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رفتار ولتامتری و تعیین ایزونیازید در داروها با استفاده از الکترود نقره اصلاح شده با اکسی فلورید نقره

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Voltammetric Behavior and Determination of Isoniazid in Pharmaceuticals by Using Silver Oxyfluoride Modified Silver Electrode

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چکیده

در مطالعه حاضر، الکترود نقره ای اصلاح شده با اکسی فلورید نقره برای اکسیداسیون الکتروکاتالیزوری ایزونیازید استفاده شد. فرآیند اکسیداسیون و سینتیک آن به وسیله روش های ولتامتری چرخه ای و کرونوآمپرومتری و تکنیک های آمپرومتری مورد مطالعه قرار گرفت. الکترود اصلاح شده یک پاسخ پایدار و خطی در گستره غلظتی ۳×۱۰^{-۴} تا $۲/۱\times۱۰^{-۳}$ مول بر لیتر با ضریب همبستگی ۰/۹۹۵۳ نشان می دهد. تعداد الکترونهای کل مبادله شده در اکسایش الکتروکاتالیزوری ایزونیازید ۴ به دست آمد. ضریب نفوذ برای ایزونیازید $۳/۱۱\times۱۰^{-۵}$ سانتی متر مربع بر ثانیه به دست آمد. حد تشخیص باروش آمپرومتری بر روی این الکترود اصلاح شده برای اندازه گیری ایزونیازید ۳/۸۵ میکرومولار به دست آمد. این روش به طور موفقیت آمیزی برای آنالیز ایزونیازید در فرمولاسیون های دارویی جامد به کار رفت. نتایج آنالیز نشان می دهند این روش می تواند در تعیین روتین ایزونیازید در محصولات آزمایش شده به کار رود.

واژه‌های کلیدی
ایزونیازید؛ الکترود اصلاح شده؛ اکسیداسیون الکتروکاتالیکی؛ اکسی فلوئورید نقره؛ اندازه گیری.

Abstract

In the present study, silver oxyfluoride modified silver electrode was employed to electrocatalytic oxidation of isoniazid. The process of oxidation and its kinetics were established by using cyclic voltammetry, chronoamperometry and amperometry techniques. The modified electrode shows a stable and linear response in the concentration range of 3×10^{-4} to 2.1×10^{-3} mol L^{-1} with a correlation coefficient of 0.9953. The overall number of electrons involved in the catalytic oxidation of isoniazid was found 4 electrons. The diffusion coefficient of 3.11×10^{-5} cm2 s^{-1} for isoniazid was also estimated using chronoamperometry study. It has been shown that using the silver oxyfluoride modified silver electrode, isoniazid can be determined by amperometry method with limit of detection of 3.85 μmol L^{-1}. The method was successfully applied for analysis of isoniazid in solid pharmaceutical formulations. The results of the analysis suggest that the proposed method has promise for the routine determination of isoniazid in the products examined.

Keywords
Isoniazid; Modified Electrode; Electrocatalytic Oxidation; Silver Oxyfluoride; Determination.

1. INTRODUCTION

Tuberculosis is one of the leading causes of death worldwide. Isoniazid (INZ), pyridine-4-carboxylic acid hydrazide, is one of the most effective tuberculostatic agents against mycobacterium strains, which is useful to prevent the development of clinical tuberculosis [1]. The importance of INZ has prompted the development of some methods for its determination including chemiluminescence [2], fluorimetry [3], spectrophoto-metry [4-5] and capillary electrophoresis [6] as well as several chromatographic methods [7–9].

Several electrochemical methods have also been studied by using different types of electrodes, such as differential pulse voltammetry at the gold electrode [10], squarewave adsorptive cathodic stripping voltammetry at the hanging mercury drop electrode [11] and cyclic voltammetry at the

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modified glassy carbon electrode [12].

In electroanalytical area, the concept of chemically modified electrodes has been developed gradually instead of conventional electrodes to improve the reactivity, sensitivity and selectivity of the electrode reactions in many applications.

