

Full Paper

Electrocatalytic Oxidation and Voltammetric Determination of Hydrazine at Bulk-Modified Carbon Paste Electrode with 1-[4-(Ferrocenyl Ethynyl Phenyl)]-1-Ethanone

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Received: 21 October 2013/ Accepted: 1 December 2013/

Published online: 28 February 2014

Abstract- The electrochemical behaviour of hydrazine studied at the surface of 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone (as an organo-metallic mediator) modified carbon paste electrode in aqueous media using cyclic voltammetry (CV) and double step potential chronoamperometry. It has been found, that under optimum condition (pH 8.00) in cyclic voltammetry, the oxidation of hydrazine is occurred at a potential about 300 mV less positive than that an unmodified carbon paste electrode. The kinetic parameters such as electron transfer coefficient, α and the catalytic reaction rate constant, k'_h were also determined using electrochemical approaches. The electrocatalytic oxidation peak current of hydrazine showed a linear dependent on the hydrazine concentration and the linear calibration plots were obtained in the ranges of 7.0×10^{-5} M - 1.8×10^{-2} M and 8.0×10^{-6} M - 1.0×10^{-3} M of hydrazine concentration with CV and differential pulse voltammetry (DPV) methods, respectively. The detection limits (2σ) were determined as 1.4×10^{-5} M and 1.2×10^{-6} M by CV and DPV methods. The RSD% for seven replicates determination of 20.0 and 50 $\mu\text{mol L}^{-1}$ of hydrazine were 1.8 and 1.6%, respectively. This method was also examined as a selective, simple and precise new method for voltammetric determination of hydrazine in real sample.

Keywords- Hydrazine, 1-[4 (ferrocenyl ethynyl) phenyl]-1-Ethanone, Organo-Metallic mediator, Electrocatalysis, Carbon paste electrode

1. INTRODUCTION

In recent years, intensive investigations have been carried out on chemically modified electrodes (CMEs), due to their fast, selective, reproducible, sensitive response and low cost for a chemical analysis [1-7]. Many different strategies have been employed for the modification of the electrodes [1-9]. Among the many different strategies used for the modification of an electrode, approach of preparing bulk-modified electrode has been of particular interest [10-15]. For this, a solid electrocatalyst is mixed with a carbon composite matrix such as carbon paste or carbon powder-epoxy resin [16-20]. It has been shown that bulk modification is flexible and easy to perform. When the electrode surface has become inactive by, e. g., poisoning of the catalyst by impurities, a fresh surface layer containing the catalyst is easily obtained by polishing.

On other hand, the practical applications of ferrocene and its derivatives can be grouped in the following main classes: absorbers of different types of radiation, including cosmic rays, regulators of combustion processes, highly effective non-toxic medicinal substances, components of various redox systems and especially as a mediator in determination on some important compound [21-23].

Hydrazine is widely used as a raw material in the manufacture of agricultural chemicals, a powerful reducing agent in fuel cell, intermediates in industrial preparations of pesticides, plant growth regulators, polymerization catalysts, corrosion inhibitor and antioxidant [24,25]. It is also very important in pharmacology, because it is recognized as a carcinogenic, hepatotoxic and mutagenic substance [5,26]. It has been reported that hydrazine and its derivatives have adverse health effects [27]. Therefore, sensitive detection of hydrazine is practically important for environmental and biological [26], which more attention has been drawn to the development of methods for determination of hydrazine. In the literatures, several methods using titrimetry [28], coulometry [29], amperometry [30,31], potentiometry [32,33], spectrophotometry [34,35] and chromatography [36-38] have been reported for the determination of hydrazine.

Investigation of electrochemical behavior of hydrazine showed a slow kinetic electron transfer in aqueous media at the surface of common electrodes. Although metals such as Pt, Au and Ag are very active in the anodic oxidation of hydrazine, they are too expensive for the practical applications. Unfortunately, hydrazine has large oxidation overpotential at ordinary carbon electrodes. It has been found that the overpotential for the oxidation of hydrazine depends on the electrode material [39], the history of the electrode and type of employed pretreatment [40]. Therefore, in this study, we describe the use of 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone as an organo-metallic mediator for the electrooxidation of hydrazine in

aqueous media. Therefore, the suitability of the 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone modified carbon paste electrode in the electrocatalytic oxidation of hydrazine and also its voltammetric determination are discussed by cyclic voltammetry, double potential step chronoamperometry and differential pulse voltammetry methods.

