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Electrocatalytic Oxidation of Hydrazine on Poly(4-Aminobenzene Sulfonic Acid)-Modified Glassy Carbon Electrode[1]

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Abstract—Electrocatalytic oxidation of hydrazine (HZ) was studied on an stable modified glassy carbon electrode (GCE) based on poly (4-aminobenzene sulfonic acid) (4-ABSA) film. The 4-ABSA-modified glassy carbon electrode was prepared by electrochemical polymerization technique in phosphate buffer solution (PBS) (pH 7.0) and its electrochemical behavior were studied by cyclic voltammetry (CV). The polymer film-modified electrode has very high catalytic ability for electrooxidation of HZ, which appeared as a reduced overpotential in a wide operational pH range of 5–10. Limit of detection (LOD) and limit of quantification (LOQ) were obtained as 1.31×10^{-7} and 4.35×10^{-7} M for CV; 7.89×10^{-8} and 2.63×10^{-7} M for CA, respectively. The results of experiments showed that prepared modified electrode have good stability, sensitivity and reproducibility for at least one month if stored dry in air.

Keywords: 4-aminobenzene sulfonic acid, modified-glassy carbon electrode, electropolymerization, electrocatalytic-oxidation, hydrazine, voltammetry

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1. INTRODUCTION

Hydrazine (N_2H_4) is the simplest diamine and the stating material in the preparation of several hydrazine derivatives. Hydrazine is used for water treatment, agriculture, pharmaceuticals chemical blowing agents and a wide variety of other applications. Also, hydrazine is very important in pharmacology because it has been recognized as a carcinogenic and hepatotoxic substance, which affects liver and brain glutathione.

Several techniques such as spectrophotometry [1], coulometry [2] potentiometry [3], titrimetry [4] and chemiluminescence [5] have been reported for the determination of hyrazine. The electrochemical techniques, which are economical, sensitive and rapid methodologies, were commenly used to determination of hydrazine [6–16]. However, the electrooxidation of hydrazine at carbon electrodes is kinetically slow and require high overpotentials. Therefore, the use of carbon electrodes is not common for hydrazine oxidation. In order to overcome these difficulties, chemically modified electrodes were used to enhance the rate of electron transfer and minimize its overpotential.

Glassy carbon modified by pyrocatechol violet [17], prussian blue [18], terpyridine manganese(II) complex [19], polypyrrole film [20], 3,4-dihydroxybenzaldehyde [21], pyrogallol red [22], poly(bromocresol purple) [23], tetrabromo-*p*-benzoquinone [24] are of various modified electrodes used in electrocatalytic oxidation of hydrazine.

Poly(4-ABSA) modified glassy carbon electrode was used determination of phenylephrine and chlorprothixene [25], hydroquinone in the presence of catechol and resorcinol [26], uric acide [27]. However, the determination of HZ at the 4-ABSA modified glassy carbon electrode has not yet been reported up to date. In this work, the direct electrochemical oxidation of HZ using the glassy carbon electrodes modified with poly (*p*-ABSA) film was investigated. The 4-ABSA modified glassy carbon electrode for electrocatalytic determination of HZ has been developed as a simple, sensitive, rapid and assay method for HZ.

2. EXPERIMENTAL

2.1. Apparatus

A potentiostat meter (VersaSTAT[3], Princeton Applied Research, USA) was used for the voltammetric measurements. All experiments were carried out in

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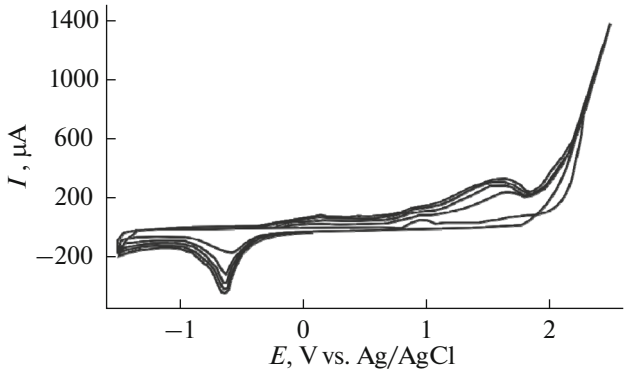


