁻ both processes were optimized. However we show that the electrochemical option, apart from providing a better form of control, generates significantly less sludge as compared with the chemical process. Furthermore, it is also shown that sludge ageing promotes the formation of soluble polynuclear species of Cr(III). Therefore, it is recommended to separate the chromium and iron-bearing phases once they are formed. We propose the optimum hydraulic conditions for the continuous reduction of Cr(VI) present in the aqueous media treated in a plug-flow reactor.

1. Introduction

Hexavalent chromium Cr(VI) is a major pollutant present in industrial wastewaters common to the metal and mineral processing, as well as plating industries. Cr(VI) is considered carcinogenic and mutagenic, and is capable of displaying considerable diffusion rates through soils and aquatic environments, as well as being a strong oxidizing agent readily absorbed through the skin; even in small quantities it irritates plant and animal tissues [1, 2]. The most probable Cr(VI) species in aqueous solution are $Cr_2O_7^{2-}$, CrO_4^{2-} and $HCrO_4^-$, the relative distribution of which as chemical species, depends on the solution pH and on the Cr(VI) concentration [3]. However, none of them form insoluble species of the pollutant, such that its separation is not feasible from the wastewater through a direct precipitation method [4].

From the electrochemical technology standpoint, previous studies were undertaken to provide new ways to reduce Cr(VI) to Cr(III). For instance, porous carbon electrodes were used to remove chromium; the mechanism involves two stages, namely, reduction of Cr(VI) to Cr(III) followed by the formation of $Cr(OH)_3$ which subsequently adheres onto the electrode surfaces. The main problem is that the process becomes inefficient as the insoluble chromium builds up on the surface [5]. Another way to effect the chromium reduction is to use copper anodes which dissolve into the chromium-containing solution, thus using advantageously the associated redox reaction to drive the reduction process. This process has been found to be limited by mass transfer, which along with inadequate hydraulic conditions results in passivation and blocking of electroactive sites [6].

To reduce significantly the concentration of Cr(VI) in aqueous solution while simultaneously converting it to trivalent chromium Cr(III), which is a thousand times less toxic than Cr(VI), the present work describes a series of experiments in which chemical and electrochemical

reduction methods are compared. The chemical method tried in this study, used $FeSO_4 \cdot 7(H_2O)$ as the reducing agent; whereas in the electrochemical technique steel electrodes (both cathode and anode) were employed in an electrochemical cell for the same purpose.

Chemical reduction takes place in acid conditions, namely at pH values below 3.0. As this process consumes protons, it becomes necessary to supply more acid to maintain a low pH [7]. However, it is shown that it is required to add an excess (50%) of the stoichiometric quantity of reducing agent to achieve the Cr(VI) removal that meets environmental standards after precipitation of the resulting Cr(III). Its main disadvantage is the large amount of sludge generated, which entrains the Cr(III)-based precipitate. Consequently, management and final disposal of this residue is quite difficult and likely to be expensive. This sludge could represent up to 50% of the total operational cost of a wastewater plant [8]. Therefore, the costs of management and final disposal of sludge must, of necessity, be taken into account in designing a wastewater treatment process. So, it is important to establish optimal conditions in which the amount of sludge generated can be minimized.

The electrochemical process involves the liberation of Fe(II) ions into the solution due to the anodic polarization of a plain carbon steel electrode [9]. These Fe(II) ions, in turn, act jointly as agents for the Cr(VI) reduction. This reaction is also favoured by low pH values, namely 2 for the present case. In this work, it is shown that there is a significant difference between the theoretical mass of iron needed to reduce Cr(VI) and the quantity required in the actual electrochemical experiments (according to Faraday's laws: <50%). From the environmental point of view, this result is encouraging since smaller quantities of sludge are produced. This fact has a significant impact on lowering final disposal costs, apart from decreasing the environmental impact.

Based on the chemical and thermodynamic characteristics of the systems, Cr(VI)–Cr(III)–H_2O–e^- and Fe(II)–Fe(III)–H_2O–e^-, we established the optimal pH needed to remove the resulting Cr(III) and Fe(III) ions from the aqueous solution by forming insoluble species (sludge generation). An electrochemical reactor that meets this feature in a continuous way is proposed in this work.

2. Experimental details

2.1. Chromium analysis

Synthetic wastewater solutions containing Cr(VI) were prepared using potassium dichromate (reagent grade) with known concentrations of Cr(VI) of 100, 200, 300 and 500 mg L^{-1} in distilled water (pH 2, adjusted by H_2SO_4). This range of Cr(VI) concentrations is commonly found in industrial plating dischargers [10]. These solutions were treated using both methods: chemical and electrochemical. Cr(VI) concentration was measured throughout treatments using the 1–5 diphenylcarbohid-

razide method (AWWA 3500-Cr D colorimetric method); using a Hach 3000 spectrophotometer with the absorption readings obtained at 540 nm [11]. The total concentration of chromium in the supernatant liquid samples was determined by atomic absorption spectroscopy using a Varian SpectrAA spectrophotometer model 10-plus [11].

2.2. Cr(VI) reduction by the chemical method

$FeSO_4 \cdot 7H_2O_{(s)}$ (reagent grade) was added to the synthetic Cr(VI) solution to change the Cr oxidation state according to the following general reaction:

$$3n\text{Fe(II)}_{(aq)} + \text{Cr}_n(\text{VI})_{(aq)} \rightleftharpoons 3n\text{Fe(III)}_{(aq)} + n\text{Cr(III)}_{(aq)}$$

(1)
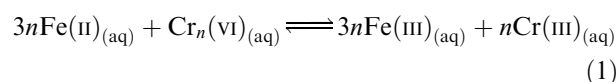
where $n = (1, 2)$ depending on the Cr(VI) concentration.

To obtain a maximum of 1 mg L^{-1} Cr(VI) concentration in the remnant liquid, different quantities of $FeSO_4 \cdot 7H_2O_{(s)}$ were tested: stoichiometric, 150 and 200% in excess. The resulting mixture was stirred to promote Reaction 1 using a stir bar and a magnetic stirrer. To remove Cr and Fe species from the aqueous phase and to pass it into the solid phase, an aqueous solution containing 1 M $Ca(OH)_2$ was added to achieve a pH value of 8.5–9.0. Maximum insolubility for both Fe(III) and Cr(III) hydroxide species is reached under the conditions stated, as predicted by the thermodynamic analysis shown below. After the solid phase (sludge) was formed, separation from the aqueous media followed by filtering. The sludge was desiccated in an oven at 105 °C and then weighted in an analytical balance. The same procedure of removal was also carried out after the electrochemical method.