2. EXPERIMENTAL

2.1. Materials

The solvent used for the electrochemical studies was twice distilled water. Buffer solution were prepared from orthophosphoric acid and its salts in the pH ranges 3.00-11.00. 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=0.1 mm) from Merck was used as the working electrode (WE) substrate. The 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon was prepared by a reported procedure [41]. Hydrazine was from Fluka and was used as received. All other reagents were of analytical grade.

2.2. Working electrode

A 1% (w/w) 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon spiked carbon powder was made by dissolving the given quantity of 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon in diethyl ether and hand mixing with 99 times its weight of graphite powder with a mortar and pestle. The solvent was evaporated by stirring a 1:1(w/w) mixture of 1% 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon spiked carbon powder and paraffin oil was blended by hand-mixing and the resulting paste was inserted in the bottom of a glass tube (with internal radius 3.0 mm). The electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon was used as a blank to determine background current.

2.3. Apparatus

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP 2061-C Electrochemical Analysis System, Behpajoo, Iran) coupled with a Pentium III personal computer connected to a HP laser jet 6L printer, and experiments were performed in a three compartment cell. A platinum wire was used as the auxiliary electrode. The 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon modified carbon paste electrode (4FEP EMCPE) and Ag|AgCl|KCl_{sat} (Metrohm) were used as the working and reference electrodes, respectively. A pH-meter (Ion Analyzer 250, Corning) was used to read the pH of the buffered solutions.

3. RESULT AND DISCUSSION

3.1. Electrochemistry of 4FEPEMCPE

The electrochemical behavior of 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone modified carbon paste electrode was investigated using cyclic voltammetry (Fig. 1A). The cyclic voltammogram exhibited an anodic peak at the forward scan of the potential related to the oxidation of the 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone to its ferrocinium form and at the reverse scan of the potential, a cathodic peak related to reduction of ferrocinium ion to ferrocene. The cyclic voltammetric data of 4FEPEMCPE in 0.1 M phosphate buffer solution (pH 7.00) at 100 mV s⁻¹ shows in Table 1). The effect of scan rates of potential (v) on the electrochemical behavior of 4FEPEMCPE shows a linear dependent of anodic and cathodic peak current *vs.* $v^{1/2}$ (Fig. 1B), that demonstrates a diffusion controlled process for Fe²⁺/Fe³⁺ redox couple of 4FEPEMCPE.

Table 1. Cyclic voltammetric data obtained for constructed 4FEPEMCPE in 0.1 M phosphate buffer solution (pH 7.00) at 100 mV s⁻¹

E_{pa} (V) ^a	E_{pc} (V) ^a	I_{pa} (μ A)	I_{pc} (μ A)	Γ_a (mol cm ⁻²)	Γ_c (mol cm ⁻²)
0.58	0.42	5.1	-4.3	3.65×10^{-9}	2.19×10^{-9}
(0.85) ^b	(2.2) ^b	(1.6) ^b	(2.3) ^b	(3.3) ^b	(2.9) ^b

^a Versus Ag | AgCl | KCl_{sat} as reference electrode.

^b The values in parentheses indicate the calculated RSD%

3.2. Electrooxidation of hydrazine at the surface of 4FEPEMCPE

It well known, the electrochemical behavior of hydrazine is dependent on pH value of the aqueous solution, whereas the electrochemical properties of Fc/Fc⁺ redox couple of this modifier are independent pH. Therefore, we studied the electrochemical behavior of hydrazine in 0.1 M phosphate buffered solution with various pH (3.00 < pH < 11.00) at the surface of 4FEPEMCPE by cyclic voltammetry. Fig. 2 shows the variation of the electrooxidation peak current (I_{pa}) of hydrazine *vs.* to pH value of aqueous buffered solutions at 4FEPEMCPE.

