Int. J. Electrochem. Sci., 5 (**2010**) 177 - 188

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrocatalytic Oxidation and Voltammetric Determination of Hydrazine by 1,1′-Ferrocenedicarboxylic Acid at Glassy Carbon Electrode

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Received: 17 January 2010 / *Accepted:* 26 February 2010 / *Published:* 28 February 2010

The homogeneous electrocatalysis of hydrazine oxidation by 1,1′-Ferrocenedicarboxylic acid (FDC) as a redox mediator was studied in aqueous medium at the surface of a glassy carbon electrode using cyclic voltammetry (CV), chronoamperometry and differential pulse voltammetry (DPV) methods. It was found that in the presence of FDC at pH 10.0, the catalytic oxidation peak current of hydrazine is high and the overpotential of hydrazine oxidation decreases about 250 mV. Based on the obtained results a mechanism for electrooxidation of hydrazine in the presence of FDC was proposed. The diffusion coefficient of hydrazine and the catalytic reaction rate constant were also determined using chronoamperometry. The experimental results showed that the mediated oxidation peak current of hydrazine is linearly dependent on the concentration of hydrazine in the ranges of 4.0×10^{-5} M – 1.0×10^{-3} M and 1.0×10^{-5} M – 2.0×10^{-4} M with CV and DPV methods, respectively. The detection limits (S/N = 3) were found to be 2.6×10^{-5} M and 6.4×10^{-6} M by CV and DPV methods, respectively. Finally, the proposed voltammetric method was used for the determination of hydrazine in water samples by the standard addition method.

Keywords: Hydrazine; 1,1′-Ferrocenedicarboxylic acid; Homogeneous electrocatalysis; Glassy carbon electrode; Cyclic voltammetry; Differential pulse voltammetry; Chronoamperometry

1. INTRODUCTION

Hydrazine is a strong reducing agent and is used as an oxygen scavenger in boilers. It is also used as a fuel in rockets and fuel cells. Hydrazine and its derivatives have found various applications as antioxidants, corrosion inhibitors, catalysts, emulsifiers, insecticides and pesticides, plant-growth regulators, photographic developers, dyes stuffs, explosives and blowing agents for plastics. On the other hand, hydrazine is highly toxic and irritant and has been recognized as a carcinogenic, mutagenic and hepatotoxic substance [1–3]. Therefore, its detection has attracted considerable analytical interest. Various methods have been reported for the determination of hydrazine, including titrimetry [4], coulometry [5], amperometry [6,7], potentiometry [8,9], spectrophotometry [10,11] and chromatography methods [12–14].

It has been found that the overpotential for the oxidation of hydrazine depends on the electrode material [15], the history of the electrode and type of employed pretreatment [16]. 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. Accordingly, much effort has been made to lower the oxidation overpotential of hydrazine, in order to facilitate its voltammetric and amperometric detection. Several approaches have been investigated to decrease the oxidation overpotential of hydrazine. One approach is the application of an electrochemically pretreated glassy carbon electrode [17]. Another promising approach is the use of suitable redox mediators for the homogeneous or heterogeneous electrocatalysis of the hydrazine oxidation. For example, redox mediators such as acetylferrocene [18], overoxidized polypyrrole [19], quinizarine [20], alizarin [21] metal hexacyanoferrates [22–24], metal pentacyanonitrosylferrates [25,26], *o*-aminophenol [1], pyrogallol red [3], pyrocatechol violet [27], chlorogenic acid [2], caffeic acid [28] and metallophthalocyanines [29–31] have shown catalytic activities toward the electrooxidation of hydrazine.

In this work, we have reported a voltammetric method for the determination of hydrazine based on its homogeneous electrocatalysis oxidation with 1,1$'$-ferrocenedicarboxylic acid (FDC) at the surface of glassy carbon electrode (GCE). The proposed voltammetric method is simple and does not need to the pretreatment or modification of the electrode.

2. EXPERIMENTAL PART

2.1. Regents and Material

All chemicals used were of analytical grade and all solutions were prepared with doubly distilled water. FDC and hydrazine (as N_2H_5Cl) (from Fluka) were used as received. Potassium chloride (from Fluka) was used as the supporting electrolyte. Buffer solutions (0.1 M, pH 3.0 – 12.0) were prepared from phosphoric acid and its salts. Hydrazine and FDC solutions were prepared just prior to use.

