Talanta 81 (2010) 1522–1528

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A novel sensor for cephalosporins based on electrocatalytic oxidation by poly(o-anisidine)/SDS/Ni modified carbon paste electrode

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ARTICLE INFO

Article history:
Received 24 December 2009
Received in revised form 21 February 2010
Accepted 24 February 2010
Available online 3 March 2010

Keywords:
O-anisidine
SDS
Cephalosporins
Electrocatalytic oxidation
Nickel

ABSTRACT

In this work for first time, the electrocatalytic oxidations of some cephalosporins were carried out by poly(o-anisidine)/SDS/Ni modified carbon paste electrode using cyclic voltammetry, chronoamperometry and chronocoulometry methods. At first, poly(o-anisidine) was formed by cyclic voltammetry in monomer solution containing sodium dodesyl sulfate (SDS), on carbon paste electrode surface. Then, Ni(II) ions were incorporated to electrode by immersion of the polymeric modified electrode having amine group in 0.1 mol L^{-1} Ni(II) ion solution. A good redox behavior was observed for the $Ni(OH)_2$/NiOOH couple on the surface of this electrode. Cephalosporins were successfully oxidized on the surface of this nickel ions dispersed poly(o-anisidine) modified carbon paste electrode. The electrocatalytic oxidation peak currents of cephalosporins were linearly dependent on their concentration. Electrode was successfully applied to determine cephalosporins in pharmaceutical preparations.

1. Introduction

Cephalosporins are the second major group of β-lactam antibiotics [1]; they are classified into four generations. These are widely used in clinical therapy for the treatment of severe defection because of their antibacterial and pharmacokinetic properties [2–6]. Up to now, several methods, such as spectrophotometric [7–10] and chromatographic [11–15] techniques, have been applied to study cephalosporins. However, the detection of these sulfur-containing compounds by spectrophotometry is not effective, because these compounds do not absorb light [16] and their derivatization is sophisticated [17,18]. So applying a simple and easy technique has been urgently desired to detect cephalosporins. Electrochemical methods, due to their rapidity, simplicity and high sensitivity in analysis, have been favored to study compounds such as cephalosporins and cepfamycins [19]. Although carbon, platinum, mercury and gold as a working electrodes have been utilized in electrochemical study of sulfur-containing compounds [20,21], the sever detection conditions can damage the electrode and fluctuating background currents can be formed on their surface [16]. To reduce these problems, some researchers used the modified electrodes. Recently, modified electrodes with metallic microparticles electrodeposited into the polymeric matrix, have been exploited to determine various species [22–24]. Among a number of polymeric metal complexes, those containing Ni(II)/Ni(III) redox couple have received considerable attention in recent years [25–27].

Nickel oxyhydroxide complex modified electrodes have been examined for many interesting reactions, such as oxidation and the determination of some organic and biologically important compounds including carbohydrates [28], alcohols [29–33], alditols [34], amino acids [35], hydrogen peroxide [36], dopamine [37] and drugs [5,38]. Nickel oxyhydroxide modified electrodes are practically appropriate for these applications because of their acceptable chemical and thermal stability.

Previously, we utilized Ni/poly(1-naphtylamine) and Ni/poly(o-aminophenol) modified carbon paste electrode for electrocatalytic oxidation of several carbohydrates [23,39] and methanol [40,41]. These studies showed that metal-polymer modified carbon paste electrodes are easy to prepare, and stable for a long period of time with acceptable reproducibility, detection limits and wide linear range responses. All these results encouraged us to continue the studies with new polymer materials.

In this work, we decided to use the above-mentioned advantageous properties of the nickel-polymer modified carbon paste electrodes again for the aim of electrocatalytic oxidation of three cephalosporin drugs containing cefixime, ceftriaxone and ceftizoxime (Scheme 1) by the use of the poly(o-anisidine). A brief glance at the literatures indicates that electrocatalytic oxidations of cefixime and ceftizoxime have not been reported with any catalyst. Nor has electrocatalytic oxidation of ceftriaxone by Ni been reported. In this context, at the first step, o-anisidine monomer was electropolymerized on the surface of carbon paste electrode in the presence of SDS. Then, nickel ions were incor-

