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A voltammetric sensor based on poly(eriochrome black T) modified glassy carbon electrode for the simultaneous determination of dihydroxybenzene isomers

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Abstract

An electrochemical sensor based on deposition of polymeric film by using electrochemical method on the surface of glassy carbon electrode was fabricated for simultaneous determination of dihydroxybenzene using differential pulse voltammetry (DPV). The sensor was constructed by simple modification of glassy carbon electrode (GCE) with a uniform electro-polymerized film of poly (eriochrome black T) (poly(EBT)). The electro-chemical behaviors of hydroquinone (HQ), catechol (CC) and resorcinol (RS) at the modified electrode were studied. The obtained peak current was linearly dependent on the HQ, CC, and RS concentrations in the range of 0.50-70.0 µM, 0.50-70.0 µM and 1.0-70.0 µM, respectively. The detection limits for HQ, CC and RS at the surface of poly(EBT)/GCE were 0.20 µM, 0.11 µM and 0.60 µM (3σ), respectively. In addition, simultaneous determination of dihydroxybenzene was evaluated in real sample of water with differential pulse voltammetry.

Keywords: Hydroquinone; Catechol; Resorcinol; Poly(eriochrome black T).

1. Introduction

Dihydroxybenzene isomers, such as hydroquinone (HQ), catechol (CC), and resorcinol (RC) have wide industrial applications as solvents or organic intermediates for the products of industries [1]. CC (1,2-dihydroxybenzene) is broadly used in the production of hair dyes, antioxidants and food additives [2]. RS (1,3-dihydroxybenzene) is generally employed to produce dyes, plastics, and synthetic fibers [3, 4]. HQ (1,4-dihydroxybenzene) is used in a wide range of applications such as polymerization inhibitors, photographic developers, food antioxidants, and rubber antioxidants [5]. Therefore, such phenolic compounds can be found in various industries effluent such as pharmaceutical, steel, paper and pulp, petrochemical, rubber, dye, textile, cosmetic, and plastic [6, 7]. These compounds are toxic with low degradability in the ecological environment and thus are considered as environmental pollutants by the US Environmental Protection Agency (EPA) and the European Union (EU) [8]. Moreover, these isomers are often coexisting in environmental samples and due to their similar structures they usually interfere with each other during their determination. Therefore, development of simple

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and rapid analytical methods and rapid analytical methods for the simultaneous and/or selective determination of dihydroxybenzene isomers is very important in analytical chemistry field. Up to now, several methods have been reported for this purpose including chromatography [9], spectrophotometry [10]. However, these methods have some disadvantages, such as the requirement for previous separation, complicated operation, and intricate chemo-metric treatments of the analytical signals. Recently, electrochemical determinations of environment have become an important study domain due to their intrinsic advantages such as wide linear analysis range, sensitivity and high efficiency, low cost, simplicity, and time saving environment electrochemical methods [11]. The main problem in the electrochemical determination of dihydroxybenzene isomers is the overlapping of the oxidation and reduction peaks of these isomers at the unmodified electrodes. This intrinsic problem could be overcome by using chemically-modified electrodes (CMEs) as electrochemical sensors. In recent years, a few CMEs have been applied as a electrochemical sensors for determination of dihydroxybenzene isomers by using different modifiers including graphene–chitosan composite [12], CTAB functionalized graphene oxide/multiwalled carbon nanotube [13], graphene/cobalt hexacyanoferrate [14], graphene doped carbon ionic liquid [15], poly-3-amino-5-mercapto-1,2,4-triazole [16], single wall carbon nanotubes [17] and multiwall carbon nanotubes [18, 19]. Some of these electrochemical sensors have a limit of detection higher than proposed electrode [12, 15, 19] or have not appropriate and wide linear dynamic range [17]. However, some of them have good and desirable analytical parameters [13, 14, 16, 18] but suffer from time of preparation electrode procedure. Moreover, in most cases the modifier films have poor homogeneity, physical stability and controllable film thickness on the surface of electrode. In this study, we describe the electro-analytical performance of poly (EBT) as an excellent modifier in the construction a voltammetric sensor for simultaneous detection of CC, HQ and RS. The sensor was constructed by simple modification of glassy carbon electrode (GCE) with a uniform electro-polymerized film of poly(EBT). The excellent oxidation peak separation and considerable improvement in the electrochemical responses of isomers allow sensitive simultaneous determination of CC, HQ and RS.