2.2. Instrumentation

The electrochemical experiments were performed using an Electrochemical Analysis System potentiostat/galvanostat (model BHP 2061-C, Behpajooh, Iran) coupled with a Pentium IV personal computer. A glassy carbon electrode ($A = 0.058$ cm^2), an Ag|AgCl|KCl$_{sat}$ electrode and a platinum wire were used as the working, reference and auxiliary electrodes, respectively. All potentials were reported with respect to this reference electrode. A pH-meter (Ion Analyzer 250, Corning) was used to read the pH of the buffer solutions. All experiments were carried out at ambient temperature.

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic Oxidation of Hydrazine in the presence of FDC at GCE in Aqueous Solution

The electrochemical behavior of FDC was studied in aqueous solution at the surface of GCE using cyclic voltammetry. Its cyclic voltammograms exhibits an anodic (E_{pa} = 0.480 V) and corresponding cathodic peaks with E_{pc} = 0.390 V and $E_{1/2}$ (= ($E_{pa} + E_{pc}$)/2) about 0.435 vs. Ag|AgCl| KCl_{sat} related to FDC/FDC$^+$ redox couple with quasi-reversible behavior ($\Delta E_p = E_{pa} - E_{pc}$ = 90 mV) at the scan rate of potential 10 mV s^{-1}.

The electrochemical behavior of hydrazine is dependent on the solution pH. Therefore, it is necessary to optimize the pH value for the efficient electrocatalysis of its oxidation. In order to determine the optimum pH for the electrocatalysis of the hydrazine oxidation by FDC, the cyclic voltammograms of 1.0 mM hydrazine were recorded in the presence of 1.0 mM FDC in 0.1 M phosphate buffer solutions with different pH values (pH 5.0–12.0) at the scan rate of 10 mV s^{-1}. The variation curve of hydrazine catalytic oxidation peak current vs. the pH of solution is shown in Fig.1. As can be seen, the value of this current is high at pH 10.0. Therefore, pH 10.0 was selected as the optimum pH for the electrocatalytic oxidation of hydrazine by FDC.

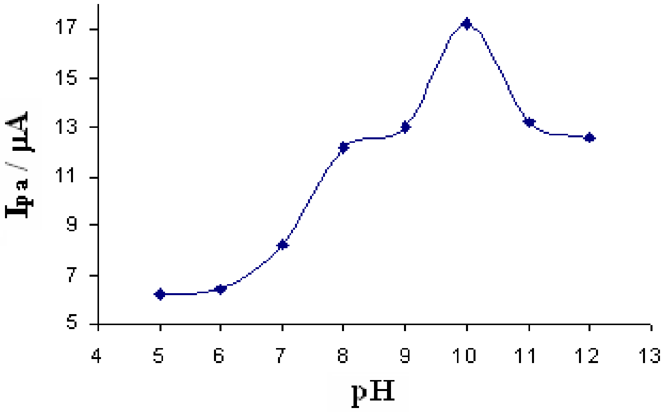

Figure 1. The variation of catalytic oxidation peak current of hydrazine vs. pH values. Data were obtained from cyclic voltammograms of 1.0 mM hydrazine in the presence of 1.0 mM FDC in 0.1 M phosphate buffer solutions containing 0.1 M KCl with various pH values (pH 5.0 – 12.0) at scan rate of 10 mV s^{-1} at the surface of GCE.

Figure 2 shows the cyclic voltammograms of 1.0 mM hydrazine in the absence of FDC (curve b), 1.0 mM FDC in the absence (curve c) and in the presence of 1.0 mM hydrazine (curve d) in 0.1 M phosphate buffer solution (pH 10.0) at scan rate of 10 mV s^{-1}. As seen, the electrochemical oxidation of hydrazine in the absence of FDC occurs irreversibly at about 750 mV vs. Ag|AgCl|KCl_{sat}, whereas, the cyclic voltammogram of FDC in the absence of hydrazine shows the oxidation and reduction of FDC/FDC$^+$ redox couple. But in the presence of hydrazine, the anodic peak current increases significantly, while the corresponding cathodic peak disappears on the reverse scan of potential. These results show that under these conditions, FDC acts as a homogeneous mediator for electrocatalytic oxidation of hydrazine. This process corresponds to an EC$'$ mechanism, where the electrochemically formed FDC$^+$ reacts with hydrazine and converts to FDC. The catalytic oxidation peak potential of hydrazine is about 500 mV vs. Ag|AgCl|KCl$_{sat}$, which is very close to the anodic peak potential of FDC. Therefore, in the presence of FDC at pH 10.0, the oxidation overpotential of hydrazine decreases about 250 mV.

