

Humic Acid/Polypyrrole on a Paraffin-Impregnated Graphite Electrode and Its Use in Arsenic Extraction

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ABSTRACT: A novel and simple electrode with rapid preparation was developed with humic acid (HA) and polypyrrole (PPy) films. The method for modified electrode preparation embraced the abrasive transfer technique on a paraffin-impregnated graphite electrode (PIGE) followed by the electrochemical incorporation of a PPy polymeric film upon bare PIGE and PIGE/HA electrodes. Cyclic voltammetry, electrochemical impedance spectroscopy, and chronoamperometry were used for the study of the modified electrodes. Morphological characterization was performed by scanning electron microscopy. The obtained results demonstrated that the presence of HA did not affect the electrical properties of the system but indeed provoked changes in the polymer morphology, turning it more granular. Next, PIGE/HA/PPy was tested in arsenic solutions [As(V)] because ar-

senic contamination of water is an important worldwide environmental issue because of the sources of arsenic contamination of water come from both natural processes and anthropogenic activities. The modified electrode displayed good and reversible extraction properties toward the analyte in acid medium and was 18% more efficient than a previously reported PPy-modified electrode (PIGE/PPy). From an environmental standpoint, this novel application of conductive polymer properties with the chelating capacity of humic substances constitutes a first step in the development of more efficient technologies for the removal of contaminants present in soil-water media. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3619–3629, 2009

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INTRODUCTION

Polypyrrole (PPy) is one of the most used polymers for the elaboration of catalytic sensors and biosensors based on immobilized enzymes, DNA sensors, and immunosensors. Its monomer, pyrrole, can be polymerized and, at the same time, electrochemically deposited upon a conducting surface a suitable electrochemical perturbation is applied; this, thus, gives rise to a modified electrode. Potentiostatic or potentiodynamic perturbations are usually used.¹ Because this kind of polymer can be *p*-doped/undoped, it has been used to extract contaminant species such as arsenic. The attained results indicate that the polymeric matrix shows a preference for AsO_4^{3-} species with increased efficiency, which was assigned to crosslinking in the polymer.² On the other hand, for the sake of decontamination, PPy coated with nylon 6,6 has been used, with very good results, to extract humic acid (HA) from aqueous systems mainly on the basis of electrostatic interactions of pyrrole with

different moieties. From the previous results, the possibility of preparing an effective modified electrode seemed feasible.³ With regard to the current state of the research, paraffin-impregnated graphite electrodes (PIGEs) have been widely used in the study of solid materials in a variety of applications,^{4–7} which have mainly considered the inclusion through the abrasive technique used in this study. Likewise, the natural anion-exchange properties of the conducting polymer PPy has been widely used in film preparation for solid-phase microextraction coupled with chromatographic techniques,^{8–10} an advanced analytical technique that allows one to obtain samples from volatile and semivolatile organic compounds.

HAs are natural polymers of high molecular weight of vegetal and animal origin that are widely distributed in nature. They are known by their high contents of P, N, and S and are partly responsible for the cation-exchange capacity, buffering capacity, and water retention in soil systems. The structure of most of these substances possesses functional groups, such as carboxylic, phenolic, hydroxyl, carbonyl, amine, amide, and aliphatic moieties, among others. Because of their polyfunctionality, HAs are considered one of the most powerful chelating agents among existing natural organic substances;

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they are capable of complexing heavy metals,^{11,12} inorganic anions and halides,^{13,14} organic acids,¹⁵ aromatic compounds,^{16,17} pesticides, and herbicides.^{18,19} Previous studies have demonstrated the importance of HA interaction with a variety of contaminants; they form complexes of different solubility and chemical and biochemical stability. Consequently, HAs are capable of modifying the availability, transport fixation, and toxicity of contaminants present in the environment.

On the other hand, the presence of arsenic dissolved in drinkable and groundwater has recently arisen as one of the main concerns at global level. In fact, depending on the country, exposure to arsenic may come from natural and industrial sources or from food and beverage ingestion. High concentrations of arsenic in drinking water (>50 $\mu\text{g/L}$) have been reported in several countries, such as Argentina, Chile, China, Japan, Mexico, Poland, Taiwan, Nepal, and parts of the United States. Indeed, important health problems have been found in northern Chile,²⁰ with over 2000 $\mu\text{g/L}$ arsenic reported in river waters situated at the pre-Andean region.²¹ However, the world's largest arsenic health issue is the pollution of drinking water aquifers in Bangladesh and West Bengal, India, which affects millions of people.^{22–25} Many countries, particularly developing ones, still use the 50- $\mu\text{g/L}$ arsenic standard because of a lack of adequate testing facilities for the determination of lower arsenic concentrations.²⁶ However, high arsenic levels in groundwater are not necessarily related to areas of high arsenic concentration. Distinctive groundwater arsenic problems occur under both reducing and oxidizing conditions in both humid/temperate and arid climates.²⁷ Among the conventional arsenic remediation techniques in aqueous systems, processes using activated alumina seem to be the most suitable if efficiency versus cost is considered.²⁸ In addition, these techniques can also remove organic contaminants, pesticides, and chlorides. However, these techniques are not massively available, and frequently, these conventional techniques possess limitations, such as the use of chemicals and their impact upon water quality, the production of large volumes of arsenic-contaminated solid residues, the often-required secondary treatments, the existence of interference, and high setup costs and poor efficiency. Recently, great efforts have been made to lower the costs. Some options are based on the coating of absorbent surfaces, for example, iron oxides, on polymeric materials; sands coated with the same kind of oxide and/or manganese compounds; and clays modified with iron oxides.^{29–34} In addition, over the past few years, studies to prevent the chemical oxidation of As(III) to As(V) have been published. This has been accomplished with different approaches, such as with UV,