2. Experimental procedure

2. 1 Chemicals and reagents

All Chemicals, reagents were purchased from Merck (Darmstadt, Germany) and were used without purification. Doubly distilled water was used to wash the glassware, and to prepare all solutions.

2.2 Apparatus

All electrochemical measurements were carried out using Ivium potentiostat-galvanostat instrument (compactSTAT.e, Netherland) equipped with a three-electrode electrochemical cell. In the three-electrode system, the silver/silver chloride (saturated KCl), platinum electrode and modified glassy carbon electrode (poly (EBT)/GCE) are used as reference, auxiliary and working electrodes, respectively. All electrodes are acquired from Azar Electrode Co. (Iran), and the GCE was polished on a polishing pad with an alumina slurry to create a clean and glossy surface before being used. A pH-meter (Metrohm 780) equipped with glass-calomel combined electrode was used for pH measurements. An ultrasonic bath (BANDELIN electronic, Digital DT510H, Germany) was used to further clean up the surface of the electrode and homogenize some of the solutions.

2.3 Preparation of modified electrode poly(EBT)/GCE

The glassy carbon electrode (GCE) was polished with 0.05 µm of alumina slurry on a polishing cloth followed by rising thoroughly with doubly distilled water until a mirror-like surface was obtained. Then, to clean the surface of the physically absorbed alumina particles, the electrode was immersed into a mixture of distilled water and ethanol and placed in an ultrasound bath for 5 minutes. To remove the chemically adsorbed compounds from the electrode surface, the cyclic voltammetry over 25 cycles ranged from -0.4 to +1.4 V (vs Ag/AgCl) 100 mVs-1 in acidic media (sulfuric acid,

0.1 mol L-1) was performed. The electrode was then transferred to electrochemical cell containing a mixture solution of 1.0 mM EBT and 0.1 M sodium hydroxide. Electro-polymerization was performed by running cyclic voltammetric technique over 25 cycles ranged from -0.4 to + 1.4 V (vs Ag/AgCl) at 100 mV s^{-1}. The electrode was then washed with distilled water and kept in 0.10 M NaOH solution. The as prepared electrode was labeled with poly(EBT)/GCE.

2.4 Analytical procedure

All measurements were carried out at room temperature. Differential pulse voltammetry (DPV) was run from 0.0 V to 0.90 V with scan rate of 50 mV s-1 (pulse amplitude of 70 mV and 50 ms pulse time). The oxidation peak currents of HQ, CC and RS (Is) were recorded at their corresponding peak potentials of 0.12, 0.26 and 0.63 V, respectively. The background voltammogram was recorded at the same condition but in the absence of HQ, CC, and RS, and the background currents at the mentioned peak potentials were also obtained (Ib). Analytical signal was defined as the difference between the background and sample peak currents (Δi=Is-Ib) and used for construction of calibration curves. After each measurement, the modified electrode was easily cleaned by electrochemical method via five potential cycles in the range -0.40-1.40 V in NaOH solution (0.10 M) and then washed with distilled water for subsequent analysis.

3. Results and Discussion

3.1 Preparation and characterization of electropolymerized polymeric film at the surface of electrode

Fig. 1. shows a continuous cyclic voltammogram (CV) recorded during the electropolymerization on the surface of GCE in 0.10 M of NaOH solution. As shown in Fig.1, the oxidation peak current of eriochrom black T reduced with increasing the number of cycles. This can be due to the formation of a polymeric film on the surface of glassy carbon electrode [20, 21].

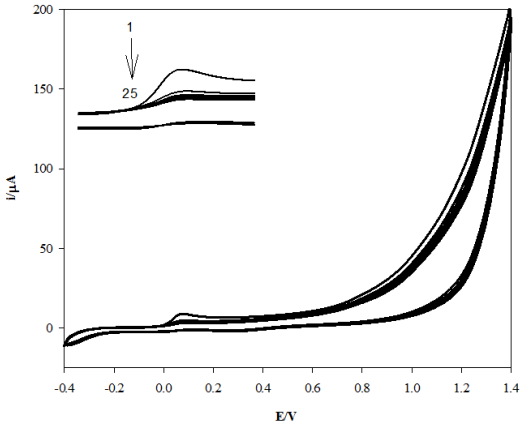


Fig. 1 Cyclic voltammograms of EBT in electropolymerization process from 1st to 25th cycles. EBT: 1.0 ×10^{-3} M; supporting electrolyte: 0.1 M NaOH; scan rate: 100 mVs^{-1}.