The electrochemical modification of electrodes with a suitable reagent has been widely used for analytical applications. The resulting electrodes were designed to provide the desired selective sites towards the analytes. Chemically modified electrodes (CMEs) are extensively researched for applications in medical diagnostics, food analysis and environmental monitoring [13−17].

An important property of CMEs is their ability to catalyze the electrode process to significantly decrease the overpotential and give more selective interaction of the electron mediator with the target analyte. These electrodes can enhance the selectivity in the electroanalytical methods.

Silver has been extensively used in a variety of applications such as catalysis, electronics, photonics and photography due to its unique properties. For example, silver has the highest electrical conductivity, thermal conductivity and reflectivity of all metals and lower cost than gold [18-19].

Also, it is a metal of commercial importance for use in high strength and corrosion resistance alloys and jewellery. Silver compounds and alloys have been widely used in dental and pharmaceutical preparations, and in implanted prosthesis [20–22].

Ag is one of important metals and can be used not only as modification metal but also as substrate metal in surface modification [23].

Ag electrode is attractive for its high catalytic activity toward the reduction of organic halides. For example, Ag electrode has been used for reductive dehalogenation of polyhalogenated phenols and Ag nanoparticles and nanorods deposited on glassy carbon substrates for the reduction of benzyl chloride [24–27].

The aim of this work is the study of the voltammetric behavior and determination of isoniazid in pharmaceuticals by using silver oxyfluoride modified silver electrode.

2. EXPERIMENTAL

2.1. Reagents and instrumentation

All chemicals used were of analytical grade from Merck (Darmstadt, Germany) and were used without further purification. INZ tablets were taken from an Iranian pharmaceutical company (Daru-Pakhsh, Iran) with claimed value of 100 mg INZ. Distilled water was used for the preparation of all solutions. All electrochemical measurements were carried out in a three electrode cell using an Autolab electrochemical system (Eco Chemie, Utrecht, the Netherlands) equipped with PGSTAT-12 and GPES software. The bare (from Azar electrode Co., Iran), or modified silver electrode was used as a working electrode, Ag/AgCl/saturated KCl (from Metrohm) and a Pt wire were used as reference and counter electrode, respectively. All experiments were carried out at room temperature.

2.2. Preparation of silver oxyfluoride modified silver electrode [28]

Prior to each experiment, the base silver electrode surface was polished with a slurry 0.05 µm alumina powder until a mirror-like surface was obtained. The electrode was then washed thoroughly with acetone and distilled water. The polished electrode was immersed in 0.1 mol L^{-1} NaF solution by applying one cycle potential scan between −1400mV and 800mV (vs. Ag/AgCl) at scan rate of $50 mVs^{-1}$. In this step, fluoride can form a complex with silver ion. Then the electrode was inserted into an electrochemical cell containing 0.1 mol L^{-1} NaOH and cycled twenty times between 170 and 800 mV (vs. Ag/AgCl) at a scan rate of 50 mV s^{-1}, regime until a stable voltammogram was obtained.

2.3. Preparation of tablet sample

Ten tablets, each containing 100mg of isoniazid, were finely powdered respectively. The white powder was accurately weighed to 1.0 g and dissolved into 10mL distilled water. The mixture was shaken for 30 min and filtered into a 50mL volumetric flask. The residue was several times washed with distilled water and solution was diluted to the mark.

3. RESULTS AND DISCUSSIONS

Electrochemical properties of the prepared SOFMS electrode were investigated. For the activation of this electrode, the electrode was placed in 0.1 mol L^{-1} NaOH and the electrode potential was cycled between 170 and 800 mV (vs. Ag/AgCl) at a scan rate of 50 mVs^{-1} for 20 cycles in a cyclic voltammetry regime until a stable voltammogram was obtained (Fig. 1).

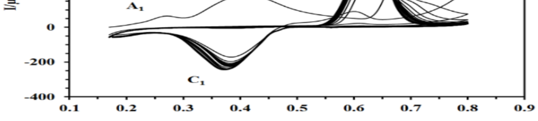


Fig.1. Repetitive cyclic voltammograms of SOFMS electrode in 0.1 mol L^{-1} NaOH in the potential range of 170 −800 mV. Potential sweep rate is 50 mV s^{-1}.

