

Electrochemical Synthesis and Characterization of New Electrodes Based on Poly-Hematoxylin Films

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ABSTRACT: The poly-hematoxylin films undoped (p-HX) and doped with strontium (p-HX-Sr) were prepared on the platinum electrodes (Pt) using cyclic voltammetry. The influence of experimental parameters, such as: anodic potential and number of voltammetric cycles on the films synthesis was investigated by electrochemical impedance spectroscopy (EIS). The results showed that, the optimal conditions to obtain the poly-hematoxylin films on platinum electrode from 10^{-2} mol L⁻¹ NaNO₃ solution, were found by recording 10 voltammetric cycles at an anodic potential of 1.5 V. Electrocatalytic activity of the poly-hematoxylin-platinum (p-HX/Pt) and poly-hematoxylin-strontium-platinum (p-HX-Sr/Pt) electrodes was tested for electrochemical degradation of benzocaine using UV-Vis spectrophotometry. Both, the mechanisms of hematoxylin (HX) polymerization, as well as benzocaine degradation were proposed. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 687–697, 2013

KEYWORDS: films; electrochemistry; degradation

Received 15 November 2012; accepted 24 February 2013; published online 2 April 2013

DOI: 10.1002/app.39218

INTRODUCTION

The interest of researchers in synthesis of organic films formed by electropolymerization on metallic surfaces increased in recent years, due to their large use in different fields such as: electrocatalysis, sensors, biosensors, molecular microelectronics, electrochromics devices, chemical modified electrodes, and also for protection against corrosion.^{1–4}

An intense interest has been in preparation, characterization and application of an important group of these polymers by the electropolymerization of simple compounds such as aniline, pyrrole, thiophene and their derivatives.^{5–8} It has been proved that the electropolymerization of compounds with more complicated structure, e.g., carbazole, safranin, phenazines, phenothiazines, and hematoxylin, is also possible resulting the polymers with bioelectrocatalytic activity.^{9–15} The main advantage of this type of sensors is that, such polymers can be grown to a controlled thickness from aqueous solutions in which the substrate are soluble and stable. Resulting sensors are reproducible and some films proved to have selective permeability to the substrate of interest. Electropolymerized or co-electropolymerized conducting polymers where obtained for special applications as sensors and biosensors.^{16–18}

Hematoxylin is extracted from the heartwood of the Central American logwood *Haematoxylon campechianum* Linnaeus. By the end of the 19th century haematoxylin, or logwood, had

been described as “without equal” as a tissue stain. Complexes between hematein and polyvalent metal cations are important nuclear dyes in histology and cytology. The whole group of complexes between hematein and trivalent metal cations are now frequently called hemalums. In the course of hemalum staining and the subsequent blueing, all color tones between red, violet, and blue can be observed.

Hematoxylin modified carbon paste electrode (HMCPE) showed excellent electrocatalytic activity toward nicotinamide adenine dinucleotide (NADH) oxidation. The electron transfer and the heterogenous rate constant for NADH oxidation were determined using cyclic voltammetry, chronoamperometry, and differential pulse voltammetry.¹⁹

A modified electrode based on hematoxylin electrodeposited on multi-wall carbon nanotubes (MWCNT) immobilized on the surface of a glassy carbon electrode was used for simultaneous or individual determination of adrenaline, ascorbic acid, and uric acid.²⁰ A new study has introduced an electrochemical DNA biosensor on the basis of the interaction of hematoxylin with 20-mer deoxyoligonucleotides for the detection of DNA hybridization.²¹ This process was observed in the potential range where the hematoxylin was electroactive by using cyclic voltammetry and differential pulse voltammetry. Poly-hematoxylin was prepared on glassy carbon electrode from 0.3 mmol L⁻¹ hematoxylin, in a phosphate buffer solution of pH = 7 in

the presence of $0.1 \text{ mol L}^{-1} \text{ NaNO}_3$ supporting electrolyte by successive cyclic voltammograms in the potential range $-0.5 \text{ V} \div 2.0 \text{ V}$ vs. Ag/AgCl reference electrode.²² The modified poly-hematoxylin electrode exhibit a good electrocatalytic activity for NADH oxidation.

Benzocaine, *p*-aminobenzoic (ethyl 4-aminobenzoate) acid ester is a drug used in odontology,^{23,24} being a local anesthetic used for reducing the pain in the mucous membranes and teguments.^{25,26} Electrochemical behaviour of benzocaine on platinum, gold and vitreous carbon electrodes, at different pH values was reported,²⁶ showing that both material as well as media pH influenced the shape of cyclic voltammogram, consequently its oxidation.²⁶

The aim of this study is the electrosynthesis and electrochemical characterization of new based poly-hematoxylin electrodes by cyclic voltammetry and electrochemical impedance spectroscopy. The modified platinum electrodes with poly-hematoxylin films undoped (p-HX/Pt) and doped with strontium (p-HX-Sr/Pt) have a good electroactivity for the electrochemical degradation of benzocaine and these are more sensitive to pH than platinum plate.

EXPERIMENTAL

The Poly-Hematoxylin Films Preparation

The poly-hematoxylin films preparation and optimal conditions of their formation on platinum electrode were performed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using a potentiostat/galvanostat Voltalab 40 with VoltMaster 4 software. A standard electrochemical cell with three electrodes was used. Both the, working and auxiliary electrodes were represented by the platinum plates (area 1 cm^2). Ag/AgCl_{sat} electrode was used as reference.

An UV-Vis spectrophotometer, VARIAN-CARY 50 type, was used to record the UV-Vis spectra of hematoxylin solutions, before and after CV. The poly-hematoxylin film was obtained on platinum electrode from an electrolyte solution (pH = 5.5) containing $10^{-4} \text{ mol L}^{-1}$ hematoxylin and $10^{-2} \text{ mol L}^{-1} \text{ NaNO}_3$ in the absence and presence of $10^{-3} \text{ mol L}^{-1} \text{ SrCl}_2$ using cyclic voltammetry, with the potential sweep rate of 100 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was measured in a frequency range from 100 kHz to 10 mHz by a perturbation signal of 10 mV amplitude peak to peak, at room temperature, after cyclic voltammetry, the relaxation time of the electrodes, in open circuit, between measurements being of 4 min.

Surface Characterization of p-HX/Pt Electrode

The surface morphologies of the unmodified and modified platinum electrodes were examined using a metallographic microscope, type Euromex with Canon camera and included Zoom-Browser - EOS Digital software.

Electrocatalytic Activity of Pt, p-HX/Pt, and p-HX-Sr/Pt Electrodes

The poly-hematoxylin films undoped (p-HX) and doped with strontium (p-HX-Sr) were prepared on platinum electrode (Pt) by scanning of 10.0 voltammetric cycles, at an anodic potential of 1.5 V in order to obtain modified platinum electrodes

(p-HX/Pt and p-HX-Sr/Pt, respectively). Their electrocatalytic activity was tested for electrochemical degradation of benzocaine. Electrochemical degradation of benzocaine was achieved on platinum electrode (Pt) from an electrolyte solution (pH = 12.2) containing $10^{-4} \text{ mol L}^{-1}$ benzocaine, ethylic alcohol 1:100 (v:v) and $10^{-2} \text{ mol L}^{-1} \text{ NaOH}$ (as support electrolyte), using cyclic voltammetry (1.0 cycle), in order to propose its electrochemical degradation mechanism.