The typical morphologies of GCE (Fig. 2A) and poly(EBT)/GCE (Fig. 2B) were characterized by scanning electron microscope. As shown in Fig. 2B, the poly(EBT) made a uniform film on the electrode surface which means that EBT was successfully polymerized on the GCE.

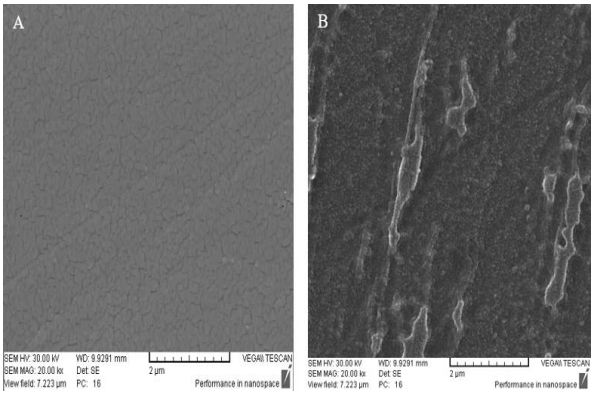


Fig. 2 SEM image of (A) GCE and (B) poly(EBT) on the surface of GCE.

The effect of pH on the electrochemical behavior of the polymeric layer deposited on the electrode surface was studied at different pHs using PBS in the range 0.3 - 7.0 by cyclic voltammetric technique. The oxidation and reduction peaks of poly (EBT) are linearly shifted by increasing of pH to the negative potentials, which indicates the presence of protons in the electrochemical oxidation process of the poly (EBT) at the electrode surface. The slope of of the linear plot of the anodic peak potential versus pH was obtained -57 mV pH^{-1}, which shows that the number of electrons and protons participating in the electrochemical oxidation process of the polymer is equal.

The dependence of electrochemical behavior of poly(EBT)/GCE on the scan rate in the range of 25-200 mV s^{-1} was investigated using cyclic voltammetry technique in PBS pH 5.0. According to the corresponding voltammograms (Fig. 3), .existence a pair of redox peak in each cycle represents the good redox activity of the poly(EBT) at the electrode surface. Also, it was found that the oxidation peak current increase with increasing scan rate with a linear regression equation of i_{pa} (μA) = 0.009υ (mV s^{-1}) - 0.3191, which indicates that the electrode process is surface-controlled. Moreover, at different scan rate, the ratio of the cathodic peak current to anodic peak current was close to unit and the peak potential separation (ΔEp = Epa − Epc) was nearly constant. These results indicate that the electrode surface reaction is quasi-reversible [22]. By comparing the peak separation potential with its theoretical value of 59/n mV at 25 ºC (or 2.303RT /nF), the number of electrons exchanged in the surface reaction process was obtained as two (n=1.8).

The concentration of electro-active species in the surface-controlled electrode process can be obtained by the following equation [23]:

$$I_p = \frac{n^2 F^2 A \Gamma v}{4 RT} \qquad (1)$$

which, n is the number of electrons involved in the electrode reaction, A is the surface geometrical area of the electrode (0.67 cm^2) and Γ is the surface coverage concentration (mol cm^{-2}). The surface coverage concentration can be calculated from the slope of anodic peak current *vs.* scan rate. According to the obtained slope (0.009), the surface coverage concentration was calculated to be 3.77 × 10^{-8} mol cm^{-2}.

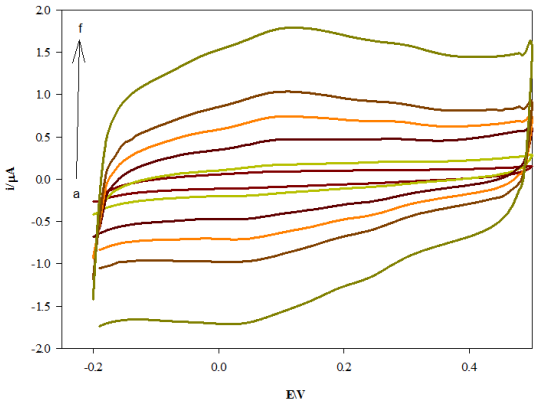


Fig. 3. Cyclic voltammograms of poly(EBT) modified glassy carbon electrode in pH=5.0 phosphate buffer solution at different scan rates. (a) 25 mV s^{-1};(b) 50 mV s^{-1}; (c) 100 mV s^{-1}; (d) 125 mV s^{-1}; (e) 150 mV s^{-1}; (f) 200 mV s^{-1}.

