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Electrokinetic removal of aluminum and chromium from industrial wastewater electrocoagulation treatment sludge

Mouna Cherifi[a], Sabir Hazourli[a], Steeve Pontvianne[b], François Lapicque[b], Jean-Pierre Leclerc[b,*]

[a]*Faculté des Sciences, Département de chimie, Laboratoire de Traitement des Eaux et Valorisation des Déchets Industriels, BP12, Annaba 23000, Algeria, Tel. +213 663243605; email: cherifimim@gmail.com (M. Cherifi)*
[b]*Laboratoire Réaction et Génie des Procédés (LRGP), CNRS – Université de Lorraine, ENSIC, 1 rue Grandville B.P. 20451, Nancy Cedex 54000, France, Tel. +33 3 83175066; email: jean-pierre.leclerc@univ-lorraine.fr (J.-P. Leclerc)*

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ABSTRACT

Treatment of industrial wastewaters by electrocoagulation is very efficient to remove numerous types of pollutant (organic, mineral, colored, metal). However, few researches are devoted to the elimination of metals contained in the generated sludge. The objective of this paper was to study the possible simultaneous removal of aluminum (issued from the electrodes) and chromium (initially present in the effluent) contained in the sludge by electrochemical migration. Electrocoagulation treatment of textile industrial wastewater in which chromium has been added was carried out using aluminum electrodes. Turbidity, COD, and TOC could be efficiently removed with abatement yields, respectively, at 97, 93, and 90%. For chromium, only 62% of the initial amount was eliminated by applying the highest current with a long operating time. The generated sludge contained high amounts of Cr and Al (749 and 1,260 mg/kg of dry sludge), far above the maximum level allowed by legislation. The possibility of removing these pollutants from the resulting sludge using electrokinetic technique was investigated. Acetic acid at 1 or 3 M and citric acid at 3 and 6 M were used as catholyte solutions to enhance the removal of aluminum and chromium (III). Best results for aluminum removal were obtained using 3 M acetic acid: up to 82% of the initial Al was recovered in the cathode chamber, whereas citric acid was more effective in chromium removal: up to 79% was transported to the cathode chamber with 6 M citric acid. Specific energy consumption is also discussed.

Keywords: Electrocoagulation; Textile wastewater; Chromium; Aluminum; Electrokinetic extraction; Sludge

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1. Introduction

Textile, tannery, and various other types of industries generate highly polluted wastewaters exhibiting high COD concentration, strong color, different pH values, sometimes high temperature, and low biodegradability [1]. Since the diversity of textile products has been increasing, different dyestuffs with highly varying chemical characteristics have been used in this sector, which complicates further the treatment of textile wastewaters [1]. Moreover, some

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*Corresponding author.

industries such as tannery industries release heavy metals. Chromium is one of the major sources of environmental pollution; it is released into aquatic environment from electroplating, metal finishing, tannery, and fertilizer industries [2]. Cr(VI) species are known to be toxic and carcinogenic, causing serious health problems, whereas Cr(III) being less toxic, can be readily precipitated out of the solution in the form of $Cr(OH)_3$ [3,4]. Chemical precipitation, adsorption by several types of adsorbents such as activated carbon, ion exchange and membrane separation, and biological methods [5] are the leading techniques for recovering and removing chromium from wastewater. These methods are often efficient, but they also present some drawbacks such as high investment and operational costs. The present study aimed at evaluating the potential of successive electrocoagulation and electrokinetic techniques for the treatment of industrial wastewater containing hexavalent chromium and separation of metal salts from sludge produced in the first step, with a view to beneficiation of the metal species and possible disposal of the treated sludge.

Electrocoagulation (EC) has been successfully used for decades to treat wastewaters issued by olive mills [6,7], oil refinery [8–10], food processing [11,12], chemical–mechanical polishing [13], tannery [14], chromium(VI) production [15], dairy [16], and paper mills [17,18]. This technique does not require supplementary addition of chemicals and because of its simple principle the investment costs are far lower than those of most conventional methods [19]. Electrocoagulation involves many chemical and physical mechanisms; aluminum or iron is dissolved by electrolysis and a range of coagulant species and hydroxides are formed, which destabilize and coagulate the suspended particles or precipitate and adsorb dissolved contaminants or remove pollutants by flotation [20,21]. The electrochemical reactions involving metal M (aluminum) as anode can be summarized as follows:

At the anode:

$$Al_{(s)} = Al^{3+}_{(aq)} + 3e^- \quad E_0 = -1.662\ \mathrm{V/NHE} \tag{1}$$

Electrolysis of water occurs at the cathode and the anode:

$$2H_2O + 2e^- = H_2 + 2OH^- \quad E_0 = -0.828\ \mathrm{V/NHE} \tag{2}$$

$$H_2O = 2H^+ + 1/2O_2 + 2e^- \quad E_0 = 1.229\ \mathrm{V/NHE} \tag{3}$$

Aluminum cathodes are usually submitted to significant corrosion by water in the presence of anions, e.g. chlorides, resulting in further hydrogen evolution:

$$Al + 3H_2O = Al^{3+} + 3/2H_2 + 3OH^- \tag{4}$$

Direct electrochemical metal reduction of Cr(VI) to Cr (III)) occurs at the cathode:

$$Cr_2O_7^{2-} + 6e^- + 7H_2O = 2Cr^{3+} + 14OH^- \quad E_0 = 1.350\ \mathrm{V/NHE} \tag{5}$$

or

$$CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3 + 5OH^- \quad E_0 = -0.130\ \mathrm{V/NHE} \tag{6}$$

Depending on the pH of the aqueous medium, different ionic species, such as $Al^{3+}_{(aq)}$, $Al(OH)_3$, $Al(OH)_2^+$, $Al(OH)_2^+$, and $Al(OH)_4^-$ can also be present in the system [22]. The suspended solid Al hydroxides can remove pollutants from the solution by sorption, co-precipitation or electrostatic attraction, followed by coagulation.

The mass of aluminum theoretically dissolved from the sacrificial anode for a particular electrical current flow in an electrolytic cell is quantified by Faraday's law [23], assuming current efficiency at unity and no occurrence of other reactions:

$$m = \frac{ItM}{n_e F} \tag{7}$$

where m is the weight of the anode material dissolved (g), I the current (A), t the electrolysis time (s), M the molecular weight of the metal (g/mol), n_e the number of electrons involved in the reaction, and F is Faraday's constant (96,485 As/mol). The mass of evolved hydrogen and formed hydroxyl ions can be calculated accordingly. However, because of significant corrosion in most cases (reaction 4), the amounts of hydrogen and Al(III) usually exceed those calculated by Faraday's law.

As mentioned below, recent studies were conducted previously on the removal of chromium from waste water by EC treatment using Al, Fe or Pt electrodes. Zongo et al. [24,25] have studied the elimination of Cr(VI) from wastewater and higher efficiency was obtained with Fe electrodes. Previous studies [26,27] reported that a significantly higher amount of sludge could be formed during the EC process. The sludge contains a high level of hydroxides of electrode metals $M(OH)_3$, and depending on the characteristics of the treated wastewater solution, chromium and other toxic elements could be found in the generated sludge, which can be a source of dangerous health and environmental consequences if improperly managed. An examination of the available literature results reveals that the quality of water treated and of the sludge formed was discussed [27,28] independent of the removal of toxic pollutants contained in the sludge.

Electrokinetic (EK) treatment can be efficient in metal removal from solid sludge [29–31], including aluminum [32]. This method consists in applying a low-level DC power to electrodes inserted in the contaminated medium [33,34]. The low-level direct current generated corresponds to the occurrence of electrode reactions, accompanied by various transport phenomena induced by both the electrical field and the physicochemical changes in the medium: electromigration, electro-osmosis, electrophoresis, and diffusion [34]. Electromigration is a mechanism of great significance for both anionic and cationic contaminants; it can be defined as the migration of ionic species towards the electrode of the opposite polarity: for example, cationic species Pb^{2+} or Cr^{3+} move to the cathode during electromigration, whereas $Pb(O_2H)^-$ or anionic Cr(VI) species such as hydrochromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$), and chromate (CrO_4^{2-}) migrate to the anode [35].