Electrocatalytic activities of Pt, p-HX/Pt, and p-HX-Sr/Pt electrodes were tested for electrochemical degradation of benzocaine by electrolyzing a solution containing $10^{-4} \text{ mol L}^{-1}$ benzocaine and $10^{-2} \text{ mol L}^{-1} \text{ NaCl}$ (pH=5.1), at a constant current density of 50 mA cm^{-2} , in static condition, for 1.0 h. Electrolysis was carried out controlled by Keithley SourceMeter 2420 3A model potentiostat/galvanostat. All experiments were performed at room temperature ($22 \pm 2^\circ\text{C}$).

Samples of $10^{-2} \text{ mol L}^{-1} \text{ NaOH}$ solutions containing $10^{-4} \text{ mol L}^{-1}$ benzocaine were used for spectrophotometric analysis, before and after cyclic voltammetry. UV-Vis spectra of $10^{-4} \text{ mol L}^{-1}$ benzocaine solutions in $10^{-2} \text{ mol L}^{-1} \text{ NaCl}$ were also recorded in order to determine the benzocaine degradation degree on Pt, p-HX/Pt and p-HX-Sr/Pt electrodes, at different reaction times: 15 min; 30 min; 45 min; 60 min, by measuring the absorbance value at λ_{max} of 279 nm. UV-Vis analysis reports were obtained using a UV-Vis spectrophotometer, VARIAN-CARY 50 type, with Cary WinUV software.

NaOH and HNO₃ solution's pH was used to study acid-base behavior of Pt, p-HX/Pt, and p-HX-Sr/Pt Pt-p-HX electrodes. In all cases pH was measured with a Hanna digital pH -meter. All reagents presented analytical purity and these were obtained from Fluka.

RESULTS AND DISCUSSION

The Preparation of Poly-Hematoxylin-Platinum (p-HX/Pt) and Poly-Hematoxylin- Strontium- Platinum (p-HX-Sr/Pt) Electrodes by Cyclic Voltammetry (CV)

The use of cyclic voltammetry provides a mean of investigation for an indirect characterization of the processes taking place. The presence of coadsorbed species has a pronounced effect on the voltammetric features of the investigated system. The cyclic voltammogram of $10^{-4} \text{ mol L}^{-1}$ hematoxylin (HX) on platinum electrode (Pt) in $10^{-2} \text{ mol L}^{-1} \text{ NaNO}_3$ solution, as support electrolyte which has a catalytic activity on the electropolymerization process^{22,27} is presented in Figure 1(a). A hematoxylin (HX) concentration of $10^{-4} \text{ mol L}^{-1}$ was employed, known to yield an optimum poly-hematoxylin (p-Hx) film on the Pt electrode, according to literature data.²² This p-HX/Pt electrode was prepared in order to be used in the study of the electrochemical degradation of benzocaine. A poly-hematoxylin film doped with strontium (p-Hx-Sr) was prepared under similar conditions, using the same electrolyte containing $10^{-3} \text{ mol L}^{-1} \text{ SrCl}_2$, in order to observe the effect of strontium ions during the preparation of the modified Pt electrode, as well as its electrocatalytic activity on the degradation process of benzocaine. The corresponding voltammogram is presented in Figure 1(b). Cyclic voltammograms, in both cases, were carried out for

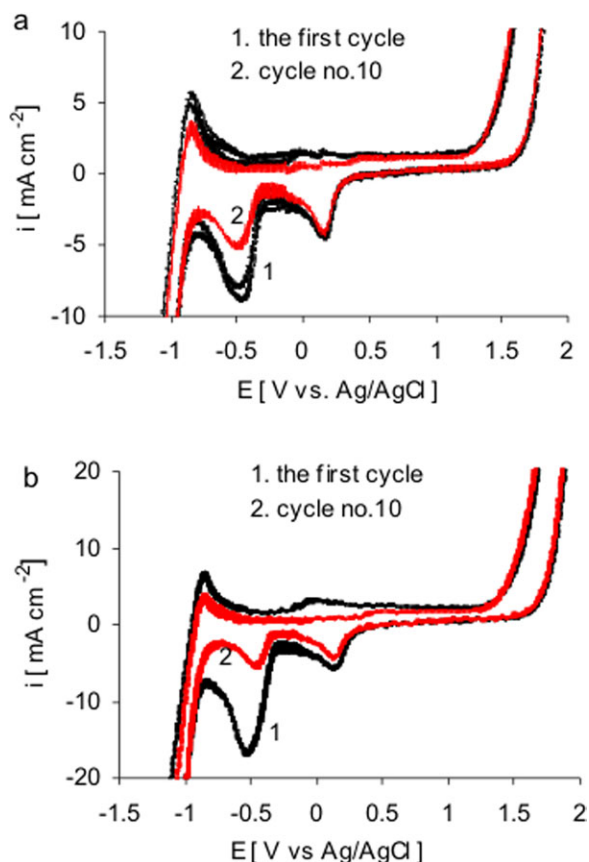
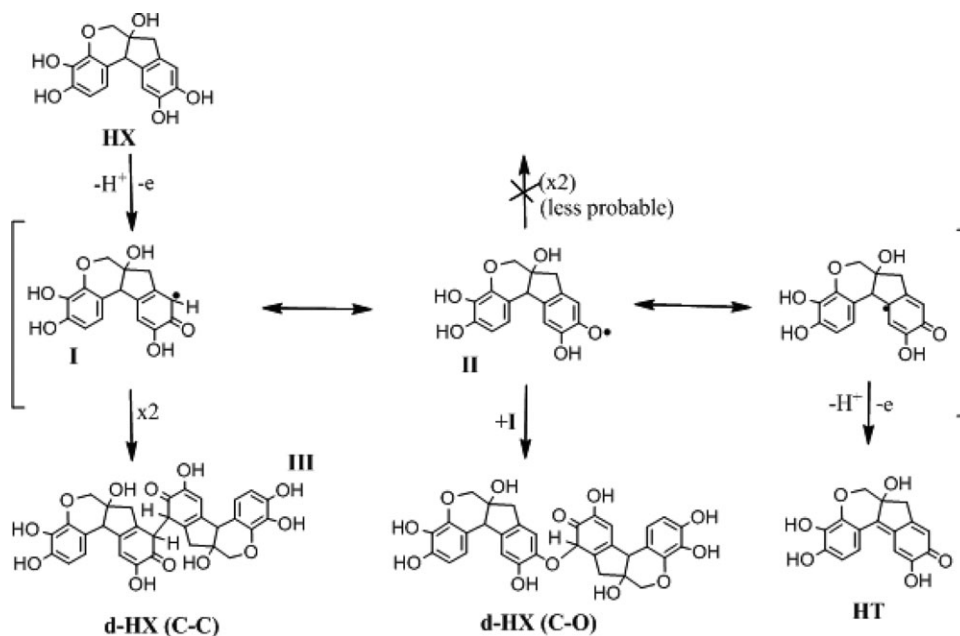


Figure 1. Cyclic voltammograms of 10^{-4} mol L^{-1} hematoxylin (HX) on platinum electrode (Pt) obtained in 10^{-2} mol L^{-1} $NaNO_3$ solution, with a scan rate of 100 mV/s, in the potential range of -1.5 to 2.0 V vs. Ag/AgCl, in the absence (a) and in the presence (b) of 10^{-3} mol L^{-1} $SrCl_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

10 cycles, the first and the last cycles being shown in Figure 1, to comment the films formation. Inert substrates, like platinum (Pt), are required as electrodes, because the electrochemical polymerization usually takes place at potentials where other metals oxidize.

