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Arsenic extraction using polypyrrole modified electrodes

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The use of a conducting polymer which can undergo p-doping-undoping, to extract arsenic is presented in this paper. As Heeger mentions [1], to explain the importance of the discovery of conducting polymers [2,3], these "offer a unique combination of properties not available from other known materials, which opens the possibility of use in a wide variety of applications". As a matter of fact, up to now, various applications have been found for these types of materials, as a function of its properties. However, the possibility of doping-undoping of the p or n type, a feature of most of these polymers, still has not been utilised for extraction of ions.

The doping-undoping process can be carried out by electrochemical methods and, in general, can be represented as follows [4,5]:

$$p\text{-}doping: \quad (\text{monomer})_x \rightarrow [(\text{monomer})^{y+}] + xy\,e^-$$

$$n\text{-}doping: \quad (\text{monomer})_x + xy\,e^- \rightarrow [(\text{monomer})^{y-}]$$

The p- or n-doping can be accomplished by partial electrochemical oxidation or reduction of the backbone π-system of an organic polymer by immersing the film in an electrolytic solution. Counter "dopant" ions are introduced, which stabilise the charge on the polymer backbone. If the process is reversible, the inversion of polarity produces the departure of the dopant ions.

Based on such processes, it is proposed to make use of this phenomenon so that the polymeric matrix can act as an "extractant" of ions: the p-doping would allow anions extraction, whereas the n-doping cations extraction [5]. The efficiency and selectivity would be determined by the structure and morphology of the matrix, and by the speciation of the electrolyte. To determine the structure and morphology of the polymeric deposit, different matrices and preparation methods can be evaluated [6], whereas for the electrolyte speciation one must resort to conventional analytical chemistry.

For this study, polypyrrole, PPy, was chosen as the polymeric electrodeposit. PPy is a conducting polymer widely studied, easy to prepare, low cost, and can be reversibly p-doped-undoped by electrochemical methods [7]. It was tested as "extractant" for arsenic in the form of an arseniate ion, AsO_4^{3-}. This form was chosen because it is the form in which arsenic is found in electro-refining cells for producing electrolytic copper, together with other metals which, under those conditions, are in the form of cations [8].

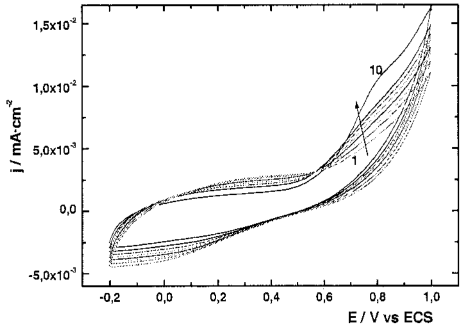


Fig. 1 Successive voltammetric scans (1 to 10) during pyrrole electropolymerization. Interface: SS/1 mM pyrrole + 3·10^{-2} M H_2SO_4.

The voltammetric profile obtained during the growing of the polymer to obtain the modified electrode, SS/Ppy, is shown in Figure 1. In spite of the fact that under those conditions an homogeneous deposit with good adherence to SS is obtained, the electro-polymerization by the potentiostatic method was carried out with the purpose of forming a more cross-linked structure. This would favour the insertion of large size anions, such as arseniate.

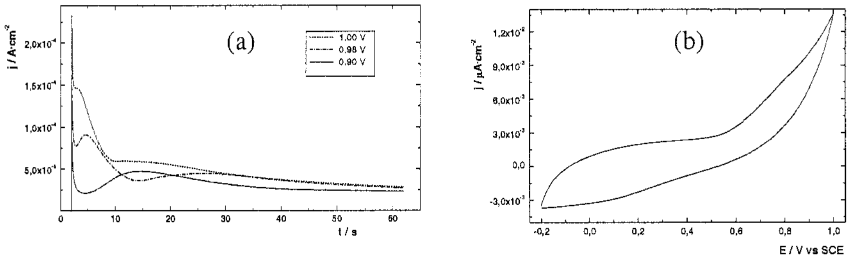


Fig. 2 (a) j/t transients during pyrrole electropolymerization (E = 0.90 to 1.00 V *vs* SCE). Interface: SS/1 mM pyrrole + 3·10^{-2} M H_2SO_4. (b) SS/Ppy response in 3·10^{-2} M H_2SO_4. Scan rate: 100 mV·s^{-1}.

The j/t transients obtained at various potentials selected from the response obtained in Figure 1 are shown in Figure 2a. These j/t responses during Ppy deposition at different potentials in the nucleation and growth potential range show that the 1.00 V potential is appropriate for the growing of the film.

The response in a solution without monomer of the deposit obtained potentiostatically is shown in Figure 2b. As can be observed, the p-doping-undoping phenomenon is clearly observed between -0.2 V and 0.8 V and the respective charges of doping-undoping confirm the possibility of reversible doping. Based on this, it was decided to use this type of modified electrode (SS/PPy) as arsenic extractant.

