

Electrochemical Sensor for Amoxicillin Using Cu/Poly (*o*-Toluidine) (Sodium Dodecyl Sulfate) Modified Carbon Paste Electrode¹

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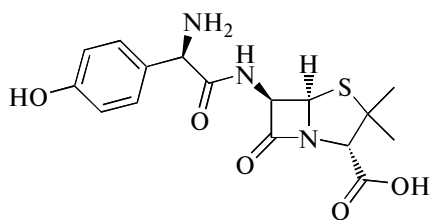
Abstract—Poly(*o*-toluidine) (sodium dodecyl sulfate) (POT(SDS)) film was electrosynthesized on carbon paste electrode (CPE) by using the cyclic voltammetry technique in aqueous solution containing *o*-toluidine (OT), sulfuric acid and SDS. Then, copper oxide was incorporated by immersion of POT(SDS)/CPE in a solution of copper sulfate and using constant potential method. Then, the electrochemical characterization of the modified electrode is presented in alkaline solution. For the first time, electrochemical behaviour of amoxicillin (AMX) at the Cu/POT(SDS)/CPE has been investigated using cyclic voltammetry (CV) and chronoamperometric method. The experimental results suggest that the modified electrode exhibits electrocatalytic effect on the oxidation of AMX resulting in a marked enhancement of the anodic peak current response. Under the selected conditions, the anodic peak current was linearly dependent on the concentration of AMX in the range 80–200 and 5–150 μM with CV and amperometric method, respectively. The detection limits (2σ) were also estimated to be 60 and 3 μM . Some kinetic parameters such as the transfer second-order rate constant ($k = 4.9 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) of AMX was calculated. Therefore, this modified electrode was a simple, rapid and new electrode to determine AMX in pharmaceutical preparations.

Keywords: electropolymerization, amoxicillin, electrocatalytic oxidation, copper

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1. INTRODUCTION

AMX (scheme), 6-(*p*-hydroxy- α -amino phenyl acetoamido) penicillanic acid, is one of the more important antibiotics used in the treatment of bacterial infections because of its fair safety and efficacy. It is the *p*-hydroxy analogue of ampicillin but possesses some significant advantage over ampicillin; include more complete gastrointestinal absorption, and little or no effect on absorption of food [1]. As the clinical use of AMX became common, methods for its quantification in drugs and biological fluids have attracted the attention of investigators. Various analytical methods have been reported for the separation and determination of AMX such as spectroscopy [2–5], capillary electrophoresis [6, 7], high performance liquid chromatography [8–10] and electrochemical methods [11, 12].



Scheme. Molecular structure of AMX.

Electrochemical techniques have shown to be excellent procedures for the sensitive determination of drugs and related molecules in pharmaceutical sample and biological fluids [13, 14]. The advancements in electrochemical techniques in drug analysis are attributed to their simplicity, low cost, and relatively short time of analysis, compared with the other techniques.

On the other hand, earlier studies with polymer modified electrodes showed an enhanced response for the determination of various biologically and clinically important species because of the increased number of active sites in the polymer film than at the monolayer-modified electrode [15].

Also, the use of noble metals such as platinum, palladium, rhodium, iridium and gold, are well-known oxidation catalysts with high activity and stability and have been successfully used incorporated in polymer modified electrodes [16–20]. However, due to the high cost of these metals, attention has been given to non noble metal based catalysts, such as copper. It has proved to be electrocatalytic active for biosensing of glucose and carbohydrates [21], saccharides, alditols, amino acids, alcohols, and amines [22], organic compounds [23], volatile organic compounds [24], cyanides [25] and nitrites [26], owing to the excellent electrocatalytic activity of copper oxide towards the oxidation/reduction of these analytes.

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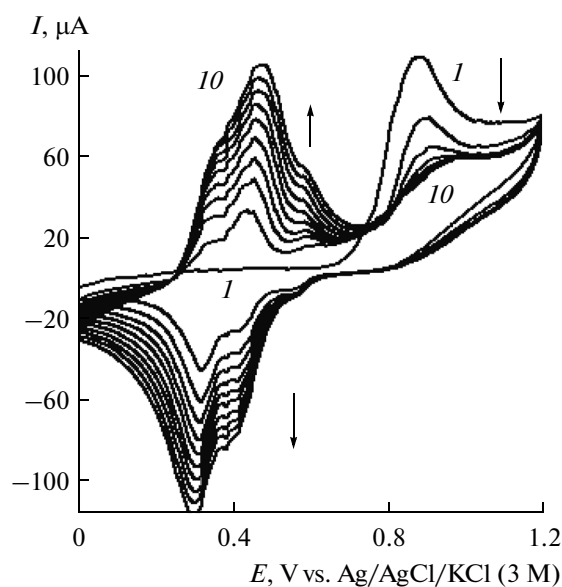


Fig. 1. Cyclic voltammograms (ten cycles) recorded during potentiodynamic growth of POT(SDS) film in a solution containing 1 mM OT, 1 mM SDS, and 0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1} .