The oxidation peak recorded at -0.8 V vs. Ag/AgCl_{sat} potential, corresponds to the oxidation of OH^- ion. The high intensity of this peak might indicate that, at this potential, pure adsorption of hematoxylin (HX) on the electrode surface might occur. At potentials of 30 mV, low intensity peaks on the first cycle are observed on both voltammograms. These peaks correspond to the oxidation of catechol groups to quinone, through intermediate species whose possible structures are depicted in Scheme 1,²² also, hematein (HT) formation being possible in this stage. Poly-hematoxylin film appearance, as shown in Figure 1, takes place at potential values higher than 0.5 V. The reduction peaks observed at 0.2 V and -0.5 V are associated with the reduction of quinone groups of poly-hematoxylin and with the reduction of other species from solution, including HT. Moreover, it can be observed that, for solutions containing strontium ions [Figure 1(b)], the peak at -0.5 V has a greater height than that shown in their absence [Figure 1(a)], suggesting that the reduction process could be enhanced by the contribution of other additional species from solution, or by the p-HX film, because strontium ions can be attached to macromolecular chains by coordinative links, with complexes formation.²⁸

During the cathodic scan of the tenth cycle, the reduction peak appeared at -0.5 V has a height considerably smaller than that resulting from the cathodic scan of the first cycle, suggesting that during the tenth scan the oxidation of HX is minimal owing to the presence of a p-HX layer. During the first cycle, the removal of the p-HX layer is possible, facilitating the formation of HT, followed by its reduction. This suggests that the presence of an adsorbed p-HX film gives rise to a decrease of



Scheme 1. The initiation stage of hematoxylin polymerization mechanism.

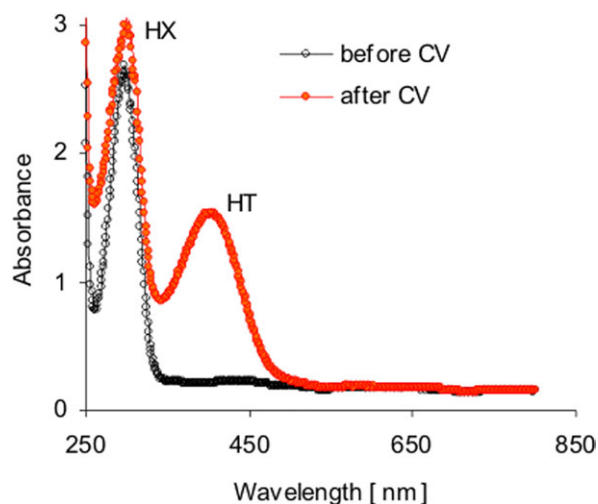


Figure 2. UV-Vis scans obtained for 10^{-4} mol L $^{-1}$ hematoxylin (HX) in 10^{-2} mol L $^{-1}$ NaNO $_3$ solution, before and after cyclic voltammetry (10 cycles). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the oxidized species formation to a certain level, and the main process that takes place might be the polymerization of HX. This tendency for HT formation, followed by its reduction, gradually increases with decreasing the number of cycles. Also, from Figure 1(a,b) it is observed that, during the anodic scan of tenth cycle, a current plateau which corresponds to a potential range between 0.5–1.25 V is formed, indicating the p-HX and p-HX-Sr films occurrence. At potential values higher than 1.25 V, the current density slowly increases, until 1.5 V, becoming more significantly, after this value. The increasing current might be due to the oxidation of -OH groups from the p-HX film and/or partially desorption of p-HX layer from platinum surface. Similar observations were reported for the electropolymerization of HX²² and pyrogallol²⁹ on glassy carbon electrodes, as well as for the polymerization of different phenolic compounds.³⁰ Also, a highly efficient noradrenaline biosensor was fabricated on the basis of hematoxylin electrodeposited on a glassy carbon electrode.³¹

The oxidation of HX to hematein (HT) may result by the steps which are shown in Scheme 1. The electrochemical oxidation of hematoxylin studied by cyclic voltammetry³² shows that in the dimerization process, hematoxylin reacts as a nucleophile with the o-quinone ring formed through the electrooxidation of hematoxylin and produces a dimer compound.³² To confirm the HT formation, UV-Vis scans of the HX solutions, before and after cyclic voltammetry are presented in Figure 2. Two adsorption peaks, at 295 nm and 415 nm, corresponding to hematoxylin (HX) and to its oxidized form, hematein (HT), respectively^{33,34} are shown on the obtained spectra. From Figure 2, it can be seen that before cyclic voltammetry, HT is presented as a flattened shoulder, indicating that the HT amount in solution is very small. After cyclic voltammetry, it can be observed that HX absorbance decreases without altering the wavelength of adsorption maximum, but at the same time, the corresponding peak of HT increases in a considerable manner.

Taking these data into account, we may conclude that: (i) the poly-hematoxylin film formation takes place above of 0.5 V; (ii) the p-HX film formation is more nuanced for the voltammetric scan of the tenth cycle; (iii) the p-HX layer is adherent and stable in the potential range between 0.5 V and 1.5 V.

Optimal Conditions of p-HX Films Formation on Platinum Electrode Studied by Electrochemical Impedance Spectroscopy (EIS)

The physico-chemical and most important electrocatalytic properties of the poly-hematoxylin films are influenced by experimental parameters like the anodic potential, the number of cycles and the presence of heavy metals ions in the electrolyte solution. The electrochemical impedance spectroscopy (EIS) is a technique that has been used for a long time to study electrochemical processes at the electrode surface. It is a valuable and convenient method to give information on impedance changes of the electrode surface in the modified process.

EIS spectra of the poly-hematoxylin films were recorded in 10^{-2} mol L $^{-1}$ NaNO $_3$ blank solution and in 10^{-2} mol L $^{-1}$ NaNO $_3$ containing 10^{-4} mol L $^{-1}$ HX, without and with 10^{-3} mol L $^{-1}$ SrCl $_2$, after cyclic voltammetry, the relaxation time of the electrodes, in open circuit, between measurements being of 4 min (Figure 3). Note that, the Nyquist spectra of undoped films obtained using cyclic voltammetry, for a constant number of cycles (10 cycles) and different anodic potentials: 0.5; 1.0; 1.5; 2.0 V [Figure 3(a)] are characterized by the capacitive loops, at high frequencies corresponding to the charge transfer processes, and by a linear region, at low frequencies, corresponding to the diffusion process. The loops are even more pronounced as the anodic potential is higher, compared with the shape of Nyquist curve obtained for the unmodified platinum electrode (Pt). Therefore, it can be stated that at an anodic potential of 0.5 V, the poly-hematoxylin film formation is less obvious. The optimal working potential that should be used in order to obtain a poly-hematoxylin film is 1.5 V, the capacitive loop being the most nuanced.