plants, and microorganism that are responsible for this oxidation,³⁵ with efficiencies over 95%.^{36–41} However, one of the main drawbacks is the acid pH at which these processes take place, whereas nearly neutral pH values are required by these hydric resources. Thus, the electroanalytical techniques, because of their versatility and the possibility of electrode and instrument miniaturization, have been of great interest for arsenic monitoring in contaminated sites.⁴² As a result of this problem, the removal of arsenic has become one of the most important challenges in contaminated water treatment, whose main requirements are high efficiency, ease of application, and low cost.⁴³

The research work presented in this article is the first approach aimed at obtaining insight into HA substance/PPy interaction with contaminants because a clear characterization of the surface under survey (electrode) is presented and further application to one of the most widespread contaminants (arsenic) was also studied. In addition, in the investigation, we developed and explored a novel, reproducible and easy-to-prepare *ex situ* remediation technique involving an environmental component, humic substances, that in the future may come from natural systems, for example, soils, and/or biosolids. This proposal differs from others because it is not included within the conventional remediation techniques but considers some adsorption components by means of electrochemical charge generation. Finally, most of the remediation techniques seek As(III) oxidation to As(V); the latter been less toxic. In this survey, the pollutant was extracted under similar conditions to those existing in soil–water systems close to mining regions in northern Chile.

A novel type of modified electrode based on the conducting polymer properties and high chelating capacity of HAs was prepared in this study. Its efficiency for interacting with contaminant species was assessed, too. The system was designed with a likely synergic effect of both compounds in mind because of the need for the enhancement of contaminant extraction efficiency through the inclusion of solid humic compounds on PIGE. Because of this new component and the positive charge of the polymeric matrix, an increase in the percentage of extracted As(V) was observed. This may have been due to the presence of humic substances, which contained phenolate in their structure. The latter might have bonded to As in AsO_4^{3-} , which bore a formal charge (+5) to bring about protonation and water release, which was previously proposed.⁴⁴ Consequently, this modified electrode represented an improvement with respect to previously proposed methods. The device was easy to prepare and highly reproducible, and very interesting potential environmental applications can be foreseen.

EXPERIMENTAL

Apparatus

All electrochemical experiments were performed with a VoltaLab PGZ100 (Radiometer Analytical, Lyon, France) potentiostat system in a glass three-compartment/three-electrode cell under an argon atmosphere. Paraffin-impregnated graphite was used as a working electrode (PIGE). A Pt wire (20 cm²) was the counter electrode. All potentials quoted in this article were measured versus a Ag/AgCl reference electrode. Electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit potential at a frequency (f) in the range 5 mHz to 1 kHz, whereas the alternating-current potential perturbation was 10 mV.

PIGE was prepared by the impregnation of spectroscopic graphite rods (diameter = 6 mm) with melted paraffin wax *in vacuo*. A homemade PIGE with a 0.28-cm² surface area was used as a bare working electrode.⁴⁵ The exposed surface of the graphite electrode was mechanically regenerated before each experiment with emery paper (grain sizes = 2000 and 2500) and thorough washing with twice-distilled water.

Chemicals and solutions

HA (Sigma-Aldrich, Milwaukee, WI) was purified by precipitation as follows. A suitably concentrated solution was adjusted to pH 1 with HCl. The obtained precipitate was filtered off and then redissolved in NaOH. The precipitation was repeated, and the second precipitate was collected, washed, air-dried, and used.

Stock solutions containing As(V) in 1 mM Na₂SO₄ + 30 mM H₂SO₄ (solution A) were prepared by dissolution of the appropriate amount of As₂O₅ in twice-distilled water according to standard procedures. Pyrrole (Sigma-Aldrich) was purified by distillation, stored at 4°C, and protected from light. All other reagents used were analytical grade (Merck SA, Darmstadt, Germany), and all solutions were prepared and deaerated with pure Ar for at least 20 min.

Preparation of modified PIGE

As for PIGE, four electrodic surfaces were characterized by cyclic voltammetry and electrochemical impedance measurements: (1) PIGE, (2) PIGE modified with HA (PIGE/HA), (3) PIGE electrochemically modified with pyrrole (PIGE/PPy), and (4) PIGE modified with HA and then electropolymerized with pyrrole (PIGE/HA/PPy). HA was transferred and immobilized onto the electrode surface with the abrasive transfer technique.⁴⁶ This was typically

achieved by the placement of some micrograms of HA sample to form a spot of finely distributed particles and gently rubbing of the lower circular surface of PIGE on this spot to transfer the sample to the electrode surface.

Electrochemical growth of the PPy films was carried out onto PIGE or PIGE/HA from 1 mM pyrrole + solution A by potentiodynamic method with the application of five successive cycles between -0.2 and 1.0 V. The morphology and microscopic structure of the bare and modified electrodes were characterized by scanning electron microscopy (SEM; model LEO 1420 VP, Leo Microscopy, Ltd., Cambridge, UK).