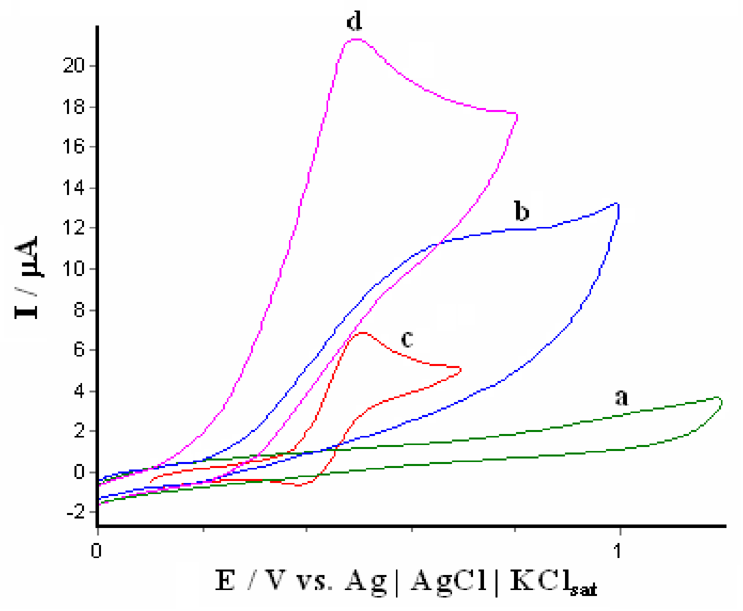

Figure 2. Cyclic voltammograms of (a) 0.1 M phosphate buffer solution (pH 10.0) containing 0.1 M KCl, (b) as (a) in the presence of 1.0 mM hydrazine, (c) as (a) in the presence of 1.0 mM FDC and (d) as (b) in the presence of 1.0 mM FDC at scan rate of 10 mV s^{-1} at the surface of GCE.

The effect of scan rate of potential on the electrocatalytic ability of FDC for electrooxidation of hydrazine was also studied. Figure 3A shows the cyclic voltammograms of 1.0 mM hydrazine in the presence of 1.0 mM FDC in 0.1 M phosphate buffer solution (pH 10.0) at various scan rates of potentials (10–200 mV s^{-1}). The plot of the catalytic oxidation peak current of hydrazine vs. $v^{1/2}$ is linear (Fig. 3B), suggesting that the reaction is diffusion limited at sufficient overpotential.

In order to get information on the rate determining step, the value of $\alpha_a n_\alpha$ (where α_a is the anodic transfer coefficient and n_α is the number of electrons involved in the rate determining step) for the electrocatalytic oxidation of hydrazine was determined. Figure 4A shows the drawn Tafel plot using the data obtained from the rising part of the cyclic voltammogram of (d) in Fig. 2. Using the slope of the Tafel plot, the value of $\alpha_a n_\alpha$ was found to be 0.42.