It can be observed [Figure 3(b)] that, maintaining the anodic potential at 1.5 V and increasing the number of cycles, the Nyquist spectrum shows more pronounced loop for 10.0 voltammetric cycles. In Figure 3(c), Nyquist diagrams corresponding to poly-hematoxylin films undoped and doped with strontium ions, obtained at an anodic potential of 1.5 V and 10.0 cycles, are compared. In the presence of strontium ions, in the electrolyte solution, the Nyquist diagram shows two loops: one at a high frequency, corresponding to the poly-hematoxylin film and the second at low frequencies, which attests the presence of strontium in the polymer film, consequently charge transfer resistance increase.

The results are consistent with those obtained by cyclic voltammetry, confirming that the optimal potential to obtain a poly-hematoxylin film is 1.5 V using voltammetric scans of 10.0 cycles. By comparing the cases of p-HX deposited from 10^{-2} mol L $^{-1}$ NaNO $_3$ solutions, containing 10^{-4} mol L $^{-1}$ HX without or with 10^{-3} mol L $^{-1}$ SrCl $_2$, on the Pt surface, it was found that the charge transfer resistance is lower in case of p-HX deposited in absence of strontium ions. This indicates that the approach of the electrochemical species to the electrode surface

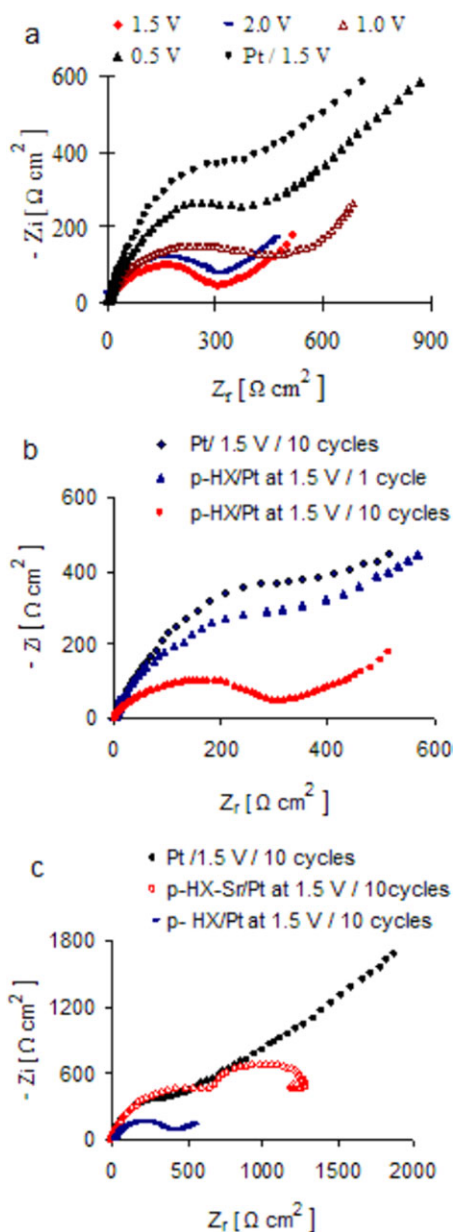


Figure 3. Nyquist spectra of the poly-hematoxylin films obtained after cyclic voltammetry in 10^{-2} mol L⁻¹ NaNO₃ blank solution and in 10^{-2} mol L⁻¹ NaNO₃ containing 10^{-4} mol L⁻¹ HX, without and with 10^{-3} mol L⁻¹ SrCl₂, relaxation time of the electrodes between measurements being of 4 min, in open circuit; (a) the influence of anodic potential on poly-HX film obtained by 10.0 voltammetric cycles; (b) the influence of voltammetric cycles number on poly-HX film obtained in potential range of -1.5 to 1.5 V; (c) the influence of strontium ions on p-HX film obtained on platinum electrode after 10.0 voltammetric cycles in potential range of -1.5 to 1.5 V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is facilitated in the case of Pt electrode modified with p-HX film undoped with strontium ions.

Surface Characterization of p-HX/Pt Electrode

The appearance of poly-hematoxylin (p-HX) film on platinum electrode surface was confirmed by microscopic images (Figure

4). Figure 4(a) shows the specific morphology of the platinum electrode before cyclic voltammetry. After ten voltammetric scans, it can be observed that, the surface morphology of the electrode is completely changed, being evidenced the feature of a coating that is assigned to p-HX film [Figure 4(b)]. In Figure 4(c), the surface morphology is shown after EIS. In this case, it is observed that the polymer film shows some discontinuities, without affecting the surface morphology and/or its texture. This attests the stability and good adhesion of p-Hx film on platinum surface.

Electropolymerization Mechanism of Hematoxylin

In the initiation stage (Scheme 1) hematoxylin molecule loses an electron and a proton with formation of an active radical (I), in equilibrium with its mesomeric forms, like (II) and (III). Similar or other mesomeric structures were reported for radicals, as intermediates in the oxidation process of HX²² and for the oxidation of other phenolic compounds.³⁰ Moreover, it was reported that the oxidation of phenolic compound produces unstable phenoxy radicals, that can be oxidized to quinones or can react to form dimers.^{22,29,30,35,36} By using these useful information, we proposed a similar mechanism for HX electropolymerization. Radical (I) can form by dimerization a new C[—]C bond [d-HX (C[—]C)]. We assume that this type of coupling is sterically disfavored, because of the steric repulsions that may appear between the two hindered aromatic rings involved in the new C[—]C bond. Radical (II) dimerization is less probable because it leads to the formation of a peroxide highly reactive. The most probable it is the reaction between the radicals (I) and (II); according to this new C[—]O bond, the corresponding [d-HX (C[—]O)] dimer with high stability may occur.

On the one hand, the position of oxygen atom inside the dimer increases the distance between molecules, and on the other hand allows their rotation; in accordance with these hypotheses, this dimer has a greater steric stability. Through the oxidation of radical (III), hematein (HT) is formed, this being the stable oxidized form of hematoxylin (Scheme 1). Five different tautomeric forms can be written for hematein, but the values of their free Gibbs energies indicate that the most stable form among them is the HT structure presented in Scheme 1.³⁷ In the propagation reaction (Scheme 2), the radical (I) attacks a new molecule forming a hematoxylin dimer [d-HX (C[—]O)].

This dimer is easily oxidized to a radical-dimer. The radical-dimer attacks a new molecule of hematoxylin and forms the [t-HX C[—]O] trimer, and this chained process continues until obtaining the stable poly-hematoxylin macromolecule. Through the proposed mechanism, a polymer chain with [—]OH and quinone groups is obtained, which could explain the acid-base behaviour of polyhematoxylin. Other radical species can be stabilized in the termination stage, through dimerization, transposition, or by the reaction of transfer chain with the solvent.