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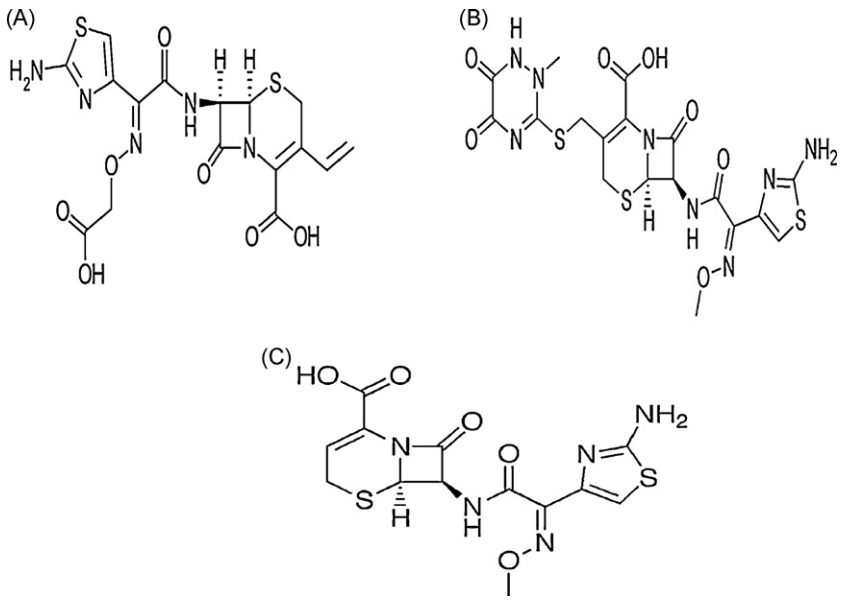
doi:10.1016/j.talanta.2010.02.062



Scheme 1. Structure of (A) cefixime, (B) ceftriaxone and (C) ceftizoxime.

porated into the polymeric matrix by immersing the polymeric modified electrode in a nickel nitrate solution. The efficiency of this nickel-modified polymeric carbon paste electrode as a sensor for the electrocatalytic oxidation and consequently the determination of the cephalosporins in alkaline medium were investigated.

2. Experimental

2.1. Reagents and materials

The solvent applied in this work was twice distilled water. Sulfuric acid from Fluka was used as the supporting electrolyte. The o-anisidine from Merck was used as it was received. Sodium hydroxide used in this work was analytical grade of Merck origin which was used without further purification. High viscosity paraffin (density: 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter: 0.10 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

2.2. Sample preparation

To analyze the tablets, the average mass of three tablets was determined. The tablets were finely powdered and homogenized in a mortar. An appropriate, accurately weighed amount of the homogenized powder was transferred into a 100 ml calibrated flask containing 50 ml of 0.1 mol L^{-1} sodium hydroxide solution. The contents of flask were sonicated for 10 min; the undissolved excipients were removed by filtration and then diluted to volume with the same supporting electrolyte. Appropriate solutions were prepared by taking suitable aliquots of the clear filtrate and then diluting them with 0.1 mol L^{-1} sodium hydroxide.

2.3. Instrumentation

Electrochemical experiments were carried out on 746VA Trace Analyzer Metrohm potentiostat with a Metrohm voltammetry cell in a three electrode configuration. An Ag/AgCl was used as reference electrode and a platinum wire was the auxiliary electrode. Working electrode was nickel/poly(o-anisidine) carbon paste electrode (Ni/POA/CPE).

2.4. Preparation of working electrode

A mixture of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulted paste was then inserted in the bottom of a glass tube (internal radius: 1.7 mm). The electrical connection was implemented by a copper wire lead fitted into the glass tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste with a stainless steel rod and smoothing the resulting surface on white paper until a smooth shiny surface was observed. Ni/POA/CPE was prepared by electropolymerization of o-anisidine at the surface of CPE in the presence of SDS and follow up incorporating the Ni ions to the polymer backbone.

3. Results and discussion

3.1. Electrochemical polymerization

Previously, poly(o-anisidine) films were obtained on the surface of Au and Pt electrodes by the use of cyclic voltammetric method [42,43]. In this work, we investigated the preparation of poly(o-anisidine) on the surface of carbon paste electrode in the absence and presence of SDS. Fig. 1A shows the typical multisweep cyclic voltammograms during the electropolymerization of o-anisidine in the absence of SDS. As it is seen in this figure, o-anisidine oxidizes irreversibly in 870 mV without corresponding cathodic processes in the reverse scan. During the next cycles, two redox peaks in lower potentials appeared and their current did not increase considerably with potential cycling. In order to grow polymer, often either high monomer concentration or long time of potential cycling can be conducted after adding 5 mmol L^{-1} anionic surfactant of SDS to monomer solution the monomer oxidation, potential was shifted to less positive potentials (by almost 100 mV, see Fig. 1B) and its oxidation current increased. Moreover, the rate of polymerization increased considerably and its growth did not stop. The effect of surfactant addition on the rate of polymerization was previously reported for other polymers [44,45].