2.3. Cr(VI) reduction by electrochemical methods

In this case the Fe(II) ions were supplied by dissolution of the plain carbon steel electrode. Metal dissolution was electrochemically induced by applying a current density of 50 A m^{-2} by means of a direct current power supply. Current density was achieved by applying a constant direct current of 5 A with voltage variation in the range 6–7 V. Further details can be found elsewhere [9]. This process was performed in a plug flow-through reactor provided with steel electrodes, which consisted of 62 plates, where 31 worked as anodes and the remainder as cathodes. The alternating stack of electrodes within the reactor was contained in an acrylic column of 1.295 m high and 0.064 m in diameter, whereby a cathode followed each anode. The area of each steel plate was 0.001625 m^2; thus, the total sacrificial electrode surface S_e was 0.10075 m^2.

The reactor column has four sampling ports at equal distances in which samples were collected to observe the changes in the Cr(VI) concentration as a function of elapsed time and reactor distance. Conditions such as
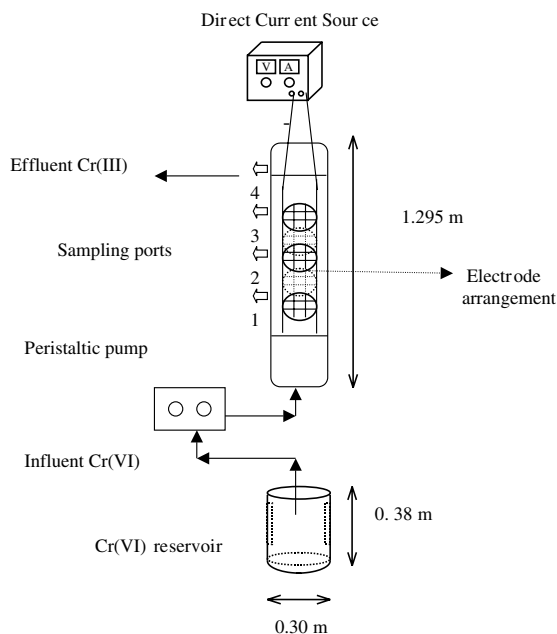
Fig. 1. Schematic diagram of the plug-flow electrochemical reactor used in the reduction of Cr(VI) to Cr(III).

pH (adding H_2SO_4) and current density were maintained at the same value throughout processing time.

The electrochemical reactor allowed both modes of operation: batch and continuous. During the batch mode, the electrochemical reactor was filled with water containing Cr(VI) without any further stirring; the volume of liquid treated each time was 2.780 L and the current was applied until the Cr(VI) concentration in solution was less that 1 mg L^{-1}. When the reactor was operated in a continuous way, the flow of solution to be treated was regulated with a peristaltic pump located at the bottom of the reactor column. Five different flow rates were tested, in the range of 261 to 550 ml min^{-1}. Figure 1 shows a schematic diagram of the electrochemical reactor.

2.4. Sludge characterization

The resultant sludge was analysed by scanning electron microscopy (SEM) and X-ray microanalysis. The normal characterization procedure of particulate aggregates was performed on a Phillips XL-30 coupled with an EDAX probe. This technique allowed us to obtain both: the micrographs that describe the morphology of sludge particle aggregates and relevant chemical information on them.

3. Results and discussion

3.1. Thermodynamical analysis

Predominance-zone diagrams (PZDs) are an important aid to gain a deeper understanding of aqueous solution chemistry by using a general donor/acceptor/particle treatment. These diagrams have been successfully used

to describe a number of different chemical system such as Ag(I)–Cl–NH_3–H^+ [12, 13] and Co(II)–Cl–NH_3–H^+ [14, 15]. In this work, the method for PDZ construction, proposed by Rojas-Hernández et al. [16, 17] and the thermodynamic data available in the literature [18, 19] were used to describe the systems: Cr(VI)–Cr(III)–H_2O–e^- and Fe(II)–Fe(III)–H_2O–e^-.

The theoretical distribution of the predominant chemical species of Cr(VI) is presented in the following one-dimensional PZD; the Cr(VI) species show both: pH and chromium concentration dependence.

For $-\log[Cr(VI)] \geq 1.9$
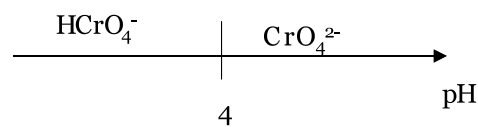
For $-\log[Cr(VI)] \leq 1.9$
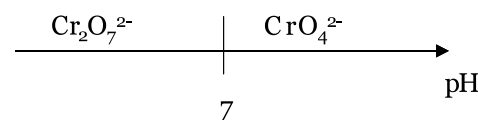
It should be pointed out from the one-dimensional PZD above, that Cr(VI) does not present any insoluble species in spite of pH variations. At this oxidation state, this metal becomes extremely mobile in aqueous and soil media, as stated previously, however the trivalent state of Cr could form highly insoluble solid species within the pH range as shown in Figure 2.

Thus, to form a Cr solid phase, which could be easy to separate from the aqueous media, it is necessary to change the Cr oxidation state. It is important to mention that in a number of papers dealing with the reduction of Cr(VI) [6, 20–23] it is common to designate a constant Cr(VI) chemical species without taking into account that the chemical conditions of the solution (i.e., [Cr(VI)], pH) are changing within the process time. Therefore, for the proposed Cr(VI) reduction reaction to become plausible, it is mandatory to consider both: the initial
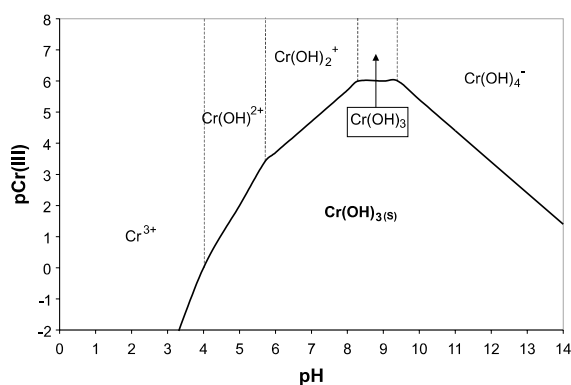