Electrochemical impedance spectroscopic technique can be used to study the electrochemical properties of the electrode interface [24]. The electro-chemical impedance studies were carried out at a frequency range of 0.1-100 kHz in 0.1 M KCl in the presence of 5.0 mM of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ as reversible redox probe. In Fig. 4, the Nyquist plots are shown for modified and bare electrodes. The semi-circle diameter in the Nyqueist plot can be used to determine the resistance to charge transfer (Rct) at the electrode/solution interface. According to the Nyquist plots in Fig. 4, the Rct was obtained 1.390 and 0.449 kΩ for the bare and modified GCE, respectively. The low Rct in the modified electrode compared with the bare electrode shows that the electron transfer process at the surface of electrode is accelerated by with the poly(EBT) film.

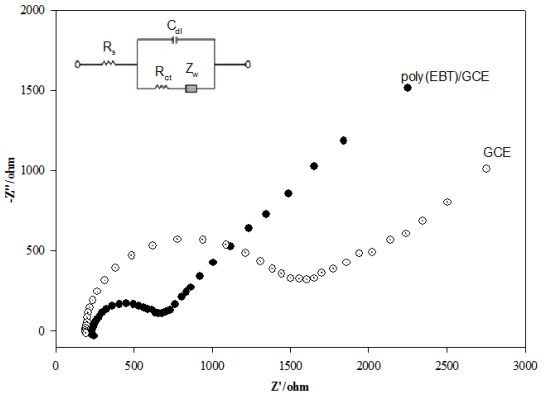


Fig. 4. Electro-chemical impedance spectra for bare GCE (a) and poly(EBT)/GCE (b). Inset shows equivalent circuit. Rs is solution/electrolyte resistance, Rct is charge-transfer resistance, Zw is Warburg impedance related to semi-infinite linear diffusion, and Cdl is double layer capacitance. Conditions: 5.0 mM of K3[Fe(CN)6]/K4[Fe(CN)6] in KCl solution (0.10 M) with frequency range of 0.1-100 kHz.

3.2 Electrochemical behavior of HQ, CC and RS on the poly(EBT)/GCE.

The electrochemical behaviors of HQ, CC and RS at the bare and modified electrodes were investigated using cyclic voltammetry. As can be seen in Fig. 5, at the bare GCE (Fig. 5 curve a), a broad oxidation peak was appeared at 0.33 V corresponding to HQ and CC, while no clear oxidation peak was observed for RS. This observation could be due to the slow electron transfer kinetic of HQ, CC and RS at the surface of bare GCE. So it is impossible to use the bare GCE for simultaneous determination of three dihydroxybenzene compounds. However, under the same conditions, all three dihydroxybenzene compounds show well-behaved oxidation peaks at the poly (EBT)/GCE (Fig. 5, curve b). The peak-to-peak separation for HQ and CC is 0.14 V, CC and RS 0.39 V. It can be concluded that the all three dihydroxybenzene can be identified separately at the poly (EBT)/GCE. The improvement in oxidation peak currents as well as the decrement in peak potential of HQ and CC at the modified electrode might be attributed to the catalytic activity of the poly(EBT) film toward the oxidation of HQ, CC and RS. The electrochemical catalytic mechanism, can be denoted as follows.

$$[\text{poly (EBT)}]_{red} \longleftrightarrow [\text{poly(EBT)}]_{ox} + 2e \qquad (2)$$

$$\left.\begin{aligned} &[\text{poly(EBT)}]_{ox} + HQ_{red} \rightarrow [\text{poly(EBT)}]_{red} + HQ_{ox} \\ &[\text{poly(EBT)}]_{ox} + CC_{red} \rightarrow [\text{poly(EBT)}]_{red} + CC_{ox} \\ &[\text{poly(EBT)}]_{ox} + RS_{red} \rightarrow [\text{poly(EBT)}]_{red} + RS_{ox} \end{aligned}\right] \qquad (3)$$