Extractions

Two electrodic surfaces, PIGE/HA/PPy and PIGE/PPy, were studied in solutions containing 1 mM AsO₄³⁻ + 1 mM Na₂SO₄ + 30 mM H₂SO₄ (solution B, cell A) and 1 mM Na₂SO₄ + 30 mM H₂SO₄ (solution A, cell B) to select the doping-undoping potentials to perform the extractions. The total volume of electrolyte in each cell was always 10.0 mL. Each extraction was carried out as follows: the modified PIGE/PPy or PIGE/HA/PPy was immersed in solution A and potentiostatically perturbed at 0.4 V for 5 min, after which it was dipped into solution B, wherein it was potentiostated at -0.5 V for 5 min. Initially and after several extractions, the arsenic concentrations in solutions A and B were determined by inductively coupled plasma/optical emission spectrometry (ICP-OES) on a Varian Liberty series II (Palo Alto, CA) instrument.

RESULTS AND DISCUSSION

Preparation and electrochemical characterization

A systematic electrochemical and morphological survey of the surfaces was accomplished to establish the most suitable modified electrode to be used in the extraction of solution A. To this purpose, every used electrodic surface was compared, that is, PIGE, PIGE/HA, PIGE/PPy, and PIGE/HA/PPy. First, PIGE was electrochemically compared with PIGE/HA, of which the latter was obtained by abrasive transfer techniques.⁴⁶ This technique is used when the compounds are insoluble in the aqueous or non-aqueous media in which the electrochemical experiment is performed.

Figure 1 depicts the stable voltammetric profile of PIGE without modification and the same PIGE modified with HA. PIGE/HA showed no redox process within the potential window applied and presented a lesser capacitive response than PIGE without modification. This may have been due to

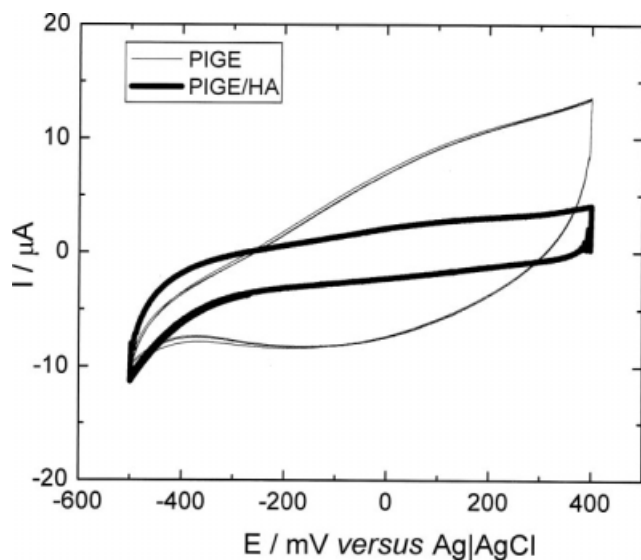


Figure 1 Potentiodynamic response of the bare PIGE (thin line) and the modified PIGE with HA (thick line) in 1 mM Na_2SO_4 and 30 mM H_2SO_4 between -0.4 and 0.5 V at 0.1 V/s (I is the current intensity, and E is the voltage).

the low conductivity of HA, which demonstrated likewise that the adsorption of HA on the PIGE surface took place. This adsorption was highly reproducible, and no loss of material was observed during the electrodynamic stabilization of PIGE/HA.

Once PIGE/HA was obtained, a thin layer of PPy was electropolymerized on the PIGE/HA surface with cyclic voltammetry to prevent likely loss by the desorption of HA. PPy was in its oxidized state, and positive charges were formed in its structure. Consequently, anions (A^-), coming from the electrolytic solution in which the film was formed, were incorporated inside the film. The anion, in addition to playing an important role in PPy synthesis, also contributed a suitable route to bring different compounds or ions to the polymeric matrix. The nature and size of the anion has an important effect on the PPy properties, which is evidenced when this polymer is obtained in the presence of small anions, such as perchlorate; this yields surfaces with ion-exchange behavior.^{47,48}

As for its preparation, PPy has been synthesized in the presence of a variety of dopants in aqueous media under similar electrochemical conditions.⁴⁹ Polymers obtained by doping with chloride, perchlorate, and acetate exhibit poor adhesion on the electroodic surface and are unstable at high temperatures. However, films obtained with sulfate and dodecyl sulfate anions are stable at high temperatures and bring about good adhesion on the electroodic surface. Furthermore, film formation depends on the pyrrole concentration, electrolyte pH, concentration of ions present in the electrolytic solution, potential window

applied (a too high potential affords films of lower conductivity and poor adhesion), and oxidation time.^{50–53} Considering the existing variables, in this study, we demonstrated that the optimum conditions for electrosynthesis to obtain thin films were those described in the Experimental section. Thus, the application of an anodic potential of 0.6 V to an aqueous solution containing pyrrole generated a noticeable layer of PPy.

Figure 2 depicts the experimental curves obtained for PIGE systems in the presence and absence of pyrrole. The inset in Figure 2 exhibits the voltammetric response of the unmodified PIGE in the absence of pyrrole. The potential window, -0.2 to 1.0 V, was the same as that selected for electropolymerization with the cathodic sweep potential starting at the open-circuit potential, 0.1 V/s, and room temperature. The charge increased as a function of the number of cycles, which is typical during the electrochemical formation of conducting polymers.^{53,54} When the same experiment was accomplished under the same conditions upon PIGE/HA in the presence of pyrrole, the same voltammetric profile was obtained during polymerization; this showed that the polymerization charge was not affected by the presence of HA on PIGE.