Electro-Oxidation Process of Benzocaine on Pt electrode Studied by Cyclic Voltammetry

The electrochemical behavior of benzocaine, in order to propose a degradation mechanism, was studied by cyclic voltammetry in

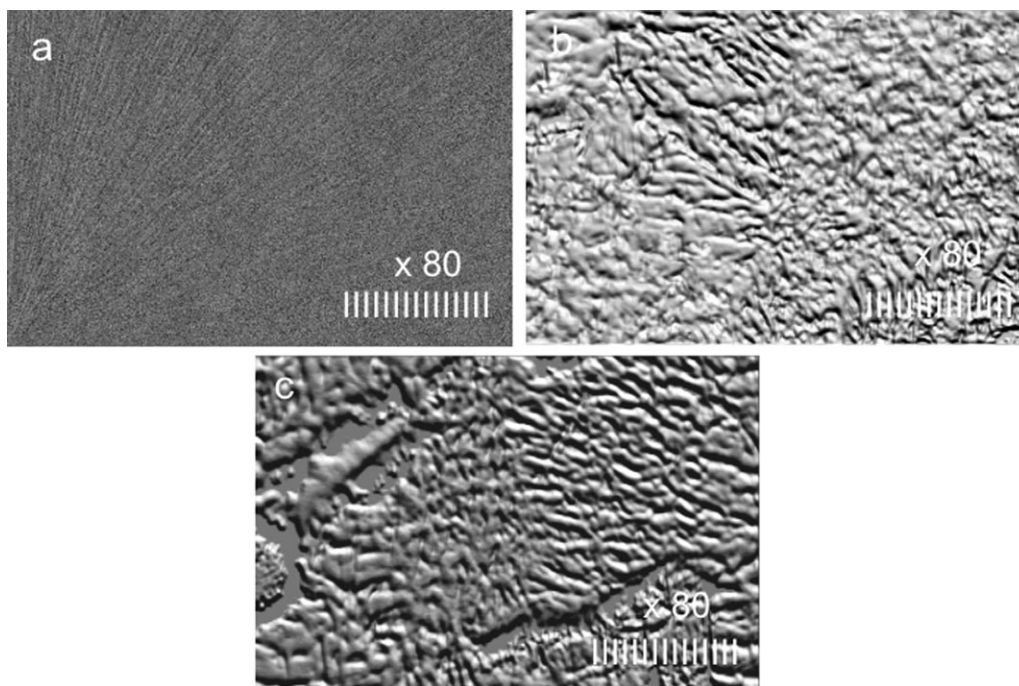


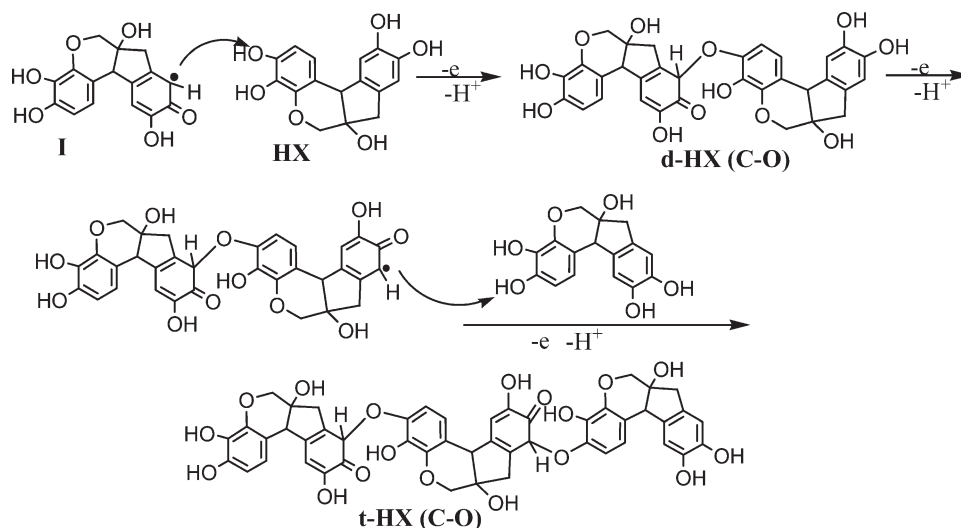
Figure 4. Microscopic images of platinum electrode surfaces: (a) reference sample, before cyclic voltammetry; (b) after 10.0 voltammetric cycles, in the potential range of -1.5 to 1.5 V vs. Ag/AgCl, of 10^{-4} mol L $^{-1}$ hematoxylin (HX) on platinum electrode (Pt) in 10^{-2} mol L $^{-1}$ NaNO $_3$ solution; (c) after EIS measured in the same conditions above mentioned, the electrodes relaxation time, in open circuit, being of 4 min between CV and EIS.

the potential range of -1.5 to 2.5 V, in the solution containing ethylic alcohol 1:100 (v:v) and 10^{-2} mol L $^{-1}$ NaOH (support electrolyte) in the absence and in presence of 10^{-4} mol L $^{-1}$ benzocaine. Figure 5 shows the cyclic voltammograms obtained in both cases.

It can be seen that the cyclic voltammogram obtained in the presence of benzocaine shows four oxidation peaks. O $_1$ and O $_2$ irreversible peaks identified at negative potentials of -0.8 V and -0.2 V, are not assigned to benzocaine electro-oxidation. These peaks are observed in the support electrolyte's cyclic voltammo-

gram too, and correspond to $-\text{OH}$ (O $_1$) ions oxidation, absorption and electro-oxidation of the ethylic alcohol (O $_2$). The irreversible peak O $_3$, from 1.2 V vs. Ag/AgCl, corresponds to the benzocaine oxidation by forming an amine radical. Through successive losses of electrons and protons, the amine radical is oxidized to a nitro compounds (Scheme 3).

With increasing anodic overvoltages, at potentials of about 1.9 – 2.0 V, an oxidation peak (O $_4$) is observed. This probably corresponds to further electrochemical oxidation of obtained derivatives (Figure 5). In the presence of protons, released in



Scheme 2. The propagation steps of the electrochemical hematoxylin polymerization mechanism.

