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Optimization of Cr(VI) electroreduction from synthetic industrial wastewater using reticulated vitreous carbon electrodes modified with conducting polymers

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ABSTRACT

In order to maintain high values of current efficiency and space–time yield during the electrochemical reduction of Cr(VI) to Cr(III), a new methodology based on the control of the applied current throughout the process was tested. The electrochemical process was carried out using a reticulated vitreous carbon electrode modified with polyaniline. Experiments to determine the reaction rate of Cr(VI) depletion as a function of current and flow velocities were performed in order to establish the relationship between the transition concentration and these operational variables. The transition concentration was the basis of the optimization procedure proposed here and it is defined as being the concentration where the kinetics changes from linear to exponential concentration dependence. The results demonstrate that for a previously optimized flow velocity, control of the current was very effective in maintaining a high space–time yield down to very low concentrations of Cr(VI) and, consequently, the energy consumption was minimized.

1. Introduction

The importance of toxic metal removal from industrial wastewaters has been discussed in several papers [1,2]. It is well known that heavy metals such as lead, copper, mercury, chromium and cadmium, when present even at very low concentrations in ionic form in aqueous solutions, can cause severe problems to human health and aquatic life [3]. Many treatment technologies have been proposed to solve this problem and replace the conventional treatment process of chemical precipitation. The sludge generated after chemical precipitation still remains very toxic and must be stored or disposed of in specially engineered landfill sites. Additionally, many valuable metals cannot be recovered/recycled when chemical precipitation is employed. Cementation, membrane processes and adsorption are examples of technologies developed to remove metal ions from wastewaters. Membrane processes are very efficient, although costly, for removal of metal ions, but as with cementation and adsorption, will only transfer the problem from the liquid to solid phase. Furthermore, when the concentration is high, adsorption is not generally efficient [3].

Electrochemical technology can overcome some of the problems associated with the processes described above. As the electron is the main reactant, electrochemical technology has been described as a *clean technology*, and presents some advantages, such as: (1) the metal can be recovered in its metallic form; (2) in many cases, when the conductivity is high enough, no chemicals (supporting electrolytes) need to be added; (3) the water in the effluent steam can be recycled to the main process; (4) process control is easily implemented since the main process variable is the electric current and, consequently, labor intensive tasks can be reduced, and (5) low operational costs make the process economically attractive [4].

In order to really make the electrochemical technology economically attractive, optimization of process variables should be performed, especially to reduce the high investment cost related to the electrochemical reactor. As industrial electrochemical processes generally operate in the galvanostatic mode, the electrodeposition rates are very high in the beginning of the process, but as the metal concentration decreases, parallel reactions become increasingly significant, reducing the current efficiency and increasing the energy consumption [4]. This problem can be solved very easily for a planar electrode, as it can be considered to have an equipotential surface. As a result the current can be controlled throughout the process in order to keep it as close to the limiting current as possible [5]. However, as the metal concentration in effluents is generally very low, porous electrodes are necessary in order to obtain a high specific surface area and high mass transfer coefficients. For a porous electrode there is a potential profile along the electric field and, consequently, different reaction zones will be present and a methodology to control the applied current in order to obtain current efficiencies close to 100% cannot be the same as for a planar electrode [6].

This paper details the use of electrochemical technology to reduce hexavalent chromium (Cr(VI)) to its trivalent form (Cr(III)). This process is very important as Cr removal from wastewaters

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using conventional techniques is only feasible for Cr(III) because it can either be easily precipitated as a hydroxide or adsorbed on a variety of organic and inorganic substrates. Additionally, compounds of Cr(VI) are reported to be highly toxic due to their carcinogenic action whereas compounds of Cr(III) are considered to be 10–100 times less toxic than Cr(VI) [7]. The use of reticulated vitreous carbon (RVC) electrodes, covered with a thin conducting polymer film, for reduction of Cr(VI) to Cr(III) has been studied by our research group for a number of years and important results concerning the polymer electrodeposition process and the effect of operational variables on the reaction rate and polymer stability have been published in the literature [8–12]. The optimization proposed in this paper took into account all this previous experience in order to establish the best conditions for Cr(VI) electroreduction.