Fig. 1. Repetitive cyclic voltammograms of 4-ABSA in 0.10 M PBS (pH 7.0) containing 2.0×10^{-3} M initial potential −1.5 V; terminal potential +2.4 V; scan rate 100 mV s^{-1}.

a three electrode system. Glassy carbon (GC) electrodes (3.0 mm diameter) were purchased from BAS and used as a working electrode. A platinum wire auxiliary electrode and a Ag/AgCl (NaCl 3 M, BAS) reference electrode were used.

The firstly, the deoxygenation process of the supporting electrolyte solutions were carried out with argon gas for 5 min before all experiments. Then, the argon gas was also passed from the solutions for 60 s after the addition of each sample solution in the experiments. In each new experiment, a new bare GC electrode surface was used. A Molspin Titration System was used to pH measurements. All experiments were carried out at ambient temperature of the laboratory (15–20°C).

2.2. Polishing and Cleaning of GC Electrodes

GC electrodes were polished successively in 1, 0.3, 0.05 μm alumina slurries made from dry Buehler alumina and ultra pure deionize water on Buehler polishing microcloth. Polished GC electrodes were sonicated in Nanopure water, in a mixture of 1 : 1 (v/v) nitric acid/water ($HNO_3 + H_2O$) (Fluka) and then, in ethanol (aldrich) for 10 min each. Before the derivatization, the cleaned electrodes were rinsed with water and dried under a stream of argon.

2.3. Preparation of Modified Electrode

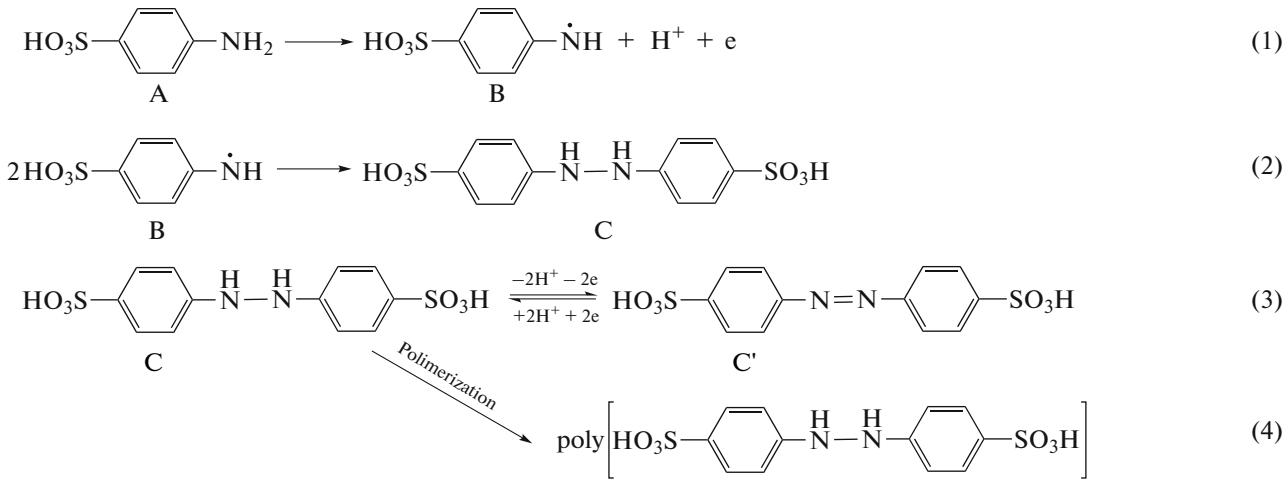
A bare GC electrode was immersed in 0.10 M PBS (pH 7.0) containing 2.0×10^{-3} M 4-ABSA solution and conditioned by cyclic sweeping between −1.5 to +2.5 V at 100 mV s^{-1} for 5 scans. Finally, the modified electrode was activated by cyclic voltammetry from −1.0 to +1.0 V at 100 mV s^{-1} for 10 scans in 0.10 M PBS (pH 7.0). Consequently, a bare GC electrode and modified GC electrode was used as a working electrode.