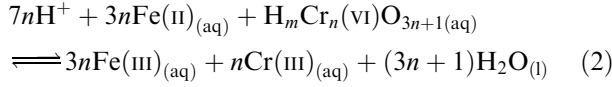Fig. 2. Predominance zone diagram for Cr(III) chemical species in aqueous solution. Solid line represents the solubility equilibrium of Cr(OH)$_{3(s)}$ and dotted line represents the predominance limits among soluble chemical species. In this diagram pCr(III)$= -\log$[Cr(III)].
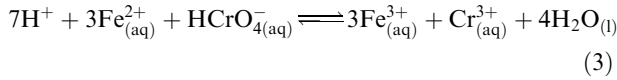
Cr(VI) concentration as well as the pH of the solution, as this can be easily inferred from the one-dimensional PZD above. Therefore, we propose the next general reaction for the Cr(VI) reduction process at pH values < 4:

$$7n\text{H}^+ + 3n\text{Fe(II)}_{(aq)} + \text{H}_m\text{Cr}_n(\text{VI})\text{O}_{3n+1(aq)}$$
$$\Longleftrightarrow 3n\text{Fe(III)}_{(aq)} + n\text{Cr(III)}_{(aq)} + (3n+1)\text{H}_2\text{O}_{(l)} \quad (2)$$

If pCr(VI) $\leqslant 1.9$ $n = 2$ and $m = 0$, while if pCr(VI) $\geqslant$ 1.9 then $n = 1$ and $m = 1$. In the pH range of 4 to 7, equilibrium between CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ is established. However, beyond pH 7, only CrO_4^{2-} will be present in the aqueous media.

As mentioned above, Cr(III) present as $\text{Cr(OH)}_{3(s)}$ can be separated from aqueous solution. Thus, in order to remove the Cr(VI), it becomes necessary to perform at least the following two steps: (i) reduction from Cr(VI) to Cr(III) and (ii) precipitation of the Cr(III) formed. From examination of Equation 2 one can observe that stage (i) requires acid media in order to displace the equilibrium to the right; therefore, a continuous proton supply is needed to maintain the pH at optimum level (i.e., pH 2). Furthermore, under this pH condition the reduction process reached equilibrium after a short time, but at higher pH values the process turned sluggish [24].

In our experimental conditions, the Cr(VI) removal process involves the following reaction:

$$7\text{H}^+ + 3\text{Fe}^{2+}_{(aq)} + \text{HCrO}^-_{4(aq)} \Longleftrightarrow 3\text{Fe}^{3+}_{(aq)} + \text{Cr}^{3+}_{(aq)} + 4\text{H}_2\text{O}_{(l)}$$
$$(3)$$

The Fe(II) and Fe(III) chemical species considered in Reaction 3 are the predominant ones at the experimental conditions as shown in Figures 3 and 4.

Once the reduction Reaction 3 takes place (by either method, chemical or electrochemical) the pH has to be increased to form insoluble species (Equations 4 and 5). Note that the insoluble products formed according to Reactions 4 and 5 will constitute the sludge in this work.
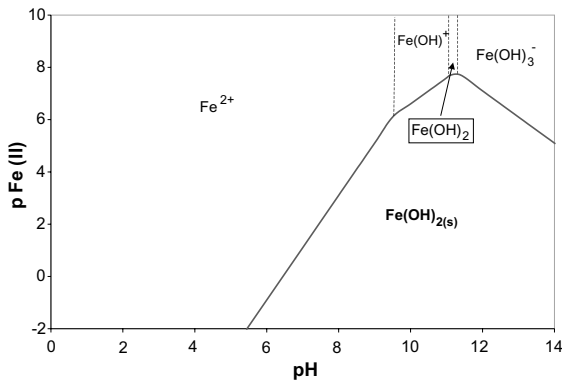

Fig. 3. Predominance zone diagram for Fe(II) chemical species in aqueous solution. Solid lines represent solubility equilibrium of Fe-(OH)$_{2(s)}$ and boundaries among soluble chemical species.
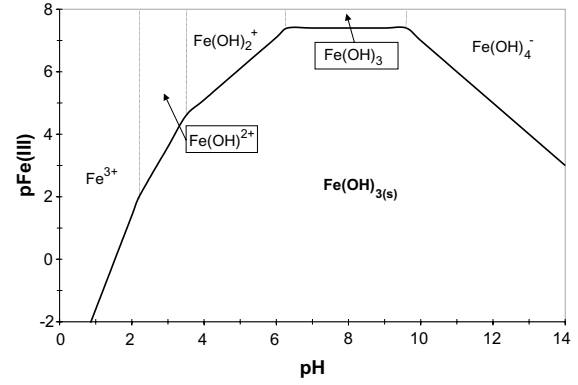

Fig. 4. Predominance zone diagram for Fe(III) chemical species in aqueous solution. Solid lines represent the solubility equilibrium of Fe(OH)$_{3(s)}$ and the boundaries among soluble chemical species.

$$\text{Cr}^{3+}_{(aq)} + 3\text{OH}^-_{(aq)} \Longleftrightarrow \text{Cr(OH)}_{3(s)} \quad (4)$$

$$\text{Fe}^{3+}_{(aq)} + 3\text{OH}^-_{(aq)} \Longleftrightarrow \text{Fe(OH)}_{3(s)} \quad (5)$$

3.1.1. *Optimal pH conditions for precipitation*
From the analysis of Figures 2 and 4, optimal pH values to form insoluble species are in the 8.5 to 10.0 pH range: in this pH range it is also possible to precipitate the excess amount of Fe(II) ions added to the solution, as could be observed in Figure 3. Note that for pH values >10, the solubility of both Cr(OH)$_3$(s) and Fe(OH)$_3$(s) increases, therefore in order to achieve the minimum quantity of metallic ions species in solution, it is fundamental to control the addition of the alkaline solution used to increase the pH.

It should be noted that at low pH values, Fe(II and III) as well as Cr(III) appear as free ions in aqueous solution, even though they are solvated. As the experiments revealed, the lower the pH, the better the reduction rates achieved. Possible charge distribution and spatial configuration changes as hydro-complexes 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, and in some cases the solution remains stable for periods as long as months or even years. Values of pH less than 3 are needed to accelerate the reduction reaction in aqueous solution [7].

