



Electrochemical removal of Cr(VI) from aqueous media using iron and aluminum as electrode materials: Towards a better understanding of the involved phenomena

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ABSTRACT

In the present work, electrocoagulation process with iron and aluminum electrodes was investigated to deepen the understanding of the mechanism of hexavalent chromium (Cr(VI)) removal. Electrocoagulation treatment efficiency was studied with regards to the abatement of Cr(VI) and the resulting species—namely Cr(III), Fe(II) and/or Fe(III). Unlike iron, aluminum electrodes were found to be unsatisfactory for Cr(VI) removal. To elucidate the removal mechanism of hexavalent chromium, different anode/cathode materials and configurations (Fe/Fe, Pt Ti (platinized titanium)/Fe, Al/Al and Pt Ti/Al) were considered. At nearly neutral pH and considering aluminum electrodes, 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. However, the contribution of the two mechanisms to Cr(VI) removal was not discriminated. On the other hand, in the case of iron electrodes, even though electrochemical reduction may contribute to chromium removal, its influence seemed to be minor since the effect was confined to less than 5% of the removal efficiency. Hence, there was essentially one real root for the reduction of Cr(VI) by electrocoagulation with iron electrodes, and it was proven to be the chemical reduction by Fe(II) anodically generated. Moreover, the resulting Cr(III) was quickly removed from solution, via efficient precipitation as Cr(OH)₃ hydroxides. Besides, the electrodisolved iron remained at low level owing to the precipitation of Fe(OH)₂ and/or Fe(OH)₃. Although chemical reduction by Fe(II) predominantly governed the removal of Cr(VI), acidic pH media was found to promote electrochemical reduction of hexavalent chromium at the cathode and accordingly to enhance Cr(VI) removal efficiency. In contrast, a delay of Cr(III) precipitation and a contamination of the electrolyte by electrodisolved iron were observed under acidic conditions. The effect of supporting electrolyte (Na₂SO₄ and NaCl) on chromium removal was also studied. No conspicuous disparity in the treatment efficiency was noted under the electrocoagulation conditions used.

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1. Introduction

Chromium ions are pollutants arising from many diverse fields such as metallurgy, electroplating, leather tanning, chemical catalysts, pigments, corrosion inhibitors and printing inks. The chemical and toxicological behaviors of chromium depend on its oxidation state: Cr(VI) or Cr(III). Because it has a high solubility in water, Cr(VI) has a significant mobility in the environment [1]. Chromium (III), on the other hand, has a low solubility in water and readily precipitates as Cr(OH)₃ [2] under alkaline or even slightly acidic

conditions. Cr(VI) is toxic to most living organisms [3–5] and a known human carcinogen by the inhalation route of exposure [6–8]. Although trivalent chromium is considered as an essential nutrient for the human body [9] and its toxicity is 500–1000 times less to a living cell than hexavalent chromium [8], exposure to excessive doses of Cr(III) for long periods of time may also cause some adverse health effects [10]. Therefore, Cr-contaminated wastewater has to be treated before being discharged. It is to note that the discharge of Cr(VI) to surface water is regulated to <0.05 mg/L, according to the United States Environmental Protection Agency (USEPA), whereas the total chromium (Cr(III), Cr(VI) and other forms of chromium) is regulated to be discharged at <0.1 mg/L [11].

Conventionally, chemical reduction–precipitation process is used to remove Cr(VI) from wastewater [12]. The method is a two-step process in which reduction and precipitation at highly acidic (pH ≈ 2) and alkaline pH conditions (pH 9–10), respectively, occur in

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Nomenclature

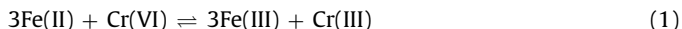
S_{TE}	effective area of electrode
d_{ie}	electrodes gap
J	current density
pH _i	initial pH of electrolyte
Cr TT	residual total chromium
Fe Th	theoretical amount of Fe ²⁺ electrogenerated during electrolysis

succession. Cr(VI) is reduced to the trivalent state, Cr(III), prior to the precipitation step. A number of chemical reductants for converting Cr(VI) to Cr(III) are described in the literature, including ferrous iron (Fe(II)) compounds [13–18], metallic iron (Fe⁰) [19,20] and reduced sulfur compounds [21]. Among these reductants, Fe(II) compounds are the most commonly used reagents reported in the literature [13–18]. Although acidic reduction with subsequent precipitation is shown to be quite efficient in treating industrial effluents, the chemical process may induce secondary pollution caused by the high amounts of added chemical substances and results in the formation of sludge which is relatively difficult to handle and dispose off.

A variation of this method that emerged in the past decade is electrocoagulation with iron electrodes which implies the reduction of Cr(VI) and precipitation of the resulting Cr(III) from the contaminated water stream in a single step by electrochemical addition of Fe(II) [22–34]. Cr(VI) was also shown to be removed from solutions by electrocoagulation with aluminum electrodes [35–37]. According to some authors [35,36], direct cathodic reduction of Cr(VI) followed by Cr(III) precipitation was suggested in this case.

In an electrocoagulation process, no addition of chemicals is necessarily needed. Small volume of sludge is produced, comparing with that in classical chemical process, which can be easily removed by decantation. Moreover, from an industrial point of view, the significant attention for electrochemical chromium removal process is due to its operational and maintenance simplicities.

Regardless of the speciation of the species taking part in the reduction of Cr(VI) by Fe(II), the simplified scheme of this reaction can be written as [13,16,25]:



Actually, reduction of Cr(VI) is more complicated. Although Cr(VI) removal by electrocoagulation process was observed to be efficient, reported reduction mechanisms from the different studies are often in some disagreement [28–30,32,35]. Moreover, despite the extensive experimental work carried out on the removal of Cr(VI) by electrocoagulation, no definitive clues mainly as to the effect of pH and supporting electrolyte on the overall performances of the process (both reduction and precipitation steps) were found in the literature.

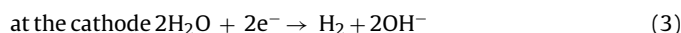
The aim of this work was to through more light on the removal mechanism of Cr(VI) by using different materials (Fe, Al, platinumized Ti) and electrode configurations. The effect of pH on the process practicability was also investigated when considering electrocoagulation with iron electrodes. Moreover, current density and supporting electrolyte were studied in term of process performances.

