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REMOVAL OF Cu(II) FROM DILUTE SOLUTIONS AT POLYPYRROLE MODIFIED ELECTRODES

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ABSTRACT

The removal of Cu^{2+} ion from dilute acidic solutions containing dissolved oxygen was investigated through its spontaneous and potentiostatic reduction at Pt and reticulated vitreous carbon (RVC) electrodes recovered with reduced polypyrrole (PPy^0). It was observed that the spontaneous Cu^{2+} ion reduction occurs only at the Pt/PPy^0 electrode. In the electroreduction procedure, a removal efficiency of 99.8% was achieved with the RVC–PPy^0 electrode after 30 min of electrolysis at −0.40 V vs. a saturated calomel reference electrode. The removal efficiency of Cu^{2+} ion from the solution was evaluated by monitoring its concentration decay through linear voltammetric measurements at a Pt ultramicroelectrode and/or by flame atomic absorption spectrometry. Due to its high efficiency and simplicity, the electroreduction procedure at the RVC–PPy^0 electrode may

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become advantageous in the removal of low-level concentrations of copper from pretreated industrial wastes.

Key Words: Polypyrrole; Cu^{2+} removal; Reticulated vitreous carbon; Pt

INTRODUCTION

Toxic species found in wastewater originated from industrial activities must be removed before discharging the effluents. The permissible concentration of metal ions has been strongly decreased, the limiting value for Cu^{2+} ion being $0.5\,mg\,L^{-1}$ in the most stringent regulations (1). Although the conventional technique of hydroxide precipitation at pH 8 allows to attain a limiting value of $1\,mg\,L^{-1}$ of cupric ion in the effluent, it generates a high salt content, which prevents the recycling and reuse of the water. Therefore, quantitative investigation on efficient and low cost processes for wastewater treatment continues to be an area of great interest.

The ability to cycle polypyrrole between oxidized and reduced states (2) suggests its application in heterogeneous oxidation–reduction reactions onto a variety of substrates recovered with this material. Among others, the applications include fields such as environment remediation, electrocatalysis, chemical sensors, batteries, and optical and electronic devices (3).

The homogeneous reaction between pyrrole [$E^0 \sim 0.20\,V$ vs. saturated calomel reference electrode (SCE)] and Cu^{2+} ion is thermodynamically spontaneous (4) so that Cu^{2+} ion may be reduced by neutral (uncharged) polypyrrole, PPy^0. On the other hand, reported studies (5) indicate that the polymer retains some of its conductive properties at potentials where it undergoes a conductor to insulator transition thus allowing metal electrodeposition on PPy^0-modified electrodes. These features lead us to investigate both the spontaneous copper deposition and its electrodeposition under potentiostatic conditions onto a reduced polypyrrole film.

Reticulated vitreous carbon (RVC) is a form of glasslike carbon combining some properties of both the glass and normal industrial carbon (6,7). It is a very inexpensive open pore material, available in several porosity grades, from 10 to 100 pores per inch (ppi). Reticulated vitreous carbon can be easily machined into various geometric shapes, it presents a high surface area, up to $66\,cm^2\,cm^{-3}$ for the 100 ppi standard (8), and it is well suited as an electrode material for flow-through cells (9).

In order to evaluate the efficiency of the copper removal procedure, the decay in the Cu^{2+} ion concentration may be conveniently monitored either by linear voltammetry or by flame atomic absorption spectrometry (FAAS). Although the latter is a usual analytical method for metal determination in the ppm range (10), electrochemical methods compete with spectroscopic ones with respect to detection limits (11) and are to be preferred whenever “in situ” or “in vivo” monitoring is required. In this case ultramicroelectrodes (UMEs) (12–14), the critical dimension of which is in the micrometer range, lead to rapid sensing because their small size enhances diffusion rates and the very small currents generated in these devices, in the order of 10^{-9} A, allow electrochemical measurements to be carried out in highly resistive media (15).

The aim of this study is the removal of Cu^{2+} ion in the $12\,mg\,L^{-1}$ concentration range from sulfuric aqueous solutions using polypyrrole covered RVC electrodes (16). The efficiency and kinetics of the metal removal process were evaluated by monitoring the concentration of the Cu^{2+} ion remaining in the solution. For a better understanding of both the spontaneous and the electroreduction reactions, preliminary studies were carried out at a Pt substrate.

EXPERIMENTAL

The electrochemical cell consisted of a conventional three-electrode assembly with a Pt wire auxiliary electrode and an SCE, to which all potentials are referred. The working electrodes were either a $2.5\,cm \times 2.5\,cm$ ($\approx 6\,cm^2$) platinum plate or an RVC prism of approximately $1.0\,cm \times 1.0\,cm \times 1.5\,cm$, fixed to a graphite rod with a conducting graphite paint from Ladd Research Industries, Inc., Burlington, VT. The platinum plate working electrode was cleaned with a 1:1 (v/v) H_2SO_4/HCl solution and heated in a Bunsen flame before using. Both in the polymerization and in the electrodeposition procedures, the auxiliary electrode was cylindrical Pt gauze. In the linear voltammetric experiments, the working electrodes were a vitreous carbon disc of 5 mm in diameter or a Pt disk UME of 2 μm radius.