Previously, we used the metal–polymer modified carbon paste electrode for electrocatalytic oxidation of some compounds [27, 28]. The results of these studies were promising. They are easy to prepare, they remain stable for a long time with high reproducibility. Further, they have detection limits as well as wide linear range responses. All these results encouraged us to pursue the inquiries with new catalyst.

Our literature survey indicates that, there is no report about Cu/POT(SDS)/CPE. In this work, we decided to preparation of this modified electrode and then using of it for the aim of electrocatalytic oxidation of amoxicillin. Also, the study aimed at examining the applicability of this modified electrode to determine amoxicillin in some real samples.

2. EXPERIMENTAL

2.1. Reagents and Materials

The solvent used in this work was twice distilled water. Sulfuric acid, OT, SDS, sodium hydroxide, copper sulfate used in this work were analytical grade of Fluka (Sydney, Australia) origin, AMX was prepared from Sari Pharmaceutical (Sari, Iran) and used without further purification. High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka (Sydney, Australia) was used as the pasting liquid for CPE. Graphite powder (particle diameter = 0.10 mm) from Merck (New Jersey, US) was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

2.2. Instrumentation

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP 2063-C Electrochemical Analysis System, Behpajoo, Iran) coupled with a Pentium IV personal computer. Voltammetry was conducted using a three-electrode cell. A modified CPE, a platinum electrode from Azar electrode (Urmia, Iran) and Ag/AgCl, KCl (3 M) from Azar electrode (Urmia, Iran) were used as working electrode, counter electrode and reference electrode, respectively.

3. RESULTS AND DISCUSSION

3.1. Preparation and Properties of Modified Electrodes

Initially, a mixture (70 : 30%, w/w) of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted in the bottom of a glass tube (internal radius = 1.7 mm). The electrical connection was via a copper wire lead fitted into the glass tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste and smoothing the resulting surface on white paper until a smooth shiny surface was observed.

The electropolymerization of OT was carried out onto the CPE substrate from a solution of 1 mM OT, 1 mM SDS and 0.1 M H_2SO_4 in the potential range 0 to 1.2 V at a scan rate of 50 mV s^{-1} . Figure 1 shows the typical multi-sweep cyclic voltammograms during the electropolymerization of OT in the presence of SDS. As can be seen in this figure, in the first anodic sweep, the oxidation of OT occurs as a distinct irreversible anodic peak ($E_{\text{pa}} = 0.85 \text{ V}$). A part of the oxidation products of OT is deposited on the electrode, as a POT film. In the first reverse cycle, the new cathodic peak is appeared at a potential around 0.3 V, confirming the initial deposition of electrooxidized products. In the second positive scan of potential, an anodic peak is appeared at a potential around 0.4 V. The oxidation peak current of monomer is decreased with increasing of the number of potential cycles up to 3rd cycle. The decreasing of oxidation current is due to the loss of activity of the electrode surface when covered with newly formed polymer film. Furthermore, under successive potential cycling, the peak currents related to the polymer are significantly increased, and their growth continued up to 10th cycle.

According to our previous works, SDS makes easier electropolymerization for monomer. Indeed, the presence of SDS decreases the monomer oxidation potential and accelerates of the polymerization [27, 28].

The redox behavior of POT(SDS) was investigated in the electrolyte solution. These results showed that

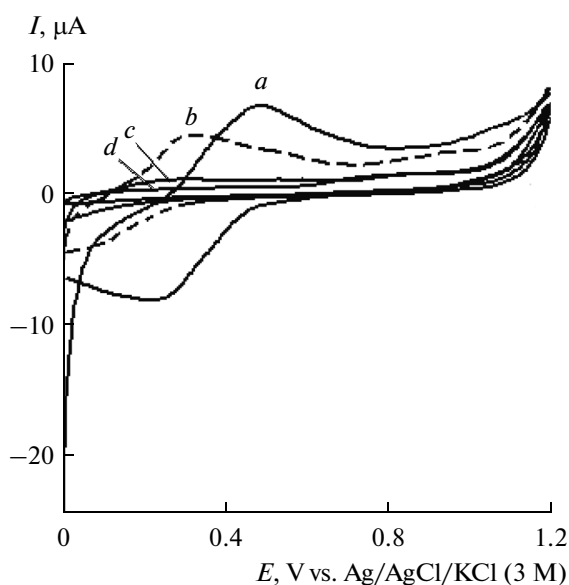


Fig. 2. Electrochemical responses of POT(SDS) at the surface of CPE in several pH: (a) 2, (b) 5, (c) 7 and (d) 11, $\nu = 50 \text{ mV s}^{-1}$.

the redox behavior of the polymeric film was strongly dependent on the pH of the electrolyte solution. Therefore, the polymer obtained shows a well-defined redox behavior in an acidic solution, but the response obtained in an alkaline solution shows a complete loss of electrode activity in the potential range of 0 to 1.2 V (Fig. 2). However, the film was not degraded under these experimental conditions, and its response was recovered when the electrode was immersed in an acidic solution.