2. Brief review on Cr(VI) removal by electrocoagulation

In its more broad definition, electrocoagulation consists of electrolysis with soluble anode, generally made of iron or aluminum. In electrocoagulation, electrode material greatly influences the effec-

tiveness of the process. In the case of the treatment of wastewater containing hexavalent chromium, the application of this technology necessarily implies a preliminarily reduction step converting Cr(VI) to Cr(III). To fulfill this reaction, iron has been reported to be the most effective electrode material owing to the in situ electrogeneration of Fe(II) species acting as reductant. However, some investigators have observed that aluminum electrodes were also almost effective for Cr(VI) removal [35–37]. Nevertheless, whatever the electrode material considered, the mechanisms proposed to explain Cr(VI) removal have been the subject of much debate and there is a rather extensive and confusing literature on the topic. At this stage, a brief review of electrocoagulation process – using aluminum and iron electrodes – in treating wastewater containing Cr(VI) seems to be essential.

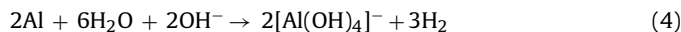
Concerning aluminum material, the main electrochemical reactions occurring at electrode surfaces during electrolysis are



Aluminum surface is known to be spontaneously covered by an oxide/hydroxide layer (passivation film) which is responsible for the electrodisolution inhibition of aluminum when anodically polarized [38]. When pH is between 4 and 8.5 [39], this layer is stable but undergoes localized attack (pitting dissolution) in halide anions presence, particularly Cl⁻ ions [40,41].

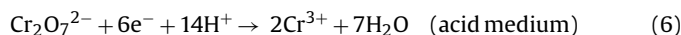
Aluminum ions (Al³⁺) produced by electrodisolution of the anode (Eq. (2)), act only as coagulant since they cannot take part in oxidation–reduction reactions. Actually, coagulation phenomena are more complex as the electrogenerated Al³⁺ ions immediately undergo spontaneous hydrolysis reactions which generate various monomeric and polymeric species such as [Al(OH)]²⁺, [Al(OH)₂]⁺, Al(OH)₃, [Al₂(OH)₂]⁴⁺, [Al₃(OH)₄]⁵⁺, [Al₆(OH)₁₅]³⁺, [Al₇(OH)₁₇]⁴⁺, [Al₈(OH)₂₀]⁴⁺, [Al₁₃O₄(OH)₂₄]⁷⁺, [Al₁₃(OH)₃₄]⁵⁺ [41–43] depending on the pH of the aqueous medium. The hydrolysis reactions make the anode vicinity acidic. Conversely, hydrogen evolution at the cathode (Eq. (3)) makes the electrode vicinity alkali. Cationic hydrolysis products of aluminum may react with OH⁻ ions to transform finally in the bulk solution into amorphous Al(OH)_{3(s)} according to complex precipitation kinetics [42,43]. In electrocoagulation process, two primary mechanisms can explain the coagulation of the negatively charged colloids by the in situ generated aluminum species: charge neutralization – minimizing the electrical repulsion between particles and favoring their agglomeration – and enmeshment of the colloids into the growing gelatinous amorphous hydroxide precipitates (sweep flocculation). The charge neutralization can be achieved – at acidic pHs – by the adsorption of the cationic hydrolyzed aluminum species (homocoagulation) or – at around neutral pH – by the coverage of negatively charged pollutant surface by the positively charged aluminum hydroxide precipitates (heterocoagulation) [43,44].

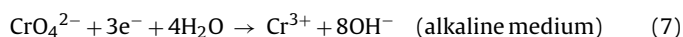
With regard to the amphoteric character of aluminum, the significant increase of the local pH at the cathode vicinity, due to hydrogen evolution (Eq. (3)), induces “chemical” attack of aluminum and its hydroxide film [41] according to the following reactions:



[Al(OH)₄]⁻ generated at the cathode vicinity is transformed finally in the bulk solution into amorphous Al(OH)₃.

When treating Cr(VI) containing solutions, an electrochemical reduction of Cr(VI) to Cr(III) at the cathode surface was proposed to occur [35,36]:





since Al^{3+} cannot reduce Cr(VI).

Furthermore, the hydroxyl ions formed at the cathode increase the pH of the wastewater, thereby inducing precipitation of Cr(III) ions as corresponding hydroxide:

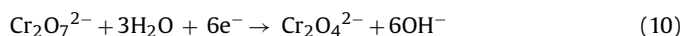


The formed aluminum species previously mentioned facilitate – by coagulation phenomena – the settling of the colloidal $\text{Cr}(\text{OH})_3$ precipitate.

In the case of iron electrodes, beside hydrogen evolution at the cathode surface (Eq. (3)), the main reaction occurring at the anode during electrolysis is

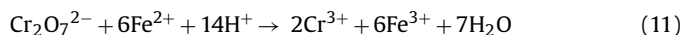


According to several authors, the Fe(II) released at the anode causes chemical reduction of Cr(VI) species (Eq. (1)) [22,28,29,32,34]. Besides, electrochemical reduction of Cr(VI) to Cr(III) at the cathode surface (Eqs. (6) and (7)) was also proposed to occur during electrocoagulation process [25,30,32]. However, its extent has never been quantified. Regardless of the involved reduction mechanism, several authors [22,30,31] claimed that the resulting Cr(III) combine with OH^- ions produced at the cathode (Eq. (2)) and precipitate as $\text{Cr}(\text{OH})_3$ (Eq. (8)). This view point was not shared by Lakshmipathiraj et al. [32] who suggested that essentially electrochemical reduction of Cr(VI) occurs at the cathode yielding to chromite formation owing to the high alkalinity produced (Eq. (3)) at the vicinity of this electrode:

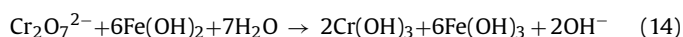
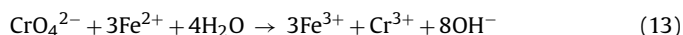


The formed chromite ions then combine with Fe^{2+} ions generated by electro-oxidation of the anode and precipitate as FeCr_2O_4 .

Under acidic conditions ($\text{pH} < 6.5$), no discrepancies as to the reaction scheme related to the chemical reduction of Cr(VI) by electrogenerated Fe^{2+} ions were found in the literature. Actually, the commonly adopted reaction scheme is



However, when the pH of the treated effluent is almost neutral or alkaline, many reaction schemes related to this reduction were found in the published accounts [22,28,29,30,32]:



The relevance of these reaction schemes will be discussed later (Section 4).

3. Materials and methods

Synthetic stock solution of 1000 mg/L Cr(VI) was prepared by dissolving the required amount of K_2CrO_4 . Solutions of lower concentrations: 45 and 180 mg/L were prepared by proper dilutions. Na_2SO_4 1 g/L and NaCl 0.5 g/L were used as supporting electrolytes. Initial pH of these model solutions was kept at its original value (near neutral) or adjusted to 2 by adding sulfuric acid.