A stock solution of 1.6×10^{-2} M in Cu^{2+} ion and 5×10^{-3} M in H_2SO_4 was prepared in double distilled water using p.a. grade reagents from Merck, Darmstadt, $CuSO_4$ being previously dried at $110 \pm 1°C$ for 6 hr.

The PPy films were electrodeposited on the Pt or RVC working electrode surface from an aqueous deaerated solution 0.1 M in pyrrole (Py) and 0.1 M in KCl, and allowed to grow for 30 min at 0.90 V using a potentiostat model DEA 332 from Radiometer, Copenhagen. After washing with distilled and deionized water, the charge stored in the film was evaluated from the voltammogram obtained in the cathodic potential scan of the electrode in deaerated 0.1 M KCl solution (voltammograms not shown).

The polymer film deposited on the electrode surface was then reduced to PPy^0 at -0.90 V for 30 min in the same 0.1 M KCl solution. Subsequently, it was thoroughly washed with water and placed in 15 mL of a 5×10^{-3} M H_2SO_4 solution (pH 2) containing 12 mg L^{-1} of Cu^{2+} ion. Copper deposition on the polymer film was then carried out under stirring and in the presence of dissolved oxygen, either at the open-circuit potential (OCP) or at an applied potential of −0.40 V. The concentration of Cu^{2+} ion remaining in the solution was monitored by FAAS at the end of each experiment using a Perkin Elmer Atomic Absorption Spectrophotometer Model 703. Additionally, in the experiments using the Pt–PPy^0 electrodes, the Cu^{2+} ion concentration decay was also followed by linear voltammetry (17) with a Pt disk UME (18,19), for which the limiting current expression is

$$i_{lim} = 4nFrDC \tag{1}$$

where n is the number of electrons, F the Faraday constant, r the radius of the Pt disk, C the concentration of the electroactive species, and D its diffusion coefficient. The electrochemical cell consisted of a three-electrode assembly, a Pt disk UME of 2 μm radius, a reference SCE and a Pt auxiliary electrode. The potential of the Pt UME was swept between 0.600 and −0.350 V at 0.020 V sec^{-1} in standard and sample aerated solutions of Cu^{2+} ion in sulfuric medium, the voltammograms being obtained with an EG&G PAR Model 264A Potentiostat. The copper content of the samples was determined from a current vs. concentration calibration curve constructed by plotting the Pt UME limiting current values [Eq. (1)] measured for Cu^{2+} ion solutions of known concentration, in the concentration range of 2–12 mg L^{-1}.

RESULTS AND DISCUSSION

Preliminary experiments on the Cu^{2+} ion electroreduction at a static glassy carbon disc electrode (5 mm diameter) were carried out by cyclic voltammetry at a scan potential rate of 0.02 V sec^{-1} in aerated and deaerated solutions containing 12 mg L^{-1} of the metallic ion in 5×10^{-3} M H_2SO_4, from $E_{sa} = 0.00$ V to $E_{sc} = -1.00$ V and reverse. The voltammograms in Fig. 1 show that the Cu^{2+} ion reduction peak at −0.18 V in the deaerated solution is slightly displaced to a less negative potential in the presence of O_2 and that the peak current values for copper deposition are equivalent.

For the solution containing dissolved oxygen, the polarization curves of the glassy carbon disc working electrode rotating at several angular velocities are shown in Fig. 2. The limiting current densities obtained from these voltammograms show a linear variation with $\omega^{1/2}$, as it can be seen in Fig. 3. This behavior agrees with the Levich equation (20) according to