3.1.2. *Stability of the sludge generated*
It was reported [18] that in the Cr(III)–H$_2$O–H$^+$ system it is possible to form soluble polynuclear species of Cr(III), however this requires two or three days. Figure 5 shows the PZD of the system Cr(III)–H$_2$O–H$^+$ when polynuclear species are taken into account [25, 26]. A comparison of Figures 2 and 5 clearly reveals that the net effect of the formation of polynuclear species (in particular $\text{Cr}_3(\text{OH})_4^{5+}$) is the solubility increase of Cr(OH)$_3$(s); the latter is so important that it brings about a decrease of approximately three orders of magnitude in the pH stability range of the Cr(OH)$_3$(s)
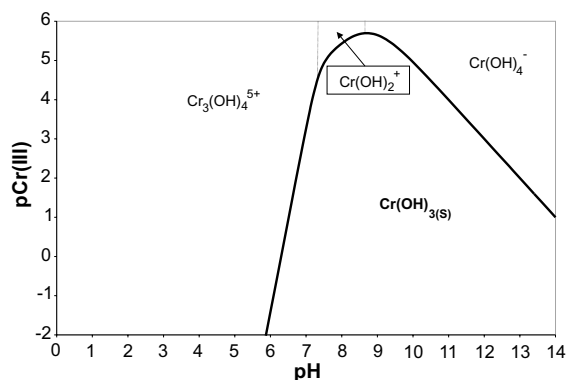
Fig. 5. Predominance zone diagram for Cr(III) taking into account the formation of polynuclear chemical species.

species. Furthermore, this indicates that as the contact time between liquid and solid phase elapses, the possibility to re-dissolve chromium in the sludge increases. Figure 5 shows the effect of formation of soluble polynuclear species on the $Cr(OH)_3$(s) solubility.

From the previous discussion, it transpires that the pH range proposed herein is the optimal for chromium removal. Moreover, the said range must be maintained to be able to proceed with separation of the solids formed, otherwise the Cr-based phases would redissolve. Even if polynuclear species are formed under these conditions, the method proposed here enables the fulfilment of the international environmental wastewater discharge limits ($[Cr_{total}] < 0.5$ mg L^{-1}) [27, 28]. Figure 6 compares the equilibria related to the formation of polynuclear species and those, which do not consider their formation. Outside this range the solubility of $Cr(OH)_3$(s) increases exponentially.

The thermodynamic analysis is in close agreement with the experimental evidence recently reported by Avena et al. [27] and Fitts et al. [28]. These authors showed that the (nonpolymerized) non-aged active monomeric hydroxide and the crystalline sample of chemical formula $Cr(OH)_3 \cdot 3H_2O$, have a layered array structure of $Cr(OH)_3(H_2O)_3$ monomers, which are linked through hydrogen bonds between the OH^- and H_2O of adjacent Cr(III) centres. Since the ageing of the active material leads to polymerization, the intermediate solids between the active and the polymeric chromium hydroxide are turned into a mixture of monomeric, oligomeric, and polymeric Cr(III) species. The longer the time and the higher the ageing temperature, the greater the proportion of oligomers or polymers. Nevertheless, although there is some agreement in the literature on the formation constants of the first and second hydrolysis products of $Cr(H_2O)_6^{3+}$, a consensus regarding the occurrence, distribution, and kinetics of higher order hydrolysis products, polymers, and hydroxide precipitates does not exist [28].

3.2. *Quantity of the sludge obtained by the chemical and electrochemical treatment*

The Cr(VI) reduction process was outlined in Section 2.2. To remove Cr and Fe species from the aqueous phase and to transfer them to the solid phase, an aqueous solution containing 1 M Ca(OH)$_2$ was added to achieve a pH value of 8.5–9.0. Maximum insolubility for both Fe(III) and Cr(III) hydroxide species is reached under the conditions stated, as predicted by the thermodynamic analysis shown above. Table 1 shows the results on the amount of sludge generated by both methods chemical and electrochemical.

From Table 1, use of the chemical method to remove Cr(VI) from solution requires, for all the different initial Cr(VI) concentrations in the solutions considered, an excess of FeSO$_4$ of 200% with respect to the stoichiometric quantity, estimated according to Reaction 3 considering 100% efficiency, to achieve a final Cr(VI) concentration that satisfactorily complies with environmental wastewater discharge limits [27, 28].

Another important aspect shown in Table 1 relates to the amount of sludge produced by each method. In all cases the quantity of sludge generated by the electrochemical technique is lower than the other one. For instance, to obtain a final Cr(VI) concentration lower than 0.5 mg L^{-1}, starting with a solution containing 500 mg L^{-1} Cr(VI), the electrochemical sludge generation corresponded to 38% respect to the chemical means. For the other different initial Cr(VI) concentrations, namely 100, 200 and 300 mg L^{-1}, there occurred a 56, 57 and 63% reduction in sludge generation, respectively. Therefore, in all cases, the sludge generated by the electrochemical method is at least 50% less compared than that resulting from the chemical method.

3.3. *Electrochemical treatment*

The theoretical variation of the Cr(VI) concentration, $[Cr(VI)](t)$ that remains in solution during the evolution of the electrochemical method can be estimated as follows. Variation of the number of moles of hexavalent chromium, remaining in solution, as a function of the

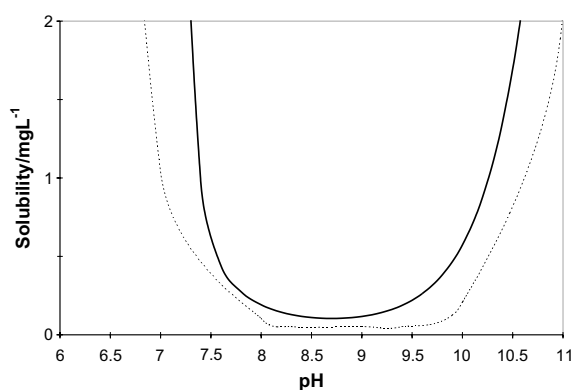*Fig. 6.* Influences of the polynuclear soluble species of Cr(III) on the $Cr(OH)_3$(s) solubility in aqueous solution. Continuous line represents solubility equilibrium of $Cr(OH)_3$(s) while dotted line shows the polynuclear species that are formed upon ageing the precipitate.