All solutions were prepared from analytical grade chemical reagents (Fluka products) and used without any further purification. Deionized water was used in all the experimental runs.

Solution pH and conductivity were measured using high precision pH meter, equipped with a combined glass electrode (METROHM, 632) and electronic conductivity meter (TACUSSEL, type CD 6NG) equipped with an immersion measurement probe, respectively.

Electrocoagulation experiments were carried out using two parallel metallic plates. Iron and aluminum plates were cut from a commercial grade iron and aluminum sheets of 2 and 3 mm thickness, respectively. The electrode surface was first mechanically polished underwater with 400 grade abrasive paper in order to ensure surface reproducibility and remove the oxide layers from the electrodes, rinsed with deionized water, degreased in acetone, and dried prior to immersion in the electrolyte [41]. For some experiments, platinized titanium (Pt Ti) mesh (Dégussa, France) was used as anode. The effective area of each electrode used was 54 cm^2 ($7\text{ cm} \times 7.7\text{ cm}$). Only one side of each electrode was taken as working surface: the second one was spared. The electrodes were connected to a digital DC power supply (CONVERGIE – CLES 60-3) with potentiostatic or galvanostatic operational options providing current and voltage in the range of 0–3 A and 0–60 V, respectively. The current was maintained constant for each run. The anode/cathode gap was kept constant at 4 cm. Note that such value was found to be satisfactory in reducing the ohmic drop [41]. A gentle magnetic stirring rate of about 250 rpm was applied to the electrolyte in all tests. Electrolyte volume used was 900 mL. The total time duration of electrolysis was modulated according to the experimental run requirements. To follow the progress of the treatment, aliquots of 20 mL were periodically taken from the reactor then filtered to eliminate sludge formed during electrolysis. The residual concentration of aqueous Cr(VI) was determined photometrically using 1,5-diphenylcarbazide by the formation of a red-purple-colored complex in weak acidic solution [45]. The absorbance of the colored Cr(VI)–diphenylcarbazide complex was measured at a wavelength of 540 nm using an UV–vis spectrophotometer (Optima SP-3000 Plus) and compared with the calibration curve. The residual concentration of total chromium (Cr(III) and Cr(VI)) and total dissolved iron (Fe(II) and/or Fe(III)) was determined by atomic absorption spectrometry (Zeenit 700 spectrophotometer – Analytikjena) after nitric acidification and suitable dilution of samples.

All electrolysis experiments were performed at $30 \pm 1^\circ\text{C}$ and were duplicated. Analyses were carried out in triplicate.

4. Results and discussion

The electrocoagulation process is affected by several operating parameters, such as electrode materials, initial pH and current density. In order to enhance the process performances, the effects of these parameters were explored.

4.1. Effect of electrode material

To through more light on the reduction mechanism of Cr(VI) with iron and aluminum electrodes, different anode/cathode configurations: Fe/Fe, Al/Al, Pt Ti/Fe and Pt Ti/Al were used in this part to carry out electrolysis tests. It is noteworthy that platinized titanium was used as reference anodic material since no electrochemical chromium oxidation (Cr(III) to Cr(VI)) can occur at its surface even at current density reaching 80 A/dm^2 [46]. For these experiments, initial chromium concentration was 45 mg/L and initial pH of the electrolyte was 7.0 (original pH of the solution). A current density of 1 A/dm^2 was applied and Na_2SO_4 (1 g/L) containing 100 ppm NaCl was used as background electrolyte. It is to be noted that NaCl was intentionally added to avoid aluminum passivation [41]. Fig. 1 shows the evolution of residual Cr(VI) concentration vs. electrolysis time for the different anode/cathode configurations considered. Table 1 gives the corresponding values of the electrolyte pH reached after 60 min of electrolysis.

Fig. 1 clearly shows that iron electrodes are effective for Cr(VI) removal to below 0.5 mg/L. Conversely, the removal is poor (resid-

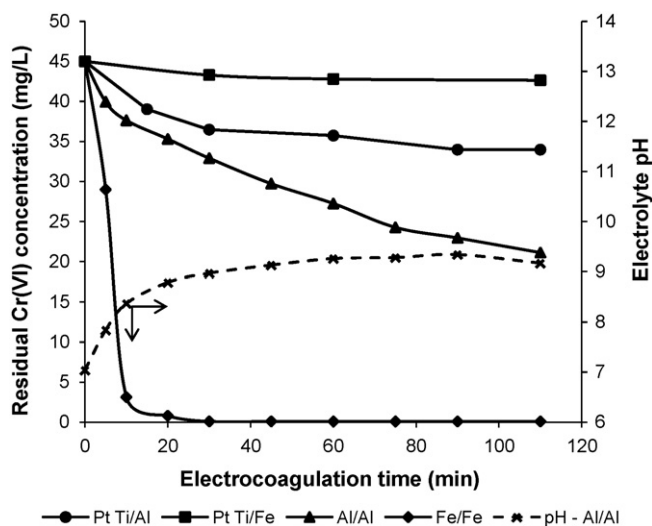


Fig. 1. Effect of different anode/cathode configurations on residual Cr(VI) concentration. Electrolyte: 45 mg/L Cr(VI) + Na₂SO₄ (1 g/L) + 100 ppm NaCl, pH_i = 7.0, $J = 1 \text{ A/dm}^2$, $S_{TE} = 2 \times 54 \text{ cm}^2$, $d_{ie} = 4 \text{ cm}$.

Table 1

Effect of anode/cathode configuration on electrolyte pH reached after 60 min of electrolysis. Electrolyte: 45 mg/L Cr(VI) + Na₂SO₄ (1 g/L) + 100 ppm NaCl, pH_i = 7.0, $J = 1 \text{ A/dm}^2$, $S_{TE} = 2 \times 54 \text{ cm}^2$, $d_{ie} = 4 \text{ cm}$.

Electrode configurations		Initial pH	pH after 60 min of electrolysis
Anode	Cathode		
Pt Ti	Fe	7.0	7.3
Pt Ti	Al		7.9
Al	Al		9.3
Fe	Fe		11.0

ual concentration of 21 mg/L after 110 min) when considering aluminum electrodes. It is to mention that, at all investigated configurations, the total chromium (Cr(VI) and Cr(III)) concentration vs. electrocoagulation time was always only little above the residual Cr(VI) concentration (not shown). Obviously, the formed Cr(III) was quickly removed from solution, via efficient precipitation as Cr(OH)₃ hydroxide.