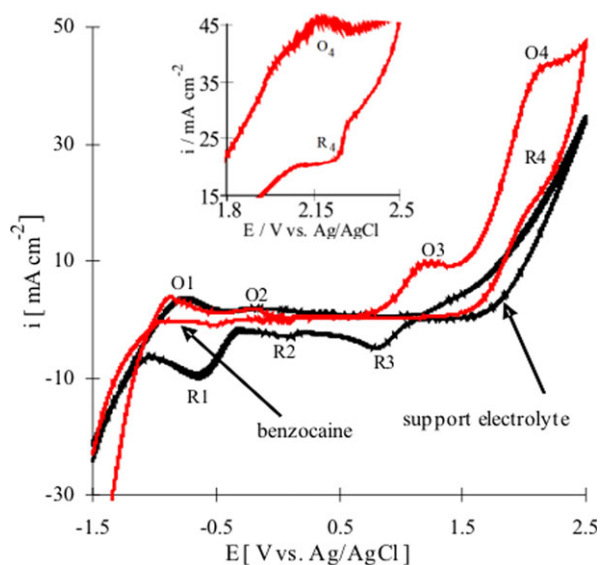
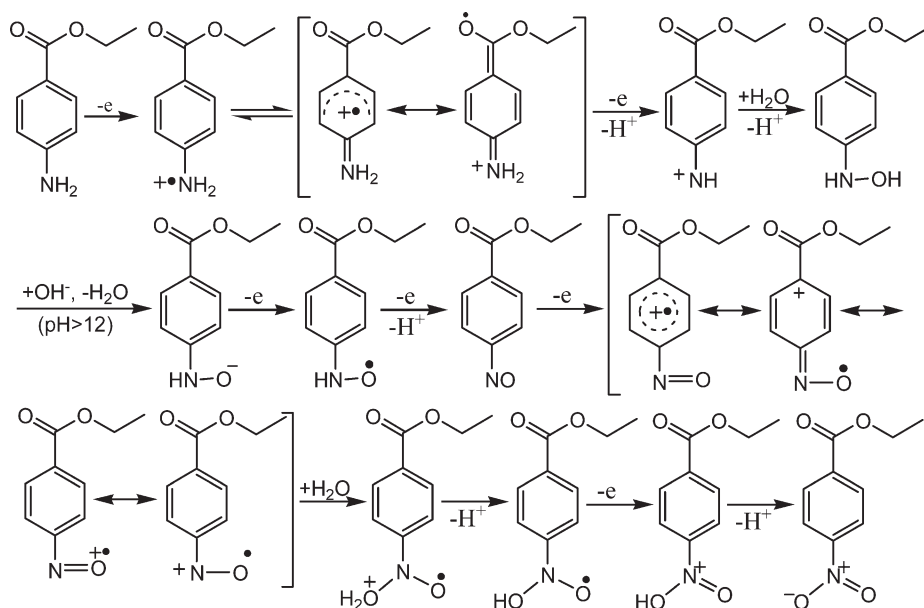


Figure 5. Cyclic voltammograms of solution containing ethylic alcohol 1:100 (v:v) and 10^{-2} mol L^{-1} NaOH (support electrolyte), and of 10^{-4} mol L^{-1} benzocaine added in the support electrolyte on platinum electrode (Pt); laboratory conditions: scan rate of 100 mV/s; pH = 12.2; room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

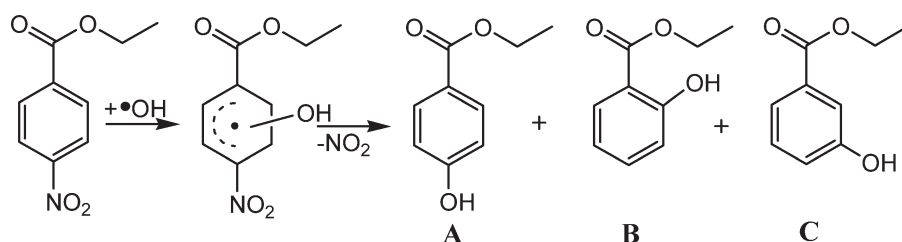
the direct oxidation process, the nitro group is partially reduced to nitroso group and/or hydroxyl amine. The process corresponds to the low intensity quasi reversible peak, R₄. The reduction peaks R₁, R₂, and R₃, identified at the potential values of -0.6, 0.1, and 0.8 V, are observed only on the cyclic voltammogram of support electrolyte, and can be attributed to the reduction of organic species, such as: acetaldehyde, acetic acid and formic acid, obtained from the electro-oxidation of the ethylic alcohol. The proposed mechanism for the electrochemical degradation of benzocaine consists in successive chemical and electrochemical stages to form the final products, such as: CO₂, H₂O, and NO₂.

In a first sequence, amine group is oxidized to NO₂. -NH₂ group has the highest susceptibility to oxidation indicating that, the peak corresponding at 1.2 V on cyclic voltammogram (O₃, Figure 5) is attributed to this oxidation. Nitrogen atom from -NO₂ group has the maximum oxidation state which may exist in organic compounds. Thus, further oxidation of the nitro-derivate involves further processes of removal of the NO₂ group. Hydroxyl radicals formed by anodic oxidation of corresponding ions attack the intermediate nitro-derivate with the elimination of -NO₂ group and formation of A, B and C products (Scheme 4).

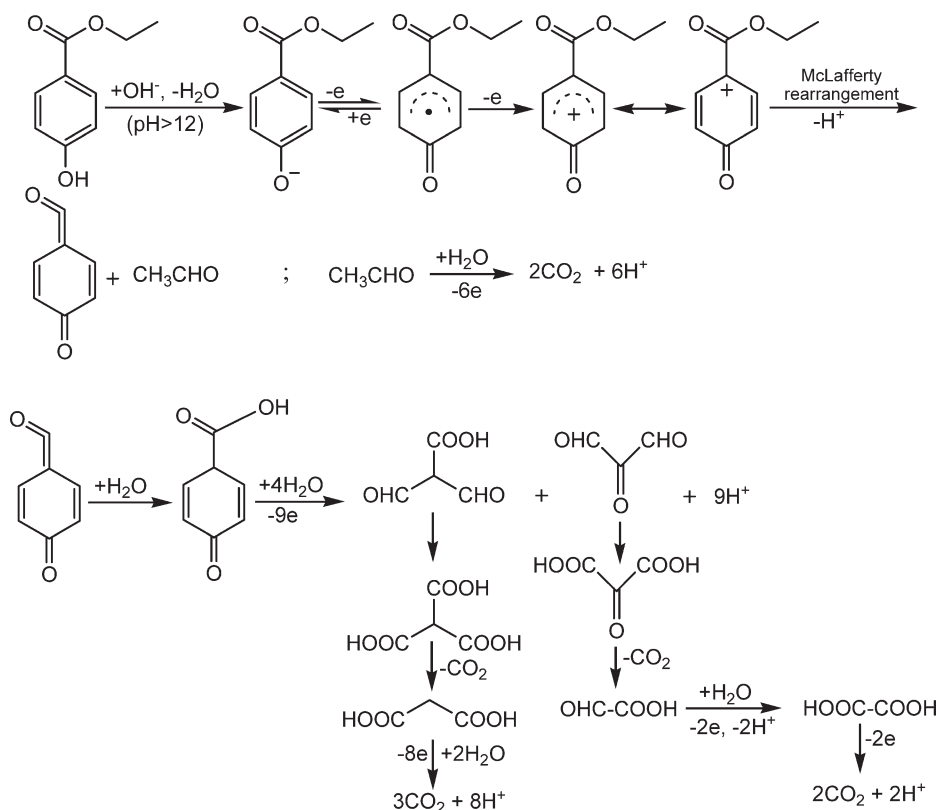
At potentials above 2.0 V, (A) intermediate oxidizes with the ring opening and smaller molecular weight intermediates are