$$1/j = 1/j_k + 1.61\nu^{1/6}/nFD^{2/3}C_0^{*}\omega^{-1/2} \tag{2}$$

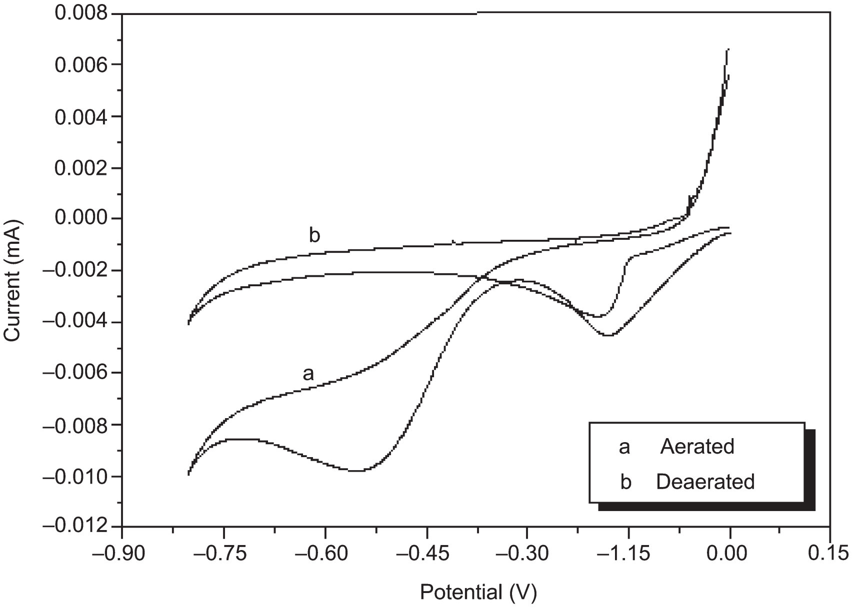

Figure 1. Cyclic voltammograms for Cu^{2+} ion reduction at a static glassy carbon disc electrode, from $E_{sa} = 0.00\,V$ to $E_{sc} = -1.00\,V$ and reverse, at a sweep rate of $0.02\,V\,sec^{-1}$. Aerated (a) and deaerated (b) solutions containing $12\,mg\,L^{-1}$ of Cu^{2+} ion in $5 \times 10^{-3}\,M\ H_2SO_4$.

where j_k is the kinetic current density obtained for the $\omega^{-1/2}$ zero value, F the Faraday constant, ν the kinematics viscosity, C_0^* the bulk concentration of the electroactive species, D its diffusion coefficient, and *n* the number of electrons. The curve j_{lim}^{-1} vs. $\omega^{-1/2}$ is a straight line, the extrapolation of which gives a positive intercept, which means that copper electroreduction is a mixed mass transport kinetic-controlled reaction. On the basis of this result, the experiments on Cu^{2+} ion electrodeposition were carried out under stirring.

Cu^{2+} Spontaneous Reduction on Pt–PPy^0

Polymerization of pyrrole on the $6\,cm^2$ Pt plate electrode was carried out for 30 min in the experimental conditions described before (21). The charge of 5.7 C (mean value) stored in the ionic polymer film was evaluated from the voltammogram obtained by scanning the potential of the Pt–PPy electrode between 0.36 and −1.60 V at $0.02\,V\,sec^{-1}$ in a 0.1 M KCl solution

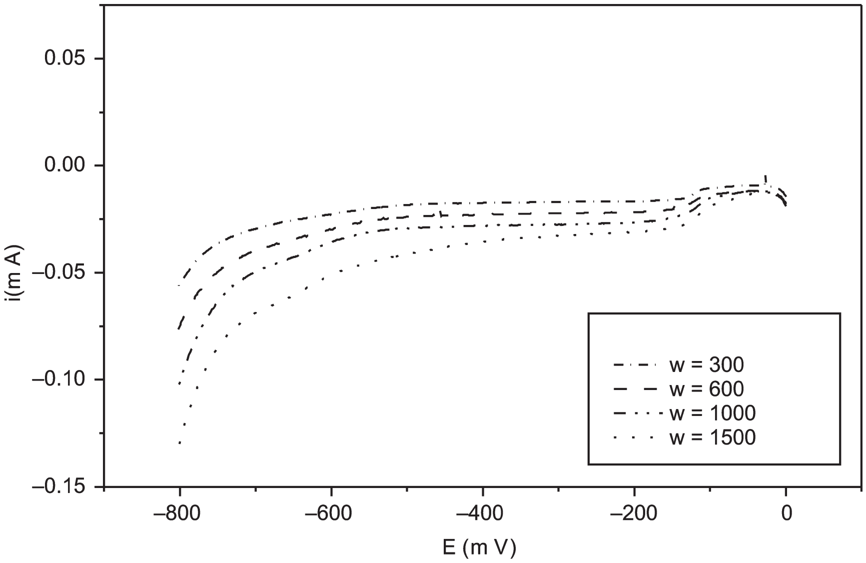

Figure 2. Linear voltammograms for Cu^{2+} ion reduction at a glassy carbon rotating disc electrode from $E_{sa} = 0.00\,V$ to $E_{sc} = -1.00\,V$, at a sweep rate of $0.02\,V\,sec^{-1}$. Aerated solution containing $12\,mg\,L^{-1}$ of Cu^{2+} ion in $5 \times 10^{-3}\,M$ H_2SO_4. The electrode rotation speeds are 300, 600, 1000, and 1500 rpm.

(voltammogram not shown). The PPy film was then reduced to PPy^0 at $-0.90\,V$ for 30 min in the same solution. Subsequently, the Pt–PPy^0 electrode was immersed in 15 mL of a solution containing $12\,mg\,L^{-1}$ in Cu^{2+} ion in $5 \times 10^{-3}\,M$ H_2SO_4, where it was allowed to react with cupric ion, in the presence of dissolved O_2 and under stirring, following the reaction:

$$Cu^{2+} + 2PPy^0 \rightleftharpoons Cu^0 + 2PPy^+ \qquad (3)$$

The Cu^{2+} ion concentration in the solution was monitored at several time intervals by linear scan voltammetry at a Pt disk UME until no change in concentration could be detected. Alternatively, the Cu^{2+} ion concentration in the solution was determined by FAAS.