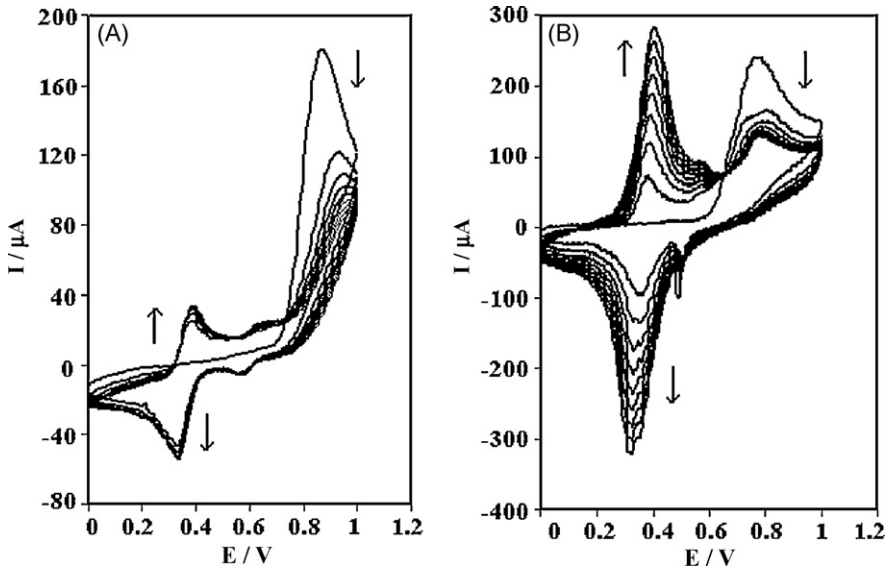


Fig. 1. Electropolymerization of POA in the solution of 5 mmol L^{-1} OA monomer/0.5 mol L^{-1} H_2SO_4 at the surface of carbon paste electrode (A) in the absence and (B) in presence of 5 mmol L^{-1} SDS at scan rate of 100 mV s^{-1}. The arrows indicate the trends of current during CVs.

After polymer was prepared, the electrode was removed, rinsed with water and the sides were wiped with soft tissue paper. The redox behavior of the film was strongly dependent on the pH of the electrolyte solution. This obtained polymer shows a well defined redox behavior in acidic supporting electrolyte solution. The response obtained in an alkaline solution (0.1 mol L^{-1} NaOH) showed a complete loss of electrode activity in the potential range from 0.0 to 0.9 V. However, the film was not damaged under these experimental conditions and its response was recovered when the electrode was immersed in an acidic supporting electrolyte solution.

3.2. Incorporation of Ni(II) ions into o-anisidine film

In order to incorporate Ni(II) ions into the POA film, the freshly electropolymerized CPE was placed at open circuit in a well stirred aqueous solution of 0.1 mol L^{-1} $Ni(NO_3)_2$. Nickel was accumulated by complex formation between Ni(II) in solution and amines sites in the polymer backbone [46,47] in a given period of time (t_a, accumulation time). The polarization behavior was examined in 0.1 mol L^{-1} NaOH for Ni/POA/CPE using cyclic voltammetry. This technique allows the oxide film formation in parallel with inspecting the electrochemical reactivity of the surface [48]. Voltammograms were recorded by cycling the potential between 0.1 and 0.65 V at 100 mV s^{-1} until a stable voltammogram was obtained. Fig. 2 shows the electrochemical response of the POA/CPE and Ni/POA/CPE after polarization in 0.1 mol L^{-1} NaOH solution.

From Fig. 2, it is seen that whereas neither oxidation nor reduction took place on the POA/CPE, a well developed redox wave was observed on the Ni/POA/CPE when the potential was swept and cycled between 0.2 and 0.65 V. These redox waves are related to the oxidation of $Ni(OH)_2$ to NiOOH and reduction of NiOOH to $Ni(OH)_2$ with a peak potential of 0.48 and 0.38 V, respectively. The surface coverage of the immobilized active substance (Ni(II)) in the films was evaluated from the charge under the current–potential wave (Fig. 2b) with correction for the baseline ($\Gamma^* = Q/nFA$). The value of Γ^* for Ni/POA/CPE was 1.43×10^{-5} mol cm^{-2}. Fig. 3 shows the cyclic voltammograms of Ni/POA/CPE in 0.1 mol L^{-1} NaOH solution at different potential sweep rates in a wide range of 10–400 mV s^{-1}. As it is seen, the peak-to-peak separation potential ($\Delta E_p = E_{pa} - E_{pc}$) of the cyclic voltammograms increased with scan rate. For $\Delta E_p > 200/n$ mV, which is commonly obtained at