After 20 runs, the SOFMS electrode shows

reproducible cyclic voltamograms. In the anodic potential sweep, the SOFMS electrode showed three anodic peaks (A_1, A_2 and A_3) appearing at 0.260, 0.399 and 0.698 V, respectively (Fig. 1).
During a reverse scan, one cathodic peak (C_1) appeared at 0.388V. The first anodic peak (A_1) is due to the electroformation of the monolayer of Ag_4OF_2. The second anodic peak (A_2) is due to the formation of the multilayer of Ag_4OF_2. The third peak (A_3) is due to the oxidation of Ag_4OF_2 to Ag_2OF_2 or direct oxidation of Ag to Ag_2OF_2. When the nuclei of Ag_2OF_2 formed at the Ag_4OF_2 surface during the anodic scan, further formation of Ag_2OF_2 became easy, and occurred at a lower potential than the initial formation of Ag_2OF_2 nuclei. The cathodic current peak C_1 is due to the reduction of Ag_2OF_2 to Ag_4OF_2 [28-29].
Next, the cyclic voltammograms of the modified electrode were recorded in 0.1 mol L^{-1} NaOH at various potential sweep rates (Fig. 2A).
With the increase of the scan rate, the redox current increased, the anodic peak shifted toward positive potential and overlapped with the oxygen evolution peak, and the cathodic peak shifted toward negative potential. The peak's currents (I_{pa} and I_{pc}) are proportional to sweep rates in the range of 5-100 mVs^{-1} (Fig. 2B), pointing to the electrochemical activity of the surface redox couple. From the slope of anodic peak currents versus scan rate and using [30]:

$$I_p = (n^2F^2/4RT)vA\Gamma^* \qquad (1)$$

where v is the sweep rate, A is the geometric surface area and Γ is the surface coverage of the redox species, the calculated value of Γ^* can be approximately 1.25×10^{-4} mol cm^{-2} for n = 2.

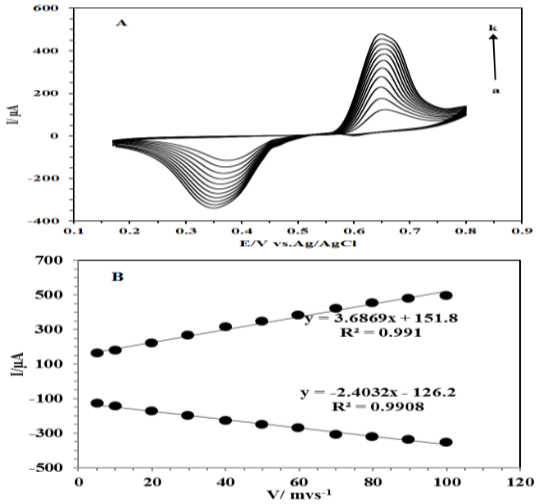


Fig. 2. (A) Cyclic voltammograms of SOFMS electrode in 0.1 mol L^{-1} NaOH at various potential scan rates: (a) 5, (b) 7, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60, (h) 70, (i) 80, (j) 90 and (k) 100 mV s^{-1}. (B) The dependency of anodic and cathodic peak currents vs. scan rate. (Inner to outer respectively).

The electrochemical oxidation of isoniazid was studied by cyclic voltammetry at the surface of the bare silver and SOFMS electrodes (Fig. 3). The oxidation of INZ shows a weak peak on the bare silver electrode but the experimental results for SOFMS electrode show well-defined anodic peak at the peak potential of 0.736 V, respect to Ag/AgCl reference electrode. It could be observed that the oxidation peak current for modified electrode significantly increased and it was almost 3 times larger than unmodified electrode. Also, as shown in Fig. 3, the potential peak at the bare silver (0.640 V) is lower than the potential peak at the SOFMS electrode (0.736 V) because the electrode response for the bare silver is controlled by diffusion while for the SOFMS electrode the response is controlled by adsorption and diffusion. The oxidation peak of INZ in 0.1 mol L^{-1} NaOH solution is irreversible and thus with increase in the peak height, the peak potential shifts to higher potential.