At the end of the experiment, the potential of the Pt–PPy^0 working electrode was scanned between 0.00 and $-1.50\,V$ at $0.020\,V\,sec^{-1}$ in 0.1 M KCl solution, a charge of mean value 2.0 C being determined in the polymer from seven replicates.

The variation of the OCP of the Pt–PPy^0 electrode vs. immersion time in the Cu^{2+} ion aerated solution (curve B) is shown in Fig. 4. It is observed

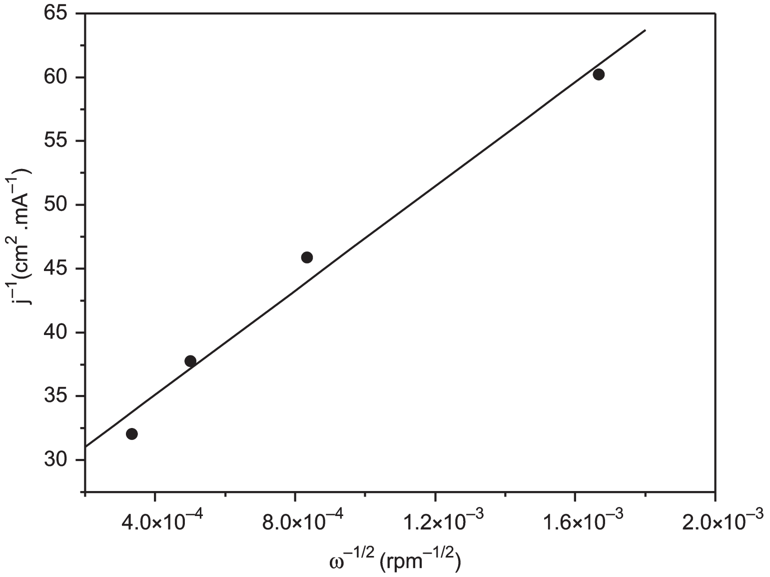

Figure 3. Linear variation of j_{lim}^{-1} with $\omega^{-1/2}$ for the reduction of Cu^{2+} ion at a glassy carbon rotating disc electrode in an aerated solution containing 12 mg L^{-1} of Cu^{2+} ion in 5×10^{-3} M H_2SO_4.

that the electrode potential stabilized at 0.050 V in approximately 60 min. For the same experimental conditions, the OCP for the Pt (curve A), RVC (curve C), and RVC–PPy^0 (curve D) electrodes stabilized, respectively, around 0.620, 0.490, and 0.450 V. Considering that the OCP is a mixed potential and that the PPy^0–electrolyte interface is the same for both the Pt–PPy^0 and RVC–PPy^0 electrodes, these experiments evidence the predominant role of the substrate–PPy^0 interface in the spontaneity of the cupric ion reduction process as compared to the RVC-solution, Pt-solution and PPy^0-solution ones.

Data on the removal of copper by spontaneous reduction onto the Pt–PPy^0electrode, at the OCP, are shown in Table 1. In the indicated time intervals, the cupric ion concentration remaining in the solution was determined by linear voltammetry at a Pt disk UME. It was observed for the given experimental conditions that a maximum decrease in Cu^{2+} ion concentration, from 12 to 4 mg L^{-1}, which is equivalent to 67% efficiency removal, is attained in 120 min. However, in spite of this significant recovery value, no characteristic metallic copper deposit could be visualized on the polymer surface, which indicates that either the reaction proceeds in the