3. RESULTS AND DISCUSSION

3.1. Electropolymarization of 4-ABSA at the GCE Surface

Figure 1 shows the voltammograms of 4-ABSA on the GCE in 0.10 M PBS (pH 7.0) containing 2.0×10^{-3} M of 4-ABSA. In the first scan, a weak anodic and cathodic peak were observed with peak potential value at E_{pa} = 0.99 V and E_{pc} = −0.70 V, respectively. In the second scan, two anodic peaks appeared with peak potentials values at +0.13 and +1.45 V, respectively. The peaks current increased upon continuous scanning, reflecting the continuous growth of the polymerization film, and a blue polymer film was formed on the GCE surface. These results indicated that 4-ABSA was deposited on the surface of GCE by electropolymerization [25–29]. The poly(*p*-ABSA) modified electrode was thoroughly washed with double-distilled water and stored in 0.1 M PBS (pH 7.0) before use.

The electropolymerization behavior of *p*-ABSA at GCE was similar to the references reported [25–29]. The reaction mechanism may be similar to that proposed in below Scheme 1.



Scheme 1. Suggested electrochemical polymerization of 4-ABSA at GCE.

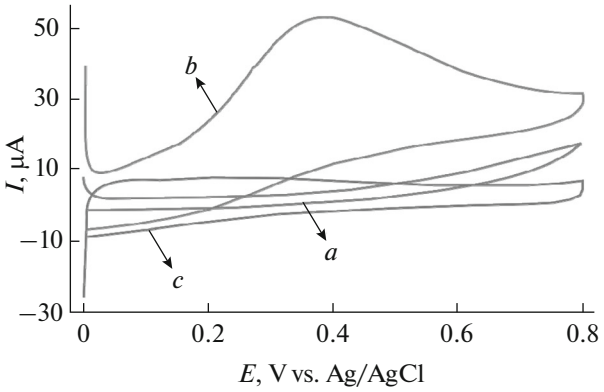


Fig. 2. Cyclic voltammograms of 3×10^{-4} M HZ at (*a*) bare (*b*) 4-ABSA modified glassy carbon electrode at pH 7 in phosphate buffer solution at scan rate 50 mV s^{-1}. The voltammogram of (*c*) is the background obtained by using the modified glassy carbon.

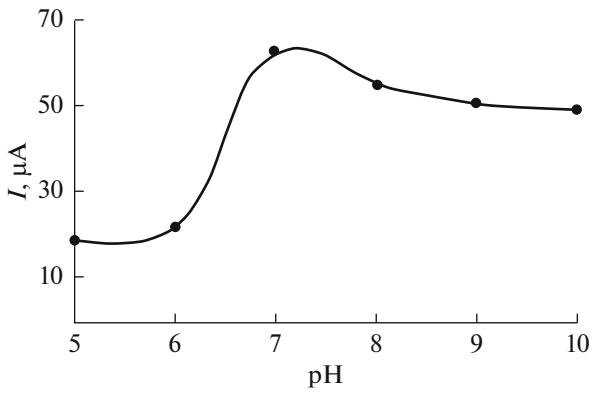


Fig. 3. Dependence of the oxidation peak current of 7×10^{-4} M HZ on pH values in 0.1 M PBS buffer, at a scan rate of 50 mV s^{-1} .