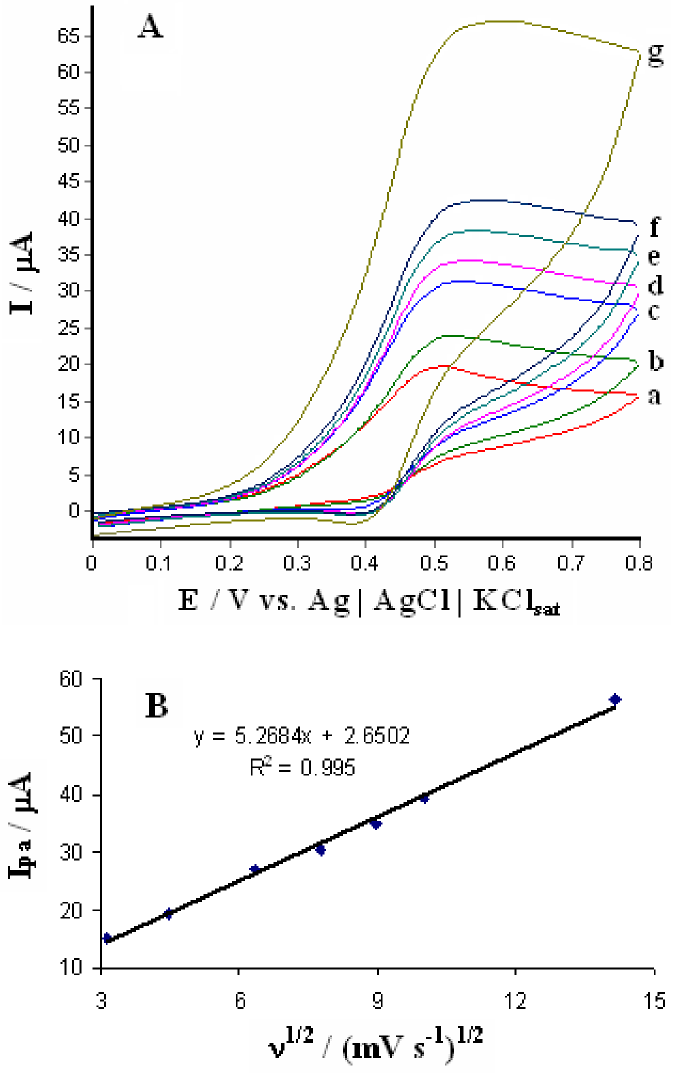

Figure 3. (A) Cyclic voltammograms of 1.0 mM hydrazine in the presence of 1.0 mM FDC in 0.1 M phosphate buffer solution (pH 10.0) containing 0.1 M KCl at various scan rates of potential (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100 and (g) 200 mV s^{-1} at the surface of GCE. (B) Plot of catalytic oxidation peak current of hydrazine vs. $v^{1/2}$.

The Tafel slope (b) was also obtained by another method using the following equation [32]:

$$E_{pa} = (b/2)\log v + \text{constant} \qquad (1)$$

As shown in Fig. 4B, the catalytic oxidation peak potential of hydrazine is proportional to log v with the slope of 0.0669 V. So, $b = 0.1338$ V. The value of $\alpha_a n_\alpha$ was calculated as 0.44 using this value of the Tafel slope. As seen, the results obtained from these two different methods are in good agreement. Therefore, the value of α_a for the electrocatalytic oxidation of hydrazine was found to be 0.43, assuming that a one-electron transfer process is the rate determining step.

According to the following equation [32]:

$$I_{pa} = 2.99 \times 10^5\, n(\alpha_a n_\alpha)^{1/2} AcD^{1/2} v^{1/2} \tag{2}$$

the total number of electrons (n) involved in the electrocatalytic oxidation of hydrazine can be obtained from the slope of the plot of I_{pa} vs. $v^{1/2}$ (Fig. 3B). The value of n was determined as $n = 3.78 \cong 4$, considering $\alpha_a n_\alpha = 0.43$, $A = 0.058$ cm^2, $c = 1.0$ mM and $D = 1.48 \times 10^{-5}$ cm^2 s^{-1} (see Section 3.3). Accordingly, the following mechanism can be proposed for the oxidation of hydrazine in the presence of FDC at pH 10.0 at the surface of GCE:

$$N_2H_4 + H_2O \rightarrow N_2H_3 + H_3O^+ + e^- \quad \text{(slow)} \tag{3}$$

$$N_2H_3 + 3H_2O \rightarrow N_2 + 3H_3O^+ + 3e^- \quad \text{(fast)} \tag{4}$$

In other words, the rate determining step is a one-electron transfer followed by a three-electron transfer to give N_2 as a final product.