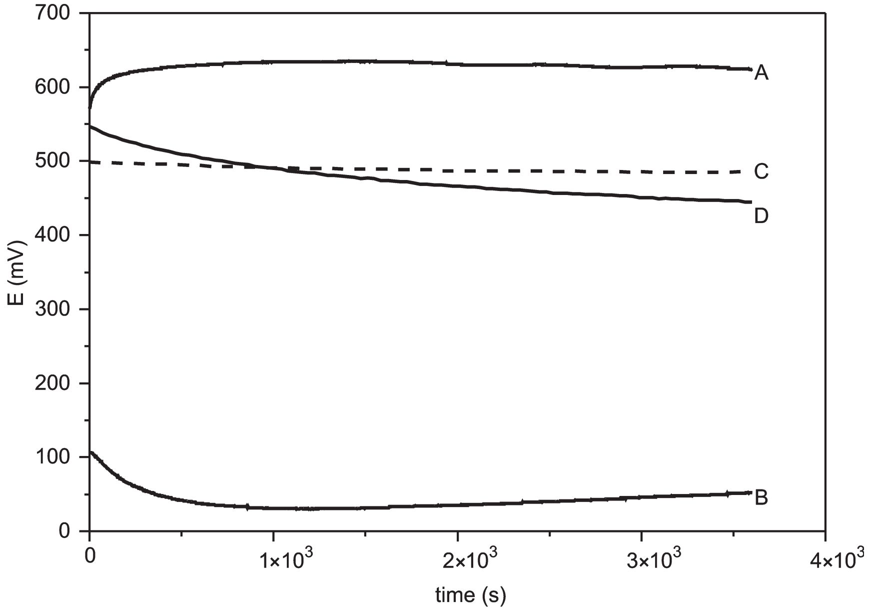

Figure 4. Open-circuit potential vs. time curves for Pt (A), Pt–PPy^0 (B), RVC (C), and RVC–PPy^0 (D) static electrodes in an aerated solution containing 12 mg L^{-1} of Cu^{2+} ion in 5×10^{-3} M H_2SO_4.

interior of the film pores or a competitive copper reoxidation process occurs at the polymer–solution interface.

In the experimental conditions of this study, the spontaneity of copper deposition at a Pt–PPy^0 cathode may be decreased due to simultaneous

Table 1. Spontaneous Copper Recovery onto the Pt–PPy^0 Electrode

Time (min)	[Cu^{2+}] (mg L^{-1}) ± SD	% Recovery
0	12.0 ± 0.5	—
30	11.5 ± 1.5	5
60	10.5 ± 2.0	16
90	7.0 ± 1.5	42
120	4.0 ± 1.0	67
150	4.0 ± 0.5	67

Reaction time, remaining Cu^{2+} ion concentration, and percent recovery for the spontaneous reaction between PPy^0 and Cu^{2+} ion. Aqueous 5×10^{-3} M H_2SO_4 containing an initial concentration of cupric ion of 12 mg L^{-1}. SD: standard deviation.

oxygen reduction and because metallic copper is slowly dissolved in dilute sulfuric medium in the presence of oxygen (22), probably with intermediate formation of hydrogen peroxide, the overall reaction being:

$$Cu + H_2SO_4 + \tfrac{1}{2}O_2 \rightleftharpoons CuSO_4 + H_2O \tag{4}$$

Notwithstanding this competing reaction, the rate of copper deposition predominates over the copper oxidation one, a slow diffusion flux of dissolved cupric ion within the pores to the PPy^0–solution interface is probably the reason for this behavior. On the other hand, the theoretical charge needed to reduce the 1.8×10^{-4} g of Cu^{2+} ion contained in 15 mL of a 12 mg L^{-1} Cu^{2+} solution being 0.55 C, then the residual charge of 2.0 C found in the polymer at the end of the experiment indicates that the polypyrrole film is reoxidized by one or more spontaneous reactions taking place simultaneously to the one between PPy^0 and Cu^{2+} ion. For example, reduction of O_2 at PPy^0 films in aqueous solution (23) has been reported, thus allowing an additional reoxidation of the reduced polymer film.

Reported works (2) have shown that the polymer electroactivity is the result of both electron transfer reactions and ionic transport between the solution and a limited number of sites in the polypyrrole film. Simultaneously to cupric ion reduction in the interior of the film, SO_4^{2-} anions must enter the polymer structure to maintain electroneutrality both in the polymer and in the solution. Therefore, it is probable that, for a 30 min grown film such as the one employed in this experiment, the rate of the reaction between cupric ion and PPy^0 is limited by ionic transport through the polymer matrix. Moreover, after Cu^{2+} ion is reduced in the outer surface sites, further PPy^0 oxidation would occur only in the interior of the polymer matrix, which could be an additional reason for the low rate of the Cu^{2+} ion spontaneous reaction at the Pt–PPy^0 electrode.

The high dispersion in the calculated standard deviation of results in Table 1 is attributed to the decrease in reproducibility observed for electrochemical measurements at UMEs. This is due to the lower current levels generated at these electrodes as compared to conventionally sized ones (19). Furthermore, it is known that PPy films obtained by electrolysis present low reproducibility (24) due to simultaneously occurring reactions between water and the cation radicals that are electrogenerated from pyrrole in the polymerization process and that are retained within the film (25). This low reproducibility was evidenced experimentally in several replicates by the difference between the polymerization charge and the stored charge in the films, for identical reaction times. The unique role of the Pt–PPy^0 interface in the spontaneous Cu^{2+} ion reduction was therefore evidenced in this experiment.

Cu^{2+} Electrodeposition at a Pt–PPy^0 Electrode

Considering that polypyrrole maintains its conductive properties to some extent, even when submitted to a reduction potential for a long time (5), electroreduction of the Cu^{2+} ion may be carried out onto PPy^0, thus increasing the rate of the ion removal.

