Electrocatalytic Oxidation of Hydrazine at Epinephrine Modified Glassy Carbon Electrode (EPMGCE).

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ABSTRACT: *A thin film of epinephrine (EP) was electrochemically deposited on the surface of glassy carbon electrode previously activated in $NaHCO_3$ solution. The cyclic voltammograms of the modified electrode indicate that the surface confined EP are strongly dependent on the solution pH, as expected for quinone/hydroquinone functionalities. The EP-modified glassy carbon electrode exhibited catalytic activity towards the electrooxidation of hydrazine, which appeared as a reduced overpotential especially in pH = 7.5. The diffusion coefficient of hydrazine was estimated using chronoamperometry. The catalytic rate constant, K_h, of the modified electrode for the oxidation of hydrazine was determined using the cyclic voltammograms recorded at low scan rates as well as the RDE voltammetric approach. It has been shown that the EP-modified electrode can be used as an amperometric sensor in the analysis of trace amount of hydrazine with high sensitivity and good limit of detection (0.83 μM). Amperometry by EP-modified electrode was used for determination of hydrazine in boiler feed water and the accuracy of the results was verified by comparison with those obtained from standard ASTM method.*

KEY WORDS: *Epinephrine, Hydrazine, Voltammetry, Amperometry, Modified electrode.*

INTRODUCTION

Hydrazine is the simplest diamine and the starting material in the preparation of several hydrazine derivatives. It is used in various area such as fuel in fuel cells, corrosion inhibitor in boilers, initiator of polymerization, starting material in the production of some insecticides and herbicides, plant growth regulator and in the preparation of several pharmaceutical derivatives [1]. Despite the wide use of hydrazine in various area, it has been known to be harmful for human life and so, its detection and determination in low concentrations in various media is highly important. Several electrochemical methods based on its reducing character were developed [2-4]. Mechanism and kinetics of hydrazine oxidation have been studied at various electrodes such as silver [5], gold [5], nickel [6], mercury [5,7,8] and platinum [7-9]. These investigations showed that the overpotentials of hydrazine oxidation at Pt, Au and Ag electrodes are smaller than at other metallic

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electrodes. However, the noble metals being expensive, are not suitable in practice and the use of carbon electrodes is not common because of the large overpotential of hydrazine oxidation at these electrodes. In order to overcome these difficulties, chemically modified electrodes with various mediators were used as hydrazine oxidation beds.

Glassy carbon modified by Nafion-ruthenium [10,11], by ruthenium, cobalt and nickel hexacyanoferrate [12-14], copper-porphyrin included zeolite [15], cobalt III/II complexes [16] and silica doped nickel phthallocyanine tetrasulfonate [17] modified carbon paste electrodes, copper [18] and cobalt [19] hexacyanoferrate and cobalt phthallocyanine [20] modified carbon electrodes, and graphite modified by cobalt naphthallocyanine [21] and Prussian blue modified carbon ceramic electrode [22] are the examples of various modified electrodes used in electrocatalytic oxidation of hydrazine.

In addition to these inorganic modifiers, several organic compounds such as 3,4-dihydroxybenzaldehyde [23,24], DNA [25], polyglutamic acid [26], chlorogenic acid [27], caffeic acid [28], pyrocatechol violet [29], quercetin [30], 4-pyridylhydroquinone [31,32] and poly(4-vinyl)pyridine [33] were also used in the preparation of glassy carbon, carbon paste, platinum or palladium modified electrodes for electrocatalytic oxidation of hydrazine.

Finally, it has been shown that the porous graphite doped with platinum microparticles [34], carbon fiber electrode modified by metallic rhodium [35,36] and even chemically activated glassy carbon electrode [4] can also be used successfully in electrocatalytic oxidation of hydrazine.

Despite so much electrodes, a literature survey confirms that effort about the preparation of new patterns for electrocatalytic oxidation of hydrazine is still in progress. However, to the best of our knowledge, epinephrine has not been used hitherto as modifier in the preparation of modified electrode for electrocatalytic oxidation of hydrazine. Accordingly, in this paper, we will describe initially the preparation, characteristics and electrocatalytic reactivity of this electrode towards hydrazine oxidation. Finally, the performance of such electrode in voltammetric and amperometric determination of hydrazine in real sample will be discussed.

EXPERIMENTAL

Chemicals

Epinephrine, (EP), or (R)-Adrenaline used as electrode surface modifier is 95% purity product from Merck and was used as received. Pure grade hydrazinium dichloride was obtained from Merck. All other chemicals used in the preparation of buffer solutions or as supporting electrolyte were analytical grade products from Merck or Fluka. Doubly distilled water was used throughout in the preparation of solutions. Hydrazine and epinephrine solutions were used as freshly prepared before each experiment.

Instrumentation

V.A. Scanner E612 as function generator in connection with Polarecord E626 as potentiostat (both from Metrohm) were used for cyclic voltammetry. A Hewlett-Pckard model 7015A X-Y recorder in connection with function generator and potentiostat was used for recording the voltammograms. Rotating disc electrode (RDE) voltammetry was carried out using a VA trace analyzer model 746 in connection with 747 VA stand as three electrode compartment holder, equipped with a RDE assembly model 628-10 (All from Metrohm). A Pentium II computer, in connection with VA trace analyzer, was used for data storage and processing. Glassy carbon disc with a diameter of 2 mm (Azar Electrode) and modified by epinephrine, (EMGCE), was used as working electrode. A platinum wire (from Metrohm) constitutes the auxiliary electrode. All potentials were quoted versus a NaCl saturated calomel electrode (from Metrohm).

EPMGCE preparation procedure

Prior to each experiment, the GC disc electrode was polished to a mirror finish using a 0.05 μm alumina slurry. The polished surface was cleaned thoroughly by washing with acetone and bidistilled water. The electrode surface was then activated electrochemically in 0.10 M sodium bicarbonate solution. The activation was performed by potential recycling between –1.10 and 1.60 V vs. ref. for 9 min. and by a scan rate of 100 mVs^{-1}. The activated electrode was then immersed in a 0.012 M solution of epinephrine in 0.30 M $HClO_4$ (pH<1) and the surface modification was achieved by 15 cycles of potential sweep between –0.10 and 0.50 V vs. ref.

and by a scan rate of 10 mVs^{-1}. The prepared electrode, after rinsing thoroughly with water, is ready to experiment. The surface coverage of EPMGCE was determined from cyclic voltammograms recorded at low scan rates and by integration of anodic peak area, assuming n = 2.