Table 1. AsO_4^{3-} extracted as a function of ExC number and electrode area

ExC	Initial AsO_4^{3-} $g{\cdot}L^{-1}$	AsO_4^{3-} after ExC $g{\cdot}L^{-1}$	Extracted AsO_4^{3-} $g{\cdot}L^{-1}$	Electrode area* cm^2
5	0.0766	0.0438	0.0328	2
10	0.0766	0.0212	0.0554	2
5	1.4442	1.2838	0.1604	6
10	1.4442	0.7834	0.6608	6

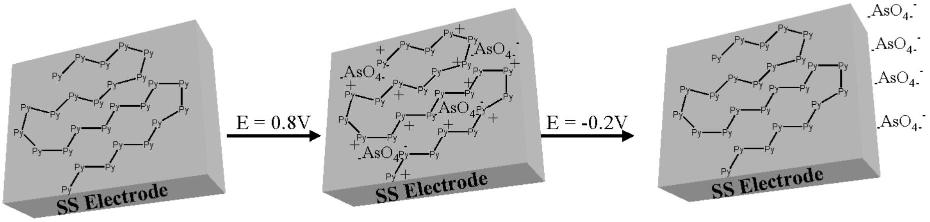
* referred to geometrical SS working electrode

The concentrations of arsenic in cell A, before and after different numbers of ExC, with the tested electrodes, are presented in Table 1. It should be noted that the HSO_4^- concentration was also controlled after performing the ExC, and it was found that it remains practically constant. This indicates that this polymeric matrix has preference for AsO_4^{3-}. This fact supports the possibility of extracting arsenic as AsO_4^{3}, using the route proposed here. Moreover, it becomes evident that, for a same solution, a larger electrode area, more amount of arsenic is extracted. This indicates that, to decrease the number of ExC and increase the efficiency of the extraction, it would only be needed to increase the area. Nevertheless, the relationship with the electrode area is not direct, because it is referred to the area of the SS support. Thus, for example, a 3 fold increase in the SS area produces a polymer effective area higher than 3 times, which is attributed to the cross-linking of the polymeric matrix.

Table 2. Doping and undoping charge as a function of ExC number for initial AsO_4^{3-} = 0.0766 $g{\cdot}L^{-1}$; SS area = 2 cm^2

ExC	***doping* charge** C	***undoping* charge** C
1	11.9	-11.8
2	11.6	-11.3
3	12.0	-11.6
4	11.6	-11.2
5	12.1	-11.5
6	12.1	-11.7
7	11.9	-11.7
8	11.6	-11.3
9	12.0	-11.6
10	11.8	-11.6

Scheme 1 shows a model of the doping-undoping process where the interaction of the arseniate ions with the pyrrole groups is also included.



Scheme 1 Interaction of arseniate ions with polypyrrole during doping-undoping process.

On the other hand, results in Table 2 confirm both the reversibility of the doping-undoping process and, the stability of the modified electrode, which can used successively, without a change in its properties.

These results ensure that practically 100% of the charge can be imputed to the arseniate anion. This is because, if the charges of the ten successive extractions are added, “undoping charge” = 115.3 C, and applying the Coulomb Law and considering that $n = 3$, the value corresponds to a total of $3.98 \cdot 10^{-4}$ moles of AsO_4^{3-}. The amount extracted can then be calculated from the total charge of doping or undoping. Since this value agrees with the value obtained in the iodometric determination (Table 1): $0.0554\ g \cdot L^{-1}$ ($5.54 \cdot 10^{-3}$ g/10 mL = $3.98 \cdot 10^{-4}$ moles) extracted when the same electrode (2 cm^2) is used and 10 ExC are performed. This is a very important result since it saves further analysis. Nevertheless, it requires that the extraction be selective.

Presently, we are studying the effect of the several variables involved in the process, on the extraction efficiency: thickness of the polymeric deposit, the film preparation method (potentiostatic or potentiodynamic), experimental conditions during electropolymerization process (pH, monomer concentration, electrolyte, etc.) area of the support electrode, number of ExC, etc. Once these variables are optimised, the selectivity of the process will be verified in the particular case of copper concentrates. However, the synopsis presented here indicates that in fact the polymer could be used as extractant for arsenic, which may have a great impact not only in the process of electro-obtention of copper, but particularly in the environmental area. Moreover, many conducting polymers are presently known, with structures than can be managed to achieve selectivity when the extraction of a particular ion is required.

In summary, these results demonstrate that conducting polymers deposited on a metallic electrode can become an interesting alternative to conventional separation methods.

Experimental

Electrochemical experiments were performed using a BAS CV-50W, and a glass three compartment-three electrodes cell under argon atmosphere. Working electrodes were

AISI 316 steel (SS) discs (0.7 cm^2) or sheets (SS) of 2 or 6 cm^2. Counter electrode was Pt wire (20 cm^2), and all potentials were measured with respect to saturated calomel reference electrode (SCE), which was connected to the analyte compartment by a Luggin capillary.

Electrochemical growth of Ppy films was carried out on SS from 1 mM pyrrole + $3 \cdot 10^{-2}$ M H_2SO_4 by potentiostatic method, applying 1.00 V during 1 hour. Subsequently, it was studied the SS/Ppy response in 1 mM AsO_4^{3-} + $3 \cdot 10^{-2}$ M H_2SO_4 (cell A), and in $3 \cdot 10^{-2}$ M H_2SO_4 (cell B), in order to select the doping-undoping potentials to perform the ExC. The total volume of electrolyte in each cell was always 10.0 mL. Each ExC was performed as follows: the SS/Ppy modified electrode was immersed in A, potentiostatically perturbed (0.8 V) during 5 min, after which was immersed in B, where it was potentiostatized at –0.2 V during 5 min. Initially and after several ExC, arsenic concentration in A and in B was determined by iodometry or atomic absorption, to verify the efficiency of the extraction. The charge of doping and undoping was also determined during each ExC.

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