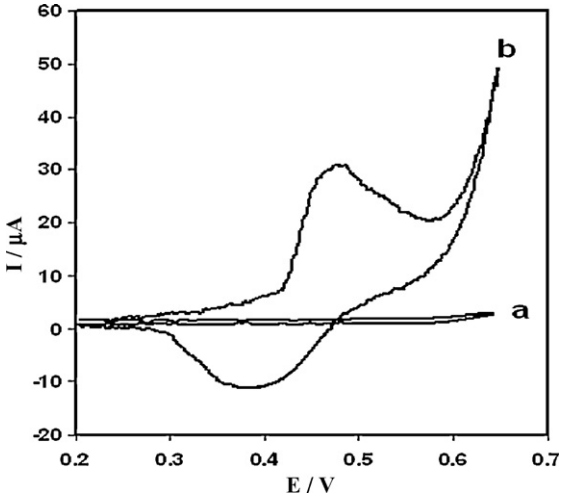


Fig. 2. Electrochemical responses of electrodes: (a) POA/CPE and (b) Ni/POA/CPE, in 0.1 mol L^{-1} NaOH solution, scan rate 10 mV s^{-1}.

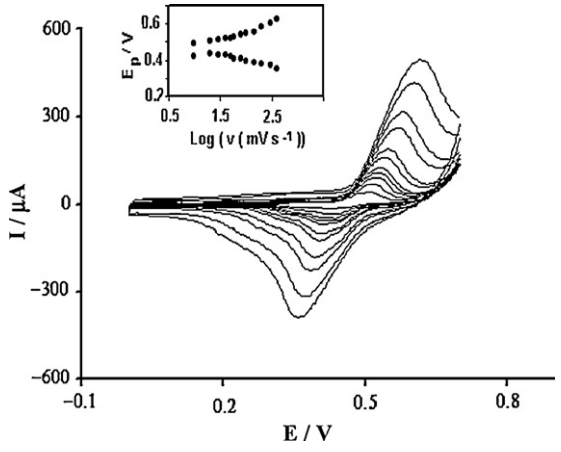


Fig. 3. Main panel: cyclic voltammograms of Ni/POA/CPE in 0.1 mol L^{-1} NaOH solution. Potential sweep rates from inner to outer are: 10, 20, 30, 40, 50, 80, 100, 150, 200, 300 and 400 mV s^{-1}. Inset: plot of E_p versus log ν for cyclic voltammograms depicted in the main panel.

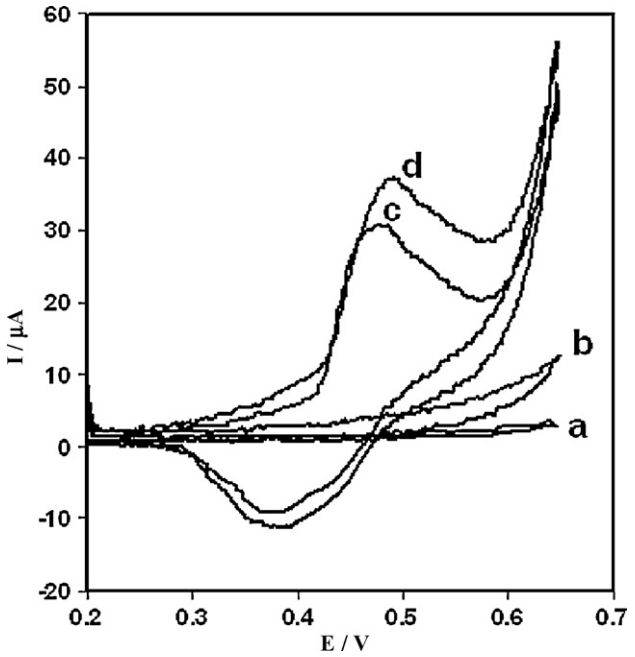


Fig. 4. Electrochemical responses of POA/CPE prepared in the presence of SDS to: (a) 0 mmol L^{-1}, (b) 0.3 mmol L^{-1} cefixime and Ni/POA/CPE to: (c) 0 mmol L^{-1} and (d) 0.3 mmol L^{-1} cefixime in 0.1 mol L^{-1} NaOH solution, scan rate 10 mV s^{-1}.

higher scan rates, the following relations were proposed by Laviron [44,49]:

$$E_{pa} = E^0 + A \ln\left[\frac{1-\alpha}{m}\right] \quad (1)$$

$$E_{pc} = E^0 + B \ln\left[\frac{\alpha}{m}\right] \quad (2)$$

where $A = RT/(1-\alpha)nF$, $B = RT/\alpha nF$ and $m = (RT/F)(k_s/n\nu)$.