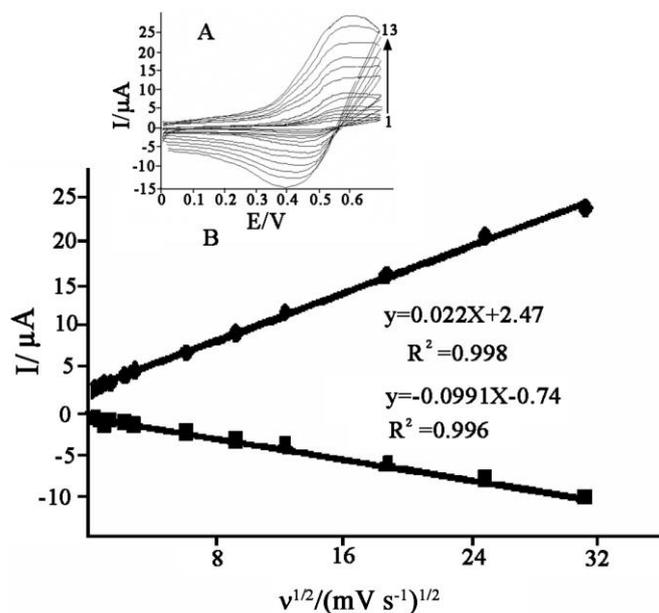


Fig. 1(A). Cyclic voltammograms of 4FEP EMCPE in 0.1 M phosphate buffer + 0.1 M LiClO_4 at pH 7.00, at various scan rates of potentials: 1) 10; 2) 20; 3) 30; 4) 40; 5) 50; 6) 80; 7) 100; 8) 200; 9) 300; 10) 400; 11) 600; 12) 800 and 13) 1000 mV s^{-1} . B) The plots of anodic and cathodic peak currents vs. $v^{1/2}$ from cyclic voltammograms of (A)

As can be seen, that maximum I_{pa} was obtained in pH 8.00. Therefore, pH 8.00 was chosen as the optimum pH for electrocatalytic oxidation of hydrazine at the surface of 4FEP EMCPE. Hence, all electrochemical experiments were done at this pH.

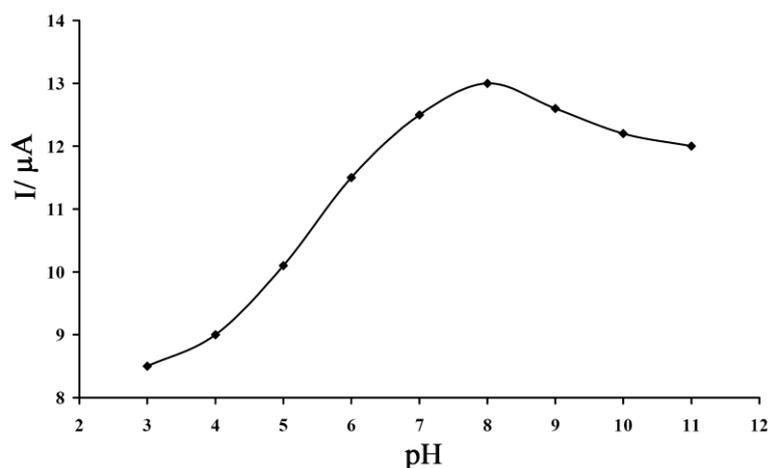


Fig. 2. Current-pH curve for electrooxidation of 7.43 mM hydrazine in 0.1 M phosphate buffer solution with various pH values: a) 3.00, b) 4.00, c) 5.00, d) 6.00, e) 7.00, f) 8.00, g) 9.00, h) 10.0 and i) 11.0 at the surface of 4FEP EMCPE as scan rate 20 mV s^{-1}

3.3. Electrocatalytic oxidation of hydrazine

The cyclic voltammograms of 4FEPEMCPE and CPE in phosphate buffer solutions (pH 8.00) in the absence and the presence of 7.43 mM hydrazine is presented in Fig. 3. In the absence of hydrazine a pair of well-defined redox peaks of 4FEPEMCPE can be observed (Fig. 3, curve c). Upon the addition of 7.43 mM hydrazine, there was a drastic enhancement of the anodic peak current, and in addition, no cathodic current was observed in the reverse scan of potential (Fig. 3, curve d). This behaviour is consistent with a very strong electrocatalytic effect. Under the same experimental condition, the direct oxidation of hydrazine at the surface of an unmodified carbon paste electrode (CPE) shows an irreversible peak at more positive potential (Fig. 3, curve b), whereas no anodic or cathodic peaks appear at the CPE in the absence of hydrazine (Fig. 3, curve a). The catalytic oxidation peak potential of hydrazine is found to be about 560 mV vs. Ag|AgCl|KCl_{sat}, whereas the oxidation peak potential of hydrazine at CPE is about 860 mV vs. Ag|AgCl|KCl_{sat}. Thus, a decrease in the over-voltage for oxidation of hydrazine at 4FEPEMCPE of is approximately shown 300 mV and an enhancement of the peak current is also achieved at modified electrode. The above results show the oxidation of hydrazine is facilitated and catalyzed by presence of 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon spiked into carbon paste electrode.