RESULTS AND DISCUSSION

The optimum conditions for preparation of EPMGCE

The effect of various parameters such as modifier solution pH, epinephrine concentration, the number of potential recycling, scan rate and sweeping potential range were examined on the performance of modified electrode, and the anodic peak current was used as a measure of the surface deposited epinephrine. Fig. 1 shows that the epinephrine contains an *o*-hydroquinone (or catechol) ring and an aliphatic secondary amine chain in its structure. The acidity constants, pK_A, reported for epinephrine in water are 8,7 and 9,9 [37], corresponding to the ionization of phenolic hydroxyl and protonated amine group respectively. Thus, in neutral pH, epinephrine exists mainly in protonated form. The electrochemical behavior of epinephrine was studied by Hawley et al. [38]. It has been shown that catechol ring in epinephrine undergoes a two-electron, two-proton oxidation process, leading to the formation of corresponding *o*-quinone. This product can enter in a cyclization reaction following a deprotonation step. Thus, the cyclization step is favored by increasing pH and vice versa.

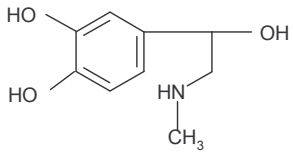
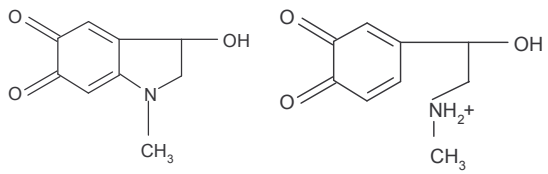


Fig. 1: The formula of epinephrine

Cyclic voltammogram of EPMGCE, prepared at pH>1, exhibits two couples of redox peaks; while at pH<1, only one couple of redox peak is observed. We assume such a behavior to the fact that at pH>1, the oxidation product of epinephrine can exist in two different forms of (**I**) and (**II**) at electrode surface, producing two different redox peaks. Whereas, at pH<1, the cyclization process is avoided and the form (**I**) is predominate. In this condition, (**I**) can attach to the preactivated GC surface functionalities whitin a Michel addition process [39], leading to a sufficiently stable epinephrine film. Thus, the solution of epinephrine in 0.30 M $HClO_4$ (pH<1) was considered as optimum for modification process, in order to obtain an stable EPMGCE with only one couple of anodic and cathodic peaks.

The effects of other parameters on the EPMGCE performance are illustrated in Fig. 2. Fig. 2A shows the effect of solution concentration of epinephrine on the surface coverage, Γ, of EPMGCE. Considering the anodic peak current as a measure of the surface coverage, it is seen that $I_{p.a}$ increases with epinephrine concentration up to 10 mM and then remains constant. This can be arisen most probably because of the saturation of whole acceptor sites on electrode surface. Thus, 12 mM solution of epinephrine in 0.30 M $HClO_4$ as considered as optimum concentration in subsequent studies.



(**II**) (**I**)

The effect of potential sweep rate on the $I_{p.a}$ is shown in Fig. 2B. On the basis of this Figure, 10 mVs^{-1} was chosen as optimum scan rate in the subsequent experiments. Fig. 2C exhibits the effect of potential cycle numbers on the epinephrine film performance. As the highest coverage is obtained for 15 cycles of potential sweep (30 min.); thus, this value was selected as optimum in subsequent studies. Finally, the effect of potential sweep range on the $I_{p.a}$ (or Γ) was investigated by preparation of EPMGCE in previously found optimum conditions, but with potential scanning in various ranges as indicated in Fig. 2D caption. The results show that the higher coverage is obtained when the potential is swept between –0.10 and 0.50 V vs. ref. Thus, this range of potential was considered as optimum value.

Stability of the modified electrode

Stability tests were carried out for electrodeposited epinephrine films under optimal conditions. Successive