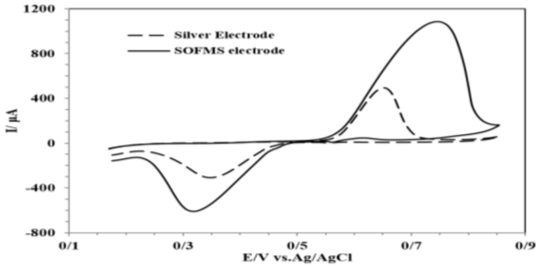
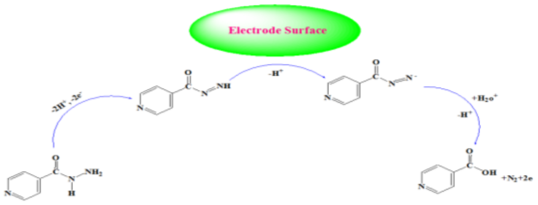


Fig. 3. Cyclic voltammograms of bare silver electrode (a) and SOFMS (b) electrode electrode in 0.1 mol L^{-1} NaOH solution in presence of 1.1 mmol L^{-1} INZ at a scan rate of 50 mV s^{-1}.

The cyclic voltammograms of SOFMS electrode were recorded in different concentrations of NaOH solution containing 0.7 mmol L^{-1} INZ (not shown). It is shown that, the high catalytic peak current is achieved above a NaOH concentration of 0.1 mol L^{-1}. So, 0.1 mol L^{-1} NaOH was chosen as an optimum supporting electrolyte. Based on the obtained results, the reaction of electrooxidation of INZ at the surface of SOFMS electrode can be written as shown on the Scheme 1.



Scheme 1. The electro-oxidation mechanism of INZ at the electrode surface.

In order to provide more evidence, the effect of the scan rate varying from 5 to 100 mV s^{-1} on the voltammetric response of SOFMS electrode in a solution containing 0.9 mmol L^{-1} INZ was studied (Fig.4A). The anodic currents increase and the peak potential shifts as the scan rate increases. When peak current values were plotted against $v^{1/2}$ (Fig. 4B), a linear relationship with $R^2 = 0.9904$ was obtained. This behavior suggests that the oxidation process is controlled by diffusion. Moreover, a plot of the scan rate normalized current ($I/v^{1/2}$) versus the scan rate exhibits the typical shape of an electrochemical (EC′) catalytic process (Fig. 4C).

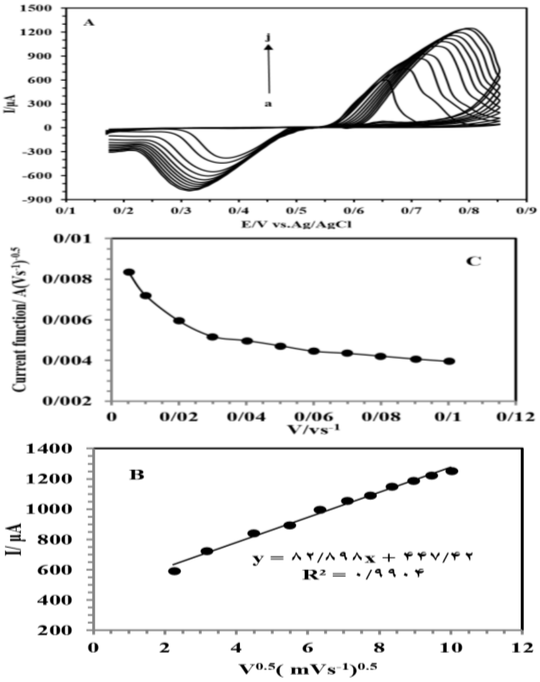


Fig. 4. (A) Cyclic voltammograms of SOFMS electrode in 0.1 mol L^{-1} NaOH containing 0.9 mmolL^{-1} of INZ at various potential scan rates (from inner to outer) 5-100 mVs^{-1}. (B) Variation of the catalytic current with the square root of sweep rate. (C) Current function vs. v for 0.1 mol L^{-1} NaOH solution in the presence of 0.4 mmolL^{-1} INZ.