In this study, the electric current and flow velocity were optimized for the electroreduction of Cr(VI) using a reticulated vitreous carbon electrode coated with an electrocatalytic polyaniline film. A methodology to control the current applied to the system was developed in order to keep the current efficiency at the desired level throughout most of the process.

2. Experimental

The experiments were performed in a plug flow reactor as described elsewhere [11]. Reticulated vitreous carbon (RVC supplied by Electrosynthesis Co.) was used as the cathode. Sixty pores per inch (ppi) RVC was employed with 4.0 cm width, 7.0 cm height and 1.27 cm thickness (specific surface area 3864 $m^2\ m^{-3}$). The RVC surface was modified by electrodeposition of polyaniline. Details of the electrodeposition process can be found in the literature [10].

Two plates of 4.0 cm × 7.0 cm of a $Ti/Ti_{0.7}Ru_{0.3}O_2$ DSA® from De Nora Brasil were used as both the counter electrode and the current feeder. The flow system consisted of one electrolyte reservoir, valves to regulate flow and a flow meter. In order to achieve high electrolyte velocities, a centrifugal pump was used to pass the electrolyte through the reactor. A schematic view of the flow system has previously been presented in the literature [11].

The electric current was supplied using a constant current source (Minipa, model 3003D, São Paulo, Brazil). In all experiments, synthetic effluents (4.0 L) prepared with different concentrations of potassium dichromate as a Cr(VI) source were employed. H_2SO_4 (0.1 M) was used as the supporting electrolyte. All reagents were of analytical grade and deionised water was used in all experiments. The temperature was maintained in the range of 26–28 °C by a thermostatic bath.

In order to perform the Cr(VI) reduction assays, the current to be applied was previously set and the current source turned on. Only following this was the main valve opened and the solution permitted to flow through the reactor. This procedure was adopted in order to avoid degradation of the conducting polymer under open circuit conditions when in contact with the highly oxidizing medium (Cr(VI)) [9]. The Cr(VI)) concentration was measured on-line using a UV–vis spectrophotometer (Ultrospec 2100pro) at a wavelength of 350 nm. The cell voltage was also measured in order to calculate the energy consumption.

3. Results and discussion

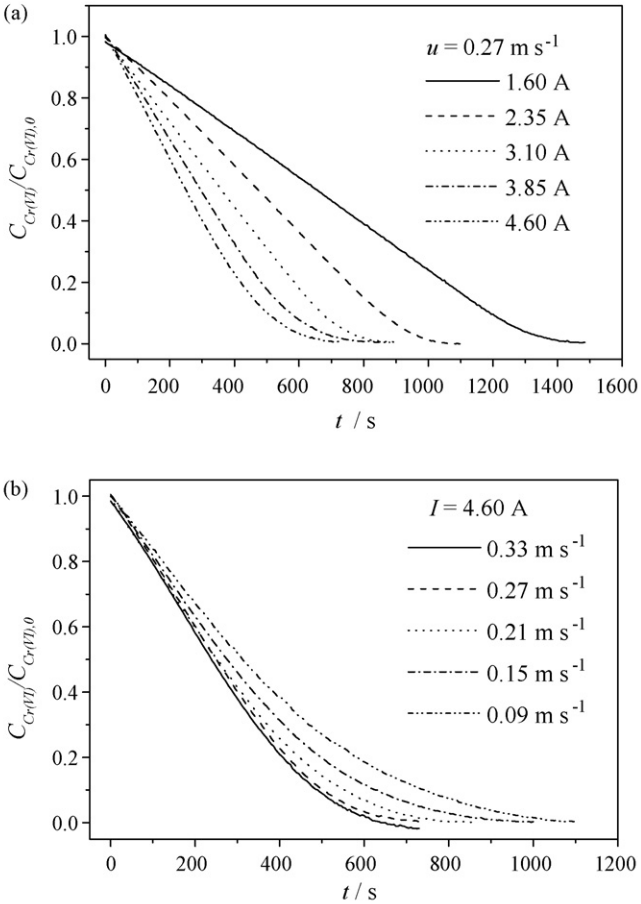

Fig. 1. Normalized Cr(VI) concentration *vs.* time for different currents (a) and for different flow velocities (b). $C_{Cr(VI),0} = 100\ mg\ L^{-1}$.