The obtained PIGE/PPy and PIGE/HA/PPy were stabilized with the same potential window into solution A. Voltammetric profiles are shown in Figure 3. Both electrodes exhibited a well-defined capacitive response. The improvement of the specific capacitance of carbon materials through faradaic reactions can be performed by the choice of a suitable monomer, such as pyrrole, that can be electropolymerized

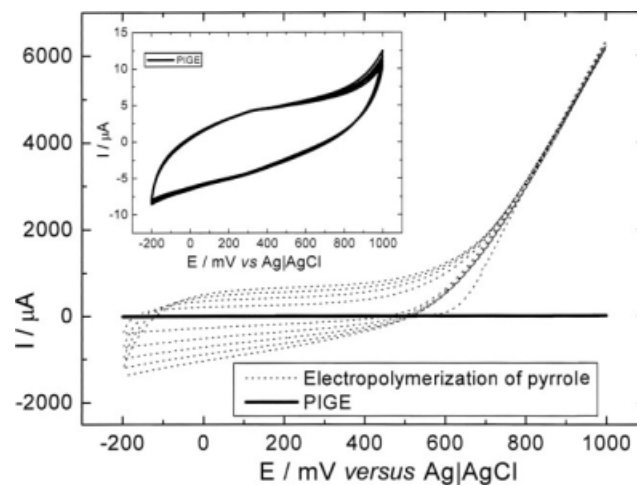


Figure 2 Typical cyclic voltammograms during electropolymerization recorded for the PIGE/pyrrole system in 1 mM Na_2SO_4 and 30 mM H_2SO_4 with different pyrrole concentrations: (—) 0 and (- - -) 1 mM (the first five cycles). The inset shows the voltammetric response of the bare PIGE between -0.2 and 1.0 V at 0.1 V/s (I is the current intensity, and E is the voltage).

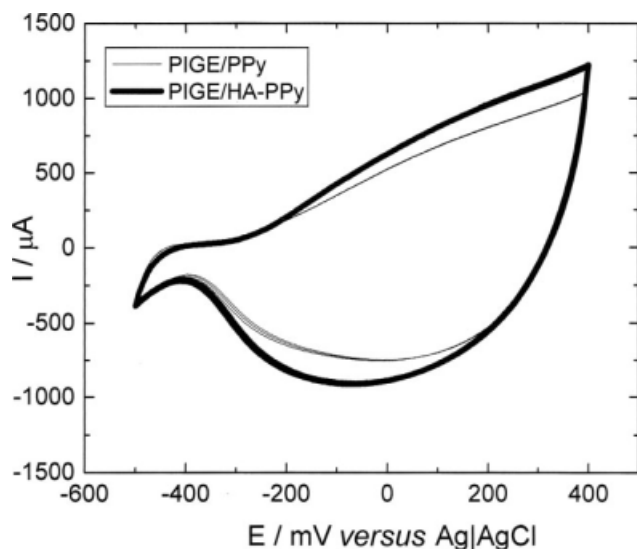


Figure 3 Potentiodynamic response of PIGE/PPy (thin line) and PIGE/HA/PPy (thick line) in 1 mM Na₂SO₄ and 30 mM H₂SO₄ between -0.5 and 0.4 V at 0.1 V/s (I is the current intensity, and E is the voltage).

upon different electrodic surfaces.^{55–57} As the polymerization charge during the electropolymerization of PIGE was not upset by the presence of HA, we can state that the capacitive response of the modified PIGE/HA/PPy was affected very little by HA because it exhibited a slightly higher response compared to that of PIGE/PPy.

EIS analysis

EIS is a powerful tool for monitoring the electrical characteristics of an electrochemical system.^{58,59} This technique was used to investigate the physical adsorption of HA upon PIGE and its subsequent interaction with pyrrole. Figure 4 shows the EIS results, displayed as Nyquist plots of Z'_{real} versus $Z''_{\text{imaginary}}$, for bare PIGE and the PIGE/HA, PIGE/PPy, and PIGE/HA/PPy modified electrodes, where Z'_{real} and $Z''_{\text{imaginary}}$ are the real variable and the negative value of the imaginary impedance variable, respectively. The electrochemical impedance measurements in this survey were carried out with solution A. In addition, each electrochemical system was measured at open-circuit potential, that is, 0.238 V for PIGE, 0.308 V for PIGE/HA, -0.151 V for PIGE/PPy, and 0.1 V for PIGE/HA/PPy. The alternating voltage was 10 mV, and the f range was 5 mHz to 1 kHz. Randles equivalent circuit was chosen to fit the obtained impedance data.⁶⁰ As Figure 4 shows, the Nyquist plots exhibited almost a straight line over the whole f range for PIGE and PIGE/HA, which is typical of a diffusion-limiting step for an electrochemical process. Similar results have been reported in other publications for an unmodified PIGE.^{59,61,62}