After reduction of the PPy deposited on Pt to PPy^0, the electrode was immersed in 15 mL of a solution, which is 12 mg L^{-1} in Cu^{2+} ion and 5×10^{-3} M in H_2SO_4. The electrodeposition of copper was then carried out at -0.40 V in the presence of dissolved O_2, the concentration decay of cupric ion in the solution being monitored by linear voltammetry at a Pt disk UME.

Data in Table 2 show that a 61% efficiency in copper recovery is attained in about 35 min, while a slow decrease in copper recovery is observed above 45 min. This behavior may be simultaneously due to oxygen reduction and due to the oxidation of the copper deposit by dissolved oxygen in sulfuric medium (22), as well as by the cathodic H_2 evolution due to H_3O^+ reduction. Therefore, in the electroreduction procedure at the Pt–PPy^0 electrode, a higher oxidation rate of copper by hydrogen constitutes an additional competing reaction, which may explain the lower efficiency copper removal (61%) value attained as compared to the one found in the spontaneous reaction (67%).

The potentiostatic reduction of Cu^{2+} ion onto Pt–PPy^0 at -0.40 V, in aqueous 5×10^{-3} M H_2SO_4 aerated solution, follows a first-order kinetics process as evidenced by the linear relation between $\log(C_{(t)}/C_0)$ and time of electrolysis shown in Fig. 5. Here, $C_{(t)}$ is the remaining Cu^{2+} ion concentration at time t, the C_0 value is 12 mg L^{-1} and the calculated values of the regression coefficient, slope, and intercept are, respectively, -0.9959, -0.0120, and 0.0202.

Table 2. Copper Recovery Through Electrodeposition onto a Pt–PPy^0 Electrode

Time (min)	$[Cu^{2+}]$ (mg L^{-1}) ± SD	% Recovery
0	12.0 ± 0.7	—
5	9.3 ± 1.3	23
15	8.0 ± 1.4	33
25	6.0 ± 0.7	50
35	4.7 ± 0.7	61
45	4.7 ± 0.7	61

Reaction time, remaining Cu^{2+} ion concentration, and percent recovery for the electrodeposition of Cu^{2+} on a Pt–PPy^0 electrode at -0.40 V. Aqueous 5×10^{-3} M H_2SO_4 containing an initial concentration of cupric ion of 12 mg L^{-1}. SD: standard deviation.

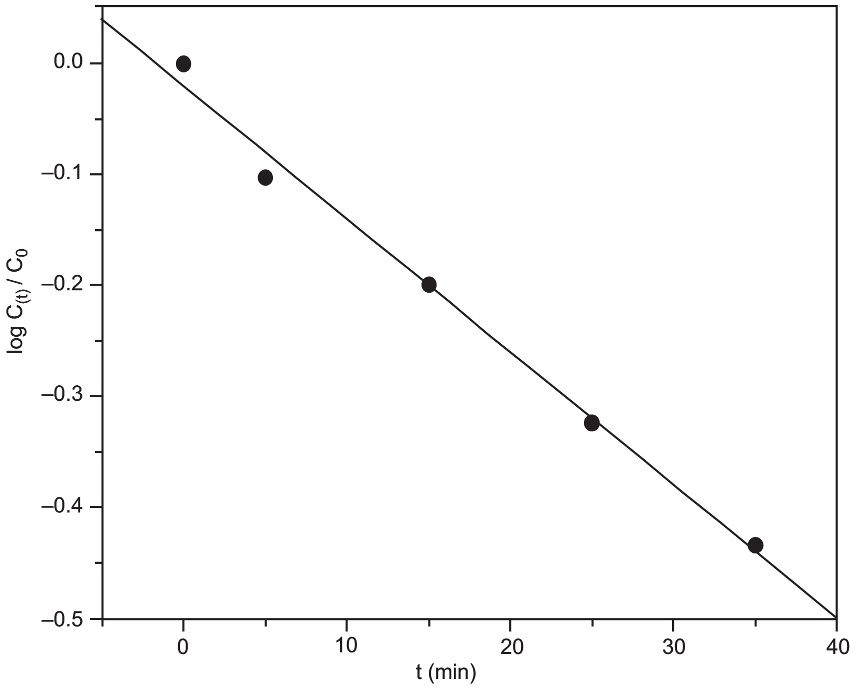

Figure 5. Linear log($C_{(t)}/C_0$) vs. time relation for the reduction of Cu^{2+} ion on Pt–PPy^0 at -0.40 V in 5×10^{-3} M H_2SO_4 aerated solution ($C_{(t)}$ is the Cu^{2+} ion concentration at time t and the C_0 value is 12 mg L^{-1}). The calculated values of the regression coefficient, slope, and intercept are, respectively, -0.9959, -0.0120, and -0.0202.

In the same experiment, the copper recovery percentage determined by FAAS for a 45 min reaction time is 54 ± 1%, this value being probably related to the lower sensitivity in copper determination by FAAS as compared to voltammetric measurements (11).