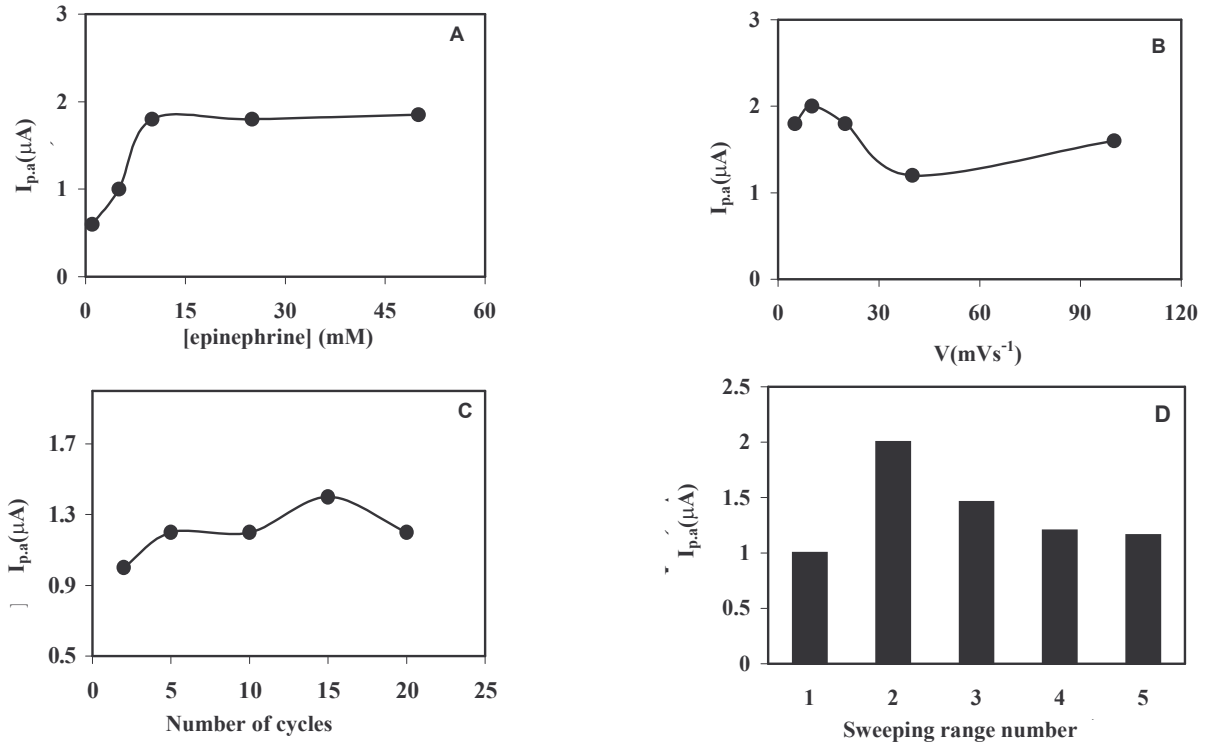


Fig. 2: Variation of anodic peak current of EPMGCE , after 100 cycles of potential sweep at 50 mVs^{-1}, as a function of: A) epinephrine solution concentration, B) scan rate, C) number of potential recycling and D) range of swept potential used in the course of modification process. In D, the numbers indicate the range of swept potential as: 1)–0.3 to 0.5, 2)-0.1 to 0.5, 3) –0.1 to 0.6, 4) 0.2 to 06 and 5) 0.2 to 0.8 volt vs. SCE.

potential scan of EPMGCE, dipped in buffer solutions with various pHs and without or with storage of electrode in dry state, were the conditions used in stability studies. The observed anodic peak current, $I_{p.a}$, considered as a measure of the electrode coverage, and its variation was illustrated in Fig. 3. It can be seen that in all pHs, the electrode coverage decreases almost abruptly during the first 20 scan, while it is slowed during the subsequent scans. We assume that the initial decay might be due to material that is weakly bound to the electrode surface, so that it can be displaced with relative ease during the potential scan or by holding in dry condition. Also, in alkaline solutions, the stability of epinephrine film is diminished which can be due to the presence of hydroxyl ions and their displacement with epinephrine molecules in electrode surface. Fig. 3 shows clearly that in the case of curve c, except for the initial 20 scan, the electrode coverage drop for subsequent scans is almost negligible. In addition, the coverage is relatively high with respect to the cases d and e. Therefor, buffer solution with pH=7 was considered as more suitable medium for electrode storage or its applications if necessary.

pH dependence of EPMGCE response

The deposited epinephrine on GC electrode surface can exhibit pH dependent peaks in cyclic voltammetry because of the presence of a catechol ring in its structure. Fig. 4A shows the voltammograms of EPMGCE in 0.10 M buffer solutions with different pHs. Fig. 4B illustrates also the variation of formal potential of the surface redox couple, taken as the average of anodic and cathodic peak potentials, as a function of solution pH.

As can be seen, the formal potential is pH-dependent and varies linearly with a slope of about 60 mV per pH unit in a wide range, which is very close to the anticipated Nernstian slope of 59 mV for a two-electron two-proton process.

However, no slope change in the potential-pH plot

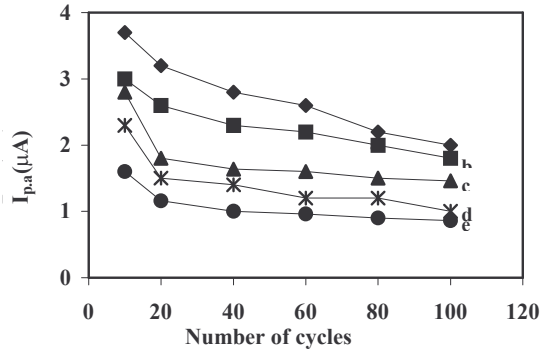


Fig. 3: Variation of anodic peak current of EPMGCE, prepared in optimum condition, against the number of potential recycling in solutions with pHs: a) 2, b) 5, c) 7, d) 5, and e) 9. In the cases of d and e, the electrode was used after 36 h. storage in laboratory atmosphere.

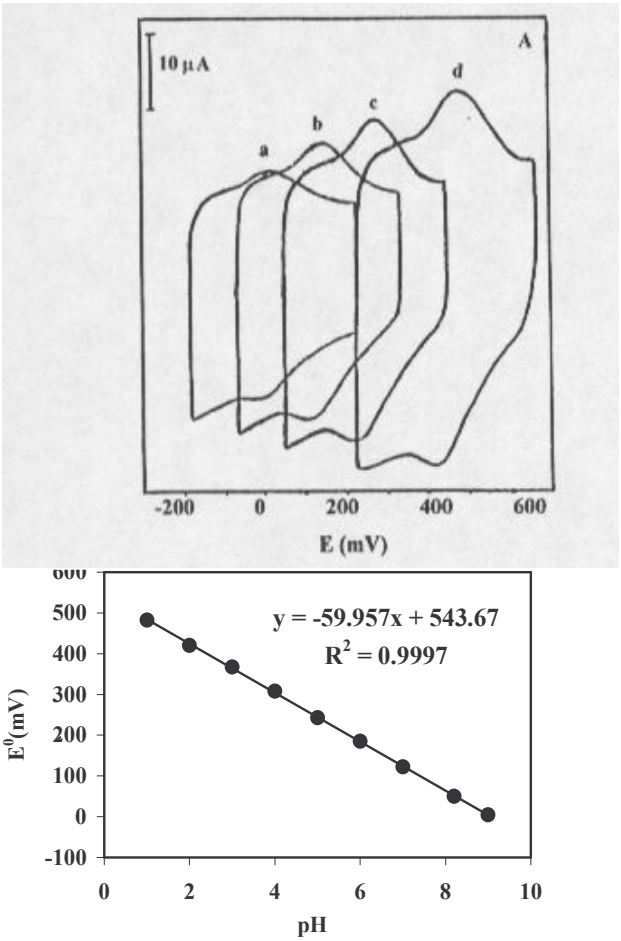


Fig. 4: A) Cyclic voltammograms of EPMGCE at buffer solutions with pHs: a) 9, b) 7, c) 5 and d) 2. Scan rate: 100 mVs^{-1}. B) Plot of formal potential ($E^{o'}$) versus pH for FPMGCE.

was observed in the pH around 8.7 (first pK_A of free epinephrine in solution [37]), most probably because of a change of pK_A for surface deposited EP. Such a change in pK_A of deposited species has also previously been reported [40-43].