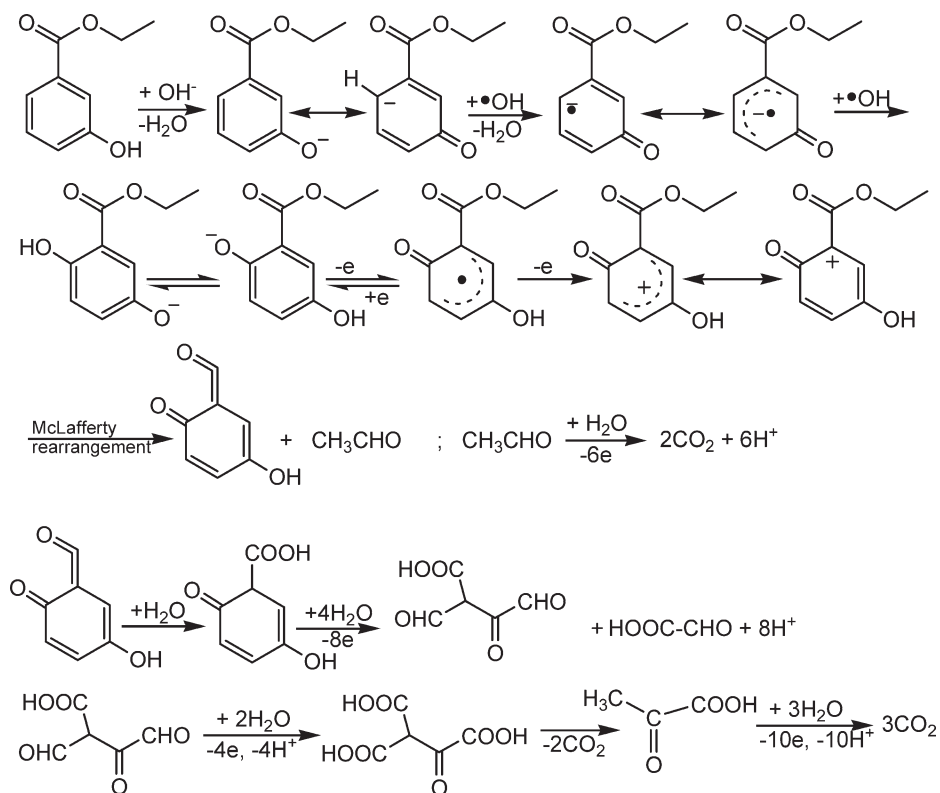
Scheme 3. Electrochemical oxidation mechanism of -NH₂ group to -NO₂ group.



Scheme 4. The mechanism of -NO₂ group elimination.



Scheme 5. Electrochemical oxidation mechanism of (A) intermediate.



Scheme 6. Electrochemical oxidation mechanism of (C) intermediate.

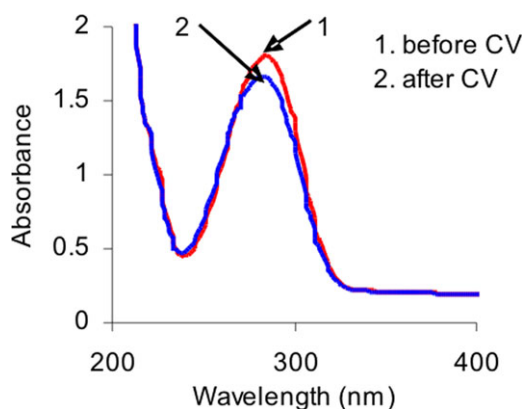


Figure 6. UV-Vis spectrophotometric scans of 10^{-4} mol L $^{-1}$ benzocaine in 10^{-2} mol L $^{-1}$ NaOH solution, before and after cyclic voltammetry. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formed, having mixed functionalities (carboxyl and carbonyl). Through carbonyl group oxidation and oxidative decarboxylation, (A) intermediate is degraded to inorganic final products (Scheme 5).

In a similar way takes place the oxidation of (B), with different oxidation of (C) (Scheme 6).

Several studies have reported different products of chemical benzocaine degradation, such as: p-aminobenzoic acid,^{38,39} ethyl ester of p-nitrobenzoic acid,^{38,39} or 4-amino-3-hydroxy-ethyl benzoate.³⁸ These studies provide that HX hydrolysis occurs under high temperature (70°C), after a period of 30 min.³⁸ In our experimental conditions p-amino benzoic acid formation is unlikely because the degradation process is not stimulated by temperature, and this occurs in short time. Thus, -NH₂ oxidation, primordial takes place, leading to the formation of ethyl ester of p-nitrobenzoic acid, corresponding to O₃ peak on the cyclic voltammogram. To confirm the benzocaine oxidation, its UV-Vis scans before and after cyclic voltammetry were recorded (Figure 6). It can be seen that, after cyclic voltammetry benzocaine absorbance decreases reaching a value of 1.66 compared with that was scanned before CV (1.8), without altering the wavelength of maximum adsorption (283 nm). This means that benzocaine was degraded in a proportion of 7.8%.

By successive oxidation and oxidative decarboxylation of intermediates, final organic products with low molecular weight like glyoxylic and pyruvic acids are formed, which can be easier oxidized than the initial (C) derivate to CO₂ and H₂O.⁴⁰