As can be seen from above Scheme 1, 4-ABSA (A) was first oxidized to free radical (B) (peak 1); the free radical (B) combined together rapidly to form hydrazobenzene sulfonic acid (C); then hydrazobenzene sulfonic acid (C) was oxidized to azobenzene sulfonic acid (C') (peak 3), and azobenzene sulfonic acid (C') was reduced to hydrazobenzene sulfonic acid (C) (peak 2) and finally the electrode surface was covered by the formed polymer (D).

3.2. Electrochemical Oxidation of HZ on 4-ABSA Modified Glassy Carbon Electrode

The electrochemical responses of HZ on the bare GC and 4-ABSA modified GC have been studied by using cyclic voltammetry. The cyclic voltammograms of 3×10^{-4} M HZ at a GC (a) and the poly(4-ABSA/GC) (b) at pH 7 in phosphate buffer solution at 50 mV s^{-1}, were shown in Fig. 2.

At the surface of bare GC electrode, a featureless voltammogram belonging to HZ was observed (Fig. 2a). However, a sharp peak was observed at 375 mV, at the surface of poly(4-ABSA/GC) electrode (Fig. 2b). In comparison with the data at the bare GC electrode, an increase in peak and a decrease in overpotential of HZ were observed at modified GC electrode.

The pH of the HZ solutions was changed using buffer solutions ranging from pH 5 to 10 and its effect on the electrochemical signal was investigated (Fig. 3). For the oxidation of hydrazine, the anodic peak potential shifts toward a less positive values with increasing pH up to 7.0. At the same time, the oxidation peak current of HZ reaches maximum at pH 7.0. Therefore, pH 7.0 was selected for further studies .

Figure 4a shows the cyclic voltammograms of the poly(4-ABSA/GC electrode in 0.1 mol L^{-1} phosphate buffer (pH 7.0) containing 3×10^{-4} M HZ at scane rates: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV s^{-1}.

The peak current values plotted against $v^{1/2}$ were shown in Fig. 4b. With increasing scan rate, the oxidation peak current increased. A good linearity between the square root of scan rate and peak current was obtained between the range of 20–100 mV s^{-1}. The linear regression equation was $I_p(\mu A) = 7.122v^{1/2} + 2.673$ with correlation coefficient ($R^2 = 0.998$) [29].

The logarithm of peak current ($\log I$) against the logarithm of scan rate ($\log v$) was shown in Fig. 5. Also, the plot of logarithm of peak current ($\log I$) versus logarithm scan rate ($\log v$) has a slope of 0.477 which is almost close to the theoretical value of 0.50. The equation was $\log I_p(\mu A) = 0.477 \log v + 0.916$ ($R^2 = 0.998$) on modified electrode [29].

Figure 6 displays the cyclic voltammograms of various concentrations of hydrazine at the poly(4-ABSA/GC) electrode in 0.1 M PBS, pH 7.0.

A plot of the peak current values as a function of the concentration was drawn (Fig. 7). The plot was linear in the concentration range of 5×10^{-6} to 1×10^{-4} M HZ. The equation was I_p (μA) = 17199c + 8.123, R^2 = 0.997 (Fig. 7) on modified electrode. The slope was 17199 μA M^{-1}, the intercept was 8.123 μA and the correlation coefficient was $R^2 = 0.997$. Limit of detection (LOD) and limit of quantification (LOQ) values was calculated using the following equations [29]:

$$\text{LOD} = 3\,s/m,\ \text{LOQ} = 10\,s/m.$$

Where, s is the standard deviation of the peak currents (for five runs) and m is the slope of the calibration curve. The achieved LOD and LOQ were 1.31×10^{-7} M and 4.35×10^{-7} M for CV on poly(4-ABSA)-modified GCE, respectively.