Treatment efficiency also results from water electrolysis at the electrodes immersed in a moisture-saturated soil/sludge. Water oxidation takes place at the anode (see Eq. (3)), which generates an acid front that causes desorption of metals and water reduction —at the cathode—as shown by Eq. (2). Hydroxide ions generated at the cathode are transported into the treated soil/sludge, causing the increase in pH near the cathode, thus reducing the migration rate of metal cations by precipitation in the form of neutral hydroxides. Different solutions have been proposed to enhance transport and extraction of species under an electric field and to prevent the formation of motionless precipitates. Neutralizing the cathodic electrolysis reaction is one of the feasible options. Therefore, the addition of weak organic acids could be used for electrode conditioning: acetic and citric acids have been reported in several studies to enhance EK operation [36–38]. Both are weak biodegradable acids, so they can be considered as environmentally safe [39]. Acetic and citric acids have been employed here as catholyte solutions, in order to prevent the formation of a high-pH zone near the cathode that could hinder the migration of Cr and Al from the sludge treated.

The paper describes the methods used and the results obtained for electrocoagulation of the wastewater considered, then for the treatment of the sludge by electrokinetic technique.

2. Experimental

Wastewater collected from the treatment station of textile plant (DMC St Amarin, France), and the physicochemical characteristics of wastewater to be treated are presented in Table 1. For the present investigation, Cr(VI) species in the form of potassium dichromate was added at 200 ppm. Treatment was carried out in an electrochemical cell operated with flow recirculation at 2.5 cm^3/min through the rectangular channel formed by the two facing electrodes of 70 × 150 mm^2, the electrode gap was fixed at 10 mm, and the cell was installed in a flow rig provided with a 2-L reservoir, a peristaltic pump, and a flow meter. Fig. 1 illustrates the experimental device used for electrocoagulation treatment. Two liters of freshly prepared Cr-containing wastewater was introduced into the tank and the run was started by imposing a fixed current in the cell. Three current intensities were employed: 0.5, 1.05, and 1.57 A, for a treatment period of 150 min. Corresponding current densities were then 48, 100, and 150 A/m^2. The cell voltage was recorded along the run time and 1-cm^3 samples were taken periodically during the experiment for turbidity, COD, TOC, and total chromium analysis. Fig. 1 represents the schematic diagram of the electrocoagulation system. pH was measured by multiparameter instrument (Consort C931), turbidity (NTU) was measured using an IR beam at 890 nm and detection of the dispersed light using a Hanna Ins. LP2000 spectrophotometer, COD level in the clear phase obtained was determined using the standardized colorimetric method with excess of hexavalent chromium and subsequent measurement of the optical density using a Hach 2400 spectrophotometer. Total chromium in the clear

Table 1
Physicochemical characteristics of industrial effluent used for the study

Parameter	Value
pH	7
Turbidity (NTU)	130
TOC (mg/L)	571
COD (mg /L)	3,480
Conductivity (mS/cm)	2.0
Temperature (℃)	18
Color, appearance	dark

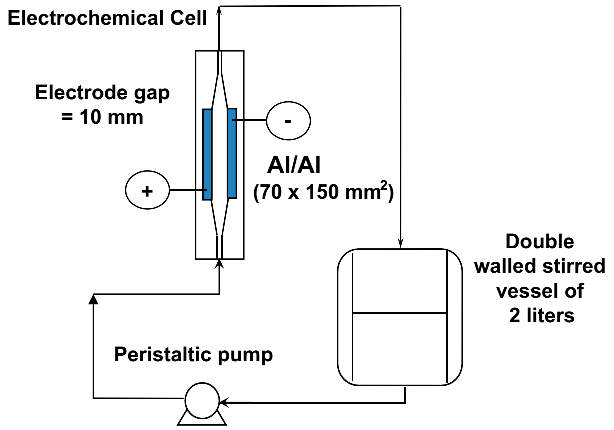


Fig. 1. Schematic representation of the experimental device for electrocoagulation treatment.

fraction was analyzed by atomic absorption using Thermo S4 Solar apparatus after acidification with 5% nitric acid. TOC was also measured in the clear fraction using Shimadzu TOC-VCSH TOC meter. The removal efficiency (R %) was calculated using the following equation:

$$R\ (\%) = \frac{X_0 - X}{X_0} \quad (8)$$

where X_0 and X represent, respectively, the initial and final turbidities, COD, TOC, and total chromium.

After completion of an EC run, wastewater sludge was allowed to settle, before collection. The sludge collected from all runs was mixed using an electric stirrer for 1 h to ensure homogenization of the solid. The moistened solid recovered was then dried in oven at 105˚C for 24 h and crushed before EK treatment. Chemical analysis of the solid obtained, following a protocol described later, led to the concentrations of Al and Cr species, found at 12.65 and 7.49 g/kg dry solid, respectively.

Fig. 2 presents the electrokinetic cell (100 × 40 × 50 mm) composed of three compartments: the central chamber being 60 mm long and containing the sludge to be treated, and two side chambers (20 mm long) in which two graphite electrodes in the form of 10-mm cylindrical rods were placed. Before introducing the sludge in the EC cell, 25 g of dry sludge was mixed with 50 ml of pure water. The anode chamber was filled with pure water at the same level of compartment containing the sludge, while the cathode chamber was filled with acetic or citric acid solutions: approx. 17 mL of the liquid was introduced in each electrode compartment. The depth of liquid or sludge in the cell compartments was then calculated to be approx. 26 mm. The cell voltage was fixed at 6 V for all tests, and the current was continuously recorded along the run. The pH in the electrolyte compartment was monitored using a Grimson pH meter. Due to the loss of liquid by evaporation from the open cell, and water transport by electro-osmosis to the cathode chamber, aliquots of the cathode solutions were poured regularly into the anode compartment and the global volume added was recorded along the runs, which were conducted for 10 or 20 d at ambient temperature, near 25˚C. The volume of solutions introduced and the other operating conditions are summarized in Table 2.

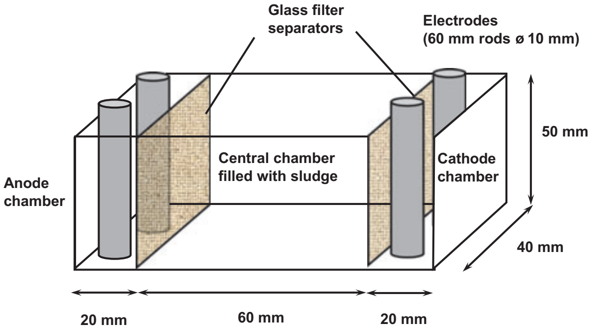


Fig. 2. Schematic view of the cell used for electrokinetic experiments.

After the EK treatment, the electrodes were removed and the cell was dried for 24 h in oven at 80˚C. The solid cake recovered could be extracted from the glass cell, making it possible to take apart the solid from the electrode chambers and the central compartment. The 6-cm-long portion recovered was cut into four sections, named S1–S4 for further analysis. Solid samples S1–S4 were diluted in deionized water to form 1/10 solid waste/water suspensions and thoroughly mixed. The pH of the obtained suspensions was measured and reported as “the final pH” of the sludge sections in the graphs presented later. Total Cr and Al concentrations were determined after digestion of 1 g of solid with 10 cm^3 of nitric acid per gram of solid by atomic absorption spectrometer (Perkin Elmer 3110). The total amount of Cr and Al recovered in the various sections and chambers was then deduced, taking into account the weight of the solid fractions. Mass balances in Al and Cr species have been controlled: for Al, the sum of the various amounts recovered corresponds to the initial amount of Al (316 mg) within 3%. For the case of chromium (187 mg introduced), the mass balance was shown to hold within 10%, which globally confirmed the accuracy of the various determinations.