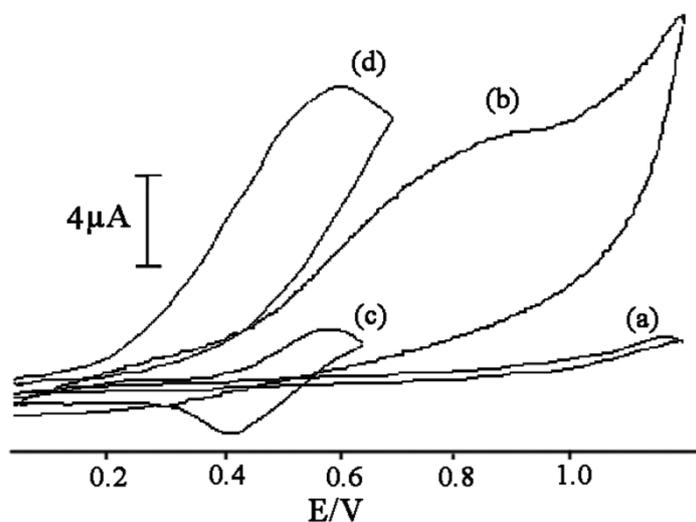


Fig. 3. Cyclic voltammograms of a) CPE in 0.1 M phosphate buffer solution (pH 8.00) at scan rate 20 mV s⁻¹ in the absence and b) in the presence of 7.43 mM hydrazine, c) as a) and d) as b) at the surface of 4FEPEMCPE

The presence of 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon as the mediator on the surface electrode provides an alternative reaction site to carbon paste for electron transfer

process of hydrazine. Therefore, the current due to the oxidation of hydrazine is increased when a 4FEPEMCPE was used.

In order to get the information on the rate determining step, Tafel slope (b) determines using the following equation for a totally irreversible diffusion controlled process [42]:

$$E_p = b/2 \log v + \text{constant} \quad (1)$$

Based on Equation 1, the slope of E_p versus $\log v$ is $b/2$, where b indicates the Tafel slope. The slope of E_p versus $\log v$ plot was found to be 0.051 V in this work (Fig. 4), thus, $b = 2 \times 0.051 = 0.102$ V. This slope value indicated an electron transfer process, which is the rate limiting step by assumption of a transfer coefficient (α) equal to 0.579.

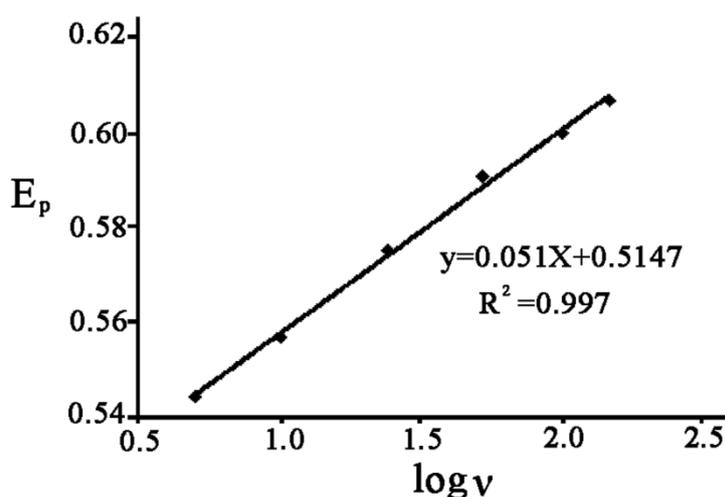


Fig. 4. The peak potential, E_p dependence on $\log(v)$ for the oxidation of hydrazine at the surface of 4FEPEMCPE

Also, The values of αn_α (where α is the transfer coefficient and n_α is the number of electrons involved in the rate determining step) were calculated for the oxidation of hydrazine at pH 8.00 at both modified and unmodified carbon paste electrodes according to the following equation [43]:

$$\alpha n_\alpha = 0.048 / (E_p - E_{P/2}) \quad (2)$$

Here, $E_{P/2}$ is the potential corresponding to $I_{P/2}$. The values for αn_α , were found to be 0.571 and 0.23 for the oxidation of hydrazine at the surface of 4FEPEMCPE and CPE, respectively. These values clearly show that not only the over-potential for hydrazine oxidation is reduced at the surface of 4FEPEMCPE, but also the rate of the electron transfer process is greatly enhanced; this phenomenon is thus confirmed by the larger I_a values recorded during cyclic voltammetry at 4FEPEMCPE.