As expected, in the potentiostatic reduction of copper, the standard deviation observed in the results is rather uniform, but now the deposition potential value is the limiting parameter and not the low reproducibility of PPy films. A more negative deposition potential would probably accelerate the removal of cupric ion, but then hydrogen evolution could disrupt the polymer adhesion to the substrate. Although the possibility of metal deposition occurring on Pt through the pores within the film has been considered (5), the small residual charge stored in PPy^0 films indicates that the remaining conductivity allows polarization of the Pt–PPy^0 electrode and the subsequent copper deposition on the polymer surface. This was in fact evidenced either visually by the characteristic color of the metallic copper deposit or by electron scanning chemical analysis (ESCA) experiments (data not shown).

Cu^{2+} Spontaneous Reduction at an RVC–PPy^0 Electrode

No spontaneous removal of cupric ion was observed at the 40 ppi RVC–PPy^0 electrode. The OCP vs. time curve for this electrode in 15 mL of a dilute sulfuric solution containing 12 mg L^{-1} of Cu^{2+} ion in the presence of O_2 is shown in Figure 4 (curve D). The potential of the modified RVC electrode stabilizes at 0.450 V in 60 min, while for the Pt–PPy^0 electrode (curve B), it stabilizes at 0.050 V.

The difference in the behavior of both the electrodes immersed in solutions of identical composition evidences the influence of the substrate in the mixed potential value. At this potential, the catalytic role of Pt in the O_2 reduction reaction (23), among other oxidation–reduction reactions that may occur, can be significant. Therefore, while the O_2 reduction reaction can be catalyzed at the Pt–PPy^0 interface, no such feature can be attributed to the RVC–PPy^0 one, the Cu^{2+} ion reduction at this electrode probably requiring a higher overpotential. Moreover, the overpotential at each substrate–PPy^0 interface is related to the mechanism of ion exchange and mass transport within the polymer film (26) in such a way that the spontaneous deposition of copper at the RVC–PPy^0 electrode is probably unfavored.

Cu^{2+} Electrodeposition at a Reticulated Vitreous Carbon Electrode

In this experiment, the 40 ppi RVC porosity and the applied potential value of −0.40 V were taken from Pletcher's investigations (27). The RVC electrode was immersed in 15 mL of a solution containing 12 mg L^{-1} of Cu^{2+} ion in 5×10^{-3} M H_2SO_4, where the electrodeposition of copper was carried out in the presence of dissolved O_2. During the experiment, the concentration of cupric ion in the solution was monitored by FAAS.

The results in Table 3 show that a 79% maximum removal efficiency, corresponding to 2.5 mg L^{-1} of Cu^{2+} ion left in the solution, is attained in 35 min. At less negative applied potentials (around −0.30 V), the reaction is slow while

Table 3. Copper Recovery vs. Time of Electrodeposition onto an RVC Electrode

Time (min)	5	15	25	35	45
Recovery (%)	21	58	68	79	79

Reaction time and percent recovery for the electrodeposition of copper from an aerated solution containing 12 mg L^{-1} of Cu^{2+} ion in 5×10^{-3} M in H_2SO_4 onto an RVC electrode under −0.40 V applied potential.

at more negative ones, the current efficiency is lower due to an increase in the O_2 and H_3O^+ reduction rates, as evidenced in the preliminary experiments using a vitreous carbon electrode (Fig. 1). The higher surface area of the RVC electrode allows an increase in efficiency recovery of copper as compared to the Pt–PPy^0 one and thus compensating for the effect of oxidation of the copper deposit by dissolved oxygen (22), and by the cathodic H_2 evolution due to H_3O^+ reduction.

Cu^{2+} Electrodeposition at the RVC–PPy^0 Electrode

This experiment allows further evaluation on the role of polypyrrole in the rate of cupric ion removal by electrolysis. The efficiency of the electrodeposition process is expected to be higher as compared to the one occurring on a smooth surface such as the bare Pt electrode one.

After reduction for 30 min of the polypyrrole recovering the RVC substrate, the electrode was thoroughly washed with water and immersed in 15 mL of the solution containing 12 mg L^{-1} of Cu^{2+} ion, the electrodeposition of which was carried out in the presence of dissolved O_2 at −0.40 V.

The concentration of cupric ion in the solution was monitored by FAAS at the end of each experiment, a 99.8% maximum efficiency in copper recovery being attained in 30 min. It was observed that the removal efficiency falls to 68.5% after 45 min of electrodeposition when the same experiment is carried out with a 10 ppi RVC–PPy^0 electrode (see Table 4).

The increased removal efficiency in this case can be ascribed to a higher overpotential for the reduction of O_2 and H_3O^+ at the RVC–PPy^0 interface, which favors the reduction of Cu^{2+}, as compared to the Pt–PPy^0 one, due to the catalytic role of Pt in these reactions. On the other hand, characteristics of the deposited polypyrrole, such as porosity, adherence, and stored charge, change according to the nature of the substrate (28).