Table 1. A comparison of the amount of sludge generated using an electrochemical treatment and chemical means

Treatment[*,‡]	Initial Cr(VI) concentration in aqueous solution /mg L^{-1}	Final Cr(VI) concentration in aqueous solution /mg L^{-1}	Amount of FeSO$_4$ added /g L^{-1}	Dry weight of sludge /g
C	100 ± 1.61	10 ± 0.79	0.96[§]	1.52 ± 0.02
C	100 ± 1.61	1 ± 0.04	1.44	1.75 ± 0.01
C	100 ± 1.61	<0.5	1.92	1.99 ± 0.01
C	200 ± 0.70	8.3 ± 0.30	1.92[§]	1.91 ± 0.01
C	200 ± 0.70	1.1 ± 0.15	2.88	2.05 ± 0.02
C	200 ± 0.70	<0.5	3.84	2.36 ± 0.01
C	300 ± 1.79	7.6 ± 0.40	2.88[§]	2.10 ± 0.01
C	300 ± 1.79	0.91 ± 0.20	4.32	2.42 ± 0.01
C	300 ± 1.79	<0.5	5.76	2.87 ± 0.01
C	500 ± 1.62	9.8 ± 0.56	4.82[§]	4.26 ± 0.01
C	500 ± 1.62	1 ± 0.10	7.23	5.01 ± 0.01
C	500 ± 1.62	<0.5	9.64	5.32 ± 0.01
EC[†]	100 ± 1.61	<0.5	–	0.88 ± 0.01
EC[†]	200 ± 0.70	<0.5	–	0.99 ± 0.01
EC[†]	300 ± 1.79	<0.5	–	1.06 ± 0.01
EC[†]	500 ± 1.62	<0.5	–	2.01 ± 0.01

[*] C chemical; EC electrochemical.
[†] Operating the electrochemical reactor in batch mode.
[‡] Treatment times, in the case of the electrochemical method are clearly shown in Figures 7(a)–(d), whereas reduction process in the chemical one requires ∼5 min in all cases.
[§] Stoichiometrical quantity.

treatment time, $n_{Cr(VI)}(t)$, can be estimated through the difference between the initial number of moles of Cr(VI) present in solution, $n_{Cr(VI)}^0$, and the number of moles of Cr(VI) that are being reduced, $n_{Cr(VI)}^{reac.}(t)$, due to Red–Ox (Reaction 3) with Fe(II) ions anodically liberated into the solution when a constant, direct current is applied to the electrode. Equation 6 shows this relationship:

$$n_{Cr(VI)}(t) = n_{Cr(VI)}^0 - n_{Cr(VI)}^{reac.}(t) \qquad (6)$$

where $n_{Cr(VI)}^{reac.}(t)$ is directly related to the number of Fe(II) moles, $n_{Fe(II)}(t)$ electrochemically formed. Therefore, considering the stoichiometric information given in Equation 3 and assuming 100% efficiency, we arrive at

$$n_{Cr(VI)}(t) = n_{Cr(VI)}^0 - \frac{n_{Fe(II)}(t)}{3} \qquad (7)$$

Due to Fe(II) ions supplied to the solution as stated in Equation 8, thus we can use the Faraday law to relate $n_{Fe(II)}(t)$ with the current applied (i), as indicated by Equation 9:

$$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2\,e^- \qquad (8)$$

$$n_{Fe(II)}(t) = \frac{i}{zF}t \qquad (9)$$

where z is the dissolution valency and F is the faradaic constant (96 500 C mol^{-1}).

Substituting from Equation 9 into Equation 7, we have

$$n_{Cr(VI)}(t) = n_{Cr(VI)}^0 - \frac{i}{3zF}t \qquad (10)$$

Multiplying Equation 10 by the chromium atomic mass (M_{Cr}) and dividing by the solution volume (V) yields

$$[Cr(VI)](t) = [Cr(VI)]_0 - \frac{M_{Cr}i}{3zFV}t \qquad (11)$$

where $[Cr(VI)](t)$ is the time variation of the hexavalent chromium concentration and $[Cr(VI)]_0$ is the initial ($t = 0$) hexavalent chromium concentration.

Finally, considering our experimental conditions ($i = 5$ A and $V = 3$ L), the appropriate physical constants, and adequate units transformation, then Equation 11 becomes

$$[Cr(VI)](t)/mg\,L^{-1}$$
$$= [Cr(VI)]_0/mg\,L^{-1} - 8.69/mg\,L^{-1}\,min^{-1}t \qquad (12)$$

During deduction of Equation 12 it was assumed that Cr(VI) reduction is solely due to the iron anodically released into solution.

Figure 7 shows the comparison of experimental data and theoretical calculations for Cr(VI) reduction as a function of time during the electrochemical treatment. For all the experimental cases, the time required to comply with international environmental wastewater discharge limits for Cr(VI) is shorter than that theoretically predicted using Equation 12.