From the impedance results, we inferred that PIGE had a charge-transfer resistance (R_{ct}) of $1.94 \times 10^5 \Omega$ and a double-layer capacitance (C_{dl}) of $10.6 \mu\text{F}$. As for PIGE/HA, the following values were found: $1.67 \times 10^5 \Omega$ and $16.7 \mu\text{F}$, respectively. The inset in Figure 4 depicts Nyquist plots for the pyrrole-modified electrodes in the absence and presence of HA. For thin layers, the kinetic control region appearing at high f values may overlap with the charge saturation region, and no diffusion region is defined.⁵⁸ In such a case, R_{ct} was 182Ω and C_{dl} was 2.7 mF for PIGE/PPy, and for PIGE/HA/PPy, R_{ct} was 89Ω and C_{dl} was 4.7 mF. These results agreed well with those obtained by cyclic voltammetry because, when pyrrole was electropolymerized on the same electrodes, they exhibited a lower R_{ct} value; that is, the obtained PPy presented higher conducting characteristics. Also, the higher C_{dl} values found demonstrated that electrodes possessing a larger superficial area were obtained, which produced rough or porous electrodes.⁵⁸

On the other hand, in Figure 4, Bode plots are depicted for the different electrodes: $\log |Z|$ versus $\log f$ and phase angle versus $\log f$ plots were drawn ($|Z|$ is the impedance modulus).

At intermediate f values, the PIGE and PIGE/HA systems showed a capacitive response because the phase angle was close to 90° , and a time constant (τ) was observed ($\tau = R_{ct} \times C_{dl}$), which indicated a redox active center for both electrodes. In addition, when we moved to low f values, the phase angle was approximately 45° , which suggested that the systems tended toward a diffusional regime. As both electrodes presented similar responses over the whole f range, we inferred that the electrical characteristics of the system were not affected in general by the presence of HA on PIGE.

On the other hand, for the PIGE/PPy and PIGE/HA/PPy systems, $\log |Z|$ versus $\log f$ graphs showed nearly the same impedance values over the whole range for each system, which indicated that the respective R_{ct} was independent of the presence of HA.

SEM morphological analysis

Figure 5 exhibits the SEM micrographs recorded for the systems under survey, namely, PIGE [Fig. 5(A)], PIGE/HA [Fig. 5(B)], PIGE/PPy [Fig. 5(C)], and PIGE/HA/PPy [Fig. 5(D)]. To determine its thickness, a PIGE/PPy cross-sectional view is shown in Figure 5(E).

Figure 5(A) depicts the morphology of an unmodified PIGE, which displayed an irregular surface structure. This morphology has been reported elsewhere.^{63,64} Figure 5(B) shows the PIGE/HA morphology. HA presented irregular aggregates on the