Experiments for five different current and flow velocity values were performed in order to evaluate their effects on the space–time yield (Y_{st}), current efficiency (CE) and energy consumption (EC) which were calculated from curves of Cr(VI) depletion against time, as exemplified in Fig. 1. From these figures, it is possible to observe two distinct regions: linear and exponential, which correspond to the region of constant and variable reaction rate and current efficiency (Fig. 2), respectively.

When the flow velocity is maintained constant and the applied current is increased, it is clear that the reaction rate also increases (Fig. 1a). In the case of a flow velocity of 0.27 $m\ s^{-1}$, there is no current effect on the current efficiency in the linear section, as can be observed in Fig. 2a. However, the concentration at which the process switches from constant to variable current efficiency (*transition concentration* – C^*) decreases, *i.e.*, the greater the current the greater the transition concentration. This means that, when working with low current values it is possible to carry out the electrochemical process at low Cr(VI) concentrations without losing efficiency when compared to working with high current values. On the other hand, the reaction rate is low and the operational time necessary to electroreduce all Cr(VI) to Cr(III) will increase.

Fig. 1b shows the influence of flow velocity on the kinetics of Cr(VI) reduction when a current of 4.60 A is applied. It is possible to observe that increasing the flow velocity will increase the reaction rate up to a value at which its effect is subsequently negligible. From the data presented in Fig. 2b it can be observed that the reaction rate does not depend on the Cr(VI) concentration, what would characterize activated control and consequently 100% of current efficiency would be expected. However, at low flow velocities the current efficiency is less than 100%, indicating that mass transfer (for currents greater than the limiting current) must also play an important role in the process. This is also corroborated by the fact that when the flow velocity is increased, the current efficiency in the region of constant reaction rate also increases.

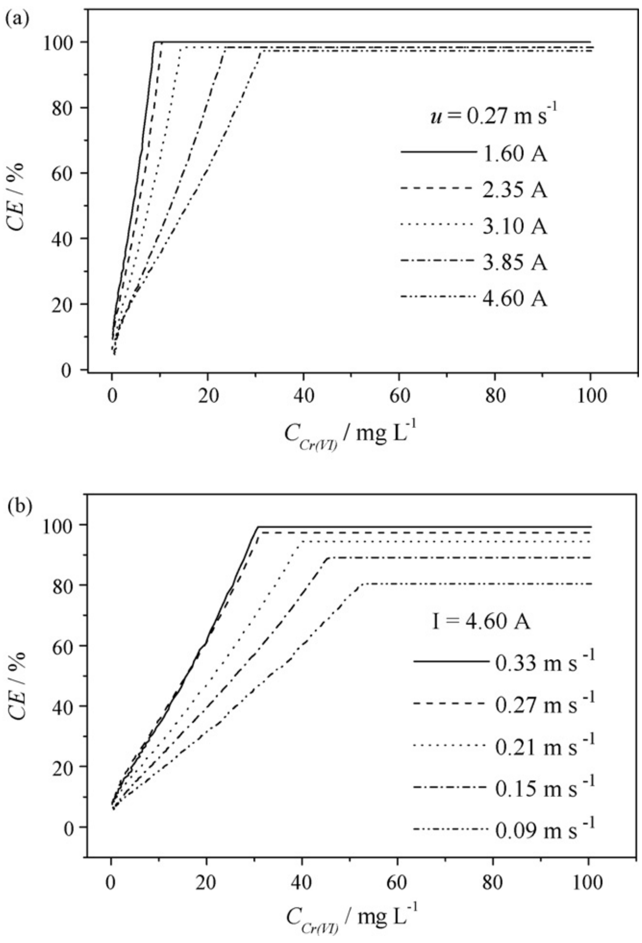

Fig. 2. Current efficiency *vs.* Cr(VI) concentration for different currents (a) and different flow velocities (b). $C_{\mathrm{Cr(VI)},0} = 100\ \mathrm{mg\ L^{-1}}$.

