



# 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.

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## 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 stream 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  $3864 \text{ m}^2 \text{ m}^{-3}$ ). The RVC surface was modified by electrodeposition of polyaniline. Details of the electrodeposition process can be found in the literature [10].

Two plates of  $4.0 \text{ cm} \times 7.0 \text{ cm}$  of a  $\text{Ti}/\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$  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.  $\text{H}_2\text{SO}_4$  (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  $26\text{--}28^\circ\text{C}$  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

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

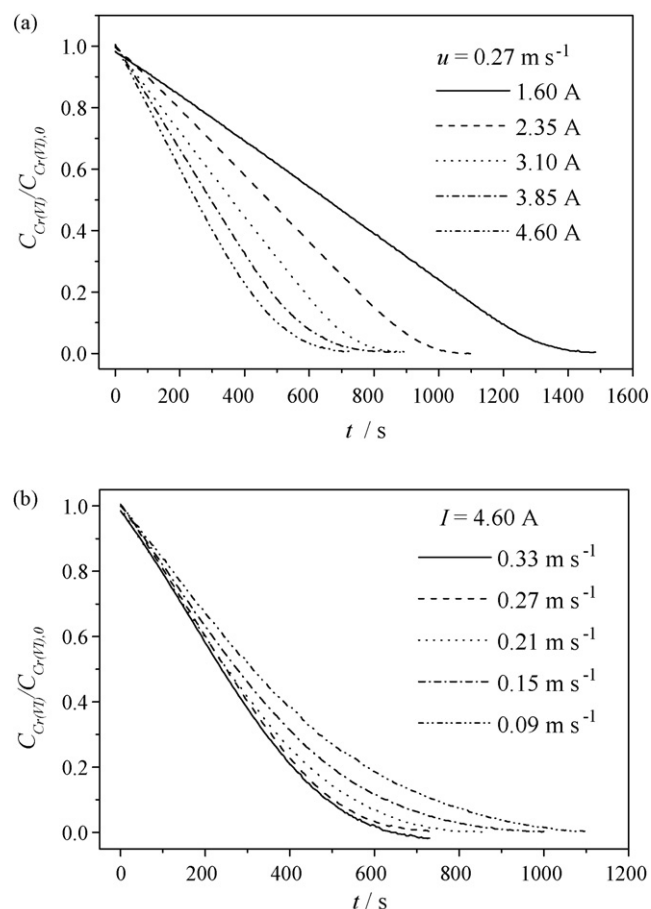


Fig. 1. Normalized Cr(VI) concentration vs. time for different currents (a) and for different flow velocities (b).  $C_{Cr(VI),0} = 100 \text{ mg L}^{-1}$ .

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  $0.27 \text{ m s}^{-1}$ , 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.

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