3.4. Chronoamperometric studies

Double step potential chronoamperometry was also employed to investigation of electrochemical behavior of aqueous buffered solution (pH 8.00) containing of various concentration of hydrazine at 4FEPEMCPE by setting the working electrode potential at 0.7 V (at the first potential step) and 0.30 V (at the second potential step) *vs.* Ag|AgCl|KCl_{sat} (Fig. 5). As can be seen, there is not any net cathodic current corresponding to the reduction of mediator in the presence of hydrazine, when the potential is stepped from 0.70 V to 0.30 V *vs.* Ag|AgCl|KCl_{sat}. However, in the presence of hydrazine, the charge value associated with forward chronoamperometry is signification greater than that observed for backward chronoamperometry (Fig. 5, insert A). Fig. 5 insert B shows the plots of currents sampled at fixed time as a function of the hydrazine concentration added to a blank solution (pH 8.00) at different times after the application of potential step. Comparing of graphs (a), (b), (c), and (d) in this figure suggests that in all cases there is a similar connection between the currents measured at a fixed time and the hydrazine concentration, but the slop of the calibration graph is increased with a decrease in the time elapsed after a potential-step application. The linearity of electrocatalytic current *vs.* $v^{1/2}$ is shown this current is controlled by diffusion of hydrazine from bulk solution toward surface of electrode that caused to near-Cottrellian behavior. Therefore, the slope of linear region of Cottrell's plot can be used to estimate the diffusion coefficient (D) of hydrazine.

A plot of I versus $t^{-1/2}$ for a 4FEPEMCPE in the presence of hydrazine given a straight line, the slop of such lines can be used to estimate the diffusion coefficient of hydrazine in the ranges (1.0 and 4.0 mM). The mean value of the D found to be $2.55 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Therefore, the results show that mediator at the surface of 4FEPEMCPE can catalyze the oxidation of hydrazine. The rate constant for the chemical reaction between hydrazine and redox sites in 4FEPEMCPE, k_h can be evaluated by chronoamperometry according to the method described in [44]:

$$I_C / I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (K_h C_b t)^{1/2} \quad (3)$$

Where I_C is the catalytic current of 4FEPEMCPE in the presence of hydrazine and I_L is the limited current in the absence of hydrazine, C_b is the bulk concentration of hydrazine (mol cm^{-3}), k_h and t are the catalytic rate constant ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and time elapsed (s) respectively. The above equation can be used to calculate the rate constant of catalytic process (k_h). The value of k_h can be simply calculated for a given concentration of substrate from the slope of I_C/I_L versus $t^{1/2}$ plot. The calculated value of K_h is $5.27 \times 10^2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ using the slope of $I_C/I_L \cdot t^{1/2}$ plot (Fig. 6). This value of k_h explains as well as the sharp feature of the catalytic peak observed for catalytic oxidation of hydrazine at the surface of 4FEPEMCPE. On the

other hand, the heterogeneous rate constant of catalytic reaction was calculated as $K'_h = 2.1 \times 10^{-3} \text{ cm s}^{-1}$.