Table 2
Operating conditions of the electrokinetic runs and volumes of complexant solution added along the runs

Run	Catholyte	Duration (d)	Volume of added solution (cm^3)
I	Acetic acid 1 M	20	6.9
II	Acetic acid 3 M	20	7.2
III	Citric acid 3 M	10	9.5
IV	Citric acid 6 M	10	10.3

3. Electrocoagulation treatment of wastewater

It has been established that the applied current has a considerable influence on the performance of the EC process via the coagulant dosage rate [14,40,41]. In order to select the best conditions to produce sludge for electrokinetic treatment, a series of experiments were conducted with currents varying from 0.5, 1.05 to 1.57 A, corresponding to current densities at 48, 100, and 150 A/m^2. The produced sludge for which high abatement rates of all the pollution criteria (TOC, COD, turbidity, and chromium concentration) with a reasonable energy cost, were then selected.

Tests have been run for 2.5 h regardless of the current applied. The cell voltage did not vary noticeably along the run, but depended largely on the current density (cd), as expected: for the three cd levels investigated, the cell voltage was measured, respectively, at 3.3, 6.0, and 8.6 V within 10%. Moreover, as often in electrocoagulation runs with Al electrodes, pH progressively increased to 9 upon dissolution of aluminum, and ranged from 8.7 to 9.2 at the end of the runs.

3.1. Turbidity and organic pollution removal

Turbidity expresses the importance of suspended matter present in wastewater. Initially, it can indicate the presence of bacteria, but more generally, the amount of suspended organic matter. In the course of the treatment, aluminum dissolution in the pH domain results in the formation of insoluble hydroxide species which contribute to the overall turbidity of the medium: as a matter of fact, negative turbidity removal values were observed for the first hour in the treatment (Fig. 3a). For longer times, trivalent Al forms settle alone or with entrapped polluting species, and the overall turbidity suddenly decreases after 75 min for the two highest cd, and 90 min at 48 mA/cm^2. Because of the threefold factor between the two extreme cd values, this behavior suggests that upon sufficient dosage of Al species, a sufficient time lapse is necessary for significant destabilization of suspended matter, then with moderate dependence on the current density, i.e. the charge passed, i.e. the amount of dissolved Al species.

COD and TOC abatement (Figs. 3b and 3c) were considerably reduced within 30 min of reaction for 0.5, 1.05, and 1.57 A with 72, 74, and 78% of COD abatement and 72, 73, and 87% of TOC removal. The two abatement degrees reach a limited value even when increasing the time of treatment, as expressed by the plateau over 30 min. Maximal abatement of turbidity and COD was improved by a higher current intensity, whereas the sensitivity on TOC removal was less important: maximal TOC removal culminated near 87%. The initial TOC content of the waste, at 571 mg/L corresponds to 47.6 mmol/L organic carbon. Therefore, because two liters of wastewater was treated per run, it may be considered that approx. 94 mmol organic carbon could be removed upon application of a charge ranging from 1,500 to 3,000 As. Oxidation of this organic matter is to require from 4 to 8 electrons per carbon atom, depending on whether this matter consists of ethers, aldehydes or ketones, or hydrocarbons: oxidation to carbon dioxide and protons would require more than 3.7 × 10^4 As. A comparison between the experimental charge passed for significant TOC abatement and the above estimate clearly shows that COD and TOC are removed by separation from the aqueous liquid, and not by faradaic

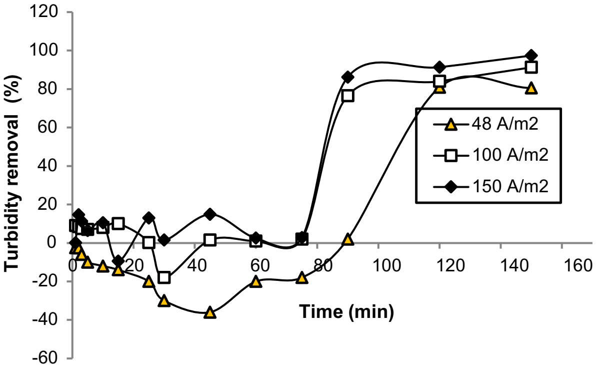


Fig. 3a. Turbidity removal vs. time for three different current intensities.

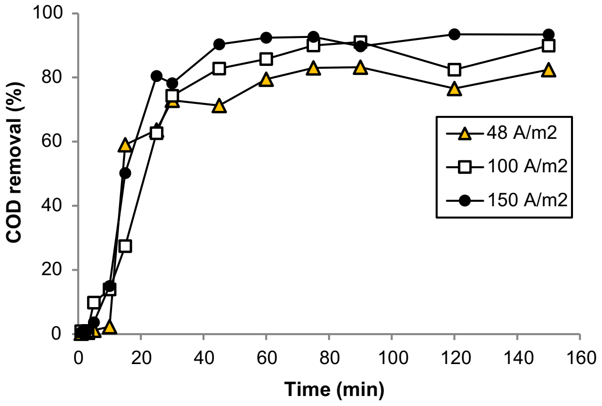


Fig. 3b. COD removal vs. time for three different current intensities.

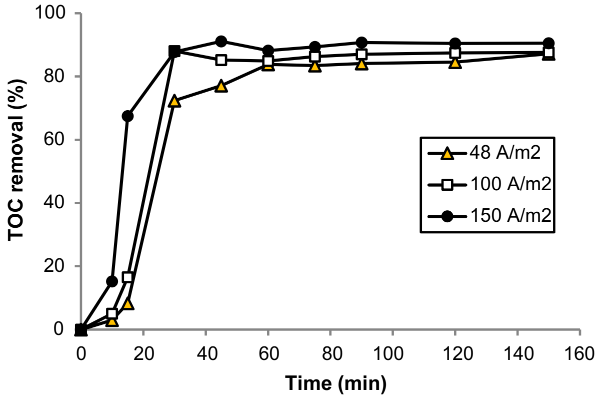


Fig. 3c. TOC removal vs. time for three different current intensities.

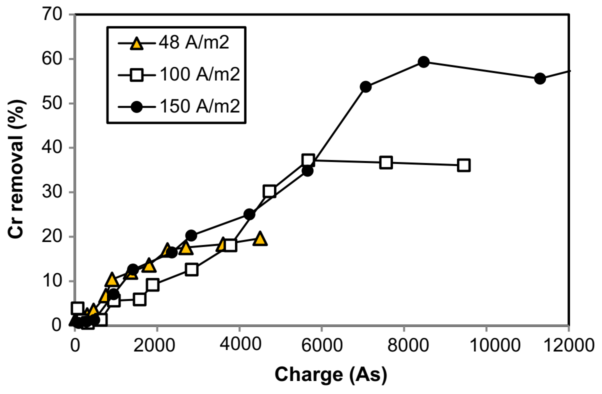


Fig. 3d. Chromium removal vs. time for three different current intensities.

oxidation, indicating once more that the energy demand of electrocoagulation is more than one order of magnitude below that for anodic oxidation.

3.2. Chromium removal

Hexavalent chromium is to be reduced at the cathode surface to Cr(III), which is prone to form insoluble $Cr(OH)_3$ species, which are incorporated in the Al-based solid flocs formed. The desired reaction occurs together with significant hydrogen evolution and Al dissolution by corrosion.

