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Analysis of the effect of polypyrrole synthesis conditions on its capacity to reduce hexavalent chromium

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Abstract

This paper reports the capacity of polypyrrole to reduce toxic hexavalent chromium (Cr(VI)). The influence of using different electrolytes during the polymer's synthesis has been studied. To improve the reduction of Cr(VI), the parameters considered were the polypyrrole morphology and the amount of conducting polymer. Polypyrrole obtained by cyclic voltammetry at a low sweep rate using KBr as supporting electrolyte showed better performance for Cr(VI) reduction compared to coatings obtained by constant potential or cyclic voltammetry at high sweep rates.

Keywords: Polypyrrole; Hexavalent chromium; Electropolymerisation

1. Introduction

Traditional techniques for removing hexavalent chromium (Cr(VI)) from industrial waste generally involve two steps: (a) chemical reduction of Cr(VI) to Cr(III) using suitable reducing agents; and (b) precipitation of Cr(III) as $Cr(OH)_3$ using, e.g. NaOH [1,2]. The development of new technologies to improve or replace the above processes is both economically and environmentally desirable. Many processes have been reported in the literature, including adsorptive [3,4], photochemical [5] and electrochemical techniques [6–8]. In the case of direct electrolysis of Cr(VI), the process is affected by poor electron transfer kinetics, low current efficiency and selectivity problems. In order to improve the efficiency of this process, different alternatives need to be investigated.

In recent years a new process involving conducting polymer films has been studied. Electrochemical polymerisation has proven to be a useful method for obtaining conjugated aromatic polymers such as polypyrrole (PPy) and polyaniline [9–11]. These conducting polymers have aroused great interest because of their possible applications [12–14]. Some of these applications are based on the phenomenon of reversible switching between oxidised and reduced forms of the polymer by electrochemical doping/undoping. This ability may be used to reduce highly toxic ions like hexavalent chromium.

The process is based on spontaneous electron transfer from the polymer to Cr(VI) present in a solution. The reaction may be represented as

$$Cr_2O_7{}^{2-}{}_{(aq)} + 6PPy_{(s)} + 14H^+ \rightarrow 2Cr^{3+}{}_{(aq)} + 6PPy^+{}_{(s)} + 7H_2O$$

The Cr(VI)/PPy system can be considered as an electrochemical cell where the electron flow from PPy to Cr(VI) is due to the variation in Gibbs energy in the reaction. The ΔG° value is -376 kJ/mol, considering that the redox potential for $Cr_2O_7{}^{-2}/Cr^{3+}$ is 1.33 V and the formal potential for PPy/PPy^+

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is −0.2 V. It is worth mentioning that the reduction process is more favourable in an acid medium [15].

Research of Cr(VI) reduction with PPy films began with Rajeshwar et al. [15–17], who performed experiments with PPy films generated over glassy carbon and platinum (Pt) electrodes using a constant potential of 0.9 V/Ag/AgCl, with KCl as the supporting electrolyte. When the films were placed in contact with solutions containing Cr(VI) it was possible to reduce almost all of the chromium present in short time lapses.

Many PPy properties such as conductivity and morphology vary according to the synthesis conditions, i.e. the solvent, electrodeposition method and the counteranion used [18–20]. A reticulated vitreous carbon (RVC) surface has been employed as a substrate for conducting polymer deposition, especially in applications where a large surface area is required. For instance, PPy has been polymerised over a variety of three-dimensional electrodes [21] in the presence of different supporting electrolytes, different sweep rates and different anodic limits, verifying the resistance of the films to the reduction of 10 ppm of Cr(VI) [22].

However, it is necessary to study the effect of changing the Cr(VI) concentration to a range similar to that of real samples handled by industry (100 ppm). It is of interest to understand the cause for this difference in reduction capacity depending on the supporting electrolyte used during electropolymerisation. This is therefore the main objective of the present work.

For this purpose, voltammetric studies of pyrrole polymerisation were performed, along with quartz microbalance analyses and morphological studies of the films obtained.

2. Experimental

Pyrrole (Aldrich) was distilled in a vacuum atmosphere prior to its use. PPy films were obtained by cyclic voltammetry (40 cycles). The working electrodes were 100, 65 and 45 ppi RVC (Electrosynthesis Company) three-dimensional meshes (1.0 cm × 1.0 cm × 0.6 cm). The counter electrode was graphite (Johnson Matthey). All the potential values are referenced to a Ag/AgCl 3.0 M KCl reference electrode. Potential control was achieved using a PAR 173.