To support the implication derived from the numerical comparison between the experimental and the theoretical iron demand above, it is necessary to postulate additional electrochemical reduction reactions, such as Equations 13–16, which must be taking place at the cathode surface. Among the latter, Equations 14 and 15 are indeed relevant as both bear the
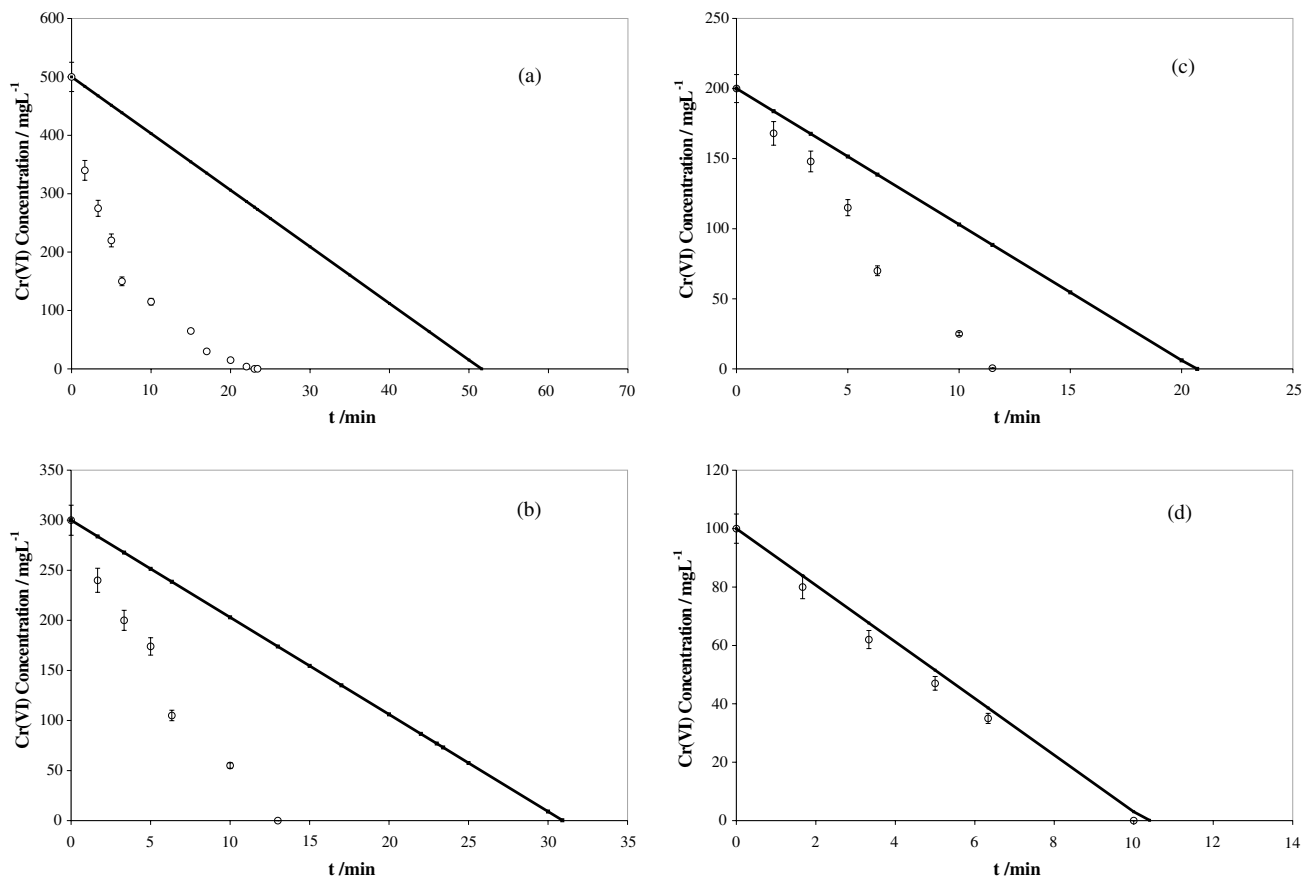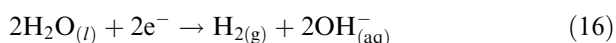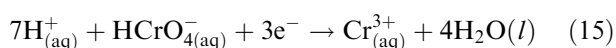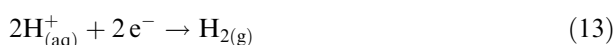
Fig. 7. Comparison of theoretical (—), according with Equation 12, and experimental data (○) for the depletion of Cr(VI) in solution as a function of electrochemical treatment time, during batch operation for different initial Cr(VI) concentration (a) 500, (b) 300, (c) 200 and (d) 100 mg L^{-1}.

potential capable of exerting further reduction, thus aiding the overall process. However, it is indeed important to draw attention to Equation 15, as it focuses predominantly onto the ancillary reduction contribution to remove the pollutant singled out for elimination purposes:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \tag{13}$$

$$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)} \tag{14}$$

$$7H^+_{(aq)} + HCrO^-_{4(aq)} + 3e^- \rightarrow Cr^{3+}_{(aq)} + 4H_2O(l) \tag{15}$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{16}$$

Taking into account their respective electrode potentials, Equations 14 and 15 are thermodynamically favoured amidst the other reactions listed above [24]. Moreover, a presence of bubbles (cf. Reaction 13) on the cathode surface was observed, although to a very limited extent with our experimental conditions (i.e., 50 A m^{-2}) although we noticed that this process was a function of the magnitude of the current density applied. Consequently, we might consider Reactions 13 and 15 in proposing a mechanism which would explain the time reduction for removal of Cr(VI) as observed.

The evidence plainly points to a significant increase in the rate of removal, a situation which entails overall process economy. However, the occurrence of Reaction 15 partly explains the observed differences between the chemical and the electrochemical method in reference to the amount of sludge generated (cf. Table 1). Nonetheless, as less iron is required to reduce the hexavalent chromium present in aqueous solution, then less Fe(OH)$_3$(s) will precipitate. Consequently, the amount of sludge diminishes.

In this paper we propose to estimate the amount of Cr(VI) cathodically reduced using the difference between the experimental and theoretical amounts of sludge produced. In this case, the theoretical procedure to estimate the quantity of sludge involves the sum of Equations 3–5, which results as

$$3H_2O_{(l)} + 5OH^-_{(aq)} + 3Fe^{2+}_{(aq)} + HCrO^-_{4(aq)}$$
$$\rightleftharpoons 3Fe(OH)_{3(s)} + Cr(OH)_{3(s)} \tag{17}$$
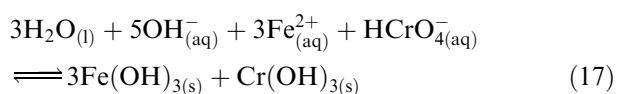
According to Equation 17 the theoretical estimation of the amount of sludge (Fe(OH)$_{3(s)}$ + Cr(OH)$_{3(s)}$) generated by complete removal of the Cr(VI) initially present in solution assuming again 100% efficiency and that Cr(VI) is the limiting reactant can be achieved.

Table 2. Experimental and theoretical quantity of sludge generated using the electrochemical treatment, for different Cr(VI) initial concentration, and the amount of Cr(VI) reduced at the cathode

Initial Cr(VI) concentration in aqueous solution /mgL^{-1}	Experimental sludge /g	Theoretical sludge /g	Difference /%	Amount of Cr(VI) reduced in the cathode /g
100 ± 1.61	0.765 ± 0.05	0.845	6.6	0.003
200 ± 0.70	0.906 ± 0.01	1.658	45.2	0.089
300 ± 1.79	1.025 ± 0.03	2.439	57.9	0.174
500 ± 1.62	1.893 ± 0.04	4.073	53.5	0.267

Table 2 shows both experimental and theoretical data related to sludge generation during the electrochemical process. From further consideration of the comparison of theoretical and experimental data, the difference between the amounts of residue generated can be ascribed to the quantity of Fe(OH)$_3$(s) that was not necessary to form due to intervention of Reaction 15. From this difference, it is possible to estimate the amount of Cr(VI) that should have been reduced in the cathode surface considering the stoichiometrical relation stated in Equation 17. Table 2 also shows the amount of Cr(VI) reduced in the cathode following the above procedure.

Table 2 shows that as the Cr(VI) initial concentration raises the amount of chromium reduced in the cathode increases. This explains the difference observed between the experimental data and the theoretical prediction made using Equation 12, (Figure 7(a)–(d)).

3.4. *Continuous Cr(VI) reduction*

The electrochemical reactor was fed continuously with an aqueous solution containing 130 mg L^{-1} of Cr(VI); once filled, a current density of 50 A m^{-2} was imposed. Table 3 gives the input and output Cr(VI) concentrations taken at the reactor's sampling port 4: it becomes straightforward that a continuous Cr(VI) reduction of 99% is achieved with a maximum flow rate of 339 mL min^{-1}.