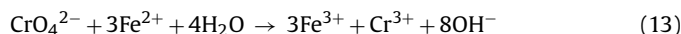
As seen from Table 1, when Fe/Fe configuration is used as anode/cathode combination, electrolyte pH value rises considerably. The pH variation during electrolysis is primary attributed to hydrogen evolution at the cathode (Eq. (3)). On the other hand, when Pt Ti/Fe is considered, merely a negligible chromium concentration decrease is observed (Fig. 1). Since electrolysis was carried out using platinized titanium as anode and iron as cathode, only electro-oxidation (Eq. (16)):



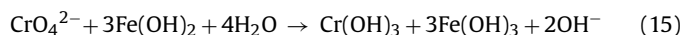
and reduction (Eq. (3)) of water were expected to happen. Accordingly, no pH change of the bulk solution could be observed. However, during these experiments, a slight pH increase is recorded (Table 1). Because Fe(II) electrogeneration was missing in this case (Pt Ti as anode), electrochemical reduction of hexavalent chromium (Eq. (7)) is suspected to take place at the cathode surface. This assumption may be suitable owing to the high alkalizing character of the latter reaction with regard to hydrogen evolution (Eq. (3)). Nonetheless, even though electrochemical reduction at the cathode may contribute to chromium removal, its influence seems to be minor since the effect is confined to less than 5% of the removal efficiency (Fig. 1). Hence, there is essentially one real root for the reduction of Cr(VI) by electrocoagulation with iron electrodes, and it is

proven to be the chemical reduction by Fe(II) anodically generated.

At this stage, it is advisable to note that according to literature [47], Cr(VI) exists in aqueous solutions only as oxyanions or oxyacids: chromate (CrO₄²⁻), monochromate (HCrO₄⁻), dichromate (Cr₂O₇²⁻) anions or chromic acid (H₂CrO₄) depending on the pH of the solution and Cr(VI) concentration. At Cr(VI) concentrations less than 10 mM (i.e. 520 mg/L), CrO₄²⁻ is the predominant species above pH 6.5, H₂CrO₄ predominates only if the pH is below 0.9, and HCrO₄⁻ predominates in the intermediate pH range of 0.9–6.5. For total concentrations of Cr(VI) greater than 10 mM, HCrO₄⁻ polymerizes to form Cr₂O₇²⁻ under acidic conditions. On the other hand, Fe(II) species globally exist as Fe²⁺ ions for pH less than 7.5 and as ferrous hydroxide Fe(OH)₂ when the pH exceeds 7.5 [48]. Considering the initial pH of the treated effluent and taking into account the pH increase occurring during electrolysis with iron electrodes, one may realize that the reaction schemes relating to the chemical reduction of Cr(VI) by Fe(II) cited earlier (Section 2) may change during the treatment process and consequently should be amended according to the species speciation [46,47] previously described. In this way, when the medium pH values are in the range of 6.5–7.5, the reaction can be written as

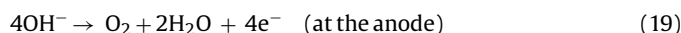
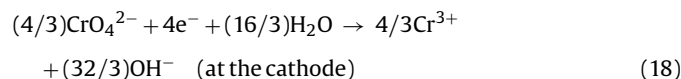
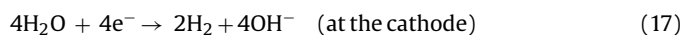


For pH values above 7.5, the corresponding reaction scheme is



According to Table 1, the solution pH rises – in the case of iron electrodes – from 7.0 to a final value of 11. The pH and concentration ranges used in these experiments imply that the CrO₄²⁻ is the predominant form of Cr(VI) present in the medium. Consequently, during electrolysis, as long as the pH remains below 7.5, the Fe(II) species released at the anode reduce Cr(VI) according to Eq. (13). When the pH value becomes higher than 7.5, Fe²⁺ ions precipitate in the bulk solution as Fe(OH)₂ and the reduction of chromium might be ascribed to Eq. (15).

Coming back to Fig. 1, one can show that in the case of Pt Ti/Al electrodes combination, chromium concentration decreases slightly but gradually to about 35 mg/L after 110 min of electrolysis. In the meantime, the solution pH increases only a little during the electrolysis (Table 1). For this configuration, only oxygen evolution (Eq. (16)) occurs at the anode, whereas hydrogen evolution and reduction of Cr(VI) to Cr(III) may take place at the cathode. For the same number of the exchanged electrons, these reactions can be written as



Besides these electrochemical reactions, “chemical” attack of the cathode (Eqs. (4) and (5)) and transformation – in the bulk solution – of the generated [Al(OH)₄]⁻ into Al(OH)₃:



occur during electrolysis. The formation of Al(OH)₃ precipitate was clearly observed during the experiments. Note that the alkalinity consumed by reaction (4) or (5) is balanced by that produced by reaction (20). Considering electrochemical reactions (Eqs. (17)–(19)), it can be stated that when hydrogen and oxygen evolutions (Eqs. (17) and (19)) are the only reactions occurring at the

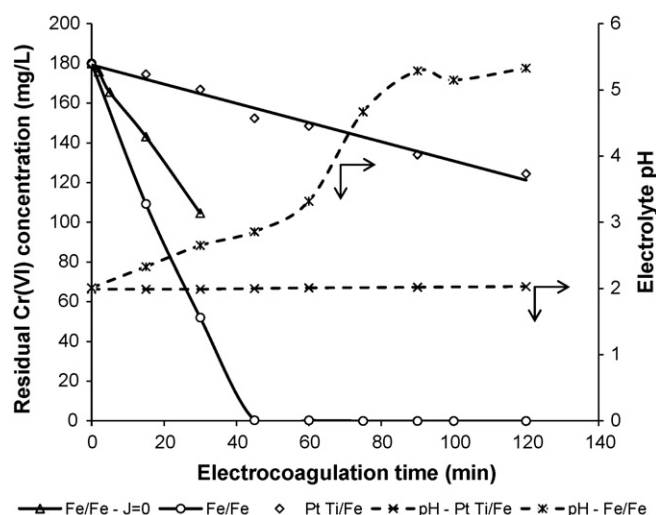


Fig. 2. Effect of different anode/cathode configurations on residual Cr(VI) concentration and electrolyte pH variation. Electrolyte: 180 mg/L Cr(VI) + Na₂SO₄ (1 g/L), pH_i = 2.0, J = 1 A/dm², S_{TE} = 2 × 54 cm², d_{ie} = 4 cm.

electrode surfaces, the solution pH should remain unchanged during electrolysis. In contrast, when Cr(VI) reduction (Eq. (18)) takes place – even partially – at the cathode, the electrolyte pH would increase due to the large amount of hydroxyl ions produced by this reaction compared to hydrogen evolution (Eq. (17)). Accordingly, the slight increase of pH experimentally observed proves that electrochemical reduction of Cr(VI) at the cathode intervenes as minor reaction during electrolysis. Note that, the precipitation as Cr(OH)₃ of the Cr(III) generated by this electrochemical reaction may slightly reduce the pH rise that would have been observed at the end of electrolysis.