Electrochemical behavior of EPMGCE

Cyclic voltammograms of an EPMGCE prepared in optimal conditions were taken in 0.15 M acetate buffer solution (pH 5) at several different potential scan rates ranging from 25 to 500 mVs^{-1} (Fig. 5A). The anodic and cathodic peak currents of the redox waves increased in proportion to the potential sweep rates below 500 mVs^{-1}, as shown in the inset of Fig. 5B, indicating that the immobilized EP exhibits electrochemical responses which are characteristic of the redox species confined on the electrode surface. In addition, the formal potential taken as the average of the anodic and cathodic peak potentials, $E^{o'}= [(E_{p.a} + E_{p.c})/2]$, is about 0.245 V vs. ref. and is almost independent of the potential scan rate for sweep rates ranging from 25 to 200 mVs^{-1}. This value is in the same order reported for chlorogenic acid modified electrode [27], but higher than those reported for caffeic acid [28] and pyrocatechol violet [29] modified GC electrodes. We assume such a difference to the effect of substituent onthe o-quinone ring in each modifier. The anodic and cathodic peak separation is about 10 mV at scan rates lower than 100 mVs^{-1}. Moreover, at scan rates below 200 mVs^{-1}, the anodic and cathodic peak potentials are independent of scan rate. Thus, the electrode process at low scan rates can be considered as a fast electron transfer reaction. At sweep rate of 500 mVs^{-1}, the peak separation increases to 20 mV, indicating the appearance of a limitation in electron transfer kinetic at higher scan rates.

Electrocatalytic oxidation of hydrazine at EPMGCE

The catalytic oxidation of hydrazine at epinephrine modified glassycarbon electrode was studied by cyclic voltammetry. Cyclic voltammograms of bare and EP modified GC electrodes,in the absence and presence of hydrazine in 0.15 M phosphate buffer(pH 7.5) are shown in Fig. 6. At bare GC electrode, the oxidation of hydrazine give rise to a little anodic current at potential very close to the positive end of sweep range,

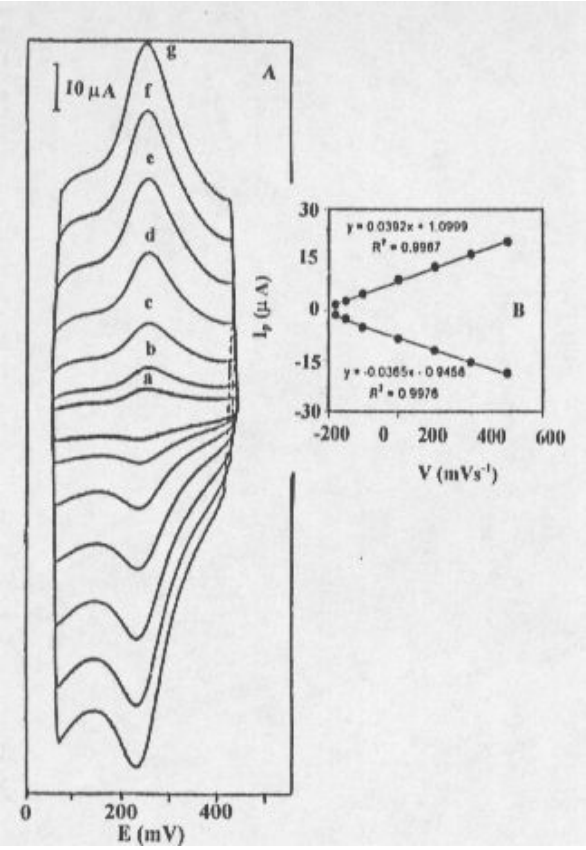


Fig. 5: A) Cyclic voltammograms of EPMGCE in 0.15 M acetate buffer (pH 5) recorded at scan rates: 2) 25, b) 50, c) 100, d) 200, e) 300, f) 400 and g) 500 mVs-1. B) Variation of anodic and cathodic peaks current versus scan rate.

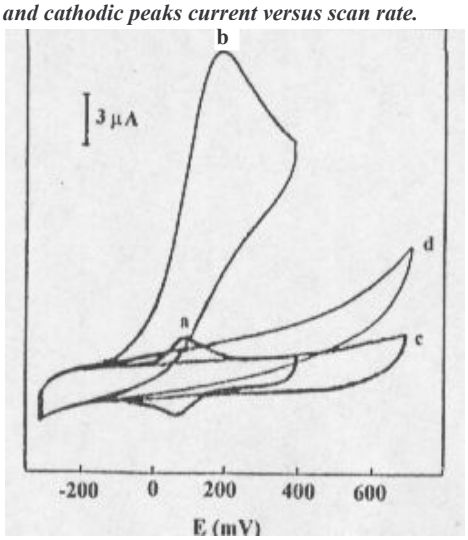


Fig. 6: Cyclic voltammograms of EPMGCE in 0.10 M phosphate buffer (pH 7.5): a) in the absence and B) in the presence of 1 mM hydrazine. C) as a and d) as b for bare GC electrode. Scan rate: 20 mVs^{-1}.