Overall, the current efficiency is improved when high flow velocities and low currents are employed (Fig. 2), suggesting an optimized operating condition in which all current is consumed in the reaction of interest. However, in a galvanostatic process, the limiting current decreases according to concentration depletion and as a result the current efficiency also decreases due to the existence of currents greater than the limiting current.

For flat electrodes it is easy to determine the optimum current to be applied (the limiting current) as a function of current, flow velocity and concentration in order to establish the optimum operating conditions or a current control to optimize the energy consumption throughout the process. However, determining the limiting current for three-dimensional electrodes is not so easy. This is due to the fact that an overpotential profile parallel to the electric field occurs and consequently, zones with different currents and electrochemical activities will also occur [11–13,19,20]. In fact, it has been experimentally proven that high overpotentials occur in the region close to the counter electrode while in the region close to the current feeder the overpotentials are very low [14,15]. Thus, for the same current, the electrode can present regions under mass transfer, mixed and activated control and the shape of the concentration *versus* time curves will depend on the extension of each region within the electrode [16,17]. For example, when current efficiency is lower than 100% in the linear region, it is possible that regions inside the electrode under activated control are predominant, but regions under mixed and mass transfer control with currents greater than the limiting are also present and decrease the current efficiency. Thus, when the flow velocity is increased, the extension of the region under mass transfer control decreases and the current efficiency increases, which explains the linear trends observed in Figs. 1b and 2b [21]. Such characteristics of porous electrodes make optimization using the limiting current procedure very difficult.

Table 1
CE^{kin}, Y_{st}^{kin}, EC^{kin}, C^* and t^* for different currents and flow velocities.

I (A)	u (m s^{-1})	CE^{kin} (%)	$Y_{st}^{kin} \times 10^3$ (kg m^{-3} s^{-1})	EC^{kin} (kWh kg^{-1})	C^* (ppm)	t^* (s)
1.60	0.33	100	11.2	3.7	8	1255
1.60	0.27	100	11.2	3.7	10	1205
1.60	0.21	100	11.2	3.2	13	1170
1.60	0.15	100	11.2	4.0	17	1100
1.60	0.09	100	11.2	4.0	21	1065
2.35	0.33	100	16.5	4.2	11	835
2.35	0.27	100	16.5	4.2	13	825
2.35	0.21	98	16.2	4.4	17	815
2.35	0.15	100	16.5	4.9	22	720
2.35	0.09	100	16.5	5.2	26	685
3.10	0.33	100	21.8	5.3	15	605
3.10	0.27	98	21.3	5.5	18	600
3.10	0.21	100	21.8	5.9	23	540
3.10	0.15	100	21.8	6.1	30	495
3.10	0.09	99	21.5	6.2	35	480
3.85	0.33	100	27.0	5.8	21	450
3.85	0.27	98	26.5	6.5	25	445
3.85	0.21	100	27.0	7.1	31	395
3.85	0.15	99	26.7	7.3	40	355
3.85	0.09	100	27.0	7.4	46	315
4.60	0.33	99	32.0	5.8	33	340
4.60	0.27	98	31.3	6.5	37	315
4.60	0.21	94	30.3	7.1	46	275
4.60	0.15	89	28.7	7.1	54	255
4.60	0.09	80	25.8	7.1	65	215

Considering the preceding discussion, the objective here is to present a simple methodology to optimize the electrochemical Cr(VI) reduction process. This is achieved by applying current control throughout the process in order to maximize the space–time yield and minimize the energy consumption. The strategy adopted is based on the dependence of the transition concentration on flow velocity and current, as can be easily observed in Fig. 2. For simplicity, the linear region will be considered to be under kinetic control since the reaction rate does not depend on the Cr(VI) concentration. Current efficiency, space–time yield and energy consumption will be referred as CE^{kin}, Y_{st}^{kin} and EC^{kin}, respectively.