For Al/Al electrodes, the decrease of residual Cr(VI) concentration (Fig. 1) and the pH rise (Fig. 1 and Table 1) observed during electrolysis are both more important than those relating to Pt Ti/Al configuration. For these two electrode combinations, the same electrochemical reactions occur at the cathode, while at the Al anode oxygen evolution is completely or partially supplanted by aluminum dissolution (Eq. (2)). Since hydrolysis of Al³⁺ species anodically released produces less acidity than oxygen evolution, it is obvious that the pH rise becomes more marked for Al/Al electrodes. Moreover, in this latter configuration, the electrodisolution of the anode and the “chemical” attack of the cathode generate a great amount of amorphous Al(OH)₃. The negatively charged CrO₄²⁻ ions should adsorb on the positively charged aluminum hydroxide precipitates – at pH values between 7 and around 9 (Fig. 1) – minimizing the electrical repulsion between the colloidal hydroxide particles favoring large aggregate formation (charge neutralization) [44]. Moreover, CrO₄²⁻ ions might be somehow incorporated into the growing Al(OH)₃ precipitates (sweep flocculation) [43] and thereby removed from the solution. Consequently, it is not discarded that these physical removal mechanisms make an explanation of the increase in the Cr(VI) abatement when passing from Pt Ti/Al to Al/Al configuration. By the way, 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 has a crucial role on chromium removal when using aluminum electrodes. This assumption could be supported by the slow decrease of residual Cr(VI) concentration observed after 75 min of electrolysis, when the pH increases over 9 (Fig. 2). This slow decrease can be explained by the formation of negatively charged aluminum hydroxide precipitate under alkaline conditions [44] which does not favor CrO₄²⁻ adsorption. Owing to the ubiquitous presence of Al(OH)₃ precip-

itate, the experimental results obtained with Pt Ti/Al and Al/Al electrodes, do not distinguish between electrochemical reduction and adsorption phenomenon contributions in the removal of Cr(VI). From an environmental standpoint, when treating wastewater containing Cr(VI) by electrocoagulation with aluminum electrodes, careful attention must be given to the generated sludge which could be contaminated by hexavalent chromium.

In the remaining experiments – because aluminum was proven to be unsatisfactory for Cr(VI) removal – only iron was used as electrode material.

4.2. Effect of initial pH

As it has been well recognized, the pH of the treated medium plays a major role in electrocoagulation process. Indeed, the nature and the efficiency of the involved electrochemical and chemical reactions are intimately related to the pH level in the system.

According to the Cr–Pourbaix diagram [39], the reduction of Cr(VI) to Cr(III) is thermodynamically favored under acidic conditions due to an increase of its standard potential with proton concentration. For this reason, the reduction step of Cr(VI) by Fe(II) or other reductant, in the conventional chemical reduction–precipitation process, is industrially realized at markedly acidic pH (2.0–3.0) [12]. Nevertheless, Eary and Rai [49] noted that when Fe(II) is added as a salt (e.g. Fe(NH₄)₂(SO₄)₂·6H₂O_(s)), efficient reduction of Cr(VI) (rapid and nearly complete) is achievable in the pH range of 2–10 even in oxygenated solutions.

When considering electrochemical processes, even highly acidic, neutral and alkaline conditions [22–35] were used for the removal of Cr(VI). For instance, Barrera-Díaz et al. [25] have proposed a working pH of 2 for Cr(VI) reduction, while Narayanan and Ganesan [33] found that effective removal of Cr(VI) was achieved when initial pH was near 8. However, in most of the works dealing with hexavalent chromium removal, the reduction of Cr(VI) by electrochemical addition of Fe(II), has been investigated predominantly to point out the Cr(VI) abatement and no so much with respect to the removal of the other resulting species – namely Cr(III), Fe(II) and/or Fe(III) – which may contaminate the treated effluent. Thus, it is still unclear if low or high pH medium is auspicious to ensure good overall performances for the electrocoagulation treatment process. With the intention of obtaining more information about this subject, the influence of acidic and nearly neutral initial pH on chromium (VI and III) removal, residual iron concentration and electrolyte pH change was studied using iron electrodes. The experiments were performed in 1 g/L Na₂SO₄ electrolyte with initial chromium concentration of 180 mg/L and two different initial pH values: 7.8 (original pH of the solution) and 2.0. A current density of 1 A/dm² was maintained. Note that a higher initial chromium concentration was used in these experiments in order to extend electrocoagulation duration and hence to make clear the effect of pH on the removal kinetics. To suitably interpret the results obtained with iron electrodes, additional electrolyses with iron anode and Pt Ti cathode were beforehand carried out.

For Pt Ti/Fe configuration, the time dependence of the residual hexavalent chromium concentration observed at acidic pH media (pH_i = 2.0) is depicted in Fig. 2. Whereas cathodic reduction of Cr(VI) (Eq. (18)) is proven to be practically negligible at nearly neutral pH media (see Section 4.1), it becomes relatively marked at pH 2.0 (Fig. 2), inducing about 33% of Cr(VI) removal after 120 min of electrolysis. However, although this electrochemical reduction produces more alkalinity than hydrogen evolution (Eqs. (17) and (18)), the solution pH shows only a slight increase during electrolysis (Fig. 2) owing to the poor intervention of this reaction on the one hand and essentially to the highly acidic initial pH of the electrolyte on the other.