Runs conducted at different cd levels revealed that the concentration of Cr(VI) species decreases regularly with time until 60–90 min (data not shown): over this period, this concentration remained nearly constant at a level directly related to the current density applied: abatement of this pollutant can be larger than 50% only with current density larger than 100 A/m^2. The data have been plotted vs. the charge passed (Fig. 3d): Cr(VI) abatement increases regularly with the charge passed up to a certain extent, which appears governed by the current density: the highest levels of Cr(VI) abatement attained approx. 20, 40, and 60% for current density 48, 100, and 150 A/m^2. The above dependence could not be interpreted directly but might be caused by inhibition of the electrode surface whose intensity would strongly depend on the cathode potential and thus on the current density. It may be postulated that the higher the current density, the higher the gas evolution rate, thus the less the significance of any surface inhibition phenomenon.

The current efficiency of the cathode for dichromate reduction is shown in Fig. 4. In spite of the appreciable scattering of the data, this efficiency ranged from 12 to 18%, except for the two or three last data of each series, corresponding to times larger than 80 min: the leveling off of Cr(VI) reduction observed in Fig. 3c is expressed here by the decrease in current efficiency. The effect of the current density appears moderate in the figure because of the dispersion of the data, but higher current yields could be obtained with the lowest current density in the first part of the treatment.

A second analysis of the experimental data was to test a simple model for direct reduction of Cr(VI) on the aluminum surface. As a matter of fact, the efficiency of the reduction conducted at constant current density i depends on whether i is larger or smaller than the limiting current density i_L defined as:

$$i_L = n_e F k_m C_{Cr(VI)} \qquad (9)$$

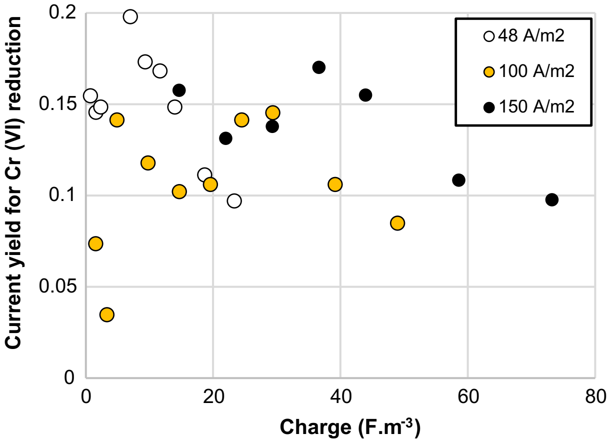


Fig. 4. Current yield vs. charge for chromium reduction.

where k_m is the mass transfer coefficient at the electrode and $C_{Cr(VI)}$ is the concentration of chromate ion in mol/m^3. The observed side evolution of hydrogen bubbles is to generate additional transfer to that afforded by the liquid flow in the cell. The approach has been treated in a previous paper in the same cell for the treatment of Cr(VI)-containing industrial wastewater [24]. From the calculations described in this paper, mass transfer coefficient was shown to be an increasing function of the current density, which is actually governing the rate of gas evolution: values for k_m had been estimated at 1.12×10^{-5}, 1.58×10^{-5}, and 1.94×10^{-5} m/s for current density at 48, 100, and 150 A/m^2. Therefore, the limiting current density at initial time i_{L0}, with $C_{Cr(VI)} = 3.85$ mol/m^3 (corresponding to the introduced 200 ppm) is in the range of 12.5–21.6 A/m^2, which is actually far below the applied cd levels. It can be observed that the ratio (i_{L0}/i) varies from 25% at 48 A/m^2 down to 14.4% at 150 A/m^2, and the values in good accordance with the experimental current yields are given in Fig. 4. Because the applied cd is always larger than the limiting cd, Cr(VI) is reduced only by a part of the current applied, namely $i_L A$. Mass balance for Cr(VI) species can be written as:

$$\frac{dn_{Cr(VI)}}{dt} = V\frac{dC_{Cr(VI)}}{dt} = -\frac{i_L A}{n_e F} = -k_m C_{Cr(VI)} \tag{10}$$

where V is the volume of the wastewater. Integration of rel. (2) yields the usual expression for the concentration of Cr(VI) at t, from which the abatement degree can be expressed:

$$X_{Cr(VI)} = 1 - \exp\left(-\frac{k_m A}{V}t\right) \tag{11}$$

Good agreement between theory and practice is shown by Fig. 5, in particular for the first hour of the treatment. For the lowest cd, the leveling off in the abatement observed after one hour cannot be predicted by the simple model. Similar deviation shows also the intermediate cd value, however after 90 min or so, whereas the agreement is quite better at 150 A/m^2. In spite of the above deviations due to possible electrode inhibition, the calculations presented could validate that Cr(VI) is reduced on the cathode surface under mass transfer conditions: Cr(III) formed was quantitatively recovered in the sludge at the end of the treatment, as revealed by chemical analysis by atomic absorption.

3.3. Discussion: charge and energy consumption for electrocoagulation treatment

With the highest current densities, the treatment can be carried out with high efficiency for the removal of turbidity, COD, TOC, and Cr(VI) as explained above. However, one of the most important parameters that greatly determine the industrial applicability of processes is the energy cost. In addition to aluminum electrodes consumed in the EC process, the major operating cost is that of electric energy consumption. The specific electric energy consumption (SEEC) is defined as the electric energy to be supplied depending on the volume of the effluent to be treated:

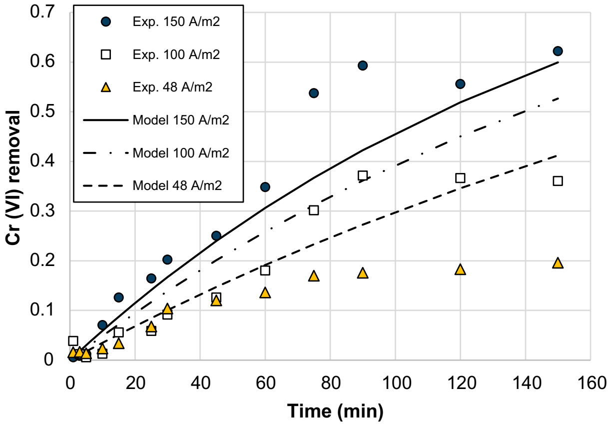


Fig. 5. Experimental and modeling chromium removal vs. time for three different current intensities.

$$\mathrm{SEEC}\ \left(\mathrm{kW\,h\,m^{-3}}\right) = \frac{ItU}{V} \tag{12}$$

where I and U, are, respectively, the current and the cell voltage. For the case of non-passivated aluminum electrodes, the following empirical relationship [25] between the electrocoagulation cell voltage and the current density can be used:

$$U = 0.1 + \frac{e}{\kappa} i + 0.20\ \ln(i) \tag{13}$$

where e is the electrode gap, at 10 mm here, and κ is the electrical conductivity of the effluent to be treated, measured at 2 mS/cm with the present solution. The experimental voltage values are in agreement within 10% of difference with the above relationship, which has been employed for the calculation of SEEC values. Depending on the current density, one-hour-long treatment consumes 0.81–6.7 kW h/m^3.

The efficiency of the electrocoagulation treatment is plotted vs. the energy demand in Fig. 6, regardless of the current density. First, turbidity removal cannot be correlated with energy consumption, as expressed by the very high dispersion of the data, since this performance criterion is largely governed by the treatment time. Therefore, low current densities are preferred for the sake of low-energy demand: for instance, 1.6 kW h/m^3 at 48 A/m^2 allows 80% turbidity abatement. Far better correlation with SEEC can be found for COD and TOC levels: in a general manner, higher abatements are obtained with higher energy consumptions, and treatment can be considered as optimal for SEEC ranging from 2 to 5 kW h/m^3. Nevertheless, as explained in Section 3.1, the level of COD abatement depends slightly on the current density—high current densities are actually more efficient. The case of hexavalent chromium is totally different since Cr(VI) is actually consumed at the electrode through a faradaic process: Cr(VI) abatement is globally improved by high energy consumptions, and extrapolation of the data indicate that more than 50 kW h/m^3 would be required for an abatement degree larger than 80%.