In order to select the potential for copper deposition on POT, CV of POT(SDS)/CPE was recorded in 0.1 M H_2SO_4 with and without 0.01 M CuSO_4 . The behavior is typical to that reported earlier involving electrodeposition of metals on polymer films [29–31]. The CV (figure not shown) consists of a prominent cathodic peak at a potential about $-0.2 \text{ V vs. Ag/AgCl}$ only in the presence of CuSO_4 and is therefore attributed to the reduction of Cu. This potential was chosen from these studies for deposition of Cu on all the substrates, either bare or POT(SDS) film covered in the present study.

The polarization behavior was examined in 0.1 M NaOH solution using CV technique. This technique allows the oxide film formation in parallel to inspecting the electrochemical reactivity of the surface. Typical cyclic voltammograms of copper oxide film in 0.1 M NaOH solution and in the potential range of -1000 to 1000 mV (potential sweep rate = 50 mV s^{-1}) is shown in Fig. 3. These voltammograms are in good agreement with those reported in the literature [32].

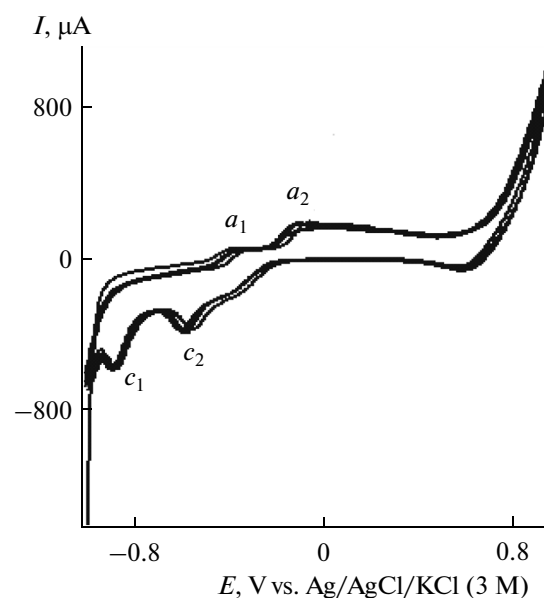
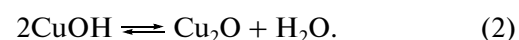
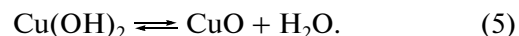
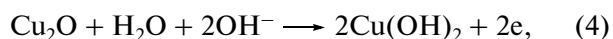


Fig. 3. Cyclic voltammograms of Cu/POT(SDS)/CPE in the potential range of -1000 , 1000 mV in 0.1 M NaOH, $\nu = 50 \text{ mV s}^{-1}$ (number of cycles = 5).

Number of well-defined peaks is observed in both the anodic and cathodic half cycles. Comparing with the literature peak a_1 is attributed to the Cu/Cu(I) redox couple. At the working pH, copper(I) hydroxide is the main product which is transformed to the corresponding oxide upon aging [33] according to the following reactions:



Peak a_2 is assigned to Cu/Cu(II) as well as Cu(I)/Cu(II) transitions through the following electrode processes [34]:



Peaks c_1 and c_2 in the cathodic half cycle are assigned to the reduction of Cu(I) to Cu and Cu(II) to Cu(I) respectively [35, 36]. Also, peak corresponds to the Cu(II)/Cu(I) couple, presumably overlapped with the anodic decomposition edge of the solvent has been estimated [34, 37, 38]. This which always appears in the course of the oxidation of copper as well as copper containing modified electrodes [39].

3.2. Electrocatalytic Oxidation of AMX on the Modified Electrode

In this work, the oxidation of AMX was first studied at modified electrode by cyclic voltammetric experi-

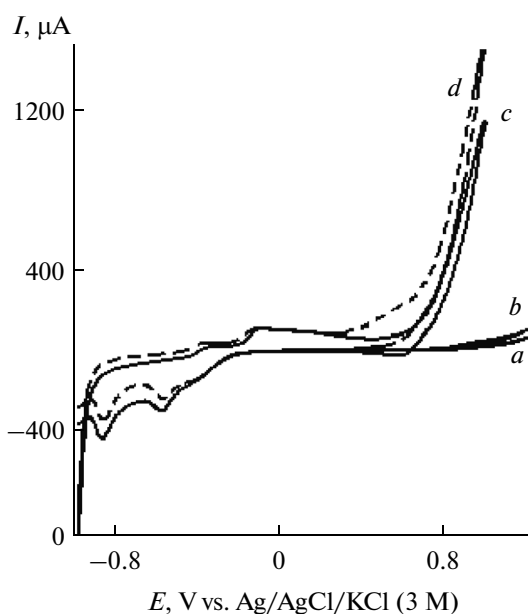
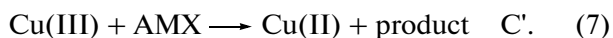
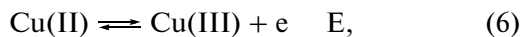