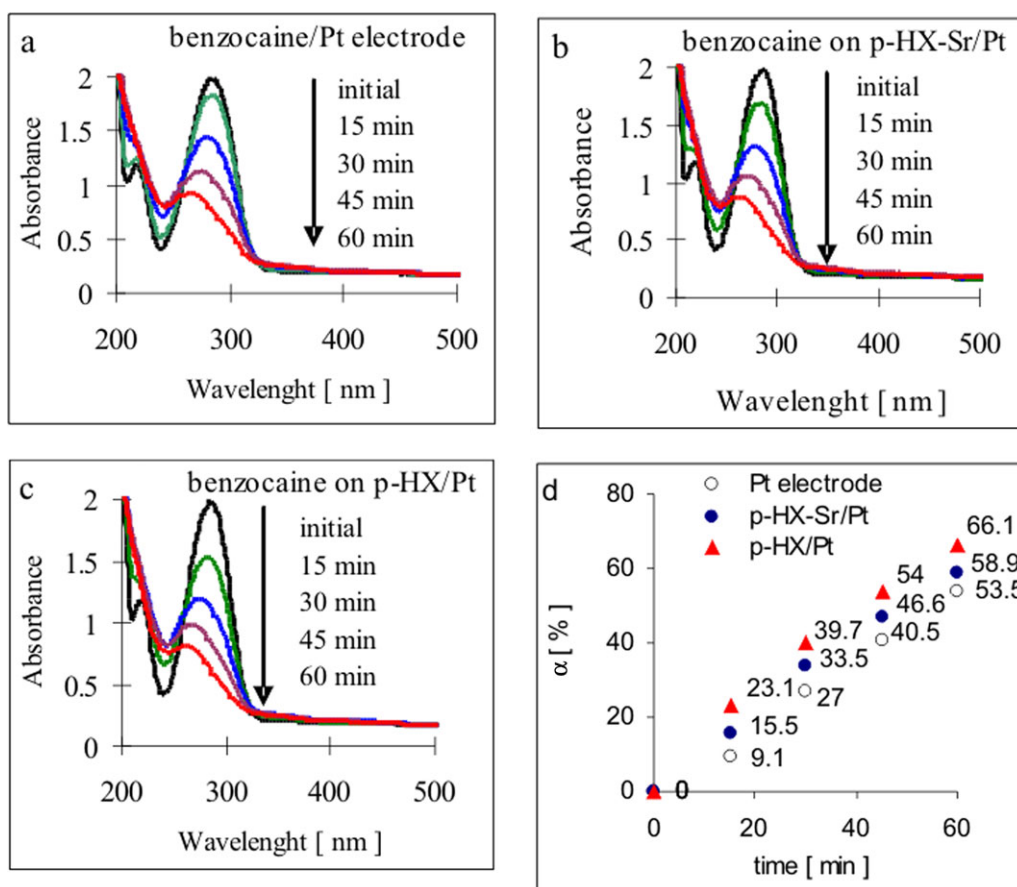


Figure 7. UV-Vis spectra and degradation degree of benzocaine in 10^{-2} mol L $^{-1}$ NaCl solution; applied current density of 50 mA cm $^{-2}$, at room temperature, on: (a) Pt electrode; (b) p-HX-Sr/Pt electrode; (c) p-HX/Pt electrode; (d) degradation degree of benzocaine on above mentioned electrodes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

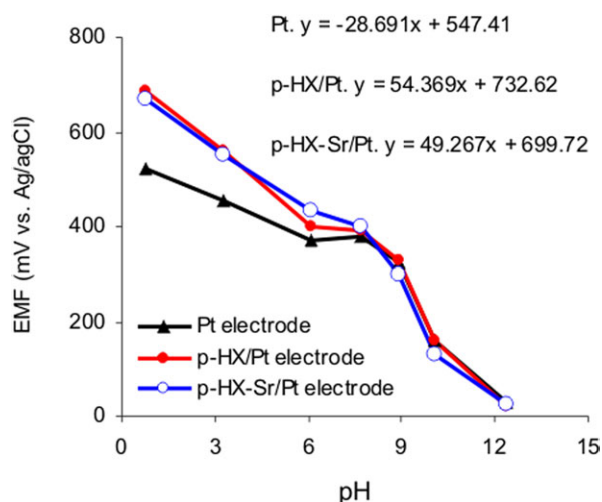
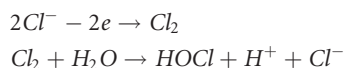


Figure 8. Electromotive force (EMF) variation with pH, corresponding to the cells, as follows: Pt- -Ag/AgCl; p-HX/Pt- -Ag/AgCl; and p-HX-Sr/Pt- -Ag/AgCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electrocatalytic Activity of Pt, p-HX/Pt, and p-HX-Sr/Pt Electrodes

The electrolyte solution containing 10^{-4} mol L $^{-1}$ benzocaine was electrolyzed in the presence of chloride ions (10^{-2} mol L $^{-1}$ NaCl) to generate active species of chlorine, in order to catalyze the degradation reaction of benzocaine. At sufficiently high concentration of chloride ions, formation and dissolution of chlorine occurs as follows:



In Figure 7(a) are presented the UV-Vis spectra recorded from 15 to 15 min for electrochemical degradation of benzocaine on platinum electrode. Also, similar spectra were obtained for degradation of benzocaine on electrochemically synthesized p-HX/Pt and p-HX-Sr/Pt electrodes [Figure 7(b,c)]. In Figure 7(d), the degradation degrees of benzocaine on three electrodes (Pt, p-HX/Pt and p-HX-Sr/Pt) are presented. These levels were calculated with the following relation, eq. (1):

$$\alpha = \frac{A_0 - A_t}{A_0} \cdot 100 \quad (1)$$

where A_0 is the initial absorbance and A_t is the absorbance at time “ t ”.

From Figure 7(d) it can be observed that on the Pt electrode, the degradation degree has the lowest value (53.5%) at the maximum electrolysis time of 1 h. Higher values of degradation degrees obtained for p-HX/Pt (66.1%) and p-HX-Sr/Pt (58.9%) electrodes, demonstrate the conductive properties of poly-hematoxylin films, and on the other hand their electrocatalytic properties.

Acid-base Behavior of Pt, p-HX/Pt and p-HX-Sr/Pt Electrodes

According to the electropolymerization mechanism, macromolecular chains present phenol and quinone groups. So, it is

therefore expected that poly-hematoxylin presents pH dependencies. Poly-hematoxylin behaviour were studied by recording the electromotive forces (EMF) values, which were determined in HCl solutions at different values of pH: 2; 4; 6 and NaOH solutions from pH = 14 to pH = 8, between Pt, p-HX/Pt and p-HX-Sr/Pt electrodes and AgAgCl_{sat}. Electromotive force dependence vs. pH is shown in Figure 8.

Note that, the electrodes show a linear variation of EMF in the pH range between 1 and 6. In the case of the p-HX/Pt electrode, electromotive force has a higher value than that corresponding to Pt electrode and as expected, a value very close to that of p-HX-Sr/Pt electrode. On the other hand, the slope (dEMF/dpH) in the range of pH (1 - 6) is almost double (see the equations inserted in the Figure 8). It can be concluded that the small changes in pH induce large variations of EMF, which means that, the poly-hematoxylin film induces at Pt substrate a greater sensitivity to pH.

CONCLUSIONS

Electrosynthesis of poly-hematoxylin films undoped and doped with strontium, on platinum electrode was performed using cyclic voltammetry. The influence of anodic potential and number of voltammetric cycles on poly-hematoxylin film formation was studied by electrochemical impedance spectroscopy. Optimal potential to obtain of poly-hematoxylin films on platinum electrode from 10^{-2} mol L $^{-1}$ NaNO $_3$ solution, were found by recording 10.0 voltammetric cycles at an anodic potential of 1.5 V. Optical microscopy images have revealed the presence of polymer films on platinum electrode surface.

Electrocatalytic activity of p-HX/Pt and p-HX-Sr/Pt electrodes was tested for benzocaine degradation from 10^{-2} mol L $^{-1}$ NaCl solution by applying in electrolysis bath a current density of 50 mA cm $^{-2}$, for 1.0 h. UV-Vis spectrophotometric scans were used to show that p-HX/Pt and p-HX-Sr/Pt electrodes have a higher electrocatalytic activity for benzocaine degradation than that platinum electrode. The highest value (66.1%) for the degradation degree of benzocaine was obtained on p-HX/Pt electrode.

The responses of p-HX/Pt and p-HX-Sr/Pt electrodes are more sensitive to pH than those of platinum electrode. Pt, p-HX/Pt, and p-HX-Sr/Pt electrodes show a linear variation of electromotive force in the pH range, of 1–6.

Both, mechanisms: of hematoxylin polymerization and benzocaine degradation were proposed. These mechanisms are in good agreement with the experimental observed data.

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