The effect of current density on treatment efficiency and energy demand is reported in Figs. 7a and 7b, for the cases of TOC and Cr(VI). Most data for TOC abatement follow the same trend with a rapid increase followed by a slightly inclined plateau (Fig. 7a). However, a closer examination of the data (Fig. 7b) reveals the strong effect of current density on the minimum SEEC values for efficient treatment: at 48 A/m^2, 0.8 kW h/m^3 suffices for 83% TOC abatement, whereas interpolation of the data yields minimum SEEC values near 1.2 and 2 kW h/m^3 at 100 and 150 A/m^2, respectively. Low current densities then appear preferable for abatement of organic matter, even though COD can be slightly more efficiently removed with high cd's (82% at 48 A/m^2 and 92% at 150 A/m^2). Removal efficiency of Cr(VI) are also dependent on the current density, with slightly higher yields at low cd, however with limited performance: high current densities are required for efficient abatement but with a far higher energy consumption.

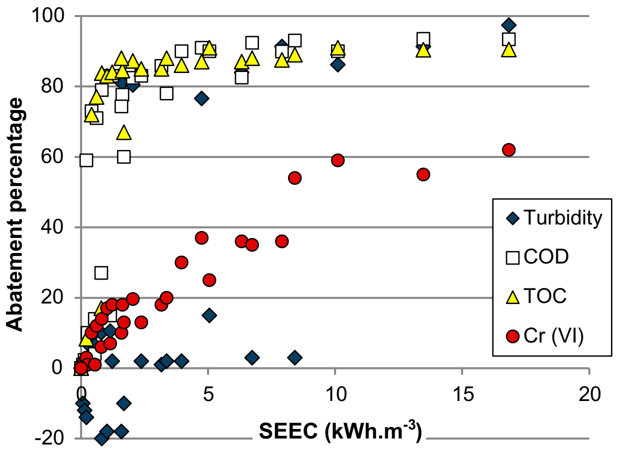


Fig. 6. Efficiency of electrocoagulation treatment vs. specific electrical energy consumption for turbidity, COD, TOC, and chromium.

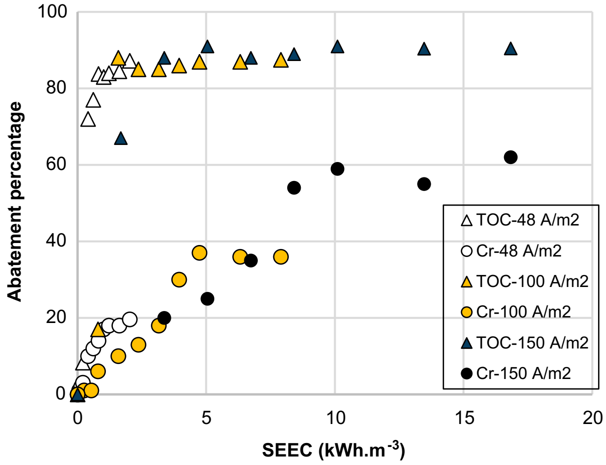


Fig. 7a. Effect of current densities on TOC and chromium abatement and specific electrical energy consumption.

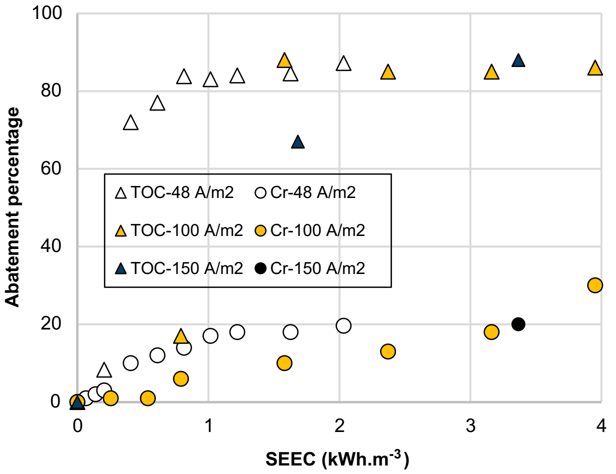


Fig. 7b. Zoom on effect of current densities on TOC and chromium abatement and specific electrical energy consumption.

Table 3
Acid–base equilibria with corresponding p*K*a values

Equilibrium	pK_a	Refs.
$H_3Cit \leftrightarrow H_2Cit^- + H^+$	3.15	Kwong et al. [44]
$H_3Cit \leftrightarrow HCit^{2-} + 2H^+$	7.92	
$H_3Cit \leftrightarrow Cit^{3-} + 3H^+$	14.35	
$AcH \leftrightarrow Ac^- + H^+$	4.76	[44]
$Al^{3+} + H_2O \leftrightarrow Al(OH)_2^+ + H^+$	5	Baes et al. [45]
$Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^+ + 2H^+$	10.20	
$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$	15.71	
$Al^{3+} + 4H_2O \leftrightarrow Al(OH)_4^- + 4H^+$	23.91	
$Cr^{3+} + H_2O \leftrightarrow Cr(OH)^{2+} + H^+$	4.15	[45,46]
$Cr^{3+} + 2H_2O \leftrightarrow Cr(OH)_2^+ + 2H^+$	9.22	
$Cr^{3+} + 3H_2O \leftrightarrow Cr(OH)_3 + 3H^+$	18.05	
$Cr^{3+} + 4H_2O \leftrightarrow Cr(OH)_4^- + 4H^+$	27.47	

4. Electrokinetic treatment of the sludge produced by electrocoagulation

The pH of the dilute sludge introduced in the central compartment was 7.72 and the initial concentrations of aluminum and chromium were 6.2 and 3.65 g/L. These concentrations exceeded by a factor larger than 2 the pollutant concentration limits for land application of sewage sludge recommended by the USEPA for Cr [42] and they are higher than the limits recommended by MENV [43] for Al. From the edition year of the two above references, the maximal authorized levels of the two metals are presumably far lower now, rendering the treatment of the sludge absolutely necessary. Before describing the experimental results obtained, speciation of trivalent Cr and Al species present in citrate or in acetate solutions have been conducted. The acid–base equilibria of the two acids and trivalent metal species are reported in Table 3.

4.1. Speciation of Cr(III) and Al(III) in the complexing solutions

The metal content in the sludge treated was 11.7 mmol Al and 3.60 mmol Cr. Taking into account the initial volume of complexant solution at the cathode and the solution aliquots added along the run, the mole amount of acetate was 23.9 or 72.6 mmol, depending on the concentration of acetic acid. For citrate, these amounts were 79.5 and 163.8 mmol. The complexing agent was present in large excess in comparison with the metal species, with exception for 1 M acetic acid. Speciation calculations were then carried out with single M metal species: the presence of the other metal species was thereafter neglected. Four (metal–complexant) systems were considered:

1. Al(III)—acetate. Complexation results in the formation of $Al(Ac)^{++}$. This species predominates in the solution in equilibrium with the remaining solid for pH up to 5 or so [47]. The presence of other complexed forms with two or more acetate ions per complex—$Al(Ac)_2^+$, $Al(Ac)_3$, etc.—is sometimes mentioned [48]. However, complexation constants leading to complex with two and three acetates are subject to controversial discussion and depend largely on the ionic strength. In the present investigation, only the formation of a single-acetate complex has been considered.
2. Al(III)—citrate. Complexation of Al salts by citrate has been evidenced by NMR by Kuan et al. [49]: three complexes, AlCi, $AlCiH^+$, and $AlCi_2^{3-}$ can be formed. In acidic media, prevalence of cationic $AlCiH^+$ can be expected, whereas for pH over 4, Al citrate are mainly in the anionic form $AlCi_2^{3-}$.
3. Cr(III)—acetate. This complexation has been studied by Silwood and Grootveld [50] using equilibrium constants obtained by Tedesco and Quintana [51] for an ionic strength at 0.1 M (only). Actually, Cr^{3+} ions can be complexed by acetate with one, two or three anions, leading, respectively, to the formation of $Cr(Ac)^{++}$, $Cr(Ac)_2^+$ and $Cr(Ac)_3$. Chromium acetate complexes are mainly in cationic forms in mild acidic solutions, whereas the neutral form predominates near pH 6.