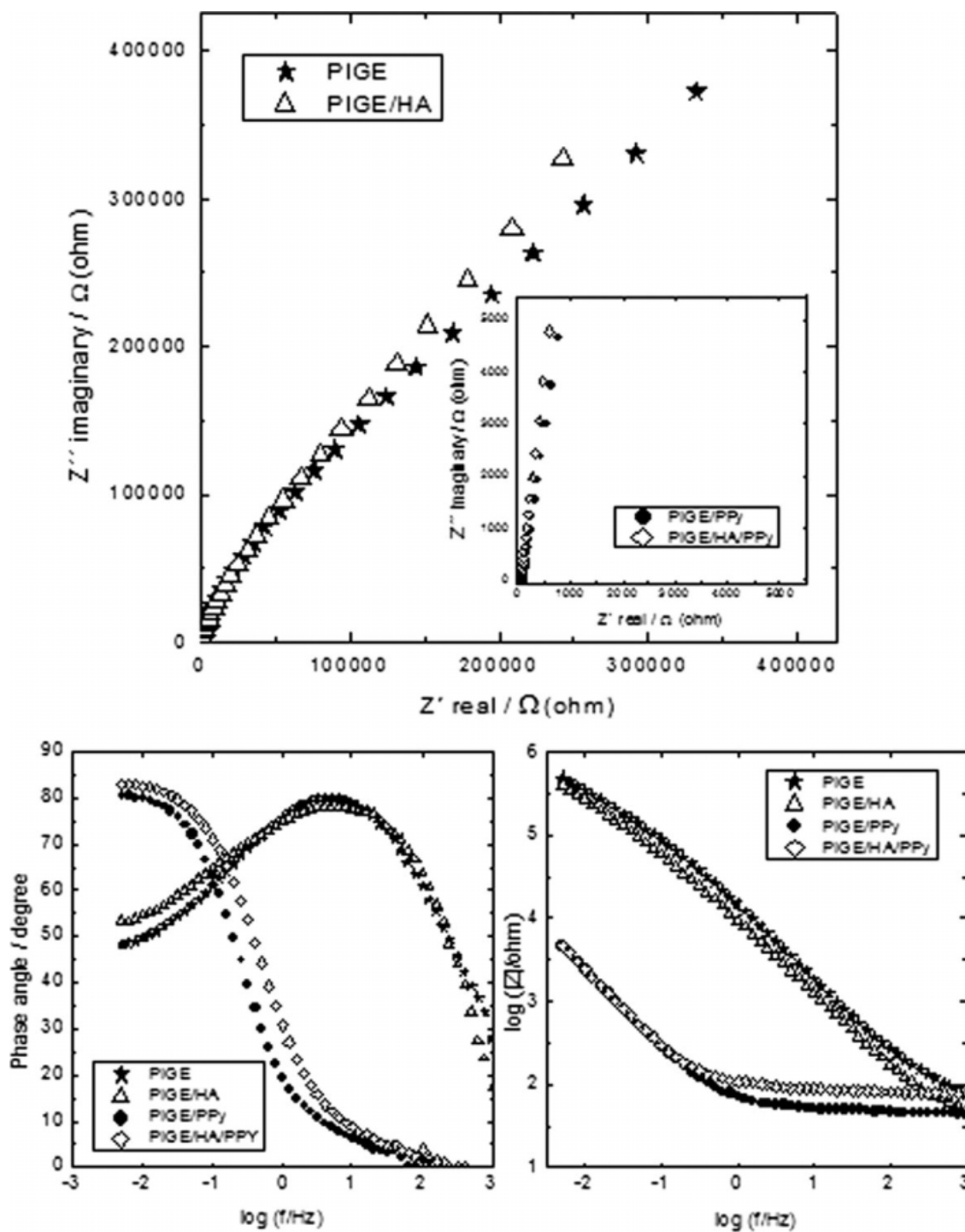


Figure 4 Nyquist plots of (★) PIGE and (△) PIGE/HA. The inset shows Nyquist plots of (●) PIGE/PPy and (◇) PIGE/HA/PPy. The lower panels present Bode plots for each electrode.

PIGE surface, and therefore, heterogeneous shapes of HA were predicted. An irregular diameter size of the particles, about 1–3 μm , was also observed. Although this particle size has been reported elsewhere, it depends on the experimental conditions.⁶⁵

Figure 5(C) illustrates the PIGE/PPy morphology. PPy usually presents nodular surface struc-

tures.^{53,66,67} However, the thinnest films exhibit less uniform surfaces, usually with little difference in the nodule diameter.⁵³ In general, the roughness and pore size of PPy films increase with film thickness.^{53,68–71}

The fundamental process in electrochemical reactions is the charge transfer between the working

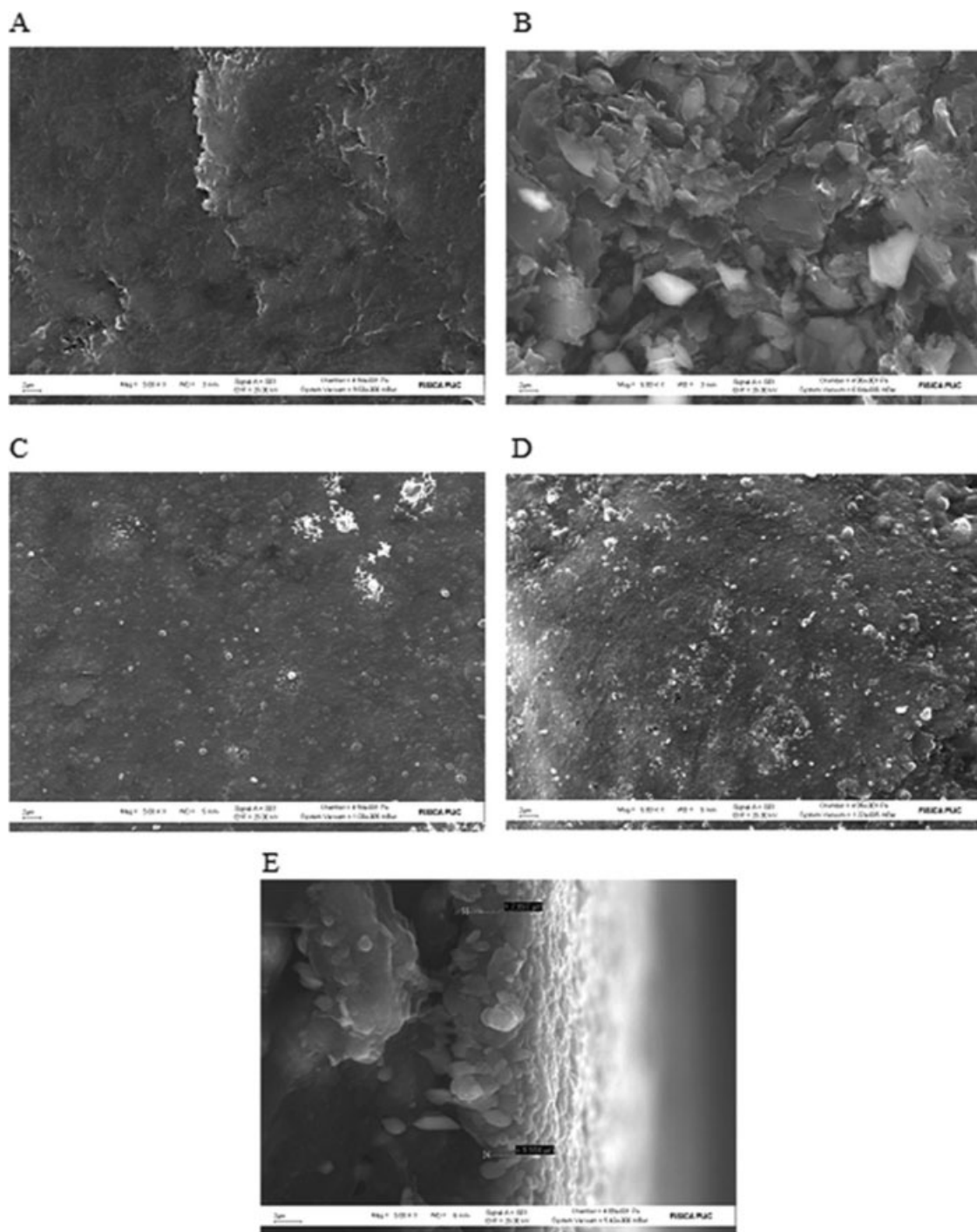


Figure 5 SEM micrographs showing the surface morphology of (A) PIGE, (B) PIGE/HA, (C) PIGE/PPy, and (D) PIGE/HA/PPy. (E) A cross-sectional view of PIGE/PPy is also shown.