From these expressions, it is possible to determine the transfer coefficient (α) by measuring the variation of the peak potentials with scan rate (ν). A plot of E_p versus log ν yields two straight lines with slopes equal to $2.3RT/\alpha nF$ and $2.3RT/(1-\alpha)nF$ for the cathodic and anodic peaks, respectively. The inset of Fig. 3 shows the plot of E_p versus log ν with slops equal to 0.164 and 0.089 for anodic and cathodic peaks. Using the slopes of plots, the value of α was determined as 0.65.

Another point in these voltammograms is that anodic and cathodic peak currents are linearly proportional to the potential sweep rate at low values from 10 to 50 mV s^{-1} (not shown). This can be attributed to an electrochemical activity of an immobilized redox couple at the surface. In the higher range of potential sweep rates (70–400 mV s^{-1}) (not shown), the peak currents depend on square root of the potential sweep rate, signifying the dominance of a diffusion process, considered as the rate limiting step in the total redox transition of the modifier film. This limiting diffusion process was also reported for other Ni modified electrodes [35,50].

3.3. Electrocatalytic oxidation of cephalosporins on the modified electrode

3.3.1. Cyclic voltammetry studies

In this work, the oxidation of cefixime was first studied at a POA/CPE electrode (without the incorporation of nickel) by cyclic voltammetric experiments in 0.1 mol L^{-1} NaOH. Typical results obtained for a potential scan from 0.2 to 0.65 V versus Ag/AgCl are shown in Fig. 4. The electrochemical response of POA/CPE in the absence of cefixime is shown in Fig. 4(a); the addition of 0.3 mmol L^{-1} cefixime to the alkaline solution did not influence the electrochemical response of the POA/CPE (Fig. 4(b)) for analytical purpose. The electrochemical response of a Ni/POA/CPE in alkaline solution (i.e., 0.1 mol L^{-1} NaOH) exhibits well defined anodic and cathodic peaks (Fig. 4(c)) associated with the $Ni(OH)_2$/NiOOH redox couple. As it is seen in Fig. 4(d), after adding cefixime (0.3 mmol L^{-1}) anodic peak current increased and cathodic peak current decreased.

This behavior is a typical observation expected from the mediated oxidation (EC′ mechanism), illustrated in the following:

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \qquad E$$

$$NiOOH + \text{cefixime} \rightarrow Ni(OH)_2 + \text{product} \qquad C'$$

Thus, the Ni/POA/CPE can catalyze the electrooxidation of cefixime due to the existence of $Ni(OH)_2$ in the poly(o-anisidine) film. This modified electrode exhibited similar electrocatalytic responses for the other cephalosporins (Fig. 5A and B), exhibiting its capability for selective oxidation of cephalosporins both in the laboratory and on a technical scale.

Cyclic voltammograms of the Ni/POA/CPE in the presence of 1.5 mmol L^{-1} cefixime at various scan rates were recorded (Fig. 6A). When scan rate increased, the peak potential for the catalytic oxidation of cefixime shifted to increasingly positive potentials, suggesting a kinetic limitation in the reaction between the redox sites of the Ni/POA/CPE and cefixime. Fig. 6B shows that the oxi-