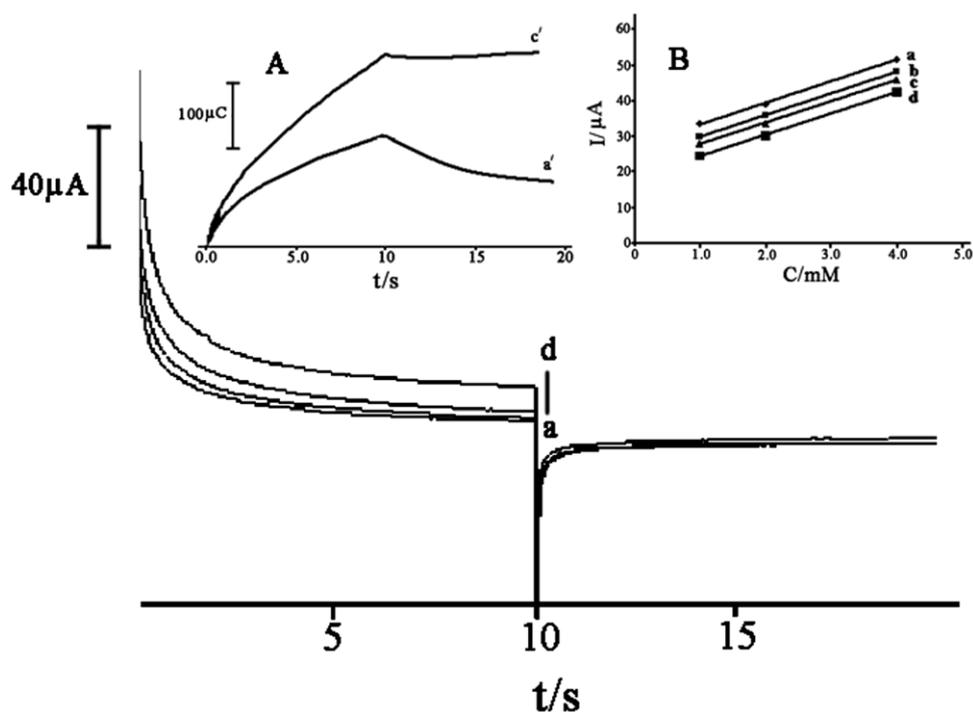


Fig. 5. Chronoamperograms obtained at the 4FEP/EMCPE in the absence a) and presence of b) 1.0, c) 2.0 and d) 4.00 mM of hydrazine in 0.1 M phosphate buffer solution (pH 8.00). First and second potential steps were 0.7 and 0.3 V. vs. Ag|AgCl|KCl_{sat}. Insert A) Shows the charge-time curves: a') for curve a) and c') for curve c). Insert B) Dependence of the fixed-time current observed for a) 0.3; b) 0.4; c) 0.515; and d) 0.67 s after the first potential step vs. hydrazine concentration derived for chronoamperograms data

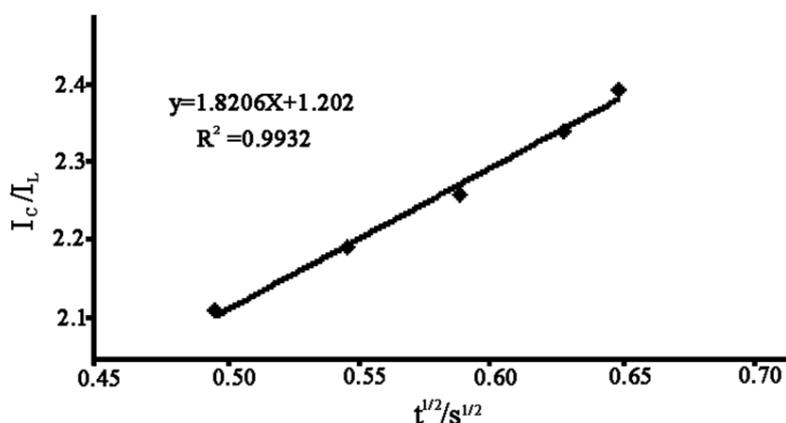


Fig. 6. Dependence of I_c/I_L on the $t^{1/2}$ driven from the chronoamperogram data

3.5. Electrocatalytic determination of hydrazine

The electrocatalytic peak current of hydrazine oxidation at the surface of the 4FEP EMCPE can be used for determination of hydrazine in solution. Therefore, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed using 4FEP EMCPE in phosphate buffer solution containing various concentration of hydrazine. The results show the electrocatalytic peak current of hydrazine oxidation at the surface of 4FEP EMCPE was linearly dependent on the hydrazine concentration, and the range of this linearity depended on the amount of mediator in the electrode matrix. The mediated oxidation peak currents of hydrazine at the surface of 4FEP EMCPE were proportional to the concentration of the hydrazine within the ranges $7.0 \times 10^{-5} \text{ M} - 1.8 \times 10^{-2} \text{ M}$ (with the correlation coefficient of 0.9936) and $8.0 \times 10^{-6} \text{ M} - 1.0 \times 10^{-3} \text{ M}$ (with the correlation coefficient of 0.9943) in the cyclic voltammetry and differential pulse voltammetry, respectively (Fig. 7 and 8). The detection limits (2σ) were $1.4 \times 10^{-5} \text{ M}$ and $1.2 \times 10^{-6} \text{ M}$ for CV and DPV, respectively. Table 2 summarized details of the methods from available references along with their analytical parameters for determination of hydrazine and compared them with the proposed method. These values are comparable to the values obtained by other research groups.