electrode surface and the molecules in the interfacial region (in solution or immobilized on the electrode surface). This heterogeneous process can be largely affected by diverse reasons: (1) the microstructure and roughness of the electrode surface, (2) active site blockade by materials adsorbed onto the electrode surface, and (3) the nature of the moieties present on the electrode surface, for example, oxides. The pres-

ence of HA affected the PPy deposit and provoked the formation of a more disperse granular morphology in PIGE/HA/PPy [Fig. 5(D)], which might have been due to the superficial adsorption of HA on the high-energy regions of PIGE, followed by nucleation and electropolymerization of PPy on them. This phenomenon has also been observed in the growth of PPy on carbon nanotubes.⁷²

TABLE I
As(V) Extracted as a Function of the Modified PIGE

Modified electrode	Extraction number	Initial As(V) (g/L)	Extracted As(V) (g/L)	Electrode area (cm ²) ^a
Acid medium				
PIGE/HA/PPy	10	0.1067	3.4×10^{-4}	0.28
PIGE/PPy	10	0.1046	2.8×10^{-4}	0.28
Alkaline medium				
PIGE/HA/PPy	10	0.1070	2.0×10^{-4}	0.28
PIGE/PPy	10	0.1070	2.0×10^{-4}	0.28

^a Referred to the geometrical PIGE working electrode.

The cross section of PIGE/PPy shown in Figure 5(E) showed a granular morphology with 7.66 μm in the thickest region and 5.55 μm in the thinnest one. This thickness was attained with just five successive potentiodynamic cycles because this electrode was to be further used for arsenic extraction from solution A as the electrolyte. As far as the polymeric film thickness is concerned, it has been reported that 10 cycles at 0.020 V/s afford films 16 μm thick.⁷³

Arsenic extraction (assay of the modified electrodes)

Tables I and II summarize the results obtained with the modified electrodes tested for arsenic extraction.

The extraction of As(V) by the PIGE/PPy and PIGE/HA/PPy electrodes was compared with both the values of transferred charge and the results obtained for concentration. The found values indicate that the amount of arsenic extracted was lower for PIGE/PPy compared to PIGE/HA/PPy. Therefore, the extraction efficiency enhancement might have been related to the kind of polymer obtained (morphology) and to the incorporation of HA as a part of the modification. Arsenic species were shown to react with HA. The interaction was postulated to involve bridging metals and deprotonated functional groups within the HA.⁷⁴ In this context, the HA we used comprised important carboxylic (5.5 ± 0.2 mequiv/g) and phenolic (1.9 ± 0.2 mequiv/g) groups, which might have supported the previously mentioned interaction. In addition, a 1 : 1 [As(V) : HA] relation was assumed for the obtained complex.⁷⁵

Contrary to As(III), inorganic species of As(V) are neutral or negatively charged, H_3AsO_4 and H_2AsO_4^- , in the pH range that we surveyed. As HAs are negatively charged, only weak interactions with As(V) could be expected. However, results have been reported that indicate the existence of strong bonding of As(V) to HA.^{44,74} These results were ascribed to a greater formal charge at the As(V) center, additional chelation, and/or stabilization effects. In this connection, when the coordina-

tion numbers are lower than 6, an exchange mechanism of the associative ligand at the center of the positively charged metal may take place.⁴⁴

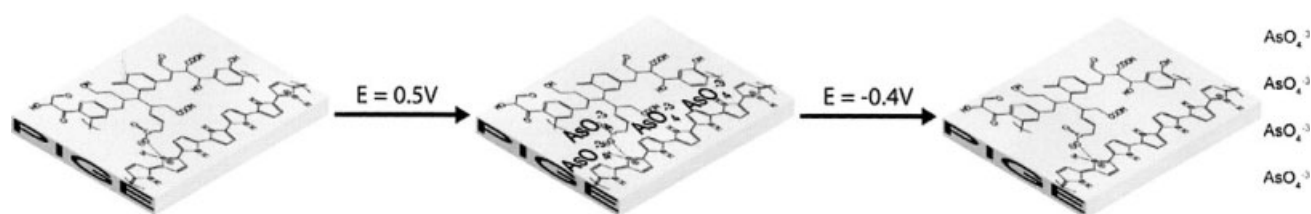
Because arsenate ion has a formal charge of +5, a phenolate addition to the electrophilic center, followed by protonation and water release, might occur. The existence of phenolate in the HAs enabled us to propose a mechanism, although the total charge was negative for both reactants, wherein the driving force may have been stabilization through the donating characteristics of phenolates, additional chelation by other moieties, and/or hydrogen bonding.⁴⁴