Fig. 1 shows the general scheme of the experimental steps. In the first step PPy was deposited on the RVC electrode from a 0.1 M pyrrole solution and a 0.1 M solution of a potassium salt (KI, KBr, KCl and KF) as the supporting electrolyte. In the second step PPy was characterised by cyclic voltammetry using the same polymerisation medium. Immediately afterwards (step 3) the polymer films were reduced at −0.9 V versus Ag/AgCl for 15 min. In the fourth step the PPy film was conditioned in a 0.1 M H_2SO_4 solution. The fifth step consisted of transferring the electrodeposited PPy to a 100 ppm Cr(VI) solution (10.0 mL) prepared with a 0.1 M H_2SO_4 solution. In step 6 the reduction of the hexavalent chromium was monitored using UV–Vis spectrometric analysis. The UV–Vis absorption spectra were measured using a Spectronic Array 3000. The Cr(VI) concentration was calculated from the intense Cr(VI) charge transfer band at 352 nm. When the Cr(VI) concentration was lower than 10 ppm, its concentration was determined by the diphenylcarbazide method using the band at 574 nm.

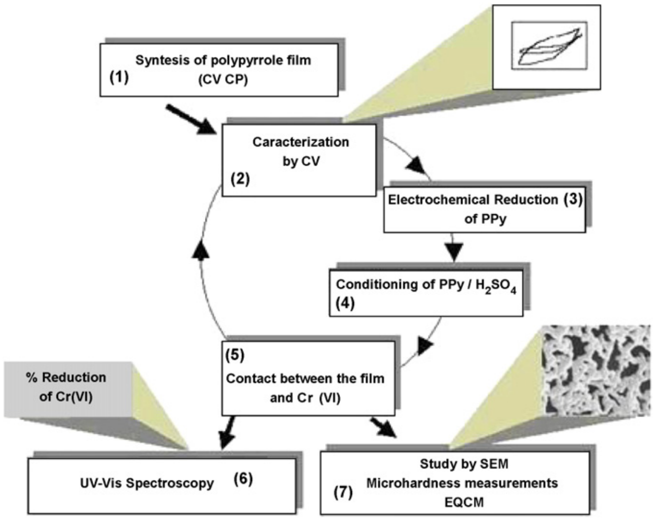

Fig. 1. General scheme of the experimental stages.

Step 7 consisted of a series of analyses. Scanning electron microscopy (SEM) was performed using a Leica s-420-s. For microhardness measurements a Fisherscope HV 100 tester was employed. Loading–unloading curves were obtained with an optimum final load value of 3 mN, in order to avoid the influence of the substrate. The testing time of the load–unload cycle was 20 s, and 15 tests were performed along the surface to generate a mean value. For EQCM experiments, a Maxtek PM-740 commercial microbalance was used. A Voltalab model 1100 potentiostat/galvanostat was employed for the synthesis and oxidation–reduction of the polymer. A three-electrode system was used, consisting of a Pt working electrode on quartz crystal (1.13 cm^2), a graphite counter electrode and a Ag/AgCl reference electrode.

3. Results and discussion

Previous studies in our working group [22] have shown that PPy films obtained by cyclic voltammetry (CV) have the property of reducing hexavalent chromium. Most films achieved a 100% reduction of Cr(VI) when placed in contact for 2 h with a 10 mL 10 ppm Cr(VI) solution. In order to learn more about their reduction properties it was decided to use the PPy films with a 100 ppm Cr(VI) solution in the same conditions. Table 1 displays the results obtained. It can be seen that the PPy films have a limited capacity. The films with the greatest efficiency were those synthesised in KI and KBr, which, respectively, achieved a 40% and 32%, reduction of Cr(VI) in a 100 ppm solution.

In search of better conditions, the synthesis method was modified by changing the potential sweep rate from 100 to 20 mV/s while leaving the same potential limits (−0.3 to 0.9 V versus Ag/AgCl). The results obtained are also shown in Table 1. The use of KI, KCl and KBr as supporting electrolytes led to 93%, 97% and 91% reductions, respectively, in the Cr(VI) present in solution. When KF was used, the reduction capacity of the PPy