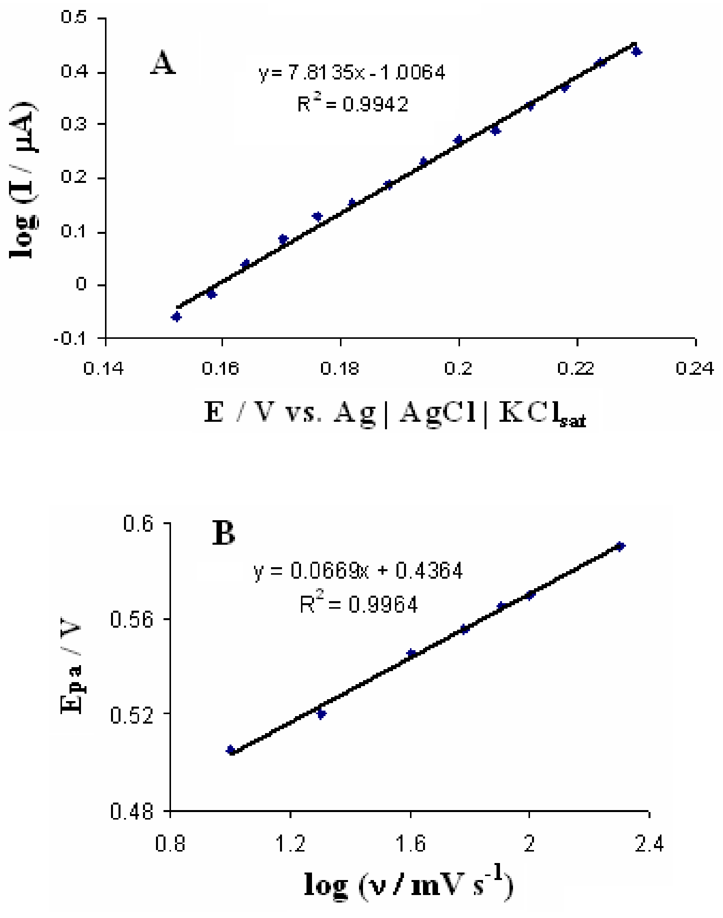

Figure 4. (A) Tafel plot drawn using data obtained from rising part of cyclic voltammogram (d) in Fig. 2. (B) Plot of catalytic oxidation peak potential of hydrazine vs. log v. Data was obtained from cyclic voltammograms of Fig. 3A.