Figure 8 shows the data obtained for continuous Cr(VI) removal in the electrochemical reactor as a function of time, for each sampling port applying the optimal flow rate (339 mL min^{-1}).

From the curves in Figure 8 it stands out that for all ports, the initial concentration of Cr(VI) appears smaller respect to that indicated in the Figure caption as the initial condition. This is explained by the rapid removal
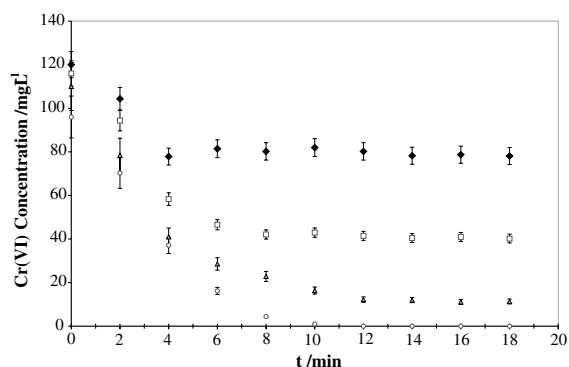

Fig. 8. Time-dependence of Cr(VI) removal measured at the different sample ports: (◆) port 1, (□) port 2, (▲) port 3 and (○) port 4. Experimental conditions for operating the electrochemical reactor: initial Cr(VI) concentration 130 mg L^{-1}, current density 50 A m^{-2} and a flow rate 339 mL min^{-1}.

effected, before passing any current through the reactor, during the initial contact between the incoming Cr(VI)-bearing solution with the steel electrodes in the reactor. This evidence shows that electroless corrosion of inexpensive plain carbon-steel electrodes is only able to produce some Cr(VI) removal. Unfortunately, this is not enough to achieve compulsory discharge limits for Cr(VI); clearly the most important consideration is that the shorter the time (and energy) consumed to achieve the most extensive removal of the pollutant, then the most effective is the process. Therefore, with an external electron supply the removal process accelerates. At this point, is important to stress that such an external source may well be one of the existing, standard power supplies in chromium-plating plants, which after working for primary production purposes, it may then be put to carry out just-as-important removal work, which would be plainly desirable to comply with mandatory contaminant concentration limits, using the environmentally

Table 3. Influence of the flow rate on the continuous Cr(VI) reduction in a plug-flow electrochemical reactor

Flow /mL min^{-1}	Initial Cr(VI) concentration /mg L^{-1}	Final Cr(VI) concentration* /mg L^{-1}	Cr(VI) removal /%
550	130 ± 1.38	54.23 ± 0.95	57.93
486	130 ± 1.38	45.33 ± 1.92	64.73
394	130 ± 1.38	31.25 ± 0.30	75.97
339	130 ± 1.38	<0.5	99.99
261	130 ± 1.38	<0.5	99.99

*Evaluated at port 4 (exit).

[†] Detection limit of the diphenilcarbazide method for Cr(VI) quantification is 10 μg L^{-1}.

friendly and economical procedure, as outlined in this work. For all cases, steady state conditions are reached after 10 min, and that under such a regime it is assured that traversing the reactor favours continuous Cr(VI) removal, which enables the user to fulfill international standards. It is inferred from experimental results in Figure 7(d) that operating the reactor in batch mode needed 10 min to reduce Cr(VI) to a concentration value lower than 0.5 mg L^{-1}, and from Figure 8, during continuous operation, it is possible to note that a similar time is required in port 4 to achieve a Cr(VI) concentration lower than 0.5 mg L^{-1}. Therefore, similar results are obtained with both reactor operating modes: batch and continuous, which suggests that a similar rate determining step controls the continuous reduction of Cr(VI) as that previously described. However, the continuous mode offers quite a significant advantage, since it opens the possibility for online treatment of the rinsing waters from plating facilities.

3.5. Sludge features

3.5.1. Sludge settling behaviour
It is a common practice to estimate the sludge settling rate (v_s) of a solid phase (S) mixed in the bulk of a liquid phase, filling a graduated cylinder with 1 L of the mix and reading the evolution of the height (H) of S as a function of time (t), then v_s can be estimated by Equation 18:

$$v_s = \frac{dH}{dt} \tag{18}$$

The behaviour of the sludge produced under two different conditions, with and without polymer addition to the mix, are now described:
(a) Settling rates without polymer. The inset in Figure 9 shows the plots depicting the settling characteristic of the solid sludge without polymer. Here there is a similar trend for both chemical and electrochemical sludge. When $dH/dt = 0$, the topmost compaction zone is reached. For the sludge chemically produced, this
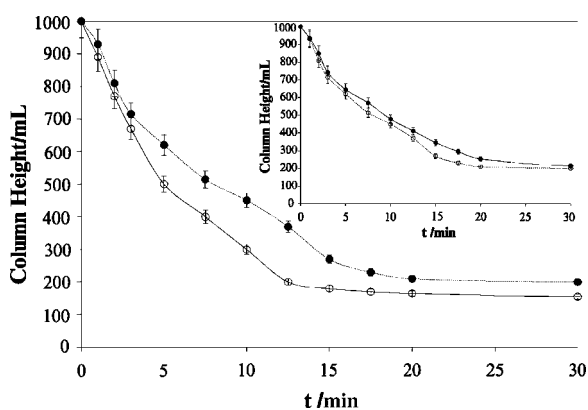
condition is attained after 30 min elapsed, whereas that formed electrochemically required only 20 min, thus a 33% reduction in time is achieved.
(b) Settling rates with polymer. To increase the settling rate of the precipitate, 2 ml of a commercially available cationic polymer was added per litre of the mix. Figure 9 shows how the settling velocity of the sludge is increased when the polymer was added. The main effect of the polymer was the same for both types of sludge, to diminish the time required to reach the topmost compaction zone, 20 min for the chemically formed and 15 min in the case of the electrochemical one. Therefore, a 33% time reduction is achieved when the polymer is added to the sludge chemically formed and 25% for the other. Moreover, when the polymer was added, the electrochemically generated sludge requires 25% less time to reach the compaction zone compared with the chemical precipitate. Thus, the use of such polymer decreases the processing time in the clarifier, increasing the throughput for whole process.