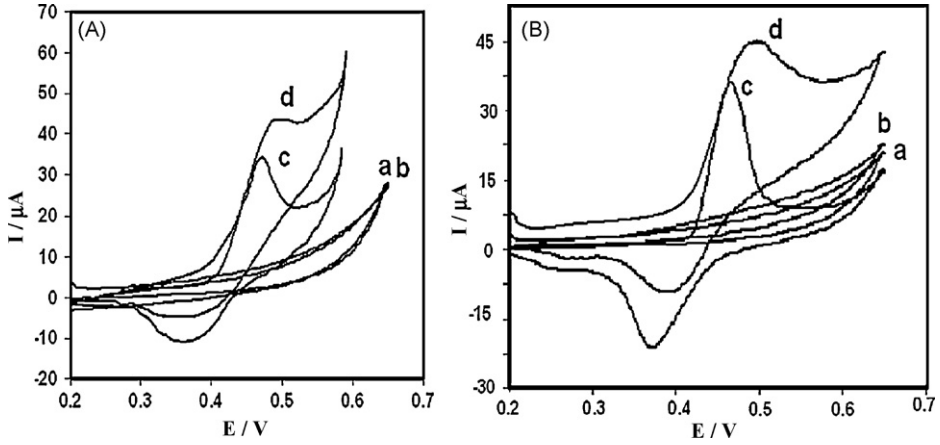


Fig. 5. (A) Electrochemical responses of POA/CPE to: (a) 0 mmol L^{-1}, (b) 0.3 mmol L^{-1} ceftriaxone and Ni/POA/CPE to: (c) 0 mmol L^{-1} and (d) 0.3 mmol L^{-1} ceftriaxone in 0.1 mol L^{-1} NaOH solution, scan rate 10 mV s^{-1}. (B) Such as (A) for ceftizoxime.

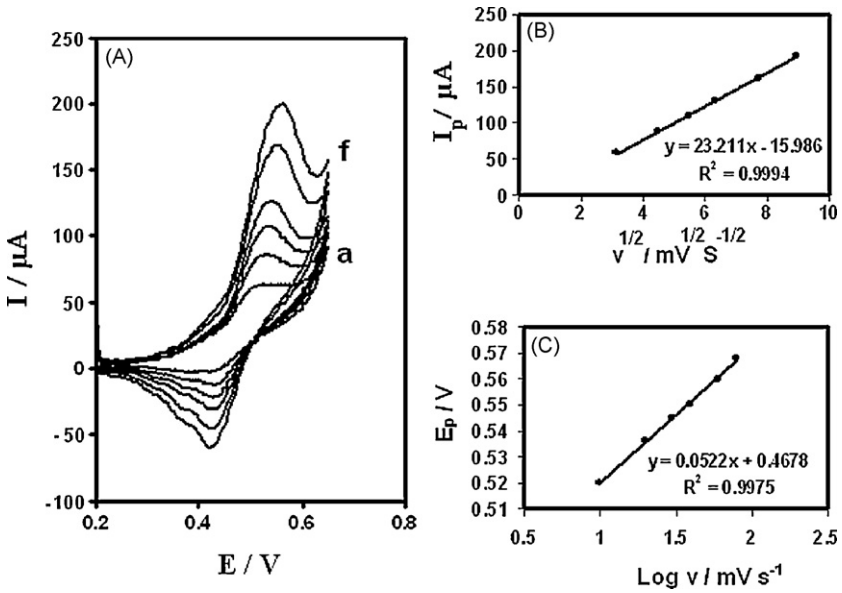


Fig. 6. (A) cyclic voltammograms of the Ni/POA/CPE in 0.1 mol L^{-1} NaOH solution containing 1.5 mmol L^{-1} cefixime at the scan rates: (a) 10 mV s^{-1}, (b) 20 mV s^{-1}, (c) 30 mV s^{-1}, (d) 40 mV s^{-1}, (e) 60 mV s^{-1} and (f) 80 mV s^{-1}, respectively. (B) Variations of I_{pa} versus $v^{1/2}$. (C) Dependence of the peak potential, E_p on log v for the oxidation of cefixime at Ni/POA/CPE.

dation current for cefixime increased linearly with the square root of the scan rate, suggesting that the reaction is mass transfer controlled.

In order to obtain information about the rate determining step, the Tafel slope, b, was determined applying the following equation, which is valid for a totally irreversible diffusion controlled process [51].

$$E_p = \frac{b}{2}\log v + \text{constant}$$

On the basis of the above equation, the slope of E_p versus log v plot is $b/2$, where b indicates the inverse of Tafel slope. As it is seen in Fig. 6C, the slope of the E_p versus log v plot was found to be 0.0522 V for cefixime, so, b = 0.1044 V. This slope indicates that a one electron transfer process is the rate limiting step, assuming a transfer coefficient of α = 0.56 for cefixime. By the use of this method, values of α for ceftriaxone and ceftizoxime were calculated and reported in Table 1.