For determination of the transfer coefficient and the number of electrons involved in the rate determining step, Tafel plot was drawn using the data from the raising part of the current voltage curve at a scan rate of 5 mV s^{-1}. The Tafel slope was 50.4 mV $decade^{-1}$ and by considering that α equal to 0.42, the results indeed suggest two electron transfer process in the rate determining step for the electrocatalytic oxidation of INZ. Based on the proposed mechanism, the rate-determining step is a chemical reaction and an electrochemical step containing a 2e $2H^+$ is before form it. The Tafel slope could be calculated by another method, i.e. it can be determined from the following equation [31]:

$$E_p = b/2 \log v + k \quad z \qquad (2)$$

where v is the scan rate, b is the Tafel slope and k is a constant value. The plot of E_p vs log (v) was drawn and the slope of this plot is 33.5 mV, therefore the Tofel slope becomes 67 mV $decade^{-1}$. This result is close to that obtained from the raising part of voltammogram recorded at the 5 mV s^{-1}. If α was assumed equal to 0.56, n_α is equaled 1.8 that closed to 2. Total number of electrons in oxidation process was calculated according to the following equation for a totally irreversible diffusive process [32]:

$$I_p = 3.01 \times 10^5 n[(1-\alpha)n_\alpha]^{1/2} ACD^{1/2} v^{1/2} \qquad (3)$$

with considering α = 0.42, $n_\alpha = 2$, $D = 3.11\times10^{-5}$ $cm^2\ s^{-1}$ (see chronoamperometric studies) and A = 0.0314 cm^2, it is estimated that the total number of electrons involved in the anodic oxidation of INZ is n ≅ 4. The total number of electrons involved in the oxidation process, was also determined by performing a complete electrolysis 10 ml of 0.1 mmol L^{-1} of isoniazid and 4 electrons was conformed.With the increase of INZ concentration, the anodic peak current gradually increased (Fig.5).

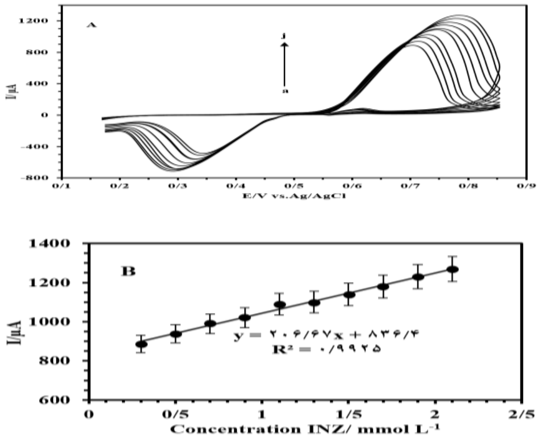


Fig. 5. (A) Cyclic voltammograms of a SOFMS electrode in the presence of various INZ concentrations: (a)–(j): 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5, 1.7, 1.9 and 2.1 mmolL^{-1}, respectively, at a scan rate of 50 mV s^{-1}, in 0.1 molL^{-1} NaOH solution. (B) Variation of anodic peak current vs. INZ concentration.

The characteristic shape of cyclic voltammogram in this potential region indicates that the signal is due to the oxidation of INZ. The catalytic peak current is proportional to the concentration of INZ in the range of 0.3 mmol L^{-1} to 2.1 mmol L^{-1}. The linear regression equation is I (μA) =206.67C $_{INZ}$ (mmol L^{-1}) + 836.4(R^2=0.9925). In order to evaluate the reaction kinetics, the oxidation of INZ on SOFMS electrode was investigated by chronoamperometry. Chronoamperometry, as well as cyclic voltammetry has been employed for the investigation of the processes occurring via an ErCi mechanism [33].