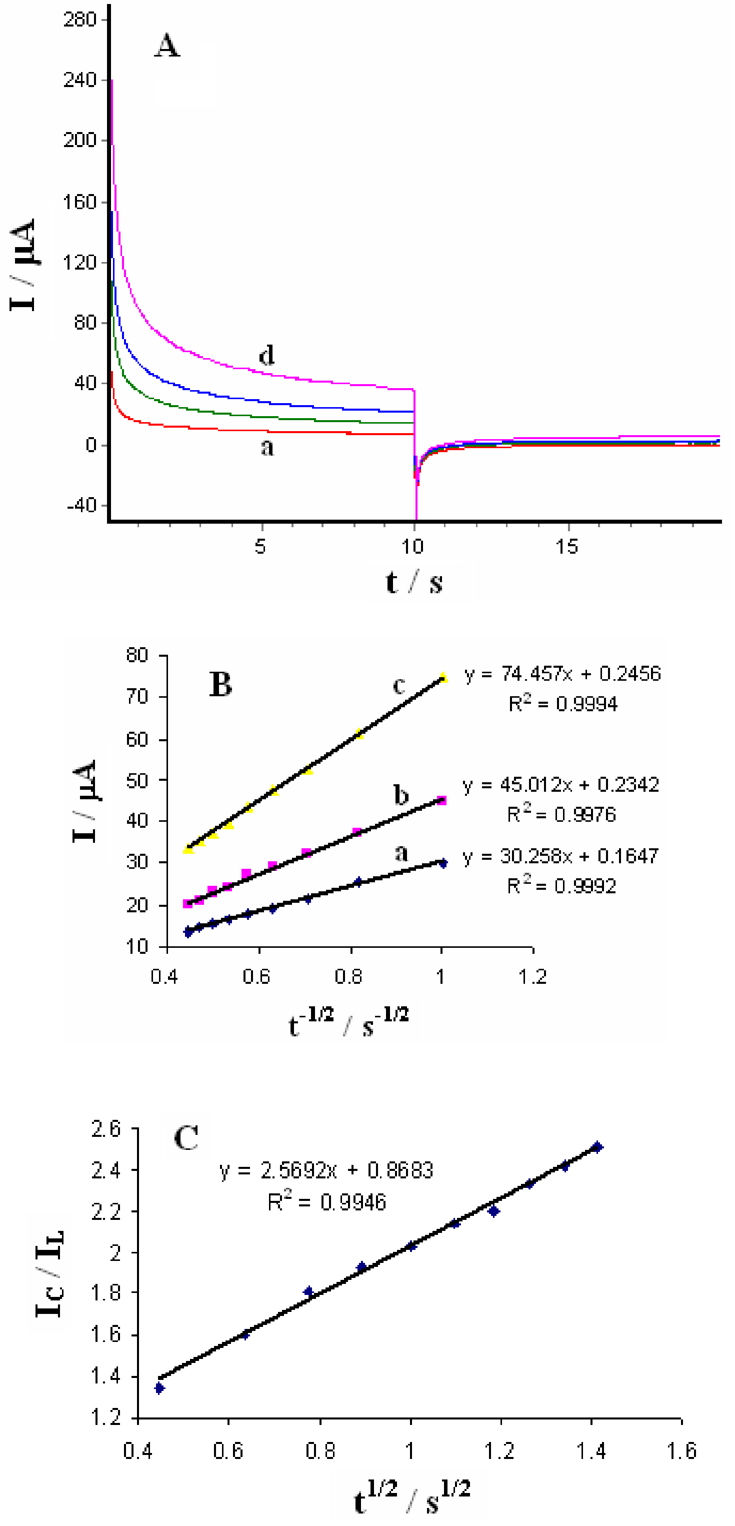

Figure 5. (A) Double potential step chronoamperograms of 1.0 mM FDC in 0.1 M phosphate buffer solution (pH 10.0) containing 0.1 M KCl in the absence (a) and in the presence of (b) 0.5, (c) 1.0 and (d) 2.0 mM hydrazine. First and second potential steps were 550 and 300 mV vs. Ag|AgCl|KCl$_{sat}$, respectively. (B) Cottrell plots drawn using data obtained from chronoamperograms (b), (c) and (d). (C) Plot of I_C/I_L vs. $t^{1/2}$. Data were obtained from chronoamperograms (a) and (d).