Fig. 4. Voltammetric responses for AMX obtained at the surface of POT(SDS)/CPE, solutions: (a) 0.1 M NaOH, (b) 1 mM AMX in 0.1 M NaOH, (c) and (d) are the same as (a) and (b) but for Cu/POT(SDS)/CPE, $v = 20 \text{ mV s}^{-1}$.

ments in 0.1 M NaOH. Typical results obtained at potential scan rate of 20 mV s^{-1} are displayed in Fig. 4. The electrochemical response of POT(SDS)/CPE in the absence and presence of AMX is exhibited; the addition of 1 mM AMX to the alkaline solution causes no effect on the electrochemical response of the POT(SDS)/CPE. The electrochemical response of a Cu/POT(SDS)/CPE after adding 1 mM AMX in alkaline solution (i.e., 0.1 M NaOH) exhibits an increasing in the anodic current and a decreasing in the cathodic current. This behavior is typical of that expected for the mediated oxidation (EC' mechanism) as follows [40, 41]:



3.3. Optimization of Electrode Variables for Efficient Performance of Cu/POT(SDS)/CPE Towards AMX Oxidation

3.3.1. Effect of cycles number on the electrocatalytic oxidation current of AMX. Electrochemical polymerization offers the possibility of controlling the thickness and homogeneity of POT film on the electrode surface. The influence of cycle numbers for preparation of the POT(SDS) films on the electrocatalytic oxidation of AMX was investigated and the corresponding results are shown in Fig. 5a. Under the constant conditions, the anodic peak current rises progressively for cycle numbers up to 20 cycles and drops afterwards. This implies that the electrocatalysis

of AMX oxidation is sensitive to thickness of the polymer film. The increasing in the anodic peak current for cycle numbers up to 20 cycles may be due to the occupation of copper in the pores of polymers with the real sizes. The decreasing in anodic peak current for AMX oxidation beyond 20 cycles may be due to lessening of real surface area of copper ions by the excessive presence of polymers on the electrode surface.

3.3.2. Effect of copper concentration. Figure 5b shows the affect of the concentration of copper dispersed in POT(SDS) on the maximum oxidation currents of 1 mM AMX in 0.1 M NaOH. It was observed, the oxidation current shows a maximum values for copper concentration of about 0.025 M, while for copper loading higher than 0.025 M, the currents decreased gradually owing probably to the coalescence of microparticles favoring island growth leading to a decrease in surface area and hence the activity.

3.3.3. The Effect of accumulation time. The electrocatalytic oxidation peak currents increased gradually with increasing of accumulation times. The maximum value was got at 500 s then leveled off, so 500 s was chosen as the optimum time, which indicated that saturated accumulation on the Cu/POT(SDS)/CPE had been achieved (Fig. 5c).

3.3.4. NaOH concentration. The potential for AMX oxidation appears to be strongly dependent on NaOH concentration (Fig. 6). It is observed that as the concentration of NaOH is increased from 0.1 to 1 M, the AMX oxidation peak is shifted to less positive values. It has been reported [34] that some of the oxidation peaks of Cu shift towards more negative values of potential as the alkali concentration increases and is also shown in Fig. 6. Hence it is probable that the reactive redox species of Cu is generated at less positive potentials as the concentration of NaOH is increased so that the AMX oxidation peak is also shifted towards less positive values. As regards the oxygen evolution reaction, its potential is also observed to decrease with increase in pH of the medium.

3.4. Effect of Scan Rate

The effect of scan rate (v) on the peak current (I_p) of AMX at the surface of Cu/POT(SDS)/CPE was also examined employing CV by varying the scan rate from 25 to 600 mV s^{-1} . A linear relationship was observed (as depicted in Fig. 7) between the oxidation peak current and the square root of scan rate with a significant correlation coefficient of 0.990 which indicates that the electrode process is diffusion-controlled within the scan rate range studied. A linear relationship was also observed between $\log I_p$ and $\log v$ over the scan range $25\text{--}600 \text{ mV s}^{-1}$ ($R^2 = 0.996$) which corresponded to the equation:

$$\log I_p = 0.54 \log v + 1.23. \quad (8)$$

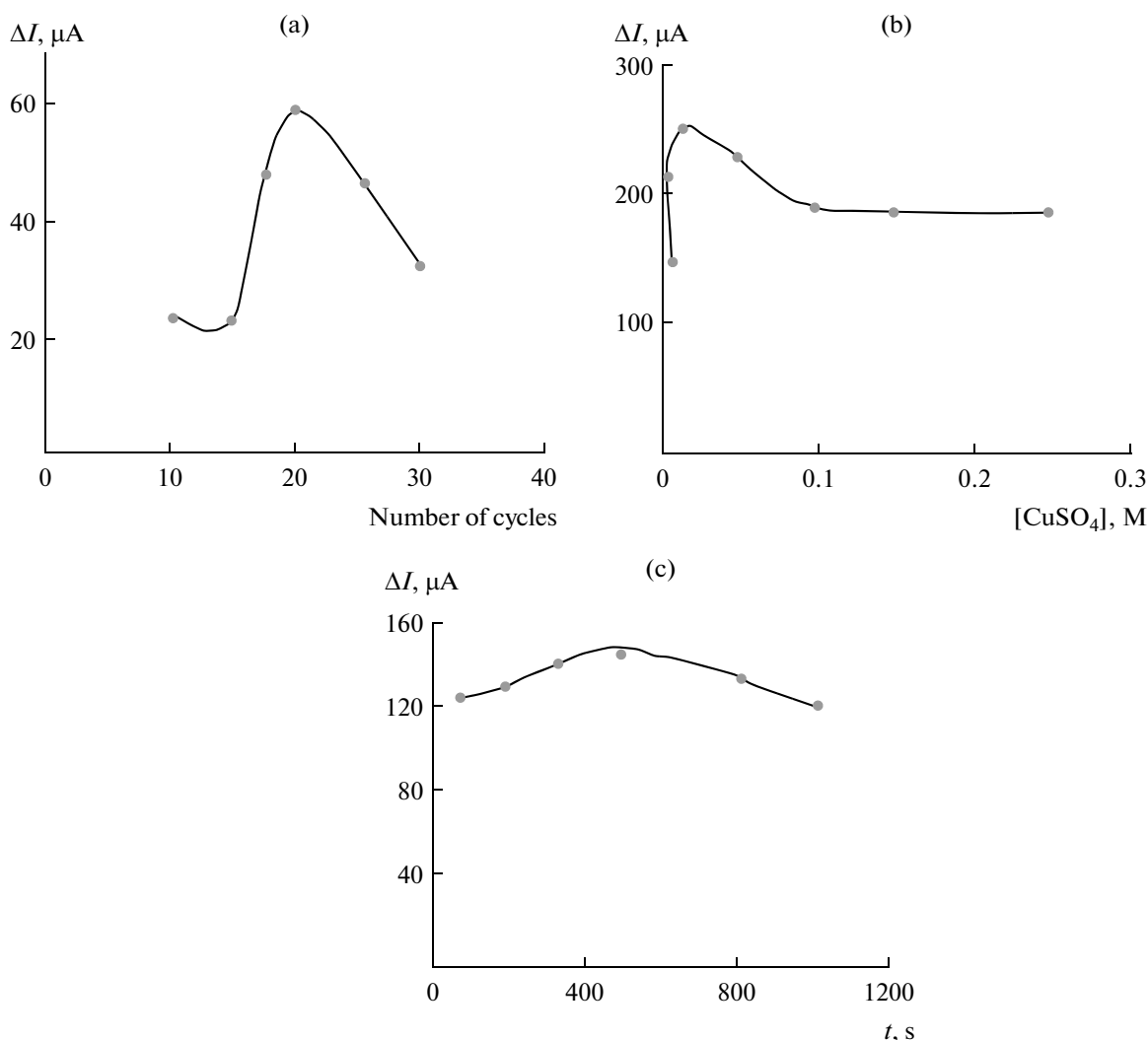


Fig. 5. Variation of currents for oxidation in presence and absence of 1 mM AMX (ΔI) in 0.1 M NaOH for (a) different cycles of polymerization (10, 15, 18, 20, 25 and 30), (b) copper concentration (0.01, 0.0125, 0.025, 0.05, 0.1, 0.15 and 0.25 M) and (c) accumulation time (100, 200, 350, 500, 800 and 1000 s) at $v = 20 \text{ mV s}^{-1}$.

The slope of 0.54 is close to the theoretically expected value of 0.50 for an ideal diffusion controlled process.

3.5. Effect of AMX Concentration

Figure 8 shows the effect of AMX concentration on the cyclic voltammograms of the Cu/POT (SDS)/CPE. As can be seen from Fig. 8, the height of the anodic peak increases with increasing AMX concentration. The characteristic shape of CV in this potential region indicates that the signal is due to the oxidation of AMX. The catalytic peak current is proportional to the concentration of AMX in the range of 0.08 to 2 mM. The linear regression equation is $I(\mu\text{A}) = 57.29 C_{\text{AMX}} (\text{mM}) + 56.38$ ($R^2 = 0.99$). The detection limit calculated from the calibration graph was 0.06 mM AMX when the signal to noise ratio was 2.

In order to enhance the sensitivity of the method (lowering the detection limit), constant potential amperometry under hydrodynamic conditions was used. Hydrodynamic amperometric responses (Fig. 9) were obtained by adding AMX to continuously stirred 1 M NaOH solutions. The inset of this figure shows the calibration graph for AMX at the modified electrode. Its response is linear for AMX within the concentration range 5–150 μM . The detection limit was 3 μM , when the signal to noise ratio was 2.