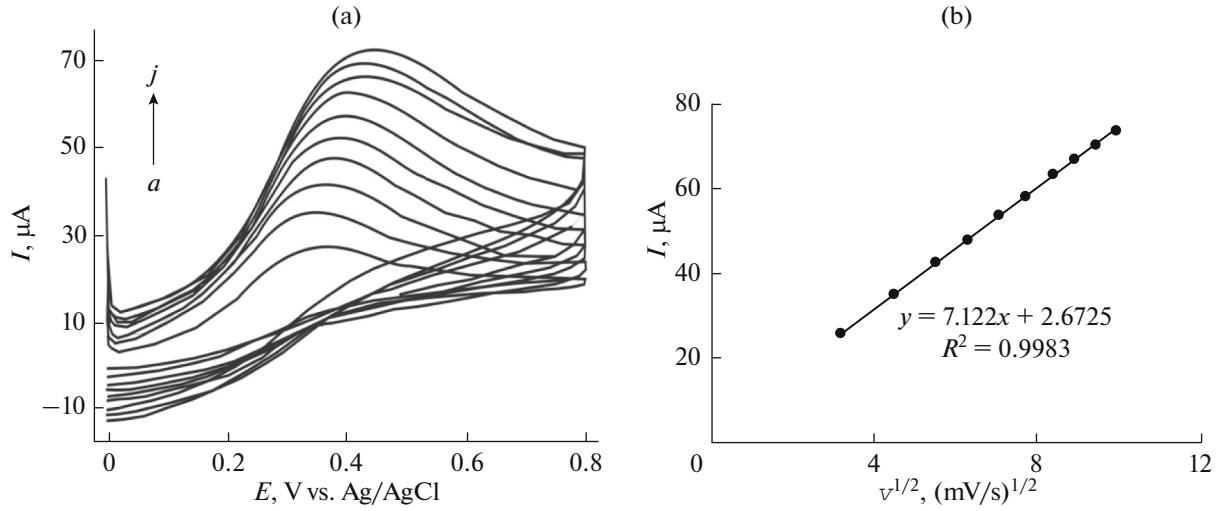


Fig. 4. (a) Cyclic voltammograms of the poly(4-ABSA/GC) electrode in 0.1 M PBS (pH 7.0) containing 3×10^{-4} M HZ at scan rates: (*a*) 10, (*b*) 20, (*c*) 30, (*d*) 40, (*e*) 50, (*f*) 60, (*g*) 70, (*h*) 80, (*i*) 90, (*j*) 100 mV s^{-1} . (b) Dependence of the peak current with square root of the scan rate in 0.1 M PBS (pH 7.0) containing 3×10^{-4} M HZ .

The electrocatalytic oxidation of HZ at the poly(4-ABSA/GC) electrode was studied by chronoamperometry. The chronoamperograms obtained for a series of HZ solutions with various concentrations as illustrated in Fig. 8a. An increase in concentration of HZ was accompanied by an increase in anodic currents obtained for a potential step of 380 mV versus reference electrode.

The current values recorded of the chronoamperograms obtained for a series of HZ solutions were used to drawn the calibration plot (Fig. 8b).

The plot drawn with current values obtained from chronoamperometric response was linear in the concentration range of 5×10^{-6} to 1×10^{-4} M HZ. The LOD and LOQ values obtained from this calibration plot are 7.89×10^{-8} and 2.63×10^{-7} M, respectively [29].

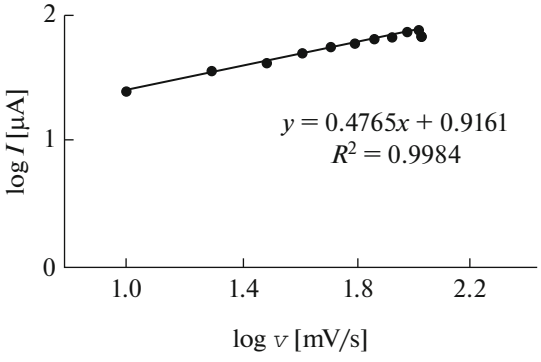


Fig. 5. Dependence the logarithm of peak current (log *I*) against the logarithm of scan rate (log *v*) at the poly(4-ABSA/GC) electrode in 0.1 M PBS (pH 7.0) containing 3×10^{-4} M HZ. Scan rates: 10, 20, 30, 40, 50, 60,70, 80, 90, 100 mV s^{-1} .