but no cathodic peak is observed in reverse scan (curve d). At the EP modified electrode, oxidation of hydrazine exhibits a typical electrocatalytic response with an anodic peak current that was greatly enhanced over that observed for the modified electrode alone and with virtually no current on the cathodic sweep (Fig. 6, curve b). The peak potential value of 160 mV is very close to that of the surface-confined mediator anodic peak potential in the absence of hydrazine (Fig. 6, curve a). The anodic peak current dependence to hydrazine concentration in the range of 0.10 – 10 mM is shown as cyclic voltammograms of Fig. 7. The inset A of this Figure illustrates the volltammograms obtained for higher concentrations of hydrazine. The inset B shows clearly that the I_p vs. hydrazine concentration plot is constituted from two linear segments with different slopes corresponding to two different ranges of substrate concentration. We ascribe this to a change in catalytic reaction conditions arising from the formation of nitrogen gas bubbles at the surface of the modifier as has already been reported [29,45]. Indeed, at low substrate concentrations the gas formed, being negligible, takes away easily the electrode surface by diffusion andthus, it has no effect on the normal diffusion of hydrazine towards the electrode surface [gas evolution unaffected (GEU) zone]. While, for high concentrations of hydrazine, gas formation at the electrode surface slackened to some extent the normal diffusion of substrate [gas evolution affected (GEA) zone]. Accordingly, the first part of the peak current vs. hydrazine concentration plot (Inset B of Fig. 7), which corresponds to a range of 0.10 to 6.5 mM of hydrazine can be accepted as useful dynamic range for hydrazine determination by voltammetry at EPMGCE. Fig. 7 shows also that along with the augmentation of hydrazine concentration in solution, the cathodic peak begins to disappear and the anodic peak potential shifts towards more positive value, indicating that the electrocatalytic process is controlled by charge transfer kinetic between EP film and hydrazine. Fig. 8 illustrates the cyclic voltammograms of a 2 mM solution of hydrazine in 0.15 M phosphate buffer (pH 7.5) at various scan rates. The Inset A of this Figure exhibits that the hydrazine peak currents vary linearly with $v^{1/2}$, confirming the diffusion controlled nature of the electrode process. However, the linear variation of ydrazine peak potentials,

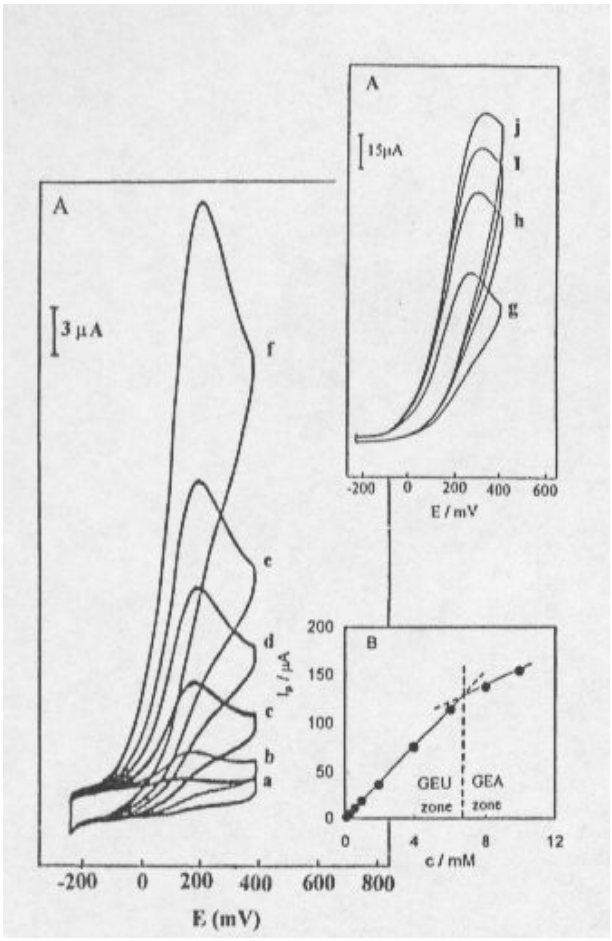


Fig. 7: A) Cyclic voltammograms obtained for EPMGCE in 0.15 M phosphate buffer (pH 7.5) containing: a) 0, b) 0.1, c) 0.3, d) 0.6, e) 1, f) 2, g) 4, h) 6, i) 8 and j) 10 mM of hydrazine. Scan rate: 20 mVs^{-1}. B) Plot of I_p versus hydrazine concentration. GEU and GEA indicate gas evolution affected and gas evolution unaffected zones respectively.

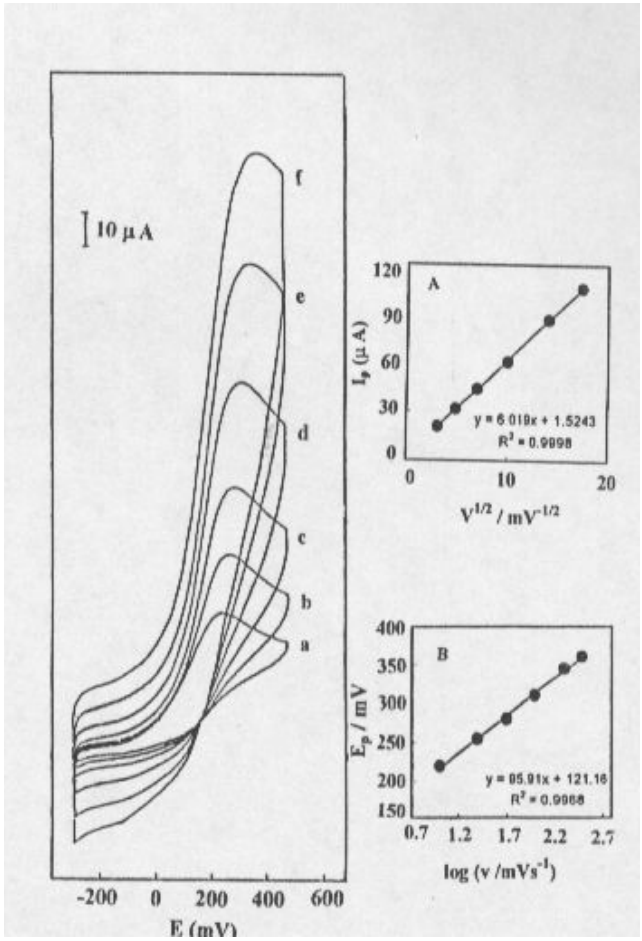


Fig. 8: Cyclic voltammograms of 2 mM hydrazine at EPMGCE, recorded in 0.15 M phosphate buffer (pH 7.5) at scan rates: a) 10, b) 25, c) 50, d) 100, e) 200 and f) 300 mVs^{-1}. Inset A: Variation of peak current with square root of scan rate. Inset B: Variation of peak potential as a function of log(scan rate).