3.6. Chronoamperometric Studies

Chronoamperometry as well as other electrochemical methods was employed for the investigation of electrochemical processes at Cu/POT(SDS)/CPE. The main panel of Fig. 10 represents the current–time profiles obtained by setting the working electrode potential

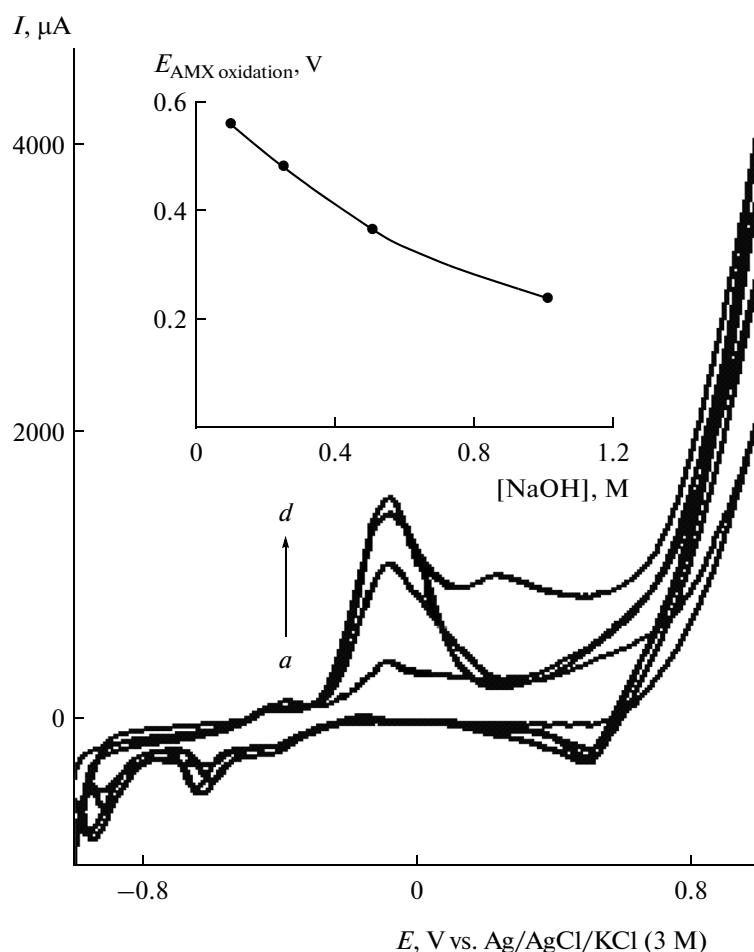


Fig. 6. Main panel: effect of NaOH concentration on the CV response of Cu/POT(SDS)/CPE in the absence of AMX. Inset: effect of NaOH concentration on oxidation potential of 1 mM AMX on Cu/POT(SDS)/CPE at 20 mV s^{-1} .

at 600 mV for various concentrations of AMX. The rate constant for the chemical reaction between the AMX and redox sites of Cu/POT(SDS)/CPE can be evaluated by chronoamperometry according to the method described in the literature [42].

$$I_C/I_L = \lambda^{1/2} [\pi^{1/2} \text{erf}(\lambda^{1/2}) + \exp(-\lambda)/\lambda^{1/2}], \quad (9)$$

where I_C is the catalytic current of the Cu/POT(SDS)/CPE in the presence of AMX, I_L is the limiting current in the absence of AMX and $\lambda = kc_0t$ (c_0 is the bulk concentration of AMX) is the argument of the error function. In the cases where λ exceeds 1.5, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_C/I_L = \pi^{1/2} \lambda^{1/2} = \pi^{1/2} (kc_0t)^{1/2}, \quad (10)$$

where k , c_0 and t are the catalytic rate constant ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), AMX 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 of

Fig. 10 shows one such plot, constructed from the chronoamperogram of the Cu/POT(SDS)/CPE in the absence and presence of 0.1 mM AMX. The mean value for (k) was found to be $4.9 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

3.7. Determination of AMX in Real Sample

The applicability of the proposed method for the sample dosage form was examined by analyzing the tablets. It was found that the drug concentrations determined using this method is in good agreement with the reported values. The value of experimentally determined drug and the declared value in tablet are tabulated in Table 1.

3.8. The Electrode Stability, Repeatability and Reproducibility

To verify the durability and long-term stability of Cu/POT(SDS)/CPE, 40 consecutive cyclic voltammograms using this electrode were recorded in 1 M NaOH solution (data not shown). It was found that