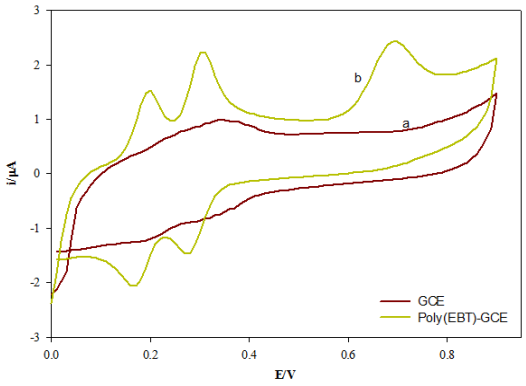
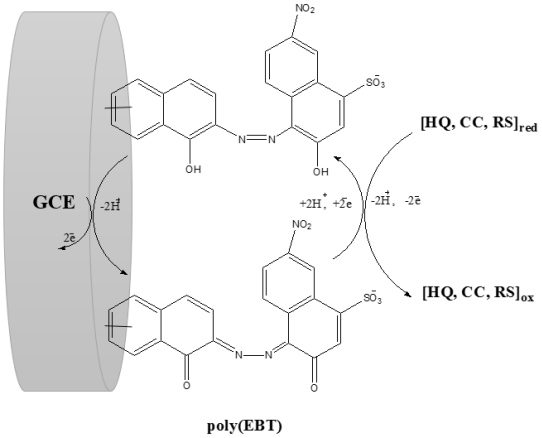


Fig. 5 Cyclic voltammograms of the mixture containing HQ, CC and RS at the bare glassy carbon electrode (a) and the poly(EBT) modified electrode (b) in pH 5.0 phosphate buffer solution. Concentration of HQ, CC and RS: 2.0×10^{-5} M and scan rate: 100 mV s^{-1}.



Scheme 1. Electrocatalytic oxidation reaction of HQ, CC and RS at the poly(EBT)/GCE.

3.3 Effect of pH on the oxidation of HQ, CC and RS at poly(EBT) modified electrode

Electrochemical oxidations of HQ, CC and RS (10.0 μM) in phosphate buffer with different pH in the range of 0.2 to 9.0 were studied using cyclic voltammetric technique. Regarding the recorded voltammograms (Fig. S1 Supporting Information), it is clear that the oxidation peak potentials of HQ, CC and RS are shifted to negative potentials by increasing pH value, which indicates the role of proton in the electrochemical oxidation of HQ, CC and RS. Also, the dependence of the oxidation peak potentials on pH is linear for all three species and follows the succeeding equations:

HQ: $E(V) = 0.473 - 0.0519pH \quad R^2 = 0.9965$ (4)

CC: $E(V) = 0.581 - 0.0523pH \quad R^2 = 0.9976$ (5)

RS: $E(V) = 0.969 - 0.0526pH \quad R^2 = 0.9939$ (6)

The slopes of the linear graphs for all three component are close to the Nernstian value (59 mV), which indicates that the number of electrons and protons in the electrochemical oxidation process of HQ, CC and RS at the modified electrode surface is equal.

3.4. Optimization of experimental conditions

The experimental conditions for simultaneous determination of HQ, CC and RS were investigated to get the maximum response. The experimental conditions such as pH of the supporting electrolyte, pulse amplitude, and scan rate were studied using the one-at-a-time method.

In order to determine the best pH for the measurement of the species, the differential pulse (DP) voltammograms on the surface of poly(EBT)/GCE for

solutions containing 10.0 µM of three analytes buffered at different pH in the range of 2.0-9.0 were recorded. The results obtained are summarized in Fig. 6. According to results, the highest current response was found for solutions with a pH of 5.0. The 0.15M phosphate buffer solution with a pH of 5.0 was chosen as the optimum supporting electrolyte for simultaneous determination of HQ, CC and RS.

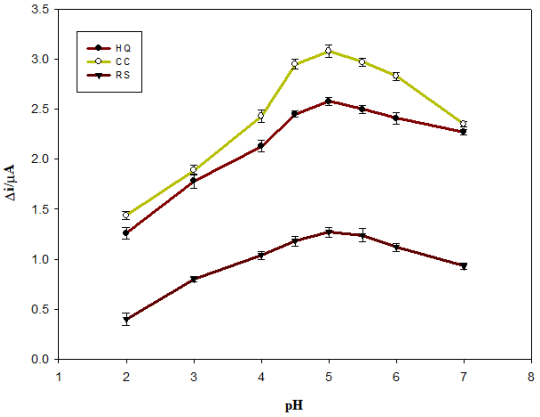


Fig. 6. Variation in analytical signal (Δi) with pH. 1.0×10^{-5} M of HQ, CC and RS.