3.3.2. Chronoamperometric studies

Double potential step chronoamperometry, as well as other electrochemical methods, was employed for the investigation of electrochemical processes at Ni/POA/CPE. The main panel of Fig. 7 represents the current–time profiles obtained by setting the working electrode potential at 500 mV (first potential step) and 350 mV (second potential step) for various concentrations of cefixime. The forward and backward potential step chronoamperometry of the modified electrode in the blank solution showed an almost symmetrical chronoamperogram, which shows that almost equal charges were consumed for the oxidation and reduction of surface confined Ni(OH)$_2$/NiOOH sites. However, in the presence of cefixime, the charge value associated with the forward chronoamperometry, Q is greater than that observed for the backward chronoamperometry (Fig. 7, inset A).

The rate constant for the chemical reaction between the cefixime and redox sites of Ni/POA/CPE can be evaluated by chronoamperometry according to the method described in the literature [52].

$$\frac{I_C}{I_L} = \gamma^{1/2}\left[\pi^{1/2}\text{erf}(\gamma^{1/2}) + \frac{\exp(-\gamma)}{\gamma^{1/2}}\right]$$

where I_C is the catalytic current of the Ni/POA/CPE in the presence of cefixime, I_L is the limiting current in the absence of cefixime and $\gamma = kc_o t$ (c_o is the bulk concentration of cefixime) is the argument of the error function. In the cases where γ exceeds 1.5, the error

Table 1
Analytical and electroanalytical parameters for oxidation of various cephalosporins at the Ni/POA/CPE.

Compounds	α	k (cm^3 mol^{-1} s^{-1})	DR (mmol L^{-1})	LOD (mmol L^{-1})
Cefixime	0.56	2.03×10^6	0.08–2	0.05
Ceftriaxone	0.54	2.7×10^6	0.06–1	0.04
Ceftizoxime	0.58	8.8×10^5	0.1–2	0.08

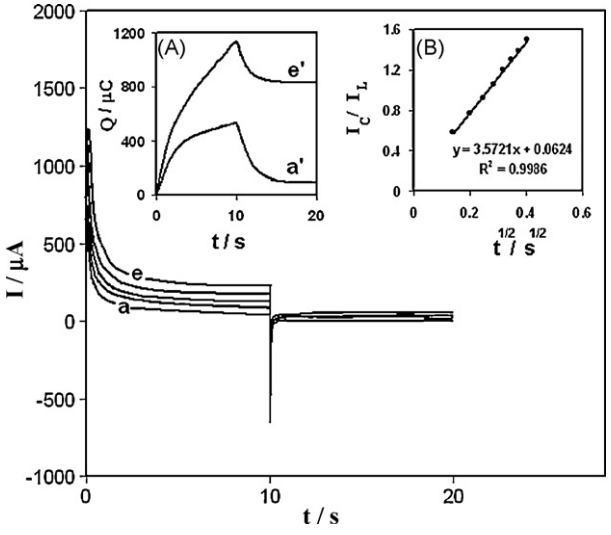


Fig. 7. Chronoamperograms obtained at the Ni/POA/CPE in the (a) absence and presence of (b) 0.2 mmol L^{-1}, (c) 0.8 mmol L^{-1}, (d) 1.4 mmol L^{-1} and (e) 2 mmol L^{-1} of cefixime in 0.1 mol L^{-1} NaOH solution, first and second potential steps were 0.5 and 0.35 V versus Ag/AgCl, respectively. Inset (A) dependence of Q (μC) versus t, (a′) and (e′), respectively derived from the data of chronoamperograms of (a) and (e). Inset (B) dependence of I_C/I_L on $t^{1/2}$ derived from the data of chronoamperogams of (a) and (e) in the main panel.