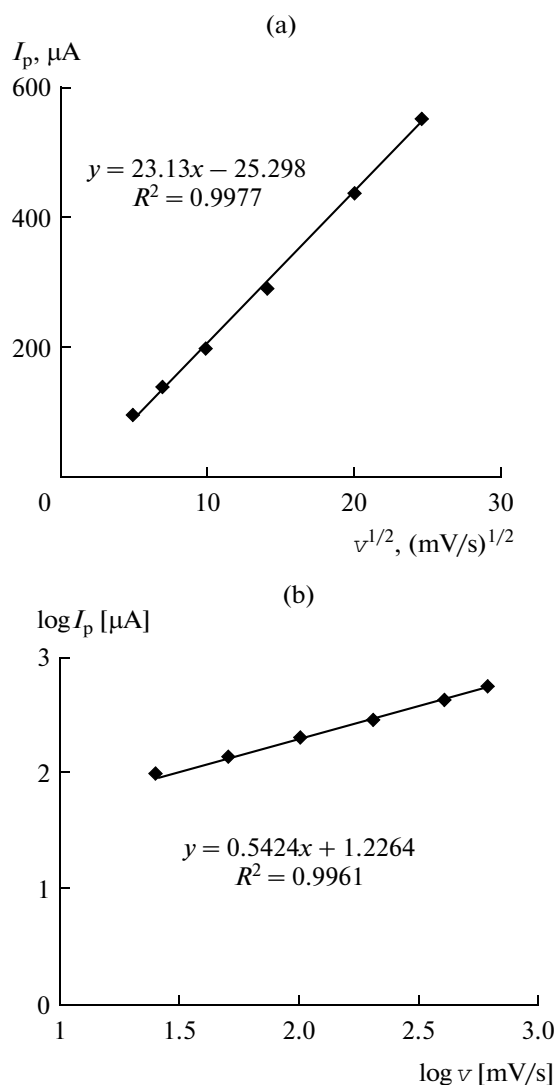


Fig. 7. (a) Variation of peak current (I_p) with square root of sweep rate ($v^{1/2}$) observed for 1 mM AMX on Cu/POT(SDS)/CPE (b) Variation of $\log I_p$ vs. $\log v$.

the peak currents changed slightly (<5%). In addition, the electrode was stored in 1 M NaOH solution when it was not in use and retained its electroactivity for 6 weeks. To investigate the repeatability of electrode, the Cu/POT (SDS)/CPE was applied to the 7 parallel determinations of 1.0×10^{-4} M AMX and the relative standard deviation (RSD) was calculated as 3.5%. Further, under the same and independent conditions, it was found that the electrocatalytic oxidation cur-

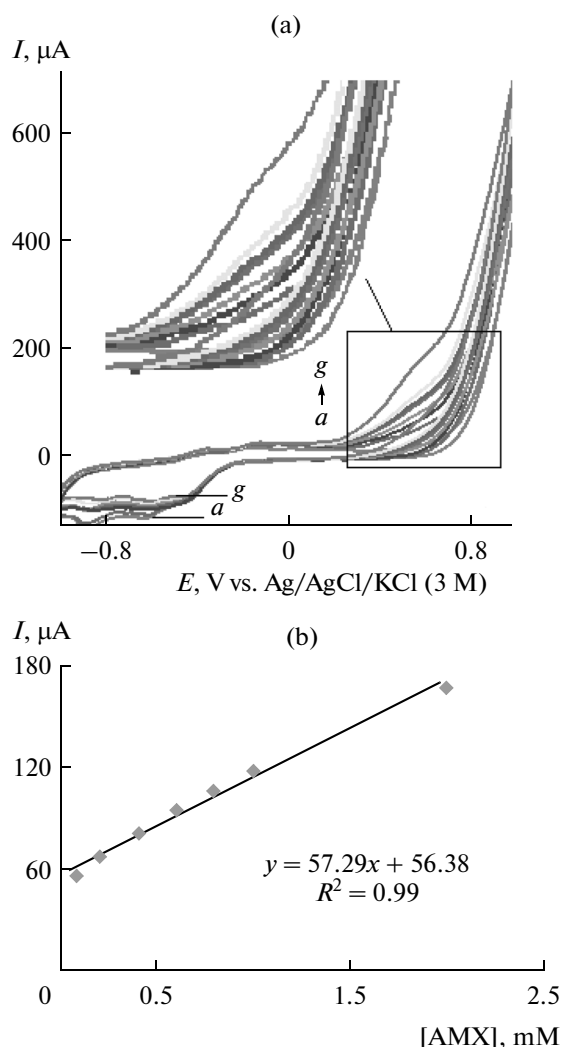


Fig. 8. (a) Current–potential curves for oxidation of AMX at the Cu/POT(SDS)/CPE in 1 M NaOH solution with different concentrations of AMX: (a) 0.08, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1 and (g) 2 mM at 20 mV s^{-1} . (b) Plot of I_p versus c .

rents of 1.0×10^{-4} M AMX almost remained the same by five Cu/POT(SDS)/CPE with a RSD of 4%, indicating a high reproducibility.