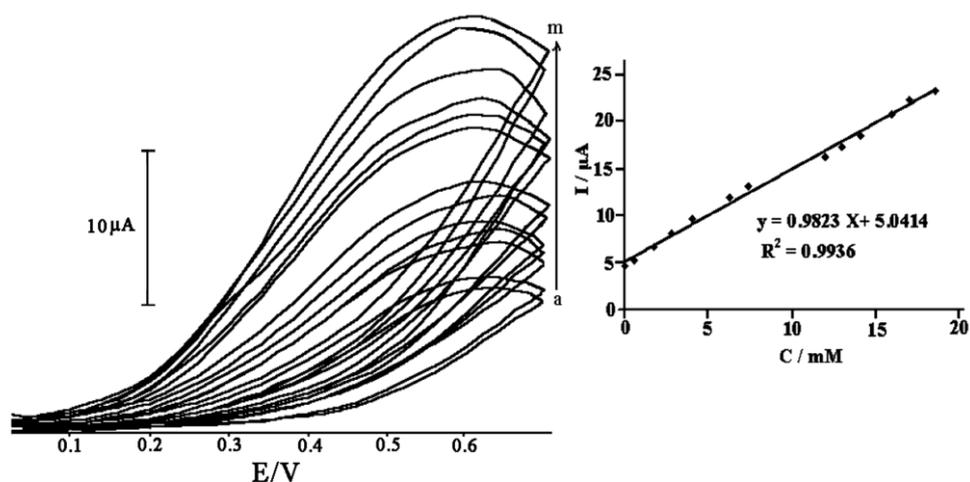


Fig. 7(A). Cyclic voltammograms of 0.1 M buffer solution (pH 8.00) in the presence of hydrazine in various concentration: 1)0.07; 2)0.62; 3) 1.80; 4) 2.85; 5) 4.09; 6) 6.32 7) 7.43; 8) 12.00; 9) 13.00; 10) 14.12; 11) 16.00; 12) 17.00 and 13) 18.58 mM at the surface of 4FEP EMCPE at $v=20 \text{ mV s}^{-1}$. B) the plot of electrocatalytic peak current of hydrazine [from CV of (A)] vs. its concentrations.

To evaluate the applicability of proposed method for voltammetric determination of hydrazine, the recovery of hydrazine was determined in drinking and river water. The

standard addition method was used for the analysis of prepared samples. The data given in Table 3 shows the satisfactory results.