The point where the Cr(VI) concentration is no longer linear with time and becomes exponential (*i.e.*, the process is no longer controlled predominantly by kinetics and starts to be predominantly controlled by mass transfer (exponential curve) was denoted by the transition time (t^*) and transition concentration (C^*), respectively. The dependence of C^* on the current and flow velocity will be the basis of the optimization process proposed and their values are presented in Table 1 as well as the values of EC^{kin}, Y_{st}^{kin} and CE^{kin}, which were calculated and determined from the curves presented in Figs. 1 and 2.

As can be seen in Table 1, for most of the experimental conditions the current efficiency was 100% or very close, and exceptions were only observed for 4.60 A. Although the high current efficiency values and low energy consumption values were observed at lower flow velocities, the low values of Y_{st}^{kin} observed under these conditions must be considered in any financial analysis as Y_{st}^{kin} will affect the reactor size and operational time. Thus, high values of Y_{st} are very desirable. It is worth mentioning that the current efficiency has a direct effect on the Y_{st} values. The lower the current efficiency, the lower the Y_{st} value.

It was observed that cell voltage is the main variable affecting the energy consumption of the electrochemical process in the region of constant current efficiency, but its influence is small and an average

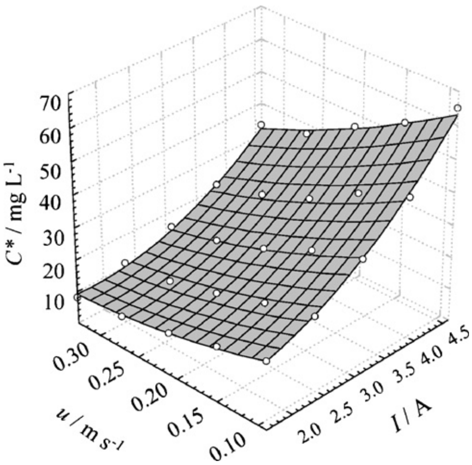

Fig. 3. Transition concentration *vs.* flow velocity and current.

energy consumption (EC^{kin}) can be calculated with deviations of less than 5% (Table 1). Otherwise, for the exponential portion of the curves of Fig. 1, the current efficiency is the main factor affecting the energy consumption and, consequently, low energy consumption values were observed.

3.1. Optimization procedure

Since the transition concentration corresponds to that in which the process stops operating at maximum current efficiency and space–time yield, as well as minimum energy consumption, an ideal process would apply a current until the transition concentration was reached, and immediately alter it, according to the value of C^*. This procedure is the basis of the optimization process proposed herein and the first step is to determine the relationship between transition concentration and applied current. The curves presented in Figs. 1 and 2 were used for this purpose and the results are shown in the surface graph in Fig. 3.

The advantage of the proposed methodology is based on the fact that the transition concentration corresponds to that in which the process changes from “kinetic control” to “mass transfer control” considering the electrochemical kinetics occurring at the same time inside of the porous electrode. As can be seen in Fig. 2, it is possible to determine the transition concentration with a precision of around 5%.

The surface graph of Fig. 3 can be represented by Eq. (1), which was obtained using the statistical technique of factorial design. This equation represents very well the experimental results considering all the significant effects ($R^2 = 0.99569$). In this case, both current and flow velocity are very important as well as their interaction.

$$C* = 24.6 - 1.4I + 2.9I^2 - 66.0u + 142.8u^2 - 27.1Iu \tag{1}$$

In Eq. (1), C^* is given in mg L^{-1}, I in Amperes and u in m s^{-1}.

After the optimum flow velocity was established, Eq. (1) can be simplified and the current can be written as a function of the transition concentration. So, the current can be controlled, *i.e.*, its value can be decreased, throughout the electrochemical process in order to keep both the current efficiency and space–time yield at their maximum and, consequently, reduce the energy consumption.