Table 4
Complexation equilibria of Al(III) species and corresponding equilibrium constants expressed as pK_a

Equilibrium	pK_a	Refs.
$Al^{3+} + Ac^{-} \leftrightarrow AlAc^{2+}$	−2.07	[47]
$Al^{3+} + Cit^{3-} \leftrightarrow AlCit$	−7.37	[47]
$Al^{3+} + Cit^{3-} + H^{+} \leftrightarrow MCitH^{+}$	−12.85	
$Al^{3+} + 2Cit^{3-} \leftrightarrow AlCit_2^{3-}$	−13.90	
$Cr^{3+} + Ac^{-} \leftrightarrow CrAc^{2+}$	−4.6	[51]
$Cr^{3+} + 2Ac^{-} \leftrightarrow CrAc_2^{+}$	−7.1	
$Cr^{3+} + 3Ac^{-} \leftrightarrow CrAc_3$	−8.6	
$Cr^{3+} + Ci^{3-} \leftrightarrow CrCi$	−8.73	[52]
$Cr^{3+} + 2Ci^{3-} \leftrightarrow CrCi_2^{3-}$	−13.3	[53]
$Cr^{3+} + 2Ci^{3-} + H^{+} \leftrightarrow CrCi_2H^{2-}$	−5.7	

(4) Cr(III)—citrate. In a more recent paper [52], only the neutral form of CrCi was considered. Previously, Tedesco and Quintana [51] considered the existence of the two anionic complexes $CrCi_2^{3-}$ and $CrCi_2H^{2-}$ with equilibria constants reported in [53]. Because of more thorough evidence of complexed forms, the existence of the above two anions has been considered in the calculations.

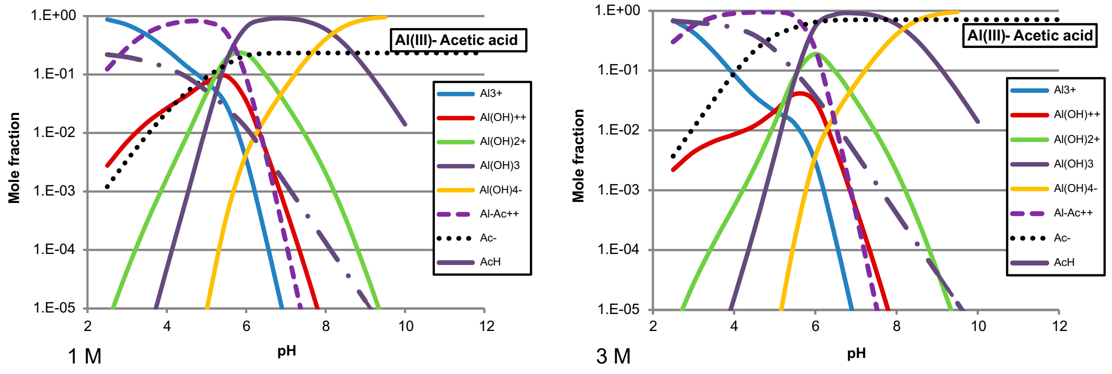
Speciation calculation were carried out depending on pH values, from 3 to 10 from the mass balances in the metal considered and the chelating agent, considering the various equilibria involved, as made in a previous study [32]. Equilibria and their constants of complexation of metal cations are given in Table 4. The concentration of total metal species and complexing agents were taken as the mole amounts given above—with the lower amount of acetate and citrate, and the total volume of liquid in the three-chamber cell.

As expected, $AlAc^{2+}$ prevails in the pH range of 4–5.5 (Fig. 8a); increasing the pH allows short predominance of $Al(OH)_2^{+}$, and mainly this of $Al(OH)_3$ for pH up to 8. Above pH 8, Al is in the anionic form $Al(OH)_4^{-}$. In the presence of citrate, $AlCiH^{+}$ predominates for pH below 5 (Fig. 8b). Over this limit, Al is exclusively in the form of $AlCi_2^{3-}$ in the range of 6–9, whereas non-complexed neutral and anionic hydroxides are only visible for pH larger than 8. Complexation by citrate appears far stronger than that with acetate, also because of the different metal-over-complexant ratios.

Chromium is strongly complexed by acetate in acidic solutions, with predominance of $CrAc^{2+}$ below pH 3.5, then $CrAc_2^{+}$ up to pH 5, followed by $CrAc_3$ in the range of 5–7.5 (Fig. 8c). Neutral hydroxide species is the major for up to pH 9.5 and anionic species $Cr(OH)_4^{-}$ prevails in more alkaline media. Finally, $CrCi_2^{3-}$ represents the major form of Cr(III) for pH ranging from 4 to 9.5 (Fig. 8d), with visible Cr^{3+} and $CrCiH_2^{+}$ forms only below pH 3.5. It can be observed that chromium is far stronger complexed by the two agents considered than aluminum, also because of the lower metal-over-complexant ratios.

4.2. Results of the electrokinetic treatment

Figs. 9a and 9b show the distribution of sludge pH, aluminum (9a), and chromium (9b) recovery after EK treatment for 6 V. The voltage has been selected so that the current density calculated over the cross section of the sludge was of a few mA/cm^2 in the first hours of the run. Sludge pH exhibits significant changes during the EK treatment. The acid front generated at anode reservoir flushed across the sludge and acetic/citric acid injected at the cathode could neutralize the generated OH^{-}. The sludge pH was lower than the initial pH, due to the addition of



1 M 3 M

Fig. 8a. Speciation diagram of the Al(III)—acetic acid system.

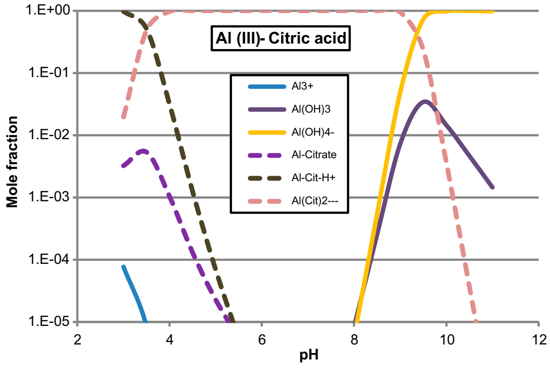


Fig. 8b. Speciation diagram of the Al(III)—citric acid system.

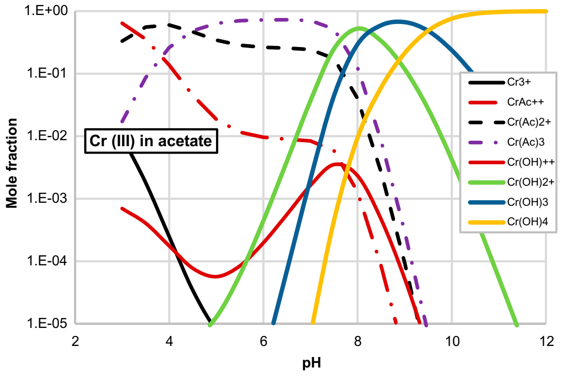


Fig. 8c. Speciation diagram of the Cr(III)—acetate system.