Complementary essays in the same experimental conditions using higher Cu^{2+} ion concentrations evidenced around 1% decrease in the removal efficiency

Table 4. Effect of Time and Dissolved O_2 on Cu Recovery at an RVC–PPy^0 Electrode

Time (min)	% Recovery in Aerated Medium	% Recovery in Deaerated Medium
45	68.5	99.9
90	85.6	99.9

Effect of time and dissolved O_2 on the percent recovery for copper electrodeposition from a 5×10^{-3} M H_2SO_4 solution containing 12 mg L^{-1} of Cu^{2+} ion at an RVC–PPy^0 electrode. Applied potential of −0.40 V and RVC porosity of 10 ppi.

for the same reduction time: the efficiency removal values of, respectively, 99.1 and 99.0% were attained for 20 and 25 mg L^{-1} Cu^{2+} ion concentrations.

Influence of Oxygen and Reticulated Vitreous Carbon Porosity on the Cu^{2+} Efficiency Removal

The effect of oxygen on the Cu^{2+} ion removal efficiency was investigated at a 10 ppi RVC–PPy^0 electrode in the same experimental conditions as before. Results in Table 4 show that, for the same electrolysis time, the copper recovery is practically complete in deaerated medium, while it decreases significantly in the presence of dissolved oxygen. Furthermore, the 99.8% removal efficiency value attained in 30 min of electrolysis using the 40 ppi RVC–PPy^0 electrode falls to 85.6% in 90 min for the 10 ppi one, as a consequence of the decrease in surface area, this behavior being already reported in the literature (27).

The significant role of both the RVC porosity and the oxygen reduction reaction is therefore evidenced. It should be emphasized that, in electroreduction procedures, besides oxygen reduction, the cathodic evolution of H_2 competes with the reduction of cupric ion (17,29–33).

Reuse of Polypyrrole Films

In the experimental conditions of this work, oxidation of PPy^0 to PPy^+ is slow (2) and the copper deposit on the polymer film dissolves in dilute sulfuric medium in the presence of oxygen (22). Hence, these properties allow reusing polypyrrole films in the removal procedures discussed before. In fact, it was experimentally observed that the PPy^0 film recovering the RVC substrate can be reused in the cupric ion electrodeposition procedure after being cleaned up from the copper deposit by immersion for 1 hr in 15 mL of a still H_2SO_4 5×10^{-3} M solution. The polymer film is then thoroughly rinsed and reduced further for 15 min in 0.1 M KCl at -0.90 V before being reused in the removal of cupric ions as described previously. Three of these experiments were performed indicating a 5% decrease in removal efficiency from the first to the third experiment. This behavior evidences that metallic copper accumulates within the pores of the electrode thus gradually reducing its area and the copper removal rate (34).

CONCLUSIONS

Polypyrrole films electrodeposited from solutions of 0.1 M in pyrrole and 0.1 M in KCl on Pt and RVC allow electrodeposition of copper to be carried out on the reduced polymer surface in the presence of oxygen.

In the described experimental conditions, the percentage efficiency in copper removal at Pt–PPy^0 electrodes is equivalent either when it is carried out at the OCP or at -0.40 V applied potential. In the latter case, a 61% efficiency in copper recovery was attained in 35 min, while a similar but slightly higher value was attained in about 2 hr in the spontaneous procedure. The oxidation of the copper deposit by dissolved oxygen and/or by H_2 formed in the cathodic reduction of H_3O^+ competes with copper deposition and seems to be responsible for the lower recovery results when the substrate is Pt. However, for the reported experimental conditions, the rate of copper deposition predominates over the copper oxidation one.

The highest removal efficiency value for copper electrodeposition, 99.8%, was achieved for the RVC–PPy^0 electrode, but this electrode showed no spontaneous removal of Cu^{2+} ion. Although the reason for this behavior is not clearly understood, it is probably related to a higher overpotential concerning the Cu^{2+} ion reduction at the RVC–PPy^0 electrode than at the Pt–PPy^0 one.

These results evidence that the nature of the substrate play a determinant role in Cu^{2+} ion reduction in the OCP procedure, while the deposition potential and the higher mass transport rate due to the RVC porosity are the limiting parameters in copper removal by electrolysis. Moreover, even in the presence of dissolved oxygen, the excellent performance of the RVC–PPy^0 electrode on copper electroreduction has been evidenced.

Application of the RVC–PPy^0 electrode in the Cu^{2+} ion electrolysis presents practical interest in the development of flow systems to remove copper and other metals from low-level concentration effluents and in polymer coverage by metallic films. It is also advantageous, especially concerning environmental applications, that the copper deposit may be cleaned up from the polypyrrole film by immersion in a dilute sulfuric acid solution so that the electrode may be reused for at least three times, a small decrease in the removal efficiency being detected at each cycle.

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