In order to optimize the pulse amplitude for DPV, the oxidation peak currents of HQ, CC and RS were measured in the pulse amplitude in the range of 10-100 mV. As the pulse amplitude increases (10-70 mV), the oxidation peak currents of the analytes increase and then remained constant. In order to achieve the best sensitivity, selectivity the value of 70 mV was chosen as the optimum value of pulse amplitude in the further studies. The influence of scan rate on the oxidation peak currents of HQ, CC, and RS studied at the range of 10 to 100 mV s^{-1}. The obtained results showed that by increasing the scan rate of 10 to 50 mV s^{-1} the oxidation peak current of analytes increased and then remained constant. So the scan rate of 50 mV s^{-1} was chosen as the optimum value in subsequent studies.

3.5. Simultaneous determination of HQ, CC and RS

The performance of the poly(EBT)/GCE in the determination of HQ, CC, and RS simultaneously in their trinary mixtures was investigated using DPV as a sensitive method with low detection limit due to low charging current in the analytical signal. For this purpose, several ternary mixtures containing three analytes were prepared in which the concentration of a species changed, while the concentration of other two species was constant at 10.0 µM and DP voltammograms of these solutions were recorded under the predefined optimal conditions (Fig. 7A, 7B and 7C). The peak currents for HQ, CC, and RS increased linearly with increases in their respective concentrations without considerable effects on the other peak currents. The obtained results (Fig. 7A) showed that the peak current for HQ increases linearly with increase in the HQ concentration, while the CC and RS responses did not change. Also, in the concentration constant of HQ and RS (10.0 µM), the increase in the peak current for CC was linear with its concentration in the range of 5.0-60.0 µM, while the oxidation peaks current for HQ and RS did not change (Fig. 7B). Fig. 7C confirms that no obvious changes took place in the HQ and CC (10.0 µM) oxidation peak currents while varying the concentration of RS.

The results clearly show that the analytical responses of HG, CC and RS are independent of each other. DPV studies were also carried out by simultaneously increasing the concentrations of all three components in their ternary mixtures. Fig. 7D shows DP voltammograms for a ternary mixture of three component with different concentration. As shown in Fig. 7D, by increasing the concentration of HQ, CC and RS simultaneously, the corresponding oxidation peak currents increase linearly. According to the results obtained, the linear dynamic ranges for HQ, CC and RS were found to be 0.5-70.0, 0.5-70 and 1.0-70 µM, respectively. The linear equations for calibration curves were obtained as follows:

$\Delta i(\mu A)=0.325C_{HQ}(\mu M) + 0.008 \quad R^2=0.9970 \qquad (8)$

$\Delta i(\mu A)=0.287C_{CC}(\mu M) + 0.176 \quad R^2=0.9963 \qquad (9)$

$\Delta i(\mu A)=0.151C_{RS}(\mu M) + 0.117 \quad R^2=0.9976 \qquad (10)$

The detection limits for HQ, CC and RS at the surface of poly(EBT)/GCE were found to be 0.20 µM, 0.11 µM and 0.60 µM (3σ), respectively.

For evaluation of reproducibility and repeatability of modified electrode, three modified electrodes were prepared in three different days and DP voltammograms of a mixture containing 10.0 µM of HQ, CC and RS