E_p, as a function of logv suggests that the electrode process can be regarded as a totally irreversible process (Inset B of Fig. 8). The slope of E_p versus logv plot is 67.45 mV. The Tafel slope can be estimated using this slope according to the equation for a totally irreversible diffusion-controlled process [44]:

$$E_p = (b \log v)/2 + constant$$

On the basis of this equation, the slope of E_p vs. logv plot is $b/2$, where b indicates the Tafel slope, Therefore b = 134.9 mV. This slope gives a value of 0.56 for charge transfer coefficient, α, assuming a one-electron transfer reaction as the rate determining step in the catalytic oxidation of hydrazine as reported for other *o*-quinone modified electrodes [27-29].

The effect of solution pH on electrocatalytic oxidation of hydrazine at EPMGCE

As stated in section 3.1, the surface coverage and the stability of the EP modified electrode depend mainly on the pH of solution where the electrode is employed. It has been shown that the electrode coverage decreases with increasing solution pH. On the other hand, electrooxidation of hydrazine being a pH dependent process, specification of an optimum pH for this process is of importance. For this purpose, the catalytic peak current and peak potential in each pH were considered as two representative factors for definition of an optimum working pH. Fig.9A illustrates the variation of oxidation peak current as a function of

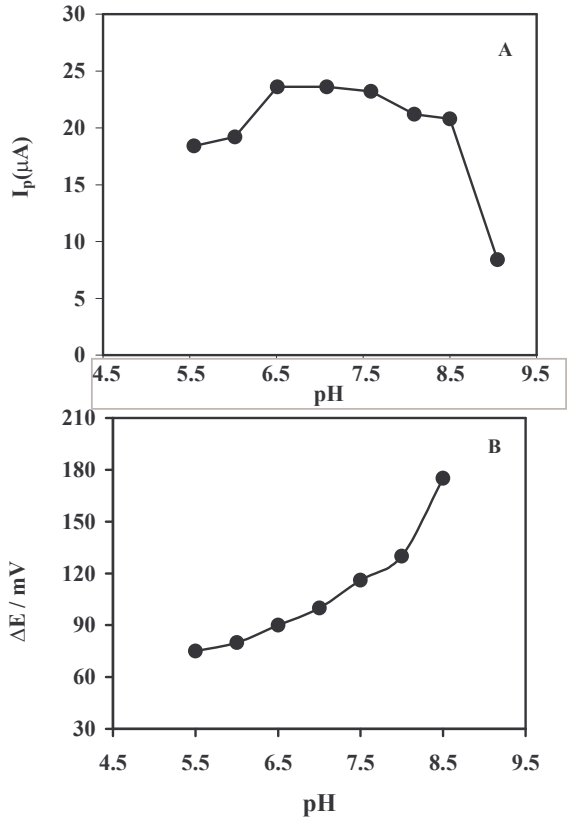


Fig. 9: The effect of solution pH: A) On the catalytic peak current and B) On the catalytic peak potential of hydrazine oxidation at EPMGCE.

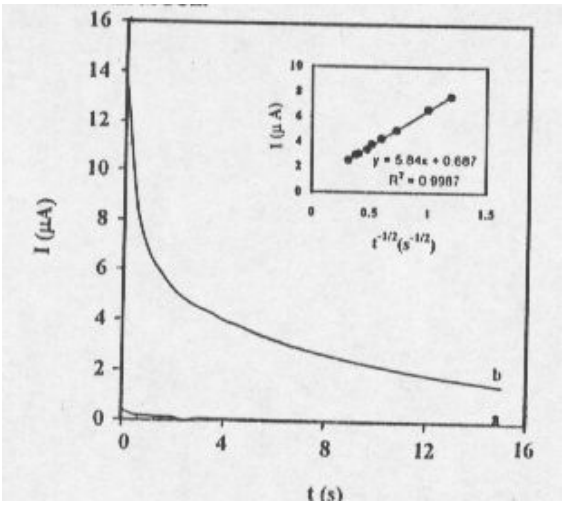


Fig. 10: Chronoamperograms obtained for EPMGCE in 0.15 M phosphate buffer (pH 7.5): A) in the absence and B) in the presence of 0.3 mM hydrazine. The working electrode potential was kept at 260 mV vs. SCE. Inset shows the corresponding I-$t^{1/2}$ plot.

pH for a 1 mM solution of hydrazine. On the basis of this Figure, The peak current increases when solution pH varies from 5.5 to 6.5 and then remains almost constant up to pH 7.5.e This indicates that the nearly neutral solutions are the more suitable media for oxidation of hydrazine. However, for pHs higher than 7.5 the peak current begins to decrease most probably because of a decrease in electrode surface coverage in more alkaline solutions.

Fig. 9B shows that the catalytic peak potential shifts towards less positive values proportionally to the augmentation of solution pH. However, in order to avoid the EP film impairment in more alkaline media, pH = 7.5 was considered as optimum value for electrocatalytic oxidation of hydrazine at EPMGCE.

Chronoamperometric studies

Chronoamperometry was used to determine the diffusion coefficient of hydrazine in solution. A step voltage of 300 mV vs. ref. was applied to EPMGCE dipped in a 0.3 mM solution of hydrazine in 0.15 M phosphate buffer (pH 7.5). The observed current being controlled by diffusion of hydrazine obeys the Cottrell equation:

$$I_d = nFAD^{1/2}C^*\pi^{-1/2}t^{-1/2}$$

where, n is the number of electrons involved in electrode process, A is the electrode geometric area in cm^2, D is the diffusion coefficient of hydrazine in cm^2s^{-1} and C^* is the bulk concentration of hydrazine in $molcm^{-3}$. The other symbols have their proper meanings. Fig. 10 exhibits the chronoamperograms obtained at EPMGCE in the absence (A) and presence (B) of hydrazine. The inset of this Figure shows the plot of I_d vs. $t^{-1/2}$ for 0.7-10s. A value of 8.3×10^{-6} cm^2s^{-1} was obtained for diffusion coefficient of hydrazine, which is in good agreement with those reported by others [27,30].