3.3. Proposed Electrochemical Oxidation Mechanism of Hydrazine at poly(4-ABSA)-modified GCE

Hydrazine was oxidized on poly(4-ABSA)-based electrode by electrochemical redox reaction. Based on the results, the following mechanisms can be proposed for the mediated oxidation of the hydrazine on the modified glassy carbon electrode. The redox transition of the poly(4-ABSA) and hydrazine species is as follows reaction mechanisms after determining the number of electrons and proton transferred.

3.4. Determining Electrons and Proton Transferred

The pH dependence of the oxidation of hydrazine was investigated. With the increasing in pH of solutions, the peak potential linearly shifts to positive values. That indicates participation of proton transfer in the electrode reaction. The linear relation between E_{pa} and pH can be expressed as [30, 31]:

The plot of the E_{pa} as a function of pH:

$$E_{pa}\ (\text{V}) = a\ \text{pH} + \text{intercept}\ (y = ax + b).$$

Where E_{pa} refers to anodic peak potential, *a* is slope, *x* is pH and *b* is intercept. From this equation, slope was found to be 53 mV/pH ($r = 0.98$). This closeness of the expected theoretical value of 59 mV/pH (Nernstain value) suggests that the number electron transferred is equal to that of the hydrogen ions taking part in the electrode reaction. In other word, the electro-

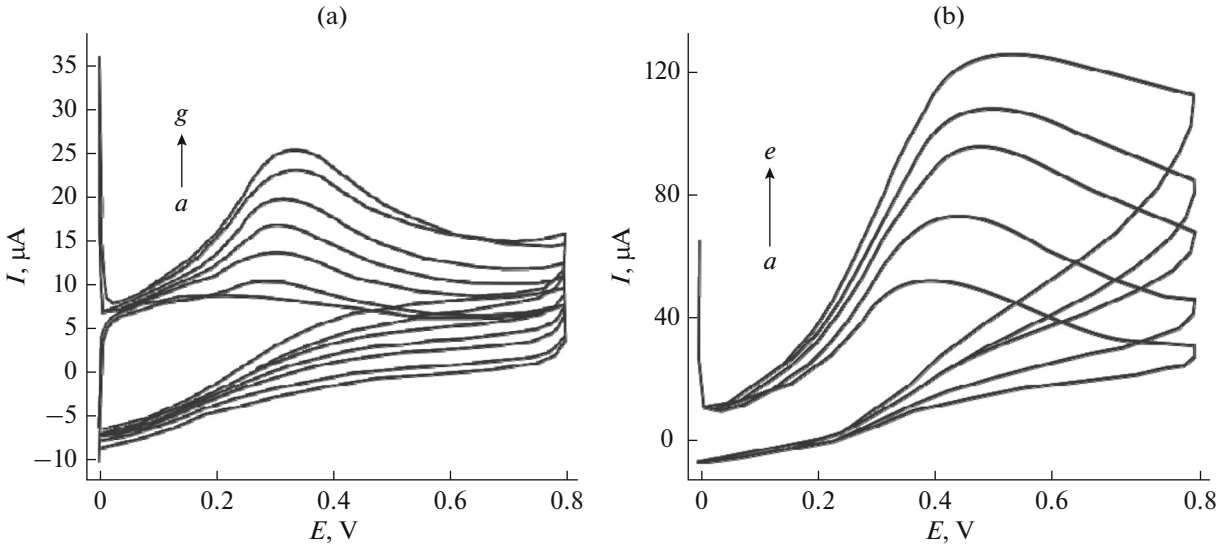


Fig. 6. Cyclic voltammograms for increasing concentrations of HZ (a) (*a*) 5×10^{-6} M, (*b*) 1×10^{-5} M, (*c*) 3×10^{-5} M, (*d*) 5×10^{-5} M, (*e*) 7×10^{-5} M, (*f*) 9×10^{-5} M, (*g*) 1×10^{-4} M; (b) (*a*) 3×10^{-4} M, (*b*) 5×10^{-4} M, (*c*) 7×10^{-4} M, (*d*) 9×10^{-4} M and (*e*) 1×10^{-3} M in 0.1 M PBS (pH 7.0) on the poly(4-ABSA/GC) electrode . Scan rate was 50 mV s^{-1} .