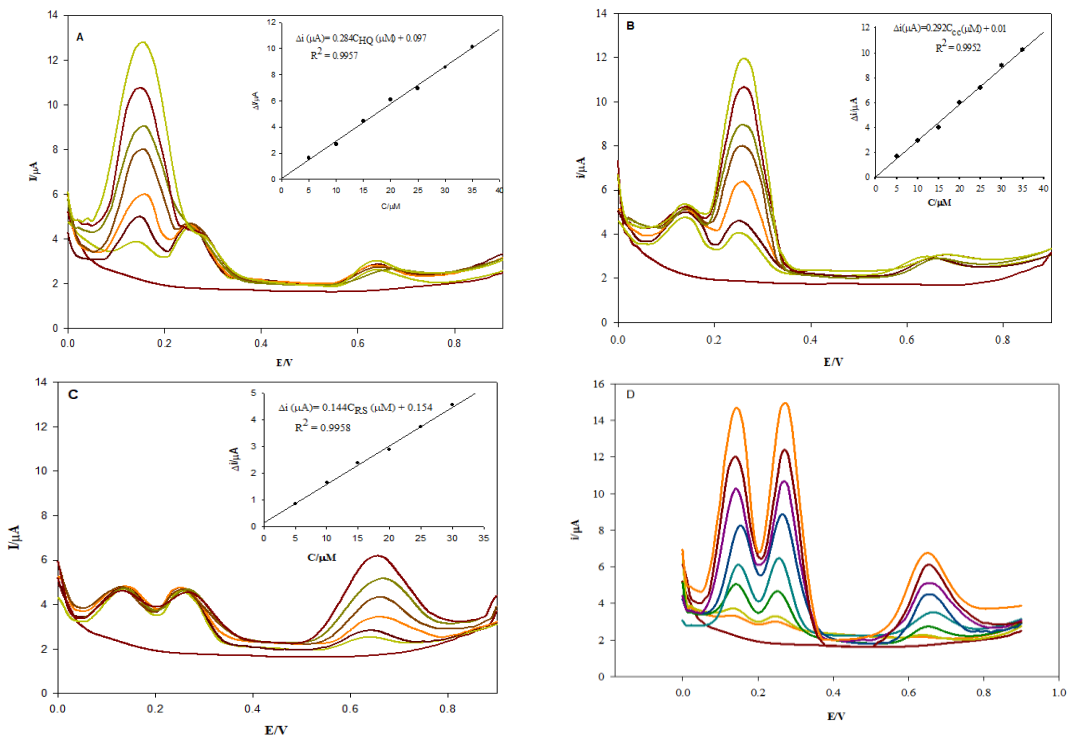


Fig. 7. (A) DPVs of HQ at poly(EBT)/GCE in the presence of 10.0 µM of CC and RS, concentrations (from 1 to 8): blank, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0 and 35.0 µM, (B) DPVs of CC at poly(EBT)/GCE in the presence of 10.0 µM of HQ and RS, concentrations (from 1 to 8): blank, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0 and 35.0 µM, (C) DPVs of RS at poly(EBT)/GCE in the presence of 10.0 µM of HQ and CC; concentrations (from 1 to 7): blank, 5.0, 10.0, 15.0, 20.0, 25.0 and 30.0 µM. and (D) DPVs of the mixture containing HQ, CC and RS at poly(EBT)/GCE in phosphate buffer solution (pH 5.0). Concentrations of the three compounds (from 1 to 9): blank, 1.0, 5.0, 10.0, 15.0, 20.0, 30.0, 35.0 and 40.0 µM for HQ, CC and RS.

were recorded (8 times) in each day. The results obtained were analyzed using the analysis of variance (ANOVA) with confidence level of 95%. The results of this study confirmed the reproducibility and repeatability of the proposed electrode preparation in different days. In order to investigate within and between electrodes precisions of propose electrode, differential pulse voltammograms of analaytes (10.0 µM) in their ternary mixture was recorded using an electrode in a day (8 replicate) and the relative standard deviations (RSD%) were calculated as 2.6% , 3.2% and 3.8% for determination of HQ, CC and RS, respectively in their mixture. Also, the RSD% was obtained for eight repetitive measurements with three electrodes (3.3%, 3.9% and 4.2% for HQ, CC, and RS respectively). These results indicated that the modified electrode had good reproducibility and repeatability.

Few electrochemical methods have reported the determination of HQ, CC and RS. A literature review on the analytical performance of CMEs (Table 1) indicated that poly(EBT)/GCE had a lower detection limit than some of the reported modified electrodes [12, 14-16, 18, 19]. Although a number of studies have reported better detection limits [17], poly (EBT)/GCE represents an expanded linear dynamic range. Some modified electrode have showed better analytical parameters in the determination of HQ, CC and RS, compared to the proposed modified electrode. However, the preparation of the proposed electrode is much easier and faster than previous reported [13].

3.6. Interference studies

The effect of different species as potentially interference substances in the simultaneous determination of HQ, CC and RS in their ternary mixture with concentration of 3.0 mg L^{-1} for each component was studied under the predefined optimal conditions. The tolerance limit, defined as the maximum concentration of the interfering substance, caused an error less than ±5% for the determination of HQ, CC and RS.

The obtained results showed that 1000-fold of methionine, L-alanine, lactose, glucose, EDTA, K^+, Na^+, Cl^-, SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, SCN^-, $H_2PO_4^-$, HPO_4^{2-}, NH_4^+, ClO_4^-, F^- and NO_3; 500-fold of thiourea, citric acid, acetate, phthalate, citrate; 100-fold of vitamin B1, vitamin B2 and uric acid; and 50-fold of dopamine, acetaminophen, l-cysteine and ascorbic acid did not affect the selectivity.