4. CONCLUSIONS

(1) CPE surface modified with Cu/POT(SDS) showed good electrocatalytic response for the oxida-

Table 1. Determination of AMX in pharmaceutical preparation using Cu/POT (SDS)/CPE

Compound	Amount labeled, g	Amount found, g	Recovery, %	RSD, % ($n = 4$)
AMX (tablet)	0.500	0.512	102	2.5
AMX (tablet)	0.200	0.208	104	3.2

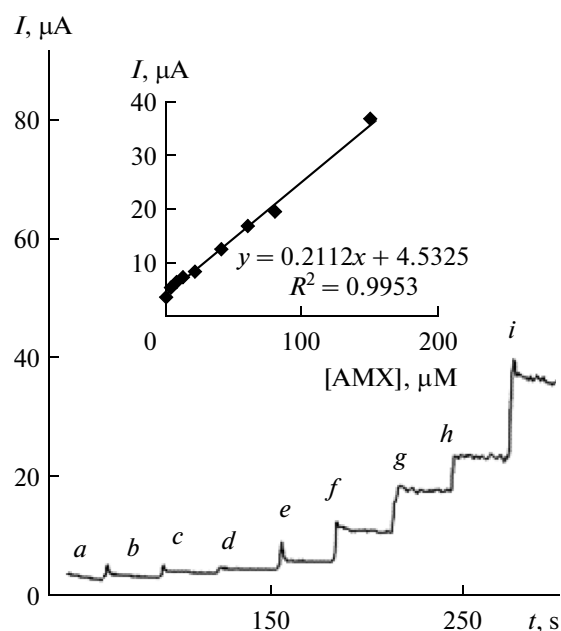


Fig. 9. Main panel: Amperometric responses of Cu/POT(SDS)/CPE in 1 M NaOH solution with different concentrations of AMX: (a) 0, (b) 5, (c) 8, (d) 12, (e) 20, (f) 40, (g) 60, (h) 80 and (i) 150 μM (Applied potential: 600 mV). Inset: Variation of amperometric current vs. AMX concentration.

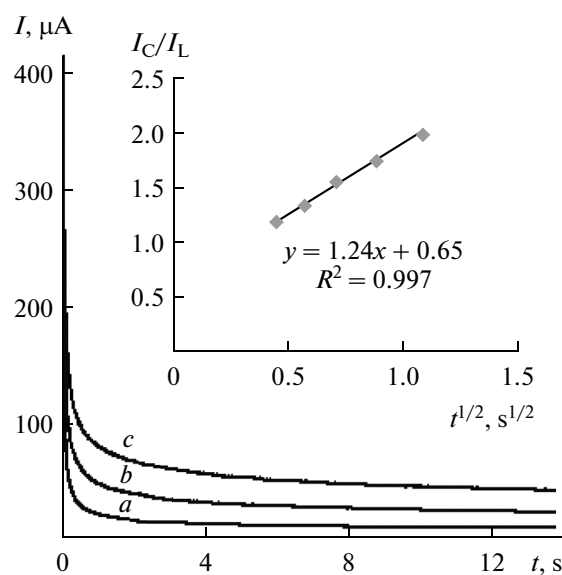


Fig. 10. Main panel: Chronoamperograms obtained at the Cu/POT(SDS)/CPE in the (a) absence and presence of (b) 0.08 and (c) 0.1 mM of AMX in 1 M NaOH solution, potential step was 600 mV versus Ag/AgCl, respectively, Inset: Dependence of I_C/I_L on $t^{1/2}$ derived from the data of chronoamperograms of (a) and (c) in the main panel.

tion of AMX using cyclic voltammetry and chronoamperometry techniques.

(2) In order to optimize of response electrode for efficient performance towards AMX oxidation, the effect of various parameters such as number of potential cycles for preparation of polymer, copper concentration, accumulation time and NaOH concentration have been investigated.

(3) Kinetically parameter, such as catalytic reaction rate constant, was determined. The value of the

rate constant (k) obtained from the chronoamperometric method indicated that the modified electrode can overcome the kinetic limitations for AMX oxidation by a catalytic process and can decrease the overpotential for the oxidation reaction.

(4) The proposed method provides a fast, sensitive and simple approach to the determination of AMX in pharmaceutical preparations.

(5) Table 2 compared the proposed electrode for AMX determination with electrodes reported in liter-

Table 2. Comparison of performances of some electrodes in electrooxidation of AMX

Electrode	Method	LDR, mM	LOD, mM	K , $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Ref.
CPE/complex oxovanadium(IV)	SWV	18.9–91.9	8.49	–	[43]
GC/PGA/GLU ^a	SWV	2–25	1.06	–	[12]
CPE/CR/Ni ^b	Amperometry	8–100	5	2.44×10^6	[44]
GC/MWCNT ^c	ASV ^d	0.6–8	0.2	–	[45]
CIM/SGD/CC ^e	Amperometry	10–65	0.53	20.9×10^4	[46]
CPE/POT (SDS)/Cu	CV	80–200	60	4.9×10^6	This work
CPE/POT (SDS)/Cu	Amperometry	5–150	3		

^a Glutaraldehyde cross-linked polyglutamic acid modified glassy carbon electrode.

^b Ni–curcumin on the carbon paste electrode.

^c Multiwalled carbon nanotube modified glassy carbon electrode.

^d Adsorptive stripping voltammetry.

^e Copper iodide modified sol–gel derived carbon ceramic.

atures. As show, the proposed electrode is comparable with other electrodes.

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