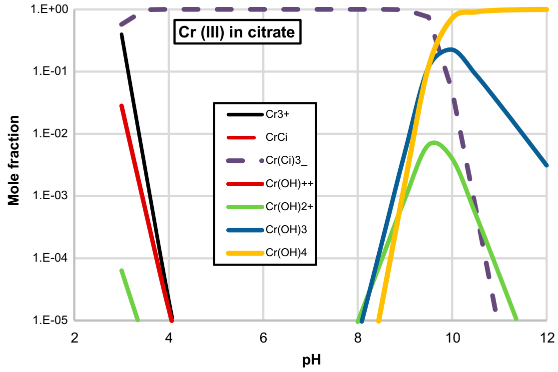


Fig. 8d. Speciation diagram of the Cr(III)—citrate system.

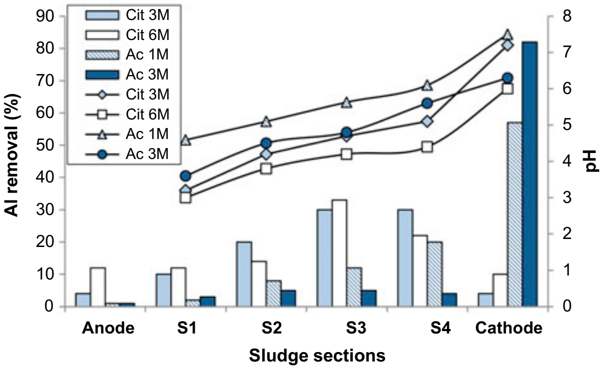


Fig. 9a. Profiles of pH and of relative Al concentrations in the cell at the end of the EK runs conducted with citric acid as catholyte solutions. Washing solution: pure water; cell voltage = 6 V.

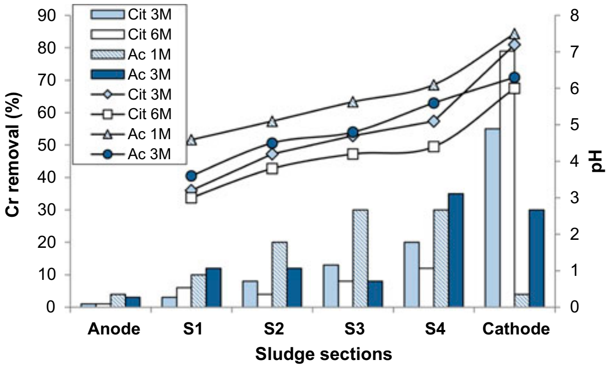


Fig. 9b. Profiles of pH and of relative Cr concentrations in the cell at the end of the EK runs conducted with citric acid as catholyte solutions. Washing solution: pure water; cell voltage = 6 V.

complexing acids along the runs. The most significant change in pH occurred with treatment with citric acid because of the high concentration used and its acidic character with its first pK_a at 3.15. The metal mass balance was satisfactory with a maximal deviation of 10% in the worst case when the metal concentration in the cell is strongly non-homogeneous.

4.2.1. Aluminum

As shown in Fig. 9a, increasing the concentration of acetic acid from 1 to 3 M at 6 V improves the removal efficiency of aluminum in the cathode chamber, with recovery yields, respectively, near 57 and 82% of the initial amount in this chamber. For possible interpretation of the different efficiencies, speciation diagram was also calculated with other concentrations of complexing acids. With 3 M acetic acid predominance of neutral form $Al(OH)_3$ is slightly retarded, allowing more efficient transport of cations towards the cathode chamber. Moreover, the pH of the cathode chamber is around 6 with 3 M acetic acid, for which both complex cations and neutral hydroxide prevail. Qualitative agreement between experiment and results of metal speciation is shown in Table 5 summarizing information from speciation calculations and giving the locations of the cathode chamber and the sludge sections, depending on the pH. The length of the arrow indicates the direction and intensity of migration phenomena.

Electrokinetic treatment of sludge with 3 and 6 M citric acid at the cathode chamber results in different behavior, with little effect of citric acid concentration: aluminum is accumulated through the sludge bed, mainly in Sections 3 and 4. This can be explained by the formation of cationic and anionic forms of aluminum complexed by citrate ions (Fig. 8b and Table 5), AlCit-H^+ (below pH 5) and $AlCit^{2-}$ (above pH 6): at the cathode, the local pH in the order of 6–7 forces Al species to migrate to the sludge and focalization is actually predicted in Section 4, with a pH near 4.7 (Fig. 9a). Citric acid is far less efficient than acetic acid for Al recovery at the cathode.

4.2.2. Chromium

Moderate chromium recovery in the cathode chamber was observed with the use of acetic acid, in particular at 1 M, for which the efficiency was at a few percentage points (Fig. 9b). Cr species appears poorly concentrated in Sections 3 and 4 of the bed, but higher focalization could be obtained with the use of 6 M acetic acid: the lower pH throughout the cell, allows the main part of the Cr species to be concentrated in Section 4 and in the cathode chamber (with 32 and 27%, respectively). Table 5 reminds that neutral $Cr(Ac)_3$ species predominates for pH ranging from 5 to 7, i.e. covering S2–S4 and the chamber with 3 M acetic acid, and only S4 and the cathode chamber with 6 M acetic acid, in full agreement with the electrokinetic experiments.

Use of citric acid as catholyte solution enhances largely chromium transport to the cathode: 57 and 79% of the initial concentration were found in the cathode chamber with 3 and 6 M acid, respectively. These good results might have been expected because of the more acidic pH in the sludge with this complexant. Furthermore, the presence of citric acid in the soil has been reported to increase the electro-osmotic flow, which favors metal removal [54,55]. Nevertheless, the examination of specification diagrams and of the location of the species at the end of the run (Table 5) predicts that the Cr species is to be concentrated in Section 2, in disagreement with the high performance for Cr recovery in the cathode chamber. The reason for this discrepancy has still not been found.

4.3. Current variations in EK runs

Electrokinetic remediation of soils or sludge can be largely hindered by the moderate conductivity of the medium, in spite of the added aliquots of acids or other complexing agents, and by the formation of neutral, insoluble compounds, e.g. metal hydroxides. In such cases, the solid formed results in local clogging of the soil pores, which has been reported to be the cause of the observed local decay of bed conductivity [56,57]. Because no reaction apart from complexation and acid–base reactions occurs in the cell, treatment cannot be restarted once the current has vanished.

As a matter of fact, EK treatment of the sludge conducted with 1 M acetic acid in the cathode was actually stopped after 5 d, since the overall current did not exceed 0.5 mA afterward—50 times below the current levels in the first hours (Fig. 10). Increasing the acid concentration to 3 M could retard the formation of $Al(OH)_3$, and the current decreased regularly down to 2 mA (approx. 0.2 mA/cm^2) at the end of the run: the different current profiles are linked to higher efficiency in concentrating the two metals in the cathode chambers. The case of citric acid is somewhat different in a way that (i) citrate is a more powerful complexant than acetate, (ii) citric acid is a stronger acid than the other acid, and (iii) the amount of citric acid introduced was 2–3 times larger than those of acetic acid. Therefore, the cell current remained at appreciable levels for the first ten days (Fig. 10), before decreasing in the second half of the 20-d-long run. The higher currents with citric acid result in higher energy consumption, but in return allow higher migration and focalization fluxes than with acetic acid.

4.4. Specific energy consumption

The specific energy consumption of the electrokinetic treatment was defined as:

$$E_s = \frac{QU_c}{n_{Al,cath}M_{Al}} \tag{14}$$

where U_c is the applied cell voltage, M_{Al} the molecular weight of aluminum, $n_{Al,cath}$ the mole amounts of Al species transferred to the cathode side, and Q the electrical charge passed during the run, calculated from the time variation of the current.