Double steps chronoamperograms were recorded by setting the working electrode potentials to desired values and were used to measure the catalytic rate constant on the modified surface. Fig. 6A shows a series of well-defined chronoamperograms for the SOFMS electrode in the absence and presence of different concentrations of INZ at an applied potential of 0.7 V versus Ag/AgCl. The plot of net current with respect to the mines square roots of time presents a linear dependency (Fig. 6B). This indicates that the transient current must be controlled by a diffusion process. The transient current is due to catalytic oxidation of INZ, which increases as the INZ concentration is raised. No significant cathodic current was observed when the electrolysis potential was stepped to 0.00 mV (*vs.* Ag/AgCl), indicating the irreversible nature of the oxidation of INZ. By using the slopes of these lines; we can obtain the diffusion coefficients of the significant according to the Cottrell equation [34]:

$$I = nFAD^{1/2}C^{*}(\pi t)^{-1/2} \qquad (4)$$

where D is the diffusion coefficient, and C* is the bulk concentration. The slopes of the resulting straight lines were then plotted versus the concentration of INZ (Fig. 6C), from which we calculated a diffusion coefficient of 3.11×10^{-5} cm^2 s^{-1} for INZ.

The rate constants of the reactions of INZ and the ensuing intermediates with the redox sites of the SOFMS electrode can be derived from the chronoamperograms according to Eq. (5) [35]:

$$I_{catal}/I_d = \lambda^{1/2}\left[\pi^{1/2}\,\mathrm{erf}(\lambda^{1/2}) + \exp(-\lambda)/\lambda^{1/2}\right] \qquad (5)$$

where I_{catal} is the catalytic current in the presence of INZ, I_d the limiting current in the absence of INZ and $\lambda=kCt$ (k , C and t are the catalytic rate constant, bulk concentration of INZ and the elapsed time, respectively) is the argument of the error function. For $\lambda > 1.5$, $erf(\lambda^{1/2})$ almost equals unity and Eq. (6) reduces to [36]:

$$I_{catal}/I_d = \lambda^{1/2}\pi^{1/2}(kCt)^{1/2} \qquad (6)$$

From the slope of the I_{catal}/I_d vs. $t^{1/2}$ plot (Fig. 6D), the value of k for 0.7 mmol L^{-1} INZ was calculated to be 3.05839×10^{5}cm^3 mol^{-1} s^{-1}.

Analytical characteristics of SOFMS electrode for the amperometric determination of INZ were estimated. Fig. 7 shows the current-time responses of the modified electrode to INZ which was successively added to the electrochemical cell containing 0.1 molL^{-1} NaOH under hydrodynamic conditions, while the electrode potential was kept at 0.600 V vs. Ag/AgCl. As shown in the figure a well-defined response was observed during the stepwise increasing of INZ concentration in the range 3- 38 µmol L^{-1}. Again, we related this to the formation of nitrogen gas bubbles at the surface of the electrode. The linear regression equation of calibration curve is expressed as I (µA) =3.4449 C_{INZ} µmol L^{-1} +251.38 with a correlation coefficient of 0.9986 (n=6). A calibration plot constructed from data of Fig. 7, gives a limit of detection (LOD) and sensitivity 1.61 µmol L^{-1} and 3.4449 µA/µmol L^{-1}, respectively [37]. The proposed method was applied to the determination of INZ in tablets by using cyclic voltammetry and amperometric methods.