3.2. Flow velocity optimization

The first step was to determine the optimum flow velocity to be used and the exponential part of the curves shown in Fig. 1b were used for this purpose. Since the exponential portions of these curves are mass transfer controlled, they were used to determine the mass transfer coefficient, k_m, as described elsewhere [18] and their dependence on the flow velocity is shown in Fig. 4. The values of k_m obtained in this work are in agreement with those of other authors using flow reactors and RVC cathodes [21].

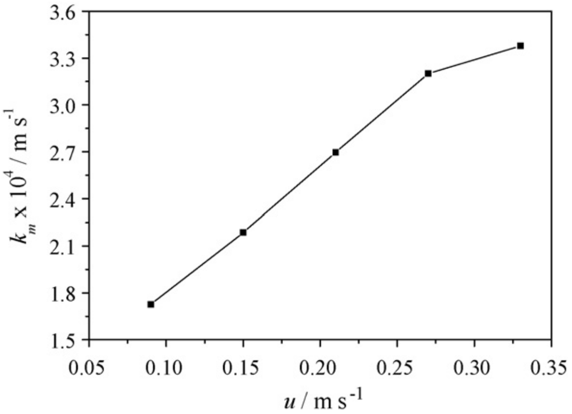

Fig. 4. Mass transfer coefficient values *vs.* flow velocity.

The increase of k_m as shown in Fig. 4 is expected since the thickness of the diffusion layer decreases when the flow velocity increases. However, since k_m is the ratio between the diffusion coefficient (D) and diffusion layer thickness (δ), its function grows monotonically and tends to an asymptotic value, as can be seen in Fig. 4. Increasing the flow velocity from 0.27 m s^{-1} to 0.33 m s^{-1} results in an increase in the mass transfer coefficient. However, it is not interesting to use 0.33 m s^{-1} given that the costs involved in pumping high flow rates will probably be greater than the benefits obtained with reaction rate improvements. In summary, flow velocities lower than 0.27 m s^{-1} cause a decrease in the current efficiency, while values greater than 0.27 m s^{-1} do not significantly improve the reaction rate. Thus, for the process studied here it was found that a flow velocity of 0.27 m s^{-1} optimizes the process when considering the current efficiency, space–time yield and energy consumption. This value was subsequently used in all experiments performed for current optimization.

3.3. Process optimization

Eq. (1) was simplified, using the value of $u = 0.27$ m s^{-1}, and resulted in Eq. (2).

$$C* = 17.2 - 8.7I + 2.9I^2 \tag{2}$$

In order to perform the experiment using optimized current control (current efficiencies of ∼100%), Eq. (2) was used to calculate the current that should be applied as a function of Cr(VI) concentration. As no electronic devices were available in the laboratory to automate this experiment at very short concentration intervals, the current was manually adjusted considering the time limitation involved. The Cr(VI) concentration was measured on line at time intervals of 5 s using a flow cell coupled to an UV–vis spectrophotometer. When a desired concentration was reached, the current was manually adjusted (decreased) according to the value calculated using Eq. (2). Fig. 5 shows the experimental conditions used to perform the optimized process. It is important to note that due to inaccuracy in the determination of the exact value of C^*, the values shown in Fig. 5 are 10% lower than those calculated from Eq. (2). This percentage was adopted as a security factor.

During the experiment, the current was maintained constant until the corresponding transition concentration was reached. At this moment a current value was set according to the values shown in Fig. 5.

Table 2
CE, Y_{st} and EC for each current range shown in Fig. 6.