3.7. Analysis of water samples

The proposed modified electrode was applied to the determination of HQ, CC and RS in tap water and spring river water. Tap water and spring water samples were collected from 10 different locations in the city of Shahrood, Iran and Farahzad spring, Shahrood, Iran, respectively. Then, 5 mL PBS (pH 5.0) and 1 mL of different standard concentrations of the HQ, CC and RS were added into 4.0 mL water sample for the determination according to the analytical procedure. None of the targeted analytes were detected in water samples. The results recoveries are listed in Table 2. It can be seen that the method showed good recoveries for the added amounts of HQ, CC and RS. Moreover, the obtained results confirmed that at 95% confidence level, there is a good agreement between the experimental and spiked values.

Table 1. Analytical parameters of some chemically modified electrodes in the determination of HQ, CC and RS.

Electrodes	LDR (µM)			DL (µM)			Technique	Reference
	HQ	CC	RS	HQ	CC	RS		
GC/GCE	1-300	1-400	1-550	0.75	0.75	0.75	DPV	[12]
CTAB-GO/MWNT /GCE	0.1-200	0.1-400	1-100	0.03	0.01	0.20	CV	[13]
CoCHF/Gr/GCE	1-150	1-200	3.5-250	0.20	0.21	0.35	DPV	[14]
Gr/CILE	10-400	10-300	1-170	1.80	0.74	0.36	DPV	[15]
Au/pAMTa-MWNTs/GCE	7.2-391	3.6-183	8.4-398	0.30	0.24	0.60	DPV	[16]
SWNT-GCE	0.4-10	0.4-10	0.4-10	0.12	0.26	0.3	DPV	[17]
MWCNT-ME	1-100	1-100	6-100	0.30	0.20	0.60	Amp	[18]
MWCNT-GCE	2-100	2-100	5-80	0.6	0.6	1.0	LSV	[19]
Poly-EBT/GCE	0.50-70.0	0.50-70.0	1.0-70.0	0.20	0.11	0.60	DPV	This work

LDR: linear dynamic range; DL: detection limit; DPV: Differential pulse voltammograms; CV: cyclic voltammetry; Amp: amprometric; LSV: linear sweep voltammetry; GC/GCE: Graphene–chitosan composite film modified glassy carbon electrode; CTAB-GO/MWNT /GCE: CTAB Functionalized Graphene Oxide/ Multiwalled Carbon Nanotube Modified glassy carbon Electrode; CoCHF/Gr/GCE: Graphene/Cobalt Hexacyanoferrate Modified Glassy Carbon Electrode; Gr/CILE: Graphene Doped Carbon Ionic Liquid Electrode; pAMTa: poly-3-amino-5-mercapto-1,2,4-triazole; MWCNT-ME: Multiwall Carbon Nanotubes Modified Electrode

Table 2. Determination of HQ, CC, and RS in water samples.

Sample	Added (μM)			Found (µM) ± CL (n=3)			Recovery (%)		
	HQ	CC	RS	HQ	CC	RS	HQ	CC	RS
tap water	0.0	0.0	0.0	ND	ND	ND	---	---	---
	10.0	10.0	10.0	9.52	9.74	9.64	95.2	97.4	96.4
	25.0	25.0	25.0	24.26	25.14	24.60	97.04	100.56	98.40
spring river water	0.0	0.0	0.0	ND	ND	ND	---	---	---
	15.0	15.0	15.0	14.85	15.20	14.92	99.00	101.33	99.47
	30.0	30.0	30.0	31.10	29.78	29.65	103.67	99.27	98.83

CL: 95% confidence limit, ND: Not detected.

4. Conclusion

In this study, a poly (EBT) modified electrode was fabricated for the simultaneous determination of HQ, CC and RS. The electro-catalytic activity of the poly(EBT) thin layer on the electrochemical oxidation of HQ, CC and RS was studied using DPV and CV techniques. The thin polymeric layer of poly(EBT) on the GCE surface increased the oxidation peak current of the analytes, which is an evidence for the electro-catalytic activity of immobilized modifier. After optimization of the analytical conditions, an electrochemical method was established for the determination of real water samples. The proposed modified electrode has a good sensitivity and selectivity for simultaneous measurement of dihydroxybenzene isomers. Analytical parameters of the method such as linear dynamic range, repeatability, reproducibility and limit of detection are desirable and suitable. The effect of the presence of foreign species on the simultaneous detection of HQ, CC and RS was studied and it was found that most of the species studied did not seriously interfere in the simultaneous determination of analytes. Finally, the proposed method was successfully applied for the simultaneous determination of HQ, CC and RS in the water sample.

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