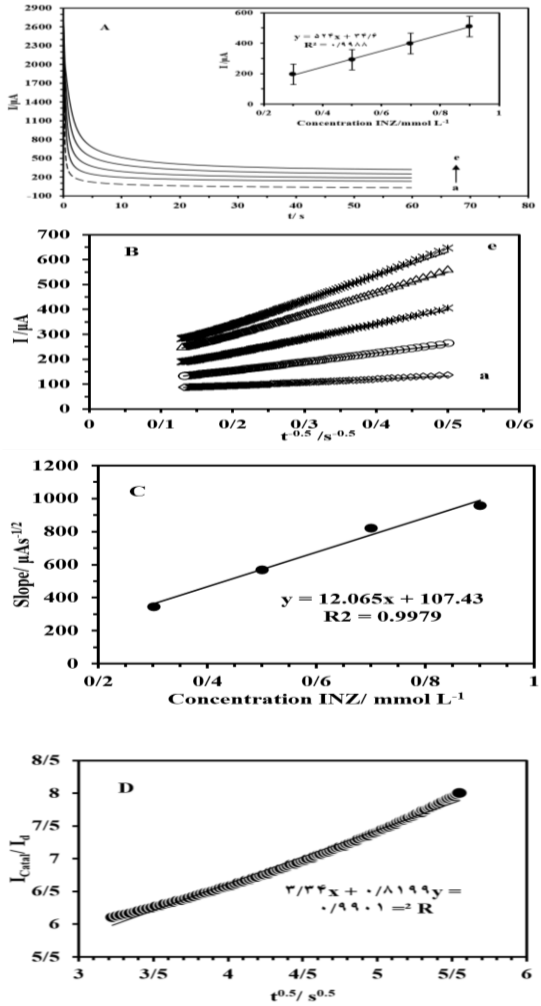


Fig. 6. (A) Chronoamperograms of SOFMS electrode in 0.1 mol L^{-1} NaOH contaning different concentrations of INZ: 0.0, 0.3, 0.5, 0.7 and 0.9 mmol L^{-1}, from (a) to (e), respectively. Potential steps were 0.7 and 0.0 V, respectively. Insets: Variation of chronoamperometric currents at *t* = 10 s vs. concentration of INZ. (B) Plot of *i* vs. $t^{-1/2}$ obtained from chronoamperometric measurements SOFMS electrode in 0.1 mol L^{-1} NaOH contaning different concentrations of INZ: 0.0, 0.3, 0.5, 0.7 and 0.9 mmol L^{-1}, from (a) to (e), respectively. (C) Dependency of I_{catal}/ I_d on $t^{1/2}$ derived from CAs of (a) and (d) in panel (A).

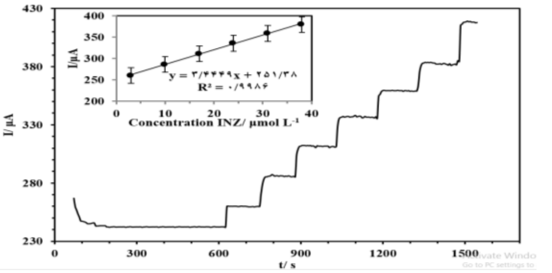


Fig. 7. The current – time profiles recorded at the SOFMS electrode during the successive addition of INZ. Inset: Typical calibration graph derived from the current – time profile.

The cyclic voltammetry and amperometric methods were used for the determination of INZ by using the standard additions method and gave mean values of 98.2 ± 0.9 and 98.8 ± 0.4 mg of INZ per tablet for three replicated respectively. The same samples were analyzed using the United States Pharmacopoeia (USP) method [38], which recommends a direct spectrophotometric measurement at 267 nm for the assay of the INZ and 98.5 mg was found for each tablet, which is in very good agreement with the declared value of 100 mg.

4. CONCLUSIONS

In the present study, the electrochemical behaviors of isoniazid at SOFMS electrode have been investigated. The modified electrode exhibits excellent and persistent electrocatalytic behavior toward INZ oxidation compared with the bare silver electrode. For SOFMS electrode, kinetic parameters such as the electron transfer coefficient (α), catalytic reaction rate constant(k) and the number of electrons involved in the rate determining step (n_α) for oxidation of INZ at the SOFMS surface were calculated as 0.51, $3.05839\times10^5 cm^3 mol^{-1} s^{-1}$ and 2, respectively. The method was successfully applied to the direct determination of INZ in pharmaceutical formulations with adequate reproducibility and sensitivity without any purification. A faster analysis for INZ can be performed by direct measurement from standard addition method.

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