Taking into account the quantity of metals (Al and Cr) removed, power consumption per kg of metal recovered has been estimated and represented in Fig. 11, together with the fraction of metal species recovered in the cathode chamber. The energy

Table 5
Qualitative description of speciation in the cell at the end of EK runs: 1 M acetic acid or 3 M citric acid. Migration direction and intensity are indicated together with the experimental locations of the various sections in the cell, with the location of the metal peak observed

pH	3	4	5	6	7	8	9	10	11
Aluminium with acetic acid									
Prevailing form	$Al(AC)^{++}$	$Al(AC)^{++}$	$Al(AC)^{++}$	$Al(OH)_3$	$Al(OH)_3$	$Al(OH)_3$	$Al(OH)_4^-$	$Al(OH)_4^-$	$Al(OH)_4^-$
Migration	→	→	→				←	←	←
Location of sections			S1	S2, S3	S4—Cathode				
Al peak location					Cathode				
Aluminium with citric acid									
Prevailing form	Al^{3+}	$Al(Ci)H^{++}$	AlCi, $Al(OH)^+$	$Al(OH)_3$, AlCi	$Al(OH)_3$, $Al(Ci)_{23}^-$	$Al(OH)_3$, $Al(Ci)_{23}^-$	$Al(OH)_4^-$	$Al(OH)_4^-$	$Al(OH)_4^-$
Migration	→	→	→	←	←	←	←	←	←
Location of sections	S1	S2, S3, S4	S4	Cathode	Cathode				
Al peak location		S3 and S4							
Chromium with acetic acid									
Prevailing form	$Cr(Ac)^{++}$	$CrAc_2^+$	$Cr(Ac)_3$	$Cr(Ac)_3$	$Cr(Ac)_3$	$C(OH)_2^+$	$Cr(OH)_3$	$Cr(OH)_4^-$	$Cr(OH)_4^-$
Migration	→	→				→		←	←
Location of sections		S1	S2, S3	S4	Cathode				
Cr peak location				S4					
Chromium and citrate									
Prevailing form	Cr^{3+}	$Cr(Ci)_2^{3-}$	$Cr(Ci)_2^{3-}$	$Cr(Ci)_2^{3-}$	$Cr(Ci)_2^{3-}$	$Cr(Ci)_2^{3-}$	$Cr(Ci)_2^{3-}$	$Cr(OH)_4^-$	$Cr(OH)_4^-$
Migration	→	←	←	←	←	←	←	←	←
Location of sections	S1	S2	S3, S4	Cathode	Cathode				
Cr peak location			S4						

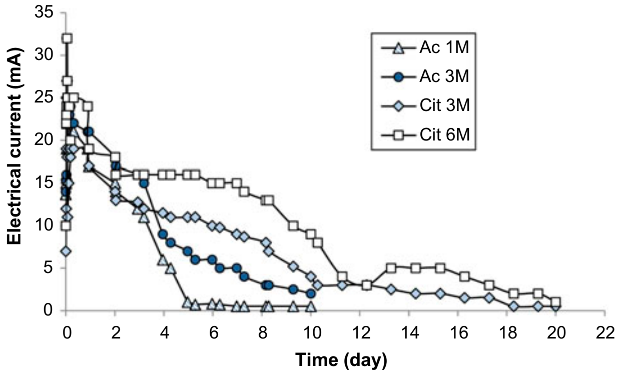


Fig. 10. Time variation of the cell current during the EK runs conducted with acetic or citric acid as catholyte solution (corresponding final distributions of pH, Al and Cr concentration are given in Figs. 9a and 9b).

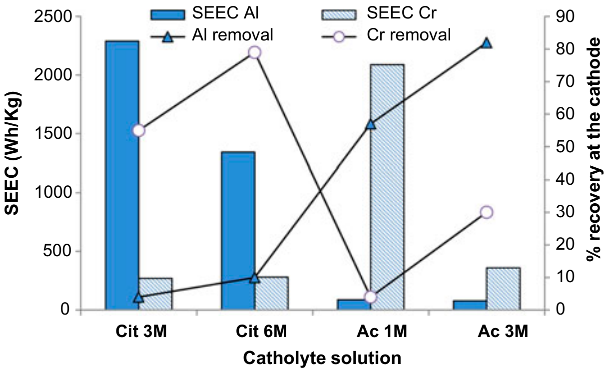


Fig. 11. Power consumption per kg of metal recovered (Al or Cr) for several types of catholyte solutions.

consumed per kg of metal recovered with 1 M acetic acid was less than with 3 M with a satisfactory aluminum recovered rate, but the use of citric acid required much more energy, in relation to the poor fraction recovered at the cathode. Comparable behavior was observed for Cr(III), but with far better performance with citric acid. Nevertheless, the energy demand obtained are very large, varying from 34 to 2,300 kW h/kg Al and from 210 to 2,080 kW h/kg Cr, depending on the complexing acid added. The high-energy demand obtained in these tests is principally due to the low metal contents in the sludge, at 1.26 wt % Al and 0.75 wt% Cr, since the other operating parameters could have been found to allow a high metal concentration in the cathode chamber.

The lowest energy consumption can be estimated from the electric charge actually consumed for transport of the complexed metal to the cathode. For this purpose, consider the case of the complex species with charge number n_{M} and whose transference number in the cell is t_{M}. The maximum mass amount of metal transferred can be related to the charge passed:

$$m_{\mathrm{M,max}} = t_{\mathrm{M}} \frac{Q}{nF} M_{\mathrm{M}} \quad \text{where subscript M is for Al or Cr} \tag{15}$$

The energy demand for the operation is actually equal to the product (QU_{c}). Therefore, the minimum specific energy consumption can be written as:

$$E_{\mathrm{s,min}} = \frac{QU_{\mathrm{c}}}{m_{\mathrm{M,max}}} = \frac{n_{\mathrm{M}} F U_{\mathrm{c}}}{t_{\mathrm{M}} M_{\mathrm{m}}} \tag{16}$$

The estimation has been made considering the present cell voltage (6 V), considering a divalent ion, e.g. AlAc^{2+} and with t_{M} = 50%: specific energy consumption could then be estimated at 23.8 and 12.4 W h/kg for recovery of Al and Cr, respectively. These values indicate that electrokinetic remediation can be an efficient technique, with fair but acceptable energy consumption, in particular for the removal of heavy, toxic metals.

5. Conclusion

The objective of this paper was to study the possibility to recover aluminum and chromium from the sludge produced by the electrocoagulation treatment of industrial wastewater using electrokinetic migration. Electrocoagulation treatment of industrial textile wastewater containing added chromium was first rapidly investigated. During the first stage of treatment, increasing current intensity slightly enhances COD and TOC removal with time. The highest current employed yields satisfactory abatement of COD and TOC, respectively, approximately 93 and 91%. Turbidity reduction necessitates a higher current density and a minimum treatment time: it reaches 97% at 150 A/m^2. Removal of Cr(VI) with Al electrodes by its reduction to Cr(III) species does not exceed 60% in all the operating conditions tested.

The obtained sludge was treated by the electrokinetic method in order to study the possible recovery of aluminum and chromium. The removal efficiency of aluminum with the addition of acetic acid as a complexing agent was higher than with citric acid. 57–82% of the initial Al was concentrated in the cathode chamber with acetic acid at 1 and 3 M. Citric acid at 3 or 6 M was not a satisfactory assistant agent and had led to Al accumulation throughout the sludge bed. The formation of $\mathrm{Al(OH)_3}$ precipitate and cationic/anionic forms of Al complexed with citric acid that migrates in contradictory directions affected the efficiency of the electrokinetic process. Chromium could be efficiently collected in the cathode chamber by use of citric acid. The specific energy consumptions were high, however mainly because of the moderate amounts of the metal species in the EC sludge. Electrokinetic method appears nevertheless promising for far larger metal contents of the sludge, i.e. after treatment of wastewater with very low contents of organic matter or non-metallic substances: the technique could be recommended downstream of the EC process for the treatment of heavy metal-containing liquid wastes.

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