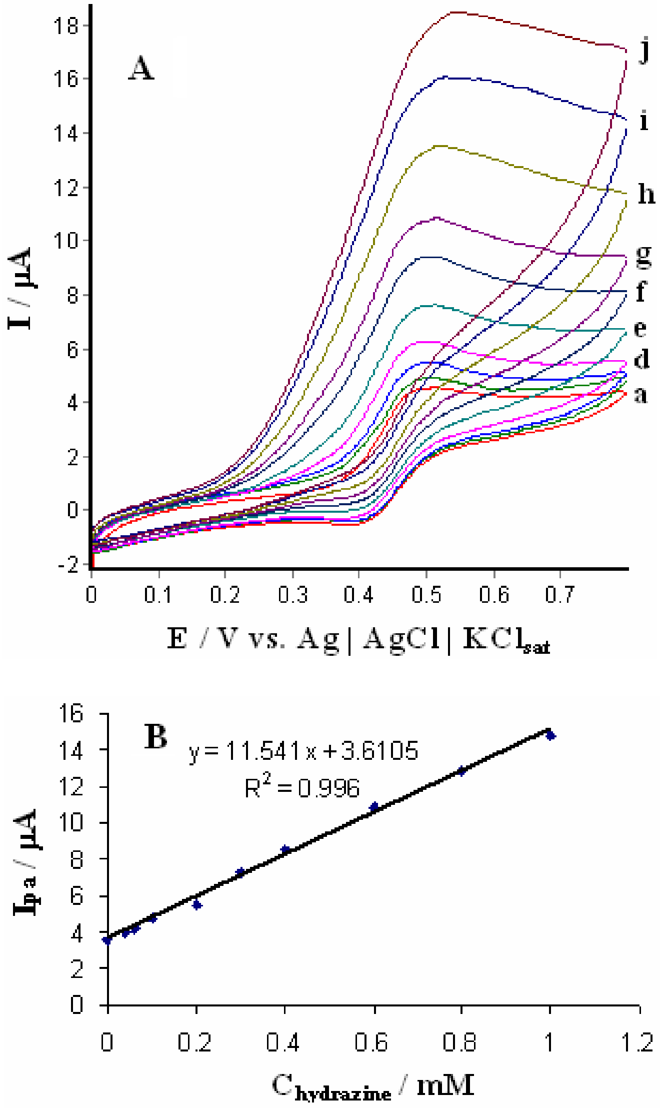

Figure 6. (A) Cyclic voltammograms of 0.5 mM FDC in 0.1 M phosphate buffer solution (pH 10.0) containing 0.1 M KCl in the absence (a) and in the presence of (b) 0.04, (c) 0.06, (d) 0.1, (e) 0.2, (f) 0.3, (g) 0.4, (h) 0.6, (i) 0.8 and (j) 1.0 mM hydrazine at scan rate of 20 mV s^{-1} at the surface of GCE. (B) Plot of catalytic oxidation peak current of hydrazine vs. concentration of hydrazine.

3.2. Chronoamperometric Studies

Chronoamperometry was used for the determination of diffusion coefficient (D) of hydrazine and catalytic reaction rate constant. The double potential step chronoamperograms of 1.0 mM FDC in 0.1 M phosphate buffer solution (pH 10.0) in the absence and in the presence of different concentrations of hydrazine were obtained by setting the potential of the glassy carbon electrode at 550 mV (as the first potential step) and 300 mV vs. Ag|AgCl|KCl$_{sat}$ (as the second potential step) (Fig. 5A). In order to determine the diffusion coefficient of hydrazine (D), the plots of I vs. $t^{-1/2}$ (Cottrell plots) were drawn using the data obtained from the chronoamperograms (b), (c) and (d) (Fig. 5B). According to the Cottrell equation [32]:

$$I = nFAcD^{1/2}\pi^{-1/2}t^{-1/2} \qquad (5)$$

the value of D can be obtained from the slopes of the linear plots of I vs. $t^{-1/2}$. The mean value of D was found to be 1.48×10^{-5} cm^2 s^{-1}, considering $n = 4$, $F = 96485$ C mol^{-1}, $A = 0.058$ cm^2 and $c = 0.5$, 1.0, 2.0 mM.