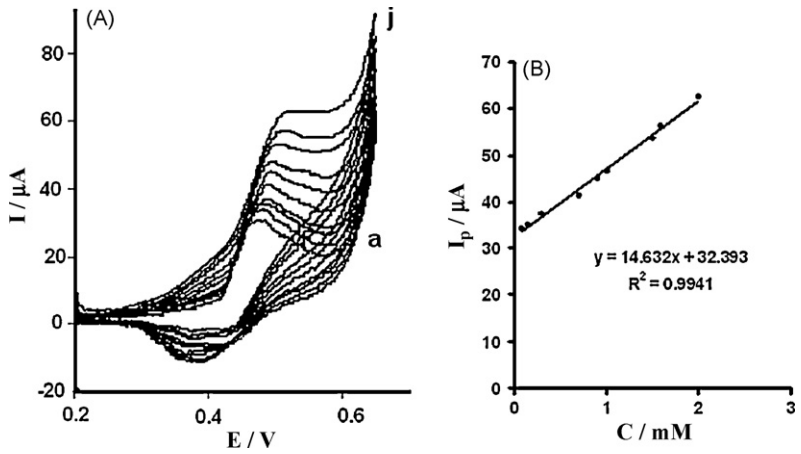


Fig. 8. (A) Current–potential curves for oxidation of cefixime at the Ni/POA/CPE in 0.1 mol L^{-1} NaOH solution with different concentrations of cefixime: (a) 0 mmol L^{-1}, (b) 0.08 mmol L^{-1}, (c) 0.15 mmol L^{-1}, (d) 0.3 mmol L^{-1}, (e) 0.7 mmol L^{-1}, (f) 0.9 mmol L^{-1}, (g) 1 mmol L^{-1}, (h) 1.5 mmol L^{-1}, (i) 1.6 mmol L^{-1} and (j) 2 mmol L^{-1}. (B) Plot of I_p versus c.

Table 2
Determination of cephalosporins in pharmaceutical preparation ($n = 5$).

Compounds	Amount labeled (g)	Amount found (g)	Percentage	RSD (%)
Cefixime (tablet)	0.2, 0.4	0.206, 0.408	103, 102	2.3, 2.4
Ceftriaxone (vial)	1.0	1.05	105	2.4
Ceftizoxime (vial)	1, 2	1.08, 2.12	108, 106	2.3, 2.5

function is almost equal to 1 and the above equation can be reduced to:

$$\frac{I_C}{I_L} = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kc_o t)^{1/2}$$

where k, c_o and t are the catalytic rate constant ($cm^3\ mol^{-1}\ s^{-1}$), cefixime concentration ($mol\ cm^{-3}$) and time elapsed (s), respectively. From the slope of the I_C/I_L versus $t^{1/2}$ plot we can simply calculate the value of k for a given concentration of substrate. Inset (B) of Fig. 7 shows one such plot, constructed from the chronoamperogram of the Ni/POA/CPE in the absence and presence of 2 mmol L^{-1} cefixime. The mean value for (k) was found to be $2.03 \times 10^6\ cm^3\ mol^{-1}\ s^{-1}$. The values of k for ceftriaxone and ceftizoxime and cefixime were found by chronoamperometry according to the method described above and are reported in Table 1.

3.3.3. *Electrocatalytic determination of cefixime*

Fig. 8 shows the cyclic voltammograms of the Ni/POA/CPE in the presence of cefixime. As it is seen in Fig. 8A, Ni/POA/CPE exhibits a well defined catalytic oxidation current increasing linearly as cefixime concentration increases. Calibration plot for analysis of cefixime (Fig. 8B) shows linear dependence of the anodic peak current on cefixime concentrations in range of 0.08–2 mmol L^{-1} and a correlation coefficient of 0.9941. A limit of detection of 0.05 mmol L^{-1} has been obtained from three times the standard deviation of the blank per the slope of calibration plot. This modified electrode exhibited similar concentration dependent profiles for ceftriaxone and ceftizoxime. The analytical parameters are listed in Table 1.

The applicability of the proposed voltammetric method for the sample dosage form was examined by analyzing the tablets and vials. It was found that the drug concentrations determined using this method are in good agreement with the reported values. The values of experimentally determined drugs and the declared values in tablets and vials are tabulated in Table 2.

4. Conclusion

In this paper POA/CPE was prepared with electropolymerization of o-anisidine on carbon paste electrode in the presence of SDS. Adding SDS to monomer solution led to increasing the polymer growth rate. Ni/POA/CPE was fabricated by open circuit accumulation of Ni(II) ions at the surface of POA/CPE and the produced electrode can catalyze the oxidation of cephalosporins via a surface layer mediated charge transfer. Using cyclic voltammetry and chronoamperometry techniques, the kinetical parameters of this drug, such as charge-transfer coefficient and catalytic reaction rate constant for oxidation, were determined. The value of the rate constant k obtained from the chronoamperometric method indicated that the modified electrode can overcome the kinetic limitations for cephalosporins oxidation by a catalytic process and can decrease the overpotential for the oxidation reaction. According to the experimental results the catalytic oxidation current of cephalosporins at the Ni/POA/CPE can be used to determine cephalosporins in aqueous solution, so an acceptable linear dynamic range and detection limit can be obtained. The electrode can be prepared simply and can be used for simple, selective and precise voltammetric determination of cephalosporins in pharmaceutical preparations.

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