3.5.2. Sludge morphology and composition
SEM analysis was carried out to observe the morphology of the sludge generated during both electrochemical and chemical Cr(VI) reduction processes. After adequate drying and mounting on the SEM studs, secondary electron images were obtained as well energy dispersive analysis taken on particles large enough to facilitate counting the radiation emitted.

Figure 10 shows typical SEM images of the particles formed: (a) chemically and (b) electrochemically. It is
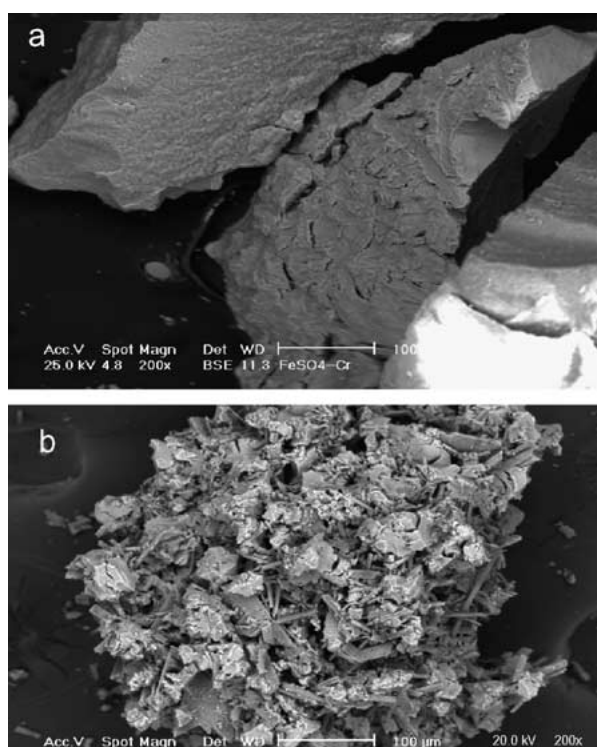

Fig. 9. Variation of the solid phase level (sludge) in a graduated cylinder as a function of the settling time for both chemically (●) and electrochemically (○) formed when a cationic polymer was added. Inset shows the same kind of curves without polymer.

Fig. 10. Microphotograph, 200×, of the sludge generated during the chemical (a) and electrochemical (b) removal of Cr(VI).

plain that both morphologies are different, while the first one appear to be dense and large the latter form clusters compounded by three kind of particles (needle-like, flake-shape and spherules), with quite a large number of them displaying a more or less defined flake-shape upon which, finer particles gather profusely, almost covering the larger ones (spherules) and other needle-like which are easily seen protruding randomly.

Elemental composition was determined from the EDAX analysis carried out on both types of sludge. It was found that they are mainly formed by iron, oxygen, chromium and calcium which confirms the formation of insoluble species such as $Fe(OH)_3$ and $Cr(OH)_3$ that are present in this structure.

3.6. Economical analysis

So far we have shown that both methods could be successfully applied to remove Cr(VI) from wastewater and that the main advantage of using the electrochemical method is to produce some 50% less sludge when compared with the chemical means. However, this might not be enough to justify its use. Therefore, an economical analysis of both techniques is required.

Table 4 shows the expenditures required to treat 1 m³ of Cr(VI)-containing wastewater using both methods. The total cost of treating this wastewater is 50% less using the electrochemical technique. Interestingly, such a difference is directly related to the cost associated for loading, transportation and disposal of the sludge, as may be deduced.

4. Conclusions

The use of thermodynamic chemical analysis allowed the construction of predominance zone diagrams. These enabled the description of the chemical systems of interest to the present work: Cr(VI)–Cr(III)–H_2O–e^- and Fe(III)–Fe(II)–H_2O–e^-, as well as the chemical interaction among the predominant species in this systems. This study allowed us to gain insight on both the chemical and electrochemical processes involved during effective Cr(VI) removal. Optimum conditions for the reduction of chromium and subsequent precipitation can be designed through the use of this methodology. Moreover, it is also shown that ageing the precipitate promotes the formation of soluble polynuclear species of Cr(III). Therefore, it is recommended that both phases should be separated as soon as they are formed.

There is a significant amount of sludge generated using the chemical method (iron sulfate); on the other hand the electrochemical means (both dissolution of iron and cathodic reduction), reduces the formation of sludge and in this way it is possible to minimise the environmental impact. Furthermore, the electrochemical means provide much better process control since electrical signals such as current and potential difference are used.

With the complexity of the system understood, an electrochemical reactor was designed and calibrated so that the international discharge limits were fulfilled effectively in a continuous way.

Both treatments studied here to remove Cr(VI) can be successfully applied. The main advantage of the elect-

Table 4. Summary of expenditures associated with the treatment of 1 m³ of wastewater containing an initial concentration of Cr(VI) of 500 mg L⁻¹ using both way to remove Cr(VI), chemical and electrochemical

Sector	Cost (US $/m³)	
	Chemical	Electrochemical (continuous mode)
Initial adjustment (pH 2)[a]	0.15	0.15
Energy consumption for electrolysis[b]	–	0.58
Chemical added $FeSO_4$[c]	0.84	–
Energy needed for pumping solution through electrochemical reactor[d]	–	0.05
Energy for stirring in the chemical method[e]	0.02	–
Base added to rise pH[f]	0.30	0.3
Polymer added[g]	0.04	0.04
Sludge loading[h]	0.12	0.05
Sludge transportation[i]	1.16	0.44
Sludge landfill[j]	1.85	0.70
Total	4.48	2.31

[a] 1 litre of H_2SO_4 needed at 0.15 $/L.
[b] Using Equation 3 in [31], we find that 5.83 kWh m⁻³ are required. The price of 1 kWh is 0.1 $.
[c] From Equation 3, considering 100% efficiency and the initial Cr(VI) concentration, 8.4 kg are required, (200% in excess of the stoichiometric amount). The price of 1 kg is 0.1 $.
[d] Considering a 3/4 h.p. neoprene pump consuming 0.53 kWh. The price of 1 kWh is 0.1 $.
[e] Considering a 1/4 variable speed stirrer consuming 0.150.53 kWh. The price of 1 kWh is 0.1 $.
[f] 1.5 kg of $Ca(OH)_2$, at 0.2 $/kg.
[g] 0.01 kg is required at 4 $/kg.
[h] Load 0.0034 $/kg, as described in [32, 33].
[i] Transportation 0.03281 $/kg, as described in [32, 33].
[j] Landfill 0.0532 $/kg as described in [32, 33].

rochemical treatment is to produce some 50% less sludge when compared with the chemical means, a factor directly reflected in the operational costs.

Acknowledgements

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