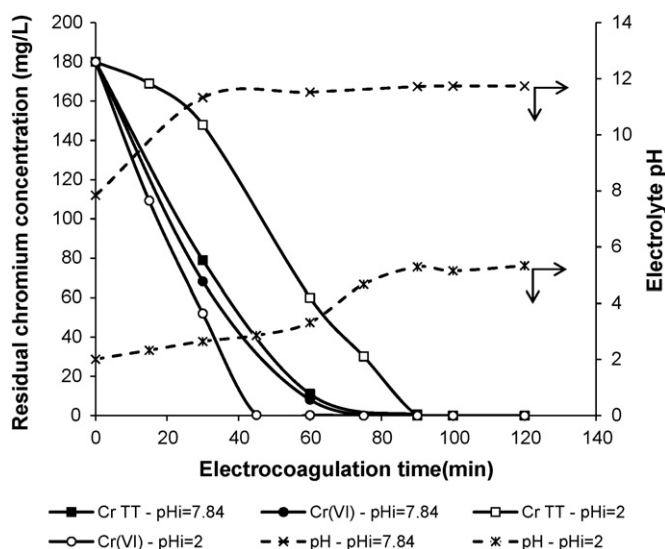


Fig. 3. Effect of initial pH solution on residual chromium concentration and pH variation. Electrolyte: 180 mg/L Cr(VI) + Na₂SO₄ (1 g/L), $J = 1 \text{ A/dm}^2$, anode: Fe, cathode: Fe, $S_{TE} = 2 \times 54 \text{ cm}^2$, $d_{ie} = 4 \text{ cm}$.

Fig. 3 shows the variation of the residual hexavalent and total chromium concentrations vs. electrolysis time for iron electrodes at initial pH values: 7.8 and 2.0. This figure also depicts the time dependence of electrolyte pH. As it can be seen, when initial pH is nearly neutral (pH_i 7.8), both Cr(VI) and total chromium are completely removed after about 75 min of electrolysis. Simultaneously, the pH increases to reach values over 11 within 30 min of electrocoagulation. Since cathodic reduction of Cr(VI) is negligible under these conditions (see Section 4.1), the pH variation currently observed is essentially attributed to both hydrogen evolution at the cathode (Eq. (3)) and chromium reduction by anodically generated Fe(II) species (Eq. (15)). Concerning the dissolved iron during electrolysis (Fig. 4), it is to be noted that residual iron concentration do not exceed 0.1 mg/L and remains at low level owing to the precipitation of Fe(OH)₂ and/or Fe(OH)₃. Consequently, residual iron species do not contaminate the electrolyte. This indicates that in addition to successful reduction of Cr(VI), precipitation of

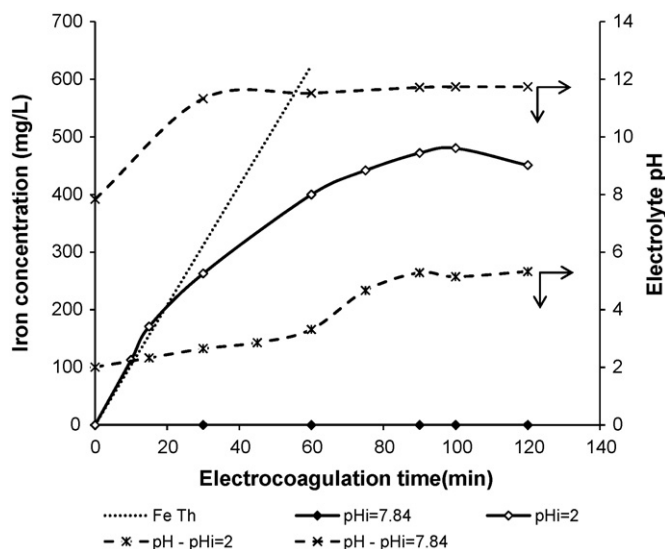
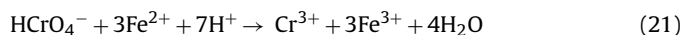


Fig. 4. Effect of initial pH solution on dissolved iron concentration and pH variation. Electrolyte: 180 mg/L Cr(VI) + Na₂SO₄ (1 g/L), $J = 1 \text{ A/dm}^2$, anode: Fe, cathode: Fe, $S_{TE} = 2 \times 54 \text{ cm}^2$, $d_{ie} = 4 \text{ cm}$.

almost all of the resulting Cr(III) and the electrodisolved iron is also achieved.

In highly acidic electrolyte (pH_i 2.0), the residual concentration of Cr(VI) dramatically decreases after only 45 min of electrocoagulation (Figs. 2 and 3). According to Fig. 2, the cathodic reduction of Cr(VI) occurring at this electrolysis time does not exceed 15%. Hence, chemical reduction by Fe(II) species – electrogenerated at the anode – predominantly governs the removal of Cr(VI). It is advisable to note here, that spontaneous reduction of Cr(VI) by metal iron (Fe⁰), taking place at open circuit, is relatively fast in acidic media and becomes very slow or absent when the electrolyte pH is slightly acidic or close to neutral. As illustration, Fig. 2 shows the decrease – vs. time – of Cr(VI) concentration originating from the spontaneous reduction of Cr(VI) by iron electrodes when the initial pH of the electrolyte is 2.0 (curve Fe/Fe–J=0). In our electrolysis experiments, this spontaneous reaction does not actually intervene since electrolyses were always started immediately after the introduction of iron electrodes in the electrochemical reactor.

Considering Fig. 3, the pH of the solution increases slightly during the first stage of electrolysis (0–60 min) to reach 3.3 at 60 min. Afterwards, an appreciable pH increase occurs. At the end stage of the experiment (90–120 min), the pH of the medium remains almost constant and the final pH value is 5.3. Note that this pH value is by far low with regard to that obtained when initial pH was 7.84 (Fig. 3). Accordingly, while the residual concentration of total chromium, during electrolysis, is only slightly greater than the hexavalent chromium concentration in the case of nearly neutral pH solution, it is being large above Cr(VI) concentration for acidic pH medium (Fig. 3). In these latter conditions, total chromium is removed after 90 min of electrocoagulation (Fig. 3). In conclusion, the high Cr(VI) removal obtained at pH_i = 2.0 since 45 min of electrolysis provides good evidence that acidic media promote Cr(VI) reduction kinetics. However, such pH conditions delay the decrease of residual concentration of Cr³⁺ ions (Fig. 3). Taking into account the pH range (0.9 < pH < 6.5) involved during the electrocoagulation treatment and the considered Cr(VI) concentrations (<520 mg/L), it may be concluded that chemical reduction of Cr(VI) by Fe²⁺ ions electrogenerated at the anode occurs according to the following reaction:



During the electrolysis, the pH rises from 2.0 to 5.3 (Fig. 3). According to literature, Cr³⁺ is significantly soluble in this pH range, since minimum solubility of Cr³⁺ is between 5.8 and 11.0 [48]. Yet, since pH ≈ 2.6, a white Cr(OH)₃ precipitate was experimentally observed very near the cathode, following the brown Fe(OH)₃ formation which has already begun since pH ≈ 2.5 too close the cathode. Thus, the decrease of residual concentration of Cr(III) observed in the pH range of 2.0–5.3 owes its origin to the precipitation of Cr(OH)₃ at the cathode vicinity where the pH is locally higher. The formed Cr(OH)₃ does not dissolve in the bulk solution for kinetic criteria.