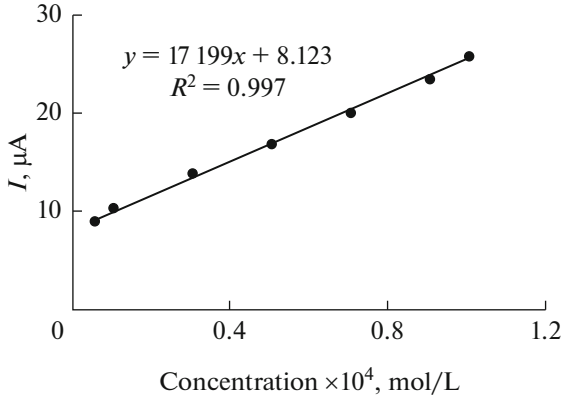


Fig. 7. Calibration plot for concentrations of HZ from cyclic voltammograms.

chemical oxidation reaction of hydrazine involves a H^+ : e ratio equal to one [30–32]. For an irreversible electrode process, according to laviron, E_{pa} is defined by the fallowing equation [30].

$$E_{pa} = E^0 + 2.303(RT/\alpha nF)\log(RTk^0/\alpha nF) + 2.303(RT/\alpha nF)\log v.$$

Where α is the transfer coefficient, k^0 the standard heterogeneous rate constant of the reaction. n the number of electrons transferred and E^0 is the formal redox potential. Other symbols have their usual meanings. Hence, The value of αn can be calculated from the slope of E_{pa} versus log *v*. In this reaction, the slope was found as 0.0591. The slope is equal to $2.303(RT/\alpha nF)$ and taking $T = 298$ K, $R = 8.314$ J K^{-1} mol^{-1} and $F = 96480$, αn was calculated as 1.01. According to Bard and Faulkner [30, 33], α can be given as

$$\alpha = 47.7/(E_{pa} - E_{pa/2})\ \text{mV},$$

where E_{pa} is the anodic peak potential, $E_{pa/2}$ is the potential where the current is at half the value. So, from this equation, the value of α was calculated as 0.254. Using this value in $\alpha n = 1.01$, then number of electrons transferred (*n*) was calculated as $4.02 \approx 4$ [30].

According to the above data, oxidation of hydrazine is four electrons and four protons process in the