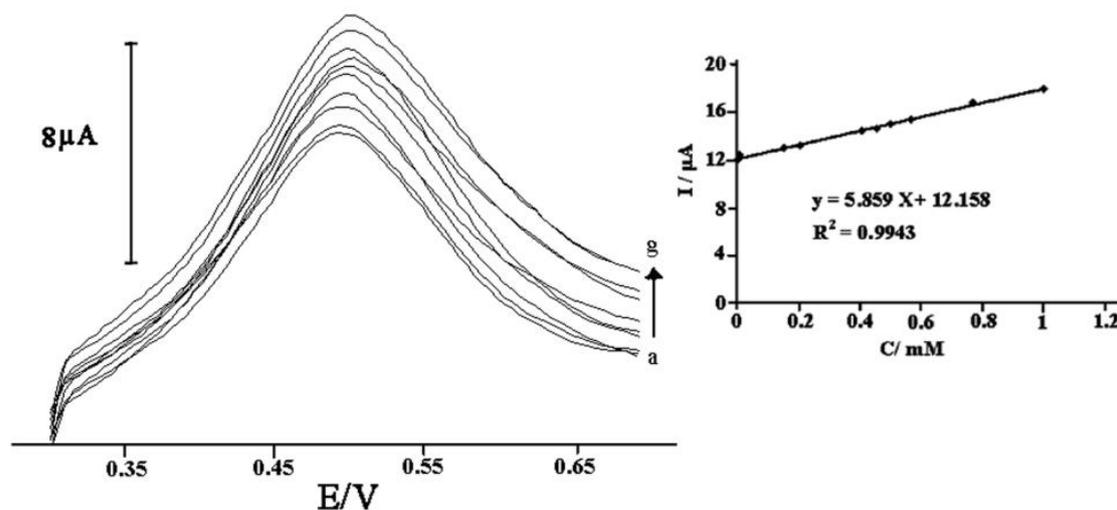


Fig. 8(A). Differential pulse voltammograms of 4FEPEMCPE in a) absence and presence of b) 0.008; c) 0.153; d) 0.206; e) 0.407; f) 0.456; g) 0.501; h) 0.568; i) 0.770 and g) 1.00 mM of hydrazine in 0.1 M phosphate buffer solution (pH 8.00). B) The plot of electrocatalytic peak current of hydrazine [from DPV of (A)] vs. its concentrations

Table 2. The reported electrodes in the literature and the proposed one for electrocatalytic determination of hydrazine

Electrode	Modifier	Methods	E_p (mV)	pH	LDR(μ M)	LOD(μ M)	Reference
GC ^a	Chlorogenic acid	CV ^b	240	----	50-1000	----	[45]
GC	Fe-tetraamino phthalocyanin	CV	300	13	1-10000	----	[46]
GC	Pyrocatechol violet	CV	240	7.5	5-40	4.2	[47]
GC	Pyrogallol red	LSV ^c	200	9	50-600	2	[48]
GC	Hydroquinone Salophen	CV	212	----	10-400	1.6	[49]
CPE	4FEPE ^d	DPV ^e	560	8	8-1000	1.4	This work

^a Glassy carbon

^d 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon

^b Cyclic voltammetry

^e Differential pulse voltammetry

^c Linear sweep voltammetry

Table 3. Determination of hydrazine in water sample

Sample	Hydrazine added (μM)	Hydrazine found (μM) ^b	Recovery (%)
Drinking water	-----	<detection limit	----
Drinking water	10.0	10.11 \pm 0.8	101.1
Drinking water	20.0	20.85 \pm 1.2	104.25
Drinking water	30.0	29.67 \pm 0.9	98.9
River water ^a	-----	<detection limit	-----
River water	15	15.04 \pm 0.45	100.2
River water	20	19.71 \pm 0.73	98.55
River water	25	25.20 \pm 1.1	100.8

^aFrom Tejan river, Sari, Mazandaran, Iran.

^bAverage of five determinations.

3.6. Interference studies

The influence of various substances as potential interference compounds on the determination of hydrazine was studied under the optimum conditions with 9.0×10^{-5} M of hydrazine concentration. The tolerance limit was defined as the maximum concentration of the potential interfering substance causes an error less than 3% for determination of 9.0×10^{-5} M of hydrazine concentration. The results are given in Table 4, shows that the peak potential and peak current varies with different metal cations, but the effects of the ions have been omitted in the presence of excess amount of EDTA (0.09 M), while almost all of anions have no effect on the peak current.

Table 4. Interference study for the determination of 90 μM hydrazine under optimized conditions

Species	Tolerance limits ($W_{\text{species}}/W_{\text{Hydrazine}}$)
NO_3^- , F^- , Br^- , CH_3COO^- , SO_4^{2-} , Citrate, EDTA, Na^+ , glucose, fructose, lactose	1000 ^a
Mg^{2+} , Zn^{2+} , Ca^{2+} , Ba^{2+} , K^+ ,	1000 ^b
Phenol	5
NH_2OH	1

^aMaximum amount tested.

^bAfter addition of 0.09 M EDTA solution.

4. CONCLUSION

Carbon paste electrode modified with 1-[4(ferrocenyl ethynyl) phenyl]-1-ethanon was used for electrocatalytic determination of hydrazine. The results show that the oxidation of hydrazine is catalyzed at pH 8.00, whereas the peak potential of hydrazine is shifted by 300 mV to a less positive potential at the surface of 4FEPEMCPE. In addition, It was shown that hydrazine can be determined using the cyclic voltammetry and differential pulse voltammetry techniques. The detection limits (2σ) were 1.4×10^{-5} M and 1.2×10^{-6} M by CV and DPV methods, respectively. The kinetic parameters such as electron transfer coefficient, α and rate constant for the chemical reaction between hydrazine and redox sites in 4FEPEMCPE, k_h were also determined using electrochemical approaches. Finally, the electrocatalytic oxidation of hydrazine at the surface of this modified electrode can be employed as a new method for the voltammetric determination of hydrazine in real samples such as drinking water and river water.

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