Concerning dissolved iron during electrolysis under acidic pH, Fig. 4 shows a sharp and continual increase of its concentration in the range of 0–60 min. Subsequently, this concentration increases less rapidly and then slightly decreases after 100 min of electrocoagulation. A first point that should be marked from these results is that dissolved iron concentration fits well to the theoretical electrogenerated Fe²⁺ (Faraday's law) in the range of 0–15 min (Fig. 4). During this electrolysis period, no precipitate was observed owing to the low pH value of the media (pH ≈ 2.3). Additionally, titration – with 0.1N KMnO₄ solution – of the whole electrolyte obtained after 15 min of electrolysis showed the quasi-absence of Fe²⁺ species. Consequently, one should conclude that the dissolved iron is entirely under Fe³⁺ form. This means that the anodically generated Fe²⁺ are imme-

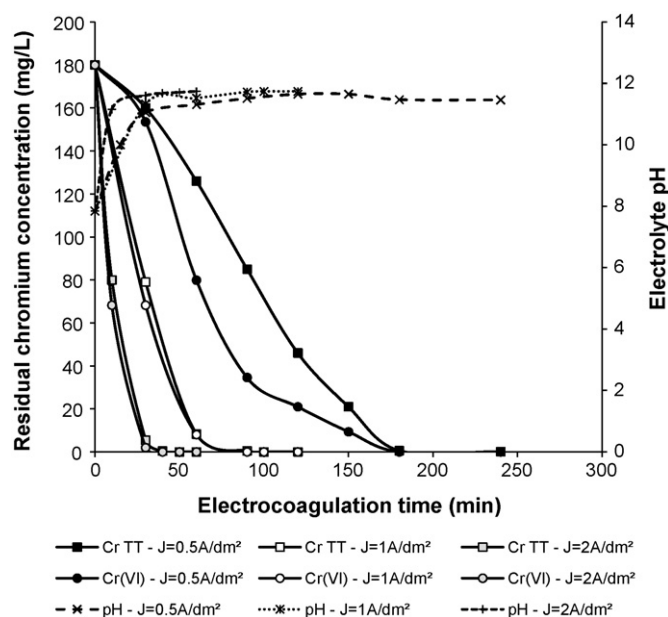


Fig. 5. Effect of current density on residual chromium concentration (Cr(VI) and total Cr) and pH variation. Electrolyte: 180 mg/L Cr(VI) + Na₂SO₄ (1 g/L), pH_i = 7.8, anode: Fe, cathode: Fe, S_{TE} = 2 × 54 cm², d_{ie} = 4 cm.

diately oxidized by Cr(VI) species present in the medium (Eq. (11)).

Secondly, when the electrolysis time reaches 25 min (pH = 2.6) dissolved iron concentration becomes below the faradic value (Fig. 4) and at the same time, a brown precipitate has clearly appeared during electrolysis. This precipitate continued to form until around 45 min of electrolysis. Throughout this electrolysis duration, Fe³⁺ ions resulting from Cr(VI) chemical reduction undergo at first hydrolysis reactions (Fe(OH)²⁺ and Fe(OH)₂⁺ formation) and finally precipitate as brown Fe(OH)₃. These reactions which are alkalinity consumers are at the origin of the slow solution pH change observed between 0 and 45 min of electrolysis.

A third point that should be noted is that after 45 min of electrocoagulation, the pH sharply increases and reaches about 5.3 at the end of 90 min (Fig. 4). This pH change is unsurprising since the production of Fe³⁺ via Cr(VI) reduction stopped to happen. Then, after 90 min, the brown precipitate has floated at the electrolyte surface whereas a green precipitate was observed to appear in the bulk solution. At the meantime, the solution pH remains almost constant (Fig. 4). Accordingly, electrogenerated Fe²⁺ ions precipitate and it is suspected to form the green Fe(II)–Fe(III) hydroxide. Finally, the slight decrease of dissolved Fe²⁺/Fe³⁺ ions suggests that longer electrocoagulation time may decrease its concentration.

4.3. Effect of current density

In all electrochemical processes, current density is an important operating parameter. The effect of current density on Cr(VI) and total chromium removal was studied and pH variation was recorded during the experimental runs. Electrocoagulation tests were carried out at current densities of 0.5, 1 and 2 A/dm². In these experiments, Na₂SO₄ 1 g/L containing 180 mg/L Cr(VI) was used. Electrolyses were carried out without further pH adjustment (pH_i = 7.8). The results are displayed in Fig. 5. This figure clearly shows that the required electrocoagulation time for the complete removal of both Cr(VI) and total chromium decreased as the current density increases. Actually, the electrocoagulation times needed for reaching complete Cr(VI) and total chromium removal are around 180, 90 and 40 min under 0.5, 1 and 2 A/dm², respectively. As seen,

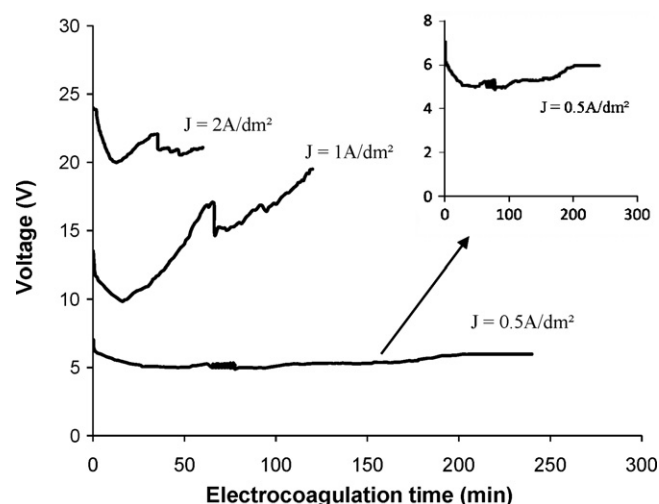


Fig. 6. Effect of current density on electrolysis voltage. Electrolyte: 180 mg/L Cr(VI) + Na₂SO₄ (1 g/L), pH_i = 7.8, anode: Fe, cathode: Fe, S_{TE} = 2 × 54 cm², d_{ie} = 4 cm.

these electrolysis times are almost inversely proportional to current density. It should be also noted that total chromium – so Cr(III) – is removed immediately after Cr(VI) reduction, except for electrolysis under 0.5 A/dm² where a difference between Cr(VI) and total chromium concentrations is observed. This fact may be due to the slow pH increase observed at 0.5 A/dm² during the first stage of electrolysis. On the other hand, for all current densities, practically the same final electrolyte pH was obtained, however, within relatively shorter times.