With regard to HA interaction with As(III) and As(V), the extent of complexation showed great variability in samples of natural organic matter in the presence of metals. A ternary complexation mechanism, in which cationic metals mediated the strong association between natural organic matter functional groups and arsenic oxyacids, was a plausible mechanism to explain the observed interactions. This assumption was supported by some experiments accomplished with fulvic materials in the presence and absence of metals such as Fe, Al, Mn, and Ca, wherein the extracting efficiency went from nil to 50% in the presence of these metals.^{76,77} Nevertheless, in our case, this kind of interaction should have been lower because of the presence of the polymer. In fact, the XPS results demonstrated that after PPy and HA were brought into contact, the $[\text{N}^+]/[\text{N}]$ rate decreased by about 15%. This suggested that some sort of adsorption occurred at specific N^+ sites and that the positively charged N atoms reacted with HA to bring about a charge neutralization.³ The process may have proceeded by the formation of organic complexes, as depicted in Scheme 1. The basic structure of HA and PPy in Scheme 1 agreed with the suggested model.⁷⁸

Although the proposed HA–As(V) interaction was valid in accordance with the preceding discussion, the morphology of the polymer might have also been involved in the improvement of extraction efficiency. In fact, the pores observed in the SEM

TABLE II
Doping and Undoping Charges as a Function of the Modified PIGE

Modified electrode	Extraction number	Doping charge	Undoping charge
Acid medium			
PIGE/HA/PPy	10	0.00810 ± 0.00181	0.01052 ± 0.00071
PIGE/PPy	10	0.00525 ± 0.00070	0.00543 ± 0.00037
Alkaline medium			
PIGE/HA/PPy	10	0.00545 ± 0.00082	0.00126 ± 0.00013
PIGE/PPy	10	0.00549 ± 0.00041	0.00200 ± 0.00025



Scheme 1 Interaction of arsenate ions with PIGE/HA/PPy during the doping–undoping process.

micrographs could have been used in the extraction of the analyte ions of interest; thus, the thickness of the film should have had an influence on the extraction efficiency, mainly because of surface increase. Although the thickness was effective in the superficial area increase because of the porous structure of the film, this did not mean that the capacity and sensitivity of the extraction increases were limitless because, after a certain thickness value, some diffusional limitations started restricting the amount of extracted analyte.⁷⁹

On the other hand, the average charge results for both modified electrodes included in Table II indicated the existence of a reversible doping/undoping process in acid medium, which meant that the stability of the electrodes remained unchanged even after 10 extractions. Furthermore, in these conditions, the transferred charge was greater for the electrode modified with HA/PPy than for that modified just with PPy, which thus presented a superior performance as an extractant. In alkaline medium, both modified electrodes presented reversibility values no better than 50%; this fact may be associated with the need to apply, under these circumstances, lengthier undoping potentials. In addition, it is likely that electrode contamination occurred because, during the undoping process, not all that was extracted in the doping stage was released. On the other hand, if the undoping charges of the 10 extractions were considered for both electrodes in acidic medium, the concentration, calculated with Coulomb's law and $n = 3$, were 5.1×10^{-3} and 2.6×10^{-3} g/L for HA/PPy and PPy, respectively. These values were clearly higher than the AsO_4^{3-} concentration found by ICP-OES and shown in Table I. This finding indicates that charge was associated not only to the extracted AsO_4^{3-} but also to other ions, such as HSO_4^- , existing at high concentrations, whose concentrations were not upset by the quantity extracted.

The results obtained in this study show the usefulness and potential applications of a novel PIGE modified by HA/PPy as an arsenic extractor because a distinct synergic effect between PPy and HA there existed. Future work to be developed will be focused on improving this system for further utilization with

other analytes. Variables, such as the polymer film thickness, number of extractions, and combined HA/PPy/HA/PPy systems, need to be studied. In addition, because of the promising results obtained in the presence of HA, the use of natural HAs, fractionated from soils derived from Chilean volcanic materials, will be considered. This will enable the likely utilization of organic fractions of renewable resources, aimed at further use of organic residues such as sludge, to be evaluated.

CONCLUSIONS

A novel ion extractant device based on a modified electrode, prepared by the adsorption of HA onto PIGE and the subsequent electropolymerization of a thin film of PPy, was elaborated and studied.

The preparation and use of the novel device allowed us to arrive at the following conclusions:

1. Morphological characterization proved that the presence of HA disturbed the PPy coating and gave rise to a more disperse granular morphology that could be ascribed to the superficial adsorption of HA on high-energy regions of PIGE followed by PPy nucleation and electropolymerization on them. Despite this, voltammetric and EIS characterization demonstrated that the modified electrode was not upset by the presence of HA because, in both its presence and absence, similar capacitive responses were attained.
2. Chronoamperometric results point to a synergic effect between PPy and HA in this electrode, which conferred the usefulness and potential applicability of the new HA/PPy-modified PIGE for arsenic extraction.
3. The efficiency of As(V) extraction improved 18% with respect to the same device in the absence of HA. A mechanism involving both arsenate and phenolate of the humic compound would account for this behavior.

Finally, the synergic effect observed enabled us to establish that the use of humic substances with

conductive polymeric matrices enhanced interaction with anionic contaminants. Consequently, further investigation must be done with the consideration that this study represents the beginning of a novel remediation technique for contaminated waters that requires the handling of selectivity and reproducibility.

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