RDE voltammetric studies

Rotating disc electrode voltammetry was used to estimate the catalytic reaction rate constant, K_h, of the reaction involved between surface deposited EP film and hydrazine. The RDE voltammograms obtained for a 1 mM solution of hydrazine in 0.15 M phosphate buffer (pH 7.5) are given in Fig. 11A. Similar voltammograms were recorded for solutions containing 0.10 and 0.50 mM of hydrazine. The plots of currents measured at 0.450 V

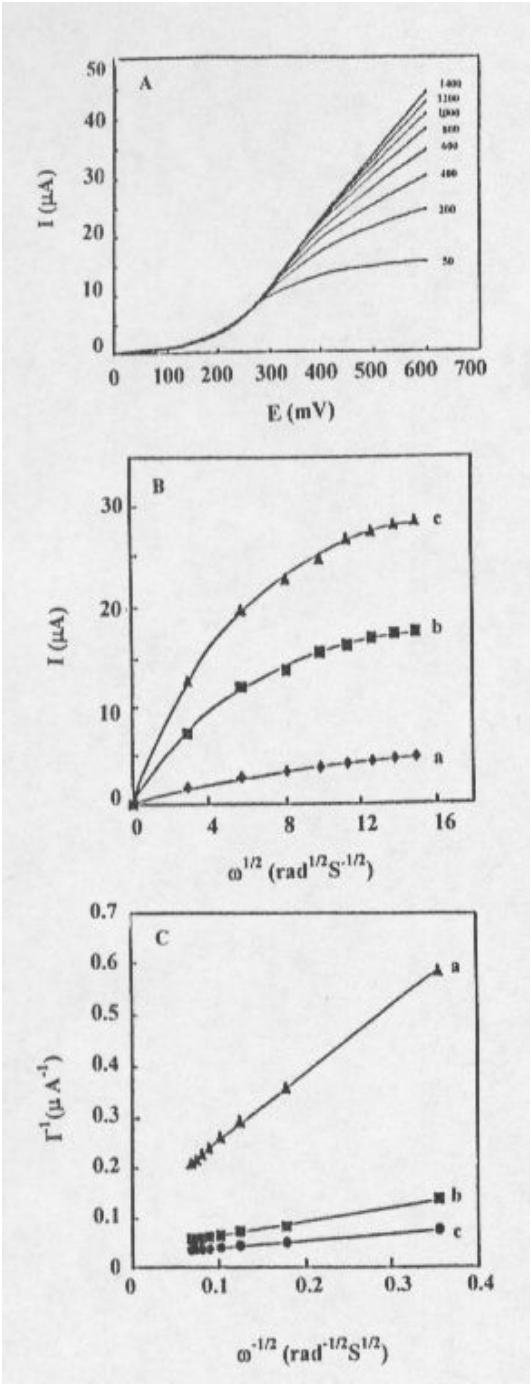


Fig. 11: A) RDE voltammograms of 1 mM hydrazine in 0.15 M phosphate buffer (pH 7.5) at various rotation rates (indicated in front of each curve). The working electrode was EPMGCE. B) plots of I versus $\omega^{1/2}$ (Levich plot) using RDE voltammograms obtained for a) 0.1. b) 0.5 and c)1 mM solutions of hydrazine. C) plots of I^{-1} versus $\omega^{-1/2}$ (Koutecky-Levich plot) on the basis of voltammograms obtained for a) 0.1. b) 0.5 and c)1 mM solutions of hydrazine.

vs. ref. as a function of $\omega^{1/2}$ (Levich plot) are shown in Fig. 11B for three different concentrations of hydrazine.

Non-linearity appeared in I-$\omega^{1/2}$ curves immediately suggests that the reaction is limited by kinetics and not by mass transport. Discarding the electron transfer between the electrode substrate and EP film to be as rate limiting, we conclude that the reaction between hydrazine and mediator EP is the rate-determining step. Under these conditions, the Koutecky-Levich equation can be used to determine the rate constant for the process. This equation can be formulated as follows [46]:

$$\frac{1}{I_{lim}} = \frac{1}{nFAK_hC^*} + \frac{1}{0.62nFA\nu^{-1/6}D^{2/3}\omega^{1/2}C^*}$$

where, C^* is the bulk concentration of hydrazine (mol cm^{-3}), ω is the angular frequency of rotation (rad. s^{-1}), D is the diffusion coefficient (cm^2 s^{-1}), n is the kinematic viscosity (cm^2 s^{-1}), K_h is the catalytic reaction rate constant (cm s^{-1}) between surface deposited EP and solution-diffused hydrazine and all other parameters have their conventional meanings. The Koutecky-Levich plots obtained from the data in Fig. 11B are shown in Fig. 11C. These plots exhibit the anticipated linear dependence between $1/I_{lim}$ and $\omega^{-1/2}$. The rate constant K_h can be calculated from the intercepts of the Koutecky-Levich plots. It was found that K_h decreases significantly with increasing the bulk concentration of hydrazine. Such an observation provides an additional evidence against the restricted access of hydrazine as the rate limiting step. From the values of the intercepts, a mean value of $(4{,}83 \pm 0.59)\times10^{-3}$ cm s^{-1} is obtained for K_h. This value is in good agreement with those reported for other electrodes modified by quinonic mediators [27,28]. Andrieux and Saveant [47] have proposed a theoretical model for electrocatalytic reactions with large catalytic rate constant, K_h. In this model, the voltammetric catalytic peak current recorded at low scan rates is proportional with bulk concentration of substrate:

$$I_{cat} = 0.496nFAD^{1/2}\nu^{1/2}C^*(nF/RT)^{1/2}$$

where, D and C^* are the diffusion coefficient (cm^2 s^{-1}) and the bulk concentration (mol cm^{-3}) of the substrate respectively and the other symbols have their usual meanings. Low value of K_h results in constant values