Fig. 6 depicts the evolution of the electrolysis voltage vs. time at different current densities. Globally, the electrolysis voltage increases with current density. Consequently, an increase of this parameter diminishes the treatment duration but leads to an increase of the cell voltage: this globally means an increase in power requirement, a prime concern of operating cost. For each current density, the cell voltage roughly decreases at first and then gradually increases. The first decrease owes its origin to the brutal pH increase (Fig. 5) observed during the first stage of electrolysis. Later, the pH remains almost constant while the conductivity of the medium decreases owing to the precipitation, as hydroxides, of the metallic species: the cell voltage increases consequently.

4.4. Effect of supporting electrolyte

In these experiments, NaCl (0.5 g/L) and Na₂SO₄ (1 g/L) were used as background salts. Initial chromium concentration of 45 mg/L was used. Electrolyses were carried out at 1 A/dm² without further pH adjustment of the electrolytes. During the course of electrolysis, Cr(VI), total chromium and residual iron concentrations were determined.

Fig. 7 displays the effect of supporting electrolyte on solution pH change and residual chromium concentration. It can be seen that the solution pH variation is practically the same for both Na₂SO₄ and NaCl background electrolytes: the pH increases from its initial value to reach a steady state at pH around 11 (Fig. 7). The results also reveal that whatever the supporting electrolyte considered, chromium removal is effective after 15 min of electrocoagulation. Fig. 7 displays however, that when NaCl is used as background electrolyte, a slight improvement of chromium removal kinetics is observed. When considering Na₂SO₄ as supporting electrolyte, these results are in disagreement with those of Lakshmipathiraj et al. [32]. Indeed, only around 17% Cr(VI) was removed from the containing Na₂SO₄ electrolyte under a current density of 1 A/dm² [32]. Moreover, the pH change observed was reported by Lakshmipathi-

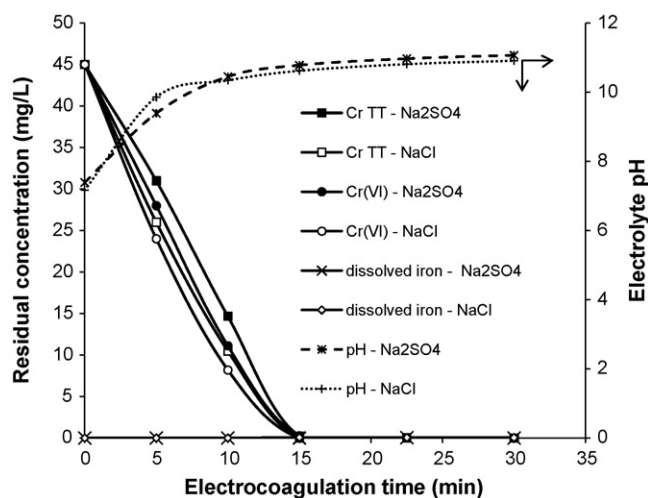


Fig. 7. Effect of supporting electrolyte on residual chromium, dissolved iron concentration and pH variation. Electrolyte: 45 mg/L Cr(VI) + Na₂SO₄ (1 g/L) or NaCl (0.5 g/L), pH_i = 7.4 and 7.2, respectively, $J = 1 \text{ A/dm}^2$, anode: Fe, cathode: Fe, $S_{TE} = 2 \times 54 \text{ cm}^2$, $d_{ie} = 4 \text{ cm}$.

raj et al. [32] to be marginal in the absence of chloride ions (pH has not exceed 6). Authors suggested passivation of iron electrodes as origin of this behavior. During our experiments, no passivation phenomenon was observed. This observation was supported by potentiodynamic polarization tests of iron in Cr(VI) media (Cr(VI) concentrations ranging from 45 to 500 ppm) containing Na₂SO₄ as background electrolyte (not shown).

Concerning dissolved iron during electrolysis, note that residual iron concentration does not exceed 0.1 mg/L and remains at low level, whatever the background electrolyte considered.

The electrolysis voltage measured at 15 min of electrolysis was about 12 and 16 V in the case of Na₂SO₄ and NaCl, respectively. To explain this difference, solution conductivities were measured. The corresponding values were 2.41 and 1.70 mS/cm for Na₂SO₄ 1 g/L and NaCl 0.5 g/L, respectively. Since passivation of iron electrodes was missing for both electrolytes, the increase of electrolysis voltage can be simply related to the increase of the ohmic potential drop of the solution.

5. Conclusion

In this study, the electrochemical removal of Cr(VI) from aqueous media using iron and aluminum as electrode materials has been investigated. The following conclusions could be drawn.

At nearly neutral pH media, although iron and aluminum materials were found to be able to remove Cr(VI) by electrocoagulation, iron electrodes were proven to be more effective than aluminum electrodes. Besides, removal mechanisms were found to be distinct when considering the different electrode materials. With aluminum electrodes, the removal efficiency obtained cannot be simply the result of electrochemical reduction of Cr(VI) to Cr(III) at the cathode surface. It has been proven that simultaneous adsorption on Al(OH)₃ precipitate occurs during electrocoagulation and participates in the removal of Cr(VI). However, no clear distinction between electrochemical reduction and adsorption phenomenon contributions was found. With iron electrodes, there is primarily one real root for the reduction of Cr(VI) by electrocoagulation and it was proven to be the chemical reduction by iron (II) anodically generated. Actually, electrochemical reduction contributed only to less than 5% of the removal efficiency of chromium. The resulting Cr(III) was quickly removed from solution, via efficient precipitation as Cr(OH)₃ hydroxide. In the case of iron electrodes,

the electrodisolved iron remained at low level owing to the precipitation of Fe(OH)₂ and/or Fe(OH)₃ and did not contaminate the solution. Cr(VI) was observed to be faster removed from the effluent by applying higher current densities. No noticeable difference in the treatment efficiency was found when Na₂SO₄ and NaCl were used as supporting electrolyte.

At acidic pH media and in the case of iron electrodes, although chemical reduction by Fe(II) was observed to mainly govern the removal of Cr(VI), electrochemical reduction contribution was found to increase comparing with nearly neutral pH media. On the other hand, acidic pH improved Cr(VI) removal. In contrast, a delay of Cr(III) precipitation and a contamination of the electrolyte by electrodisolved iron were observed.

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