Concentration interval (mg L^{-1})	I (A)	$\Delta U_{Average}$ (V)	CE (%)	$Y_{st} \times 10^3$ (kg m^{-3} s^{-1})	EC (kWh kg^{-1})
100–82	5.80	5.94	97.1	28.4	9.5
82–58	5.40	5.79	96.1	26.2	9.3
58–40	4.60	5.29	96.8	22.5	8.5
40–28	3.90	4.91	95.9	18.9	7.9
28–19	3.10	4.36	96.3	15.1	7.0
19–14	2.40	3.94	95.6	11.4	6.5
14–10	1.60	3.25	100	8.1	5.0
10–5	0.90	2.71	100	4.5	4.2
5–0	0.90	2.52	Average: 37.5	Average: 1.7	Average: 10.4

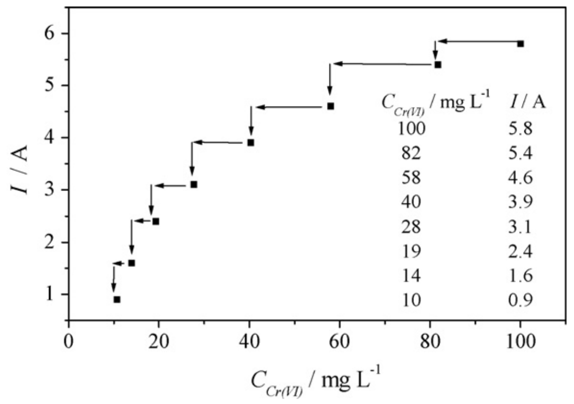

Fig. 5. Operational curve used for the current control as a function of Cr(VI) concentration.

It is important to mention that in a practical situation, the current control can be achieved using digital controllers set to supply the desired current as a function of time, since Faraday's law can be used to convert Eq. (2) into an equation of current *versus* time. If desired, the current control can be performed for time intervals of less than 1 s.

Using the procedure and operational conditions described above, the experimental curve shown in Fig. 6 was obtained. The curve presented in Fig. 6 corresponds to the normalized depletion of Cr(VI), as a function of time, considering the current applied for each Cr(VI) concentration range (as given in Fig. 5). As expected, each section of the curve that corresponds to an applied current displays linear behavior and the cell voltage, current efficiency, space–time yield and energy consumption for each section are given in Table 2. For concentrations lower than 5 mg L^{-1} it is not interesting to apply current control as the process will become extended and no significant benefits in terms of energy consumption will be gained.

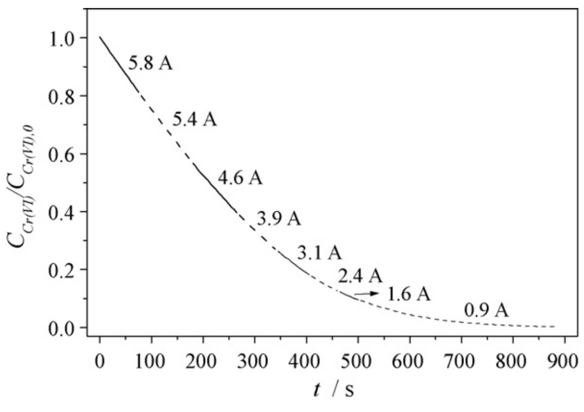

Fig. 6. Normalized Cr(VI) concentration *vs.* time for experiments carried out under current control.

As can be seen in Table 2 the proposed process based on current control was very efficient in maintaining high current efficiency (>95%) values – even at low Cr(VI) concentrations. Consequently, the space–time yield was maximized and energy consumption was minimized as almost all the applied current was used for the desired reaction.

Finally, it is worth mentioning that this optimization methodology can be applied not only for Cr(VI) reduction but also for the electrochemical treatment of effluents containing other metals (or a mixture of them). Of course, in the case of electroreduction of other metals, Eqs. (1) and (2) must be obtained considering the particular effluent under study. Additionally, another advantage of the proposed optimization methodology is that the effects of other substances commonly present in real effluents are naturally considered during the determination of the empirical equations used for optimization.

4. Conclusions

A new method to optimize the operational variables that affect the Cr(VI) electroreduction process using a polyaniline-modified RVC porous electrode was presented. The results demonstrate that a flow velocity of 0.27 m s^{-1} optimizes the hydrodynamic conditions when considering the mass transfer coefficient. Current control based on the transition concentration was proven to be a feasible and simple methodology that can be used to obtain high space–time yields and low energy consumption down to very low Cr(VI) concentrations.

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