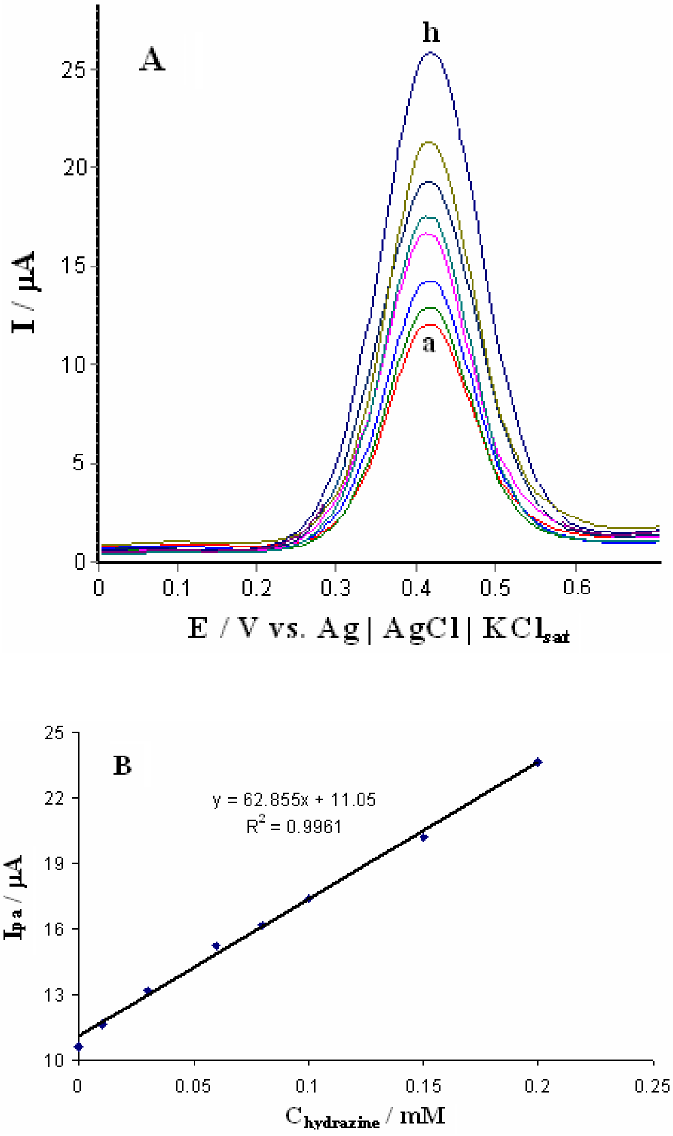

Figure 7. (A) Differential pulse voltammograms of 0.5 mM FDC in 0.1 M phosphate buffer solution (pH 10.0) containing 0.1 M KCl in the absence (a) and in the presence of (b) 0.01, (c) 0.03, (d) 0.06, (e) 0.08, (f) 0.1, (g) 0.15 and (h) 0.2 mM hydrazine at the surface of GCE. Scan rate, pulse amplitude and pulse time were 20 mV s^{-1}, 50 mV and 50 ms, respectively. (B) Plot of catalytic oxidation peak current of hydrazine vs. concentration of hydrazine.

The catalytic reaction rate constant (k) was determined according to the method described in the literature [33]:

$$I_C/I_L = (\pi kct)^{1/2} \qquad (6)$$

where I_C and I_L are the oxidation currents of FDC in the presence and in the absence of hydrazine, respectively, and c is the bulk concentration of hydrazine. The above equation was used to calculate the value of k. From the slope of the plot of I_C/I_L vs. $t^{1/2}$ for 2.0 mM hydrazine (Fig. 5C), the value of k was determined as 1.05×10^3 M^{-1} s^{-1}.

3.3. Voltammetric Determination of Hydrazine

The catalytic oxidation peak current of hydrazine was used as the analytical signal for the voltammetric determination of hydrazine by CV and DPV methods. The cyclic voltammograms and differential pulse voltammograms of 0.5 mM FDC in 0.1 M phosphate buffer solution (pH 10.0) in the absence and in the presence of various concentrations of hydrazine are shown in Figures 6A and 7A, respectively. As can be seen in Figures 6B and 7B, the mediated oxidation peak current of hydrazine is proportional to the concentration of hydrazine in the ranges of 4.0×10^{-5} M – 1.0×10^{-3} M and 1.0×10^{-5} M – 2.0×10^{-4} M in CV and DPV methods, respectively. The detection limits (S/N = 3) were determined as 2.6×10^{-5} M and 6.4×10^{-6} M with CV and DPV methods, respectively. The linear concentration ranges are dependent on the concentration of FDC.

3.4. Determination of Hydrazine in Water Samples

In order to evaluate the applicability of the proposed voltammetric method, the recoveries of hydrazine were determined in drinking water samples containing different concentrations of hydrazine by the standard addition method. The results obtained are satisfactory (Table 1) and suggest that the proposed voltammetric method can readily be applied to the determination of hydrazine.

Table 1. Determination of hydrazine in drinking water samples.

Sample	Hydrazine added (mM)	Hydrazine found (mM) [a]	Recovery (%) [a]	RSD (%)
1	0.4	0.382	95.4	2.8
2	0.6	0.587	97.8	2.2
3	0.8	0.789	98.6	2.5
4	1.0	1.016	101.6	1.8

[a] Average of three determinations.

4. CONCLUSIONS

In this work, 1,1′-Ferrocenedicarboxylic acid was used as a redox mediator for the homogeneous electrocatalysis of hydrazine oxidation in aqueous medium at the surface of GCE. It was found that in the presence of FDC at the optimum pH (10.0), the oxidation overpotential of hydrazine decreases about 250 mV. A mechanism for the oxidation of hydrazine in the presence of FDC was proposed. The diffusion coefficient of hydrazine and catalytic reaction rate constant were also determined using chronoamperometry. The experimental results showed that the catalytic oxidation peak current of hydrazine in cyclic voltammetry and differential pulse voltammetry methods is proportional to the concentration of hydrazine and can be used as the analytical signal for the voltammetric determination of hydrazine.

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