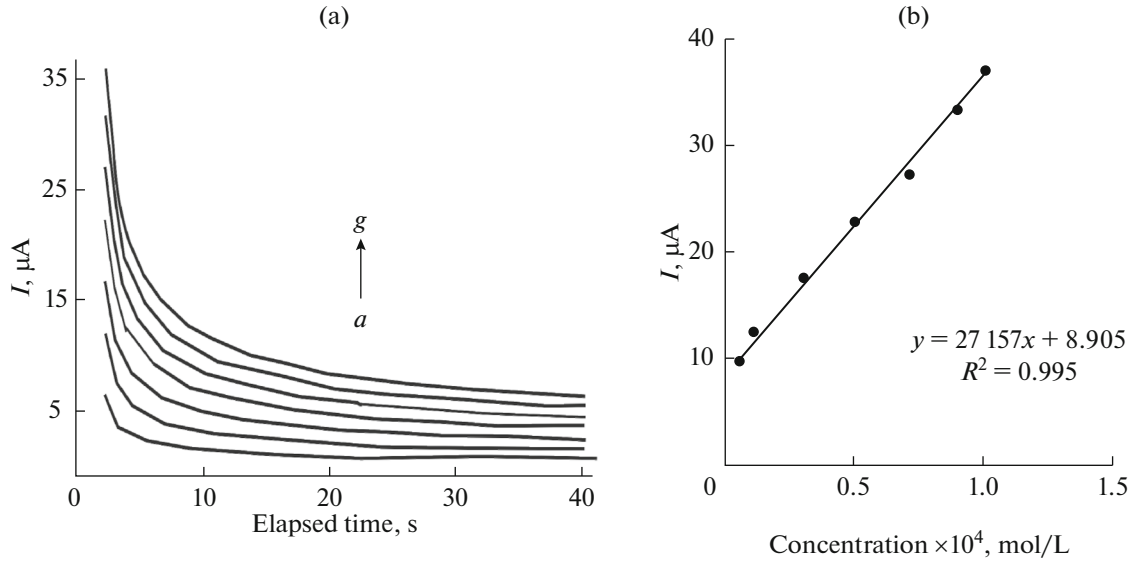
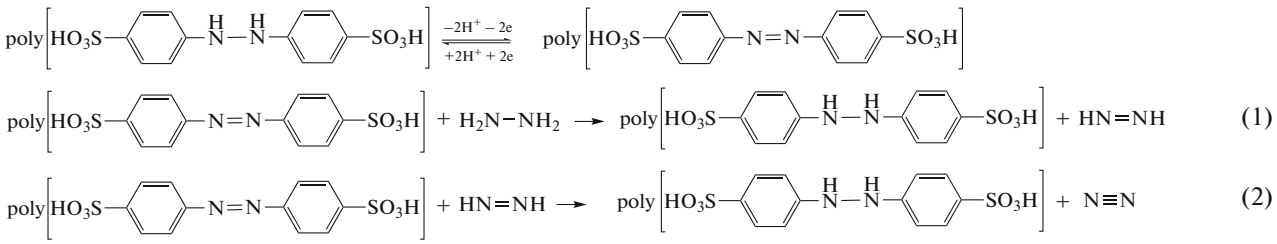


Fig. 8. (a) Chronoamperometric response of the poly(4-ABSA/GC) electrode for increasing concentrations of HZ, (*a*) 5×10^{-6} M, (*b*) 1×10^{-5} M, (*c*) 3×10^{-5} M, (*d*) 5×10^{-5} M, (*e*) 7×10^{-5} M, (*f*) 9×10^{-5} M, (*g*) 1×10^{-4} M in 0.1 M PBS (pH 7.0) containing different concentrations of HZ for a potential step of 380 mV vs. reference electrode. Variation of chronoamperometric currents at $t = 40$ s vs. concentration of HZ. (b) Calibration plot of HZ.

proposed electrochemical method (Scheme 2), good agreement with [32]:

$$N_2H_4 \rightarrow N_2 + 4\,H^+ + 4e \text{ (overall reaction).}$$

Hydrazine is irreversibly oxidized by four electron and four proton process to give N_2 as a final product.



Scheme 2. Proposed Electrochemical Oxidation Mechanism of Hydrazine at poly(*p*-ABSA)-modified GCE.

As can be seen from Scheme 2, on the poly(*p*-ABSA)- modified GCE, the reaction is formed out of hydrazine-diaza conversion by two steps (1) and (2). Hydrazine poly(*p*-ABSA) is transformed to diaza poly(*p*-ABSA) four electron and four proton process to give N_2 as a final product [32, 34].

4. CONCLUSIONS

Glassy carbon electrode coated with poly (4-aminobenzene sulfonic acid) film was used for electrocatalytic determination of HZ. It was shown that HZ can be determined using the cyclic voltammetry and amperometry techniques on the basis of its oxidation process at an overoxidation (poly(4-ABSA/GC) electrode. The modified electrode is determined stable for a long time and can be used for the electrocatalytic oxidation of HZ in phosphate buffer, pH 7.0

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