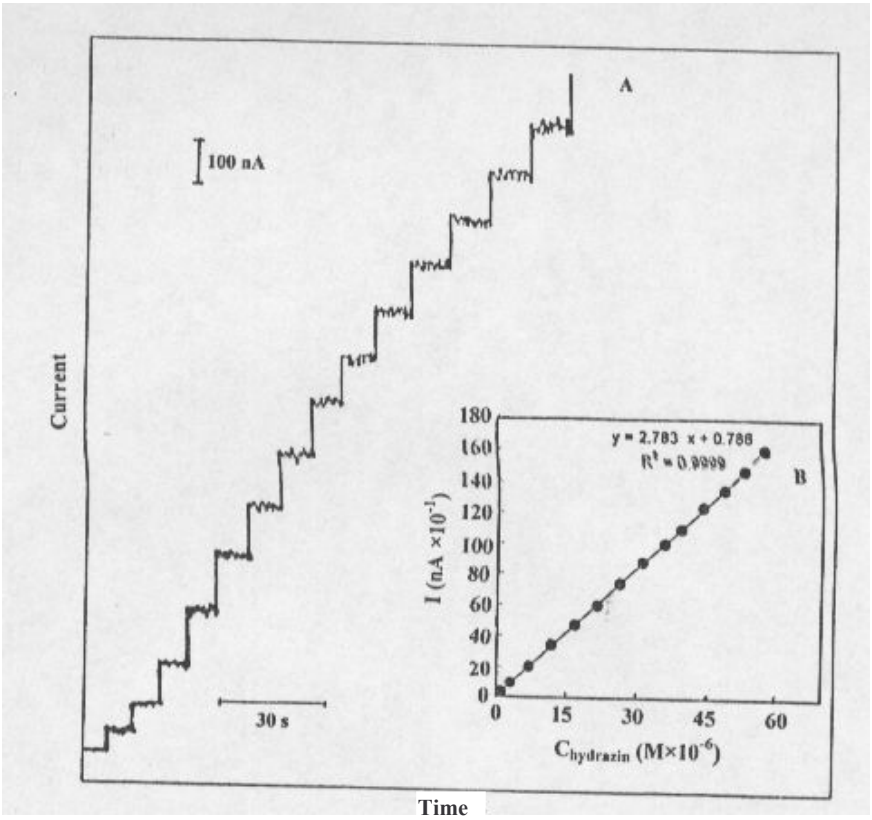


Fig. 12: Amperogram obtained for EPMGCE in 5 ml 0.15 M phosphate buffer (pH 7.5) in the course of successive addition of 0.1 mM hydrazine solution. The working electrode potential was kept in 260 mV vs. SCE. Inset shows the variation of measured current as a function of hydrazine concentration in solution.

lower than 0.496 in above equation. For a scan rate of 20 mVs^{-1}, we found the mean value of this constant to be 0.335 for a EPMGCE with a coverage of 2.7×10^{-10} $mol.cm^{-2}$ (evaluated from the cyclic voltammograms recorded at low scan rates and using the equation $\Gamma = Q/nFA$, where Q is the charge obtained by integrating the anodic peak under the background correction), a geometric area (A) of 0.031 cm^2 and considering $D = 8.3\times10^{-6}$ cm^2s^{-1} in solutions containing 0.1, 0,3 and 0.6 mM of hydrazine. According to the approach of Andrieux and Saveant and using Fig. 1 in their theoretical paper [47], a value of 4.04×10^{-3} cms^{-1} is obtained for K_h. This value is in accordance with that obtained by RDE voltammetric method.

Application of EPMGCE as amperometric sensor of hydrazine

In order to improve the l. o. d. of hydrazine determination at EPMGCE, it has been used as an amperometric sensor in moving solutions of hydrazine.

Table 1

Boiler feeding water	Amperometry with EPMGCE (ppb)	ASTM spectrophotometric method (ppb)
Sample No. 1	50.3	47.0
Sample No. 2	48.9	49.0
Sample No. 3	47.4	48.9
Sample No. 4	53.5	50.7
Mean	50.0	48.9
Standard deviation	2.6	1.5

The same three electrode system used in voltammetric procedures was adopted for amperometric measurement unless the EPMGCE potential is adjusted at 0.260 V vs. SCE and the solution is stirred regularly by a magnetic stirrer. Fig. 12 shows the amperogram obtained during the addition of successive increments of a 10^{-4} M hydrazine solution into 5 ml of 0.15 M

phosphate buffer solution (pH 7.5). The inset exhibits the corresponding amperometric calibration curve obtained by plotting the measured current after each addition of hydrazine solution vs. its concentration. As it is seen, a linear plot is obtained for hydrazine concentration ranging from 1×10^{-6} to 5.74×10^{-5} M. The calculated limit of detection (l.o.d.), using the definition: $y_{l.o.d.} = y_B + 3s_B$ [48] is 8.3×10^{-7} M.

The efficiency of EPMGCE as an amperometric sensor was also examined in the determination of hydrazine in a real sample. The feeding water from the economizer of boilers in Tabriz city thermal power plant was used for this purpose. The average value of hydrazine level, calculated from the data of four repetitive amperometric measurements by standard addition method was 50.0 ± 2.6 ppb.

The accuracy of the above amperometric determination was verified by application of standard ASTM method [49] to the quantitation of hydrazine in the same real sample. The results of both methods are collected in table 1.

No significant difference exists between the results obtained from these two methods using a *t* test at confidence level of 99.5% (P = 0.05).

CONCLUSION

Epinephrine can be oxidatively electrodeposited onto glassy carbon electrodes previously activated in alkaline solution. The redox response of the films is that anticipated for a surface-immobilized redox couple, and the pH dependence of the redox activity of these films is around 59 mV/pH unit. These films exhibit potent and persistent electrocatalytic behavior toward hydrazine oxidation. The kinetic parameters such as charge transfer coefficient, α, and the catalytic reaction rate constant, K_h, were also determined using cyclic and RDE voltammetry. It has been shown that voltammetry and amperometry by EPMGCE can be used as analytical methods for hydrazine determination in quiet and moving solutions, respectively.

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