

REDUCTION OF HEXAVALENT CHROMIUM USING POLYANILINE FILMS

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INTRODUCTION. Chromium is used in a variety of applications including electroplating, dye production, tannery, water-cooling and others. As the toxicity of hexavalent chromium as a carcinogenic agent was proven, its effluents concentration is controlled and the limit levels are very low (the Brazilian legislation limits Cr(VI) discharge in 0.1 mgL^{-1}). The reduction of Cr(VI) to its trivalent state makes it less toxic and easily adsorbed or precipitated. Thus, the reduction of Cr(VI) to Cr(III) serves to immobilize it [1]. In this paper a process using the conducting polymer polyaniline (Pani) to reduce the hexavalent chromium was studied. Two possible processes were tested: the process under open circuit conditions and the process operating under cathodic protection of the film. The polymer degradation and the Cr(VI) reduction rate were evaluated in both cases.

EXPERIMENTAL. In the experiments under open circuit conditions the polyaniline film was chemically deposited over polycarbonate particles, and then the chromium reduction took place in a fixed bed reactor with the electrolyte flowing through it.

For the experiments under cathodic protection a flow reactor with a cathode of 10 ppi reticulated vitreous carbon of $1,2 \times 2 \times 2 \text{ cm}$ was used. The counter-electrode was a DSA[®] coated with Ti/RuO₂. The reactor is sketched in figure 1. The polyaniline film was previously electrodeposited over the RVC cathode from an aniline solution [2]. Before flowing the Cr(VI) solution, a constant potential of $-0,2 \text{ V}$ (vs. SCE) was applied and then the process was carried out. The reference electrode was calomel saturated (SCE).

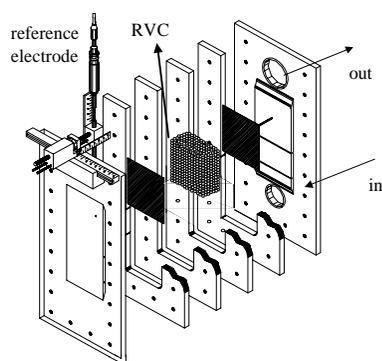


Figure 1. Exploded view of the flow reactor.

The electrolyte was prepared using HCl as support electrolyte, and K₂Cr₂O₇ was used as the source of Cr(VI).

RESULTS AND DISCUSSION. Figure 2 shows the reaction rate of Cr(VI) reduction using particles of polycarbonate covered with a Pani film. These experiments were carried out under open circuit conditions. A faster rate is observed in the beginning of the process, where the oxidation of polyaniline takes place. After that the reaction rate decreases and Pani starts to take part in a chemical reaction where the main product is p-benzoquinona, which was detected in a UV-vis analysis of the solution. At the end of the experiment it could also be observed that the Pani film was consumed and the surface of the polycarbonate was practically nude. This was observed in all studied concentrations.

Because the dichromate medium is extremely oxidizing, Pani becomes superoxidized and starts to take part in an irreversible hydrolysis reaction [3]. This process of Pani degradation makes the process under open

circuit conditions inappropriate in an industrial scale where the recycling of the polymer is necessary.

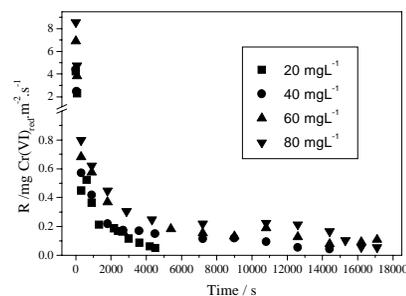


Figure 2. Reaction rate for chromium reduction tested under open circuit conditions.

To solve the degradation problem the superoxidation of the Pani film should be avoided. The application of a cathodic potential during the process of exposing the film to the Cr(VI) solution could solve the problem. The reaction rate for this process is shown in figure 3.

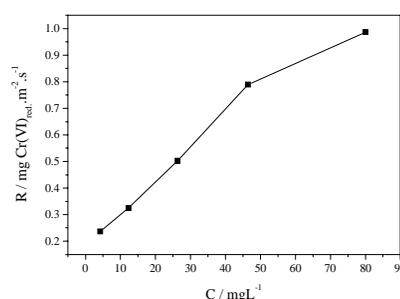


Figure 3. Reaction rate for chromium reduction under cathodic protection conditions. $C_0 = 80 \text{ mgL}^{-1}$.

As can be observed in figure 3, the reaction rates are greater than those observed in the process under open circuit conditions, and the rate is extremely dependent on the ion concentration.

The Pani film degradation was evaluated by means of the Pani film voltamograms before and after reacting with the hexavalent chromium. This is shown in figure 4.

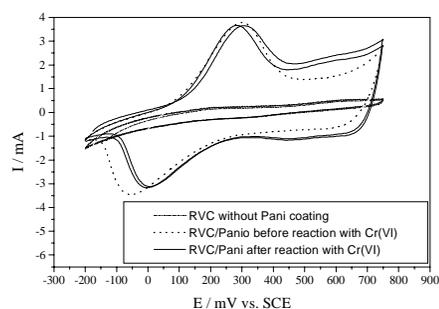


Figure 4. Voltamograms of Pani film before and after reacting with chromium.

The cathodic protection was very efficient in avoiding degradation, as can be seen in figure 4. The UV-vis spectra didn't show the presence of p-benzoquinone, also confirming that practically no degradation reaction took place. Another advantage of this process is the possibility to work the reactor continuously without the necessity to stop and recycle the polymer, as in the case of the open circuit process.

REFERENCES.

- [1] Wei C.; German S.; Basak S. and Rajeshwar R.. J. Electrochem. Soc., Vol. 140, No. 4, L60, 1993.
- [2] Huang, W-S; Humphrey B.D. and MacDiarmid A.G.. J. Chem Soc., Faraday Trans. 1, 82, 2385, 1986.
- [3] Cui, C.Q; Su, X.H. and Lee, j. Y.. Polymer Degradation and Stability 41, 69, 1993.

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