

Simultaneous Electrochemical Determination of Phenol Isomers in Binary Mixtures at a Poly(phenylalanine) Modified Glassy Carbon Electrode

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Glassy carbon electrode (GCE) is modified with electropolymerized films of phenylalanine. This poly(phenylalanine) modified electrode is used to simultaneous electrochemical determination of hydroquinone (HQ) and catechol (CC) and shows an excellent electrocatalytic effect on the oxidation of HQ and CC by cyclic voltammetry (CV) in 0.1 M acetate buffer solution (pH 5.0). In differential pulse voltammetric (DPV) measurements, the poly(phenylalanine) modified electrode could separate the oxidation peak potentials of HQ and CC present in binary mixtures by about 104 mV though the bare electrode gave a single broad response. A successful elimination of the fouling effect by the oxidized product of HQ on the response of CC has been achieved at the poly(phenylalanine) modified electrode. The determination limits for HQ and CC in binary mixtures at the poly(phenylalanine) modified electrode were found to be 1.0×10^{-6} M and 7.0×10^{-7} M, respectively. The proposed method has been applied to direct simultaneous determination of HQ and CC in a water sample with simplicity and high selectivity.

Keywords: Chemically modified electrode; Phenylalanine; Hydroquinone; Catechol; Electrochemistry

1. INTRODUCTION

The concept of chemically modified electrodes (CMEs) is one of the exciting developments in the field of electroanalytical chemistry. Many different strategies have been employed for the modification of the electrode surface. The motivations behind the modifications of the electrode surface are: (i) improved electrocatalysis, (ii) freedom from surface fouling and (iii) prevention of undesirable reactions competing kinetically with the desired electrode process [1].

The simultaneous determination of isomers is an interesting subject in electroanalysis [2-6]. The increasing demand for it has led to the development of a rapid, simple and non-separation method for the simultaneous determination of isomers where the CMEs have emerged as an efficient and versatile approach, and have attracted considerable attention over the past decades due to its advantages in terms of reduced costs, automatic and fast analysis, high sensitivity and selectivity [7-9]. Among various CMEs, polymer-modified electrodes (PMEs) are promising approach to determination of isomers.

Hydroquinone (HQ) and catechol (CC) are two isomers of dihydroxybenzenes. Dihydroxybenzenes are important environmental pollutants because they are toxic to humans and difficult to degrade. Furthermore, because HQ and CC have similar structures and properties, they usually coexist in products. Therefore, it is very important to develop simple and rapid analytical methods for dihydroxybenzene isomers [3]. The established methods for the determination of HQ and CC are commonly performed after pretreatment and separation [10]. It is important to develop a new method capable of simultaneous determination without previous separations of these compounds. HQ and CC have a basic quinone structures that might be electrochemically oxidized at a platinum or carbon electrodes [9]. The oxidation process to quinone has been widely studied from electrochemical point of view [11-12]. But so many difficulties are existed to simultaneously determine HQ and CC. The major difficulty is that the voltammetric peaks corresponding to oxidation/reduction of two phenol isomers are, in many cases, highly overlapped. Moreover, the competition of the phenolic isomers by electrode surface makes the relationship between the voltammetric response and the isomers concentrations, in the mixtures, non-linear [4]. Recently, an enormous amount of research has been devoted to the development of new chemically modified electrodes for monitoring HQ or CC [13-21].

Up to the present, few literatures for the directly simultaneous determination of HQ and CC using PME have been reported. To our best knowledge, the simultaneous determination of HQ and CC at poly(phenylalanine) modified electrode has not been reported. In an effort to develop a voltammetric method for the simultaneously selective and sensitive determination HQ and CC, the present work employed a GCE which was modified with poly(phenylalanine). The poly(phenylalanine) modified electrode could be used as a new sensor for simultaneously selective and sensitive determination of HQ and CC in binary mixtures by successful elimination of the fouling effect by the oxidized product of HQ on the response of CC. The proposed method has been applied to simultaneous determination of HQ and CC in a water sample with simplicity and high selectivity.

2. EXPERIMENTS

2.1. Reagents

L-phenylalanine (Phe), hydroquinone and catechol were obtained from Beijing Chemical Factory (Beijing, China). All other chemicals were of analytical grade and were used without further purification. A 0.1 M acetate buffer solution (ABS) was used to control the pH. All solutions were prepared with deionized water treated in a Millipore water purification system (Millipore Corp.). All experiments were carried out at room temperature.

2.2. Apparatus

Voltammetric measurements were performed with a CHI 440 electrochemical analyzer (CH Instruments, Chenhua Co. Shanghai, China). A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as reference electrode, a platinum wire counter electrode and a bare or modified glassy carbon disk working electrode (GCE). The pH values were measured with a PB-10 pH meter (Satorius). Unless otherwise stated, the electrolyte solutions were thoroughly degassed with N₂ and kept under a N₂ blanket.

2.3. Preparation of Poly(phenylalanine) Modified Glassy Carbon Electrode

Prior to electrochemical modification, the bare GCE with a diameter of 3 mm was polished with diamond pastes and alumina slurry down to 0.05 μm on a polishing cloth (Buehler, Lake Bluff, IL). Then it was rinsed with water and sonicated in 1 +1 HNO₃, acetone and water for 10 min, respectively. After being cleaned, the electrode was then placed in 0.01 M phenylalanine solution (0.1 M, pH 7.0 phosphate buffer solution) which was previously deaerated with high purity nitrogen for 10 min. The electrode was treated with cyclic scanning between -1.5 and 2.5 V at a scan rate of 100 mV s⁻¹, 8 scans. A uniform adherent blue polymer was found on the GCE surface. After modification, the modified electrode was electroactivated by cyclic voltammetry from -0.2 to 0.8 V at 100 mV s⁻¹ in pH 5.0 ABS. Then the electrode was ready for use after the final washing with water. Hereafter the modified electrode will be referred as the *p*-Phe modified electrode. The effective area of the modified electrode was determined as 7.54×10⁻² cm² from a cyclic voltammogram of 1.0×10⁻³ M K₃[Fe(CN)₆] in 0.1 M KCl.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Oxidation of HQ at the *p*-Phe Modified Electrode

Fig. 1 shows the cyclic voltammograms (CVs) at a bare GCE (Fig. 1a) and a *p*-Phe modified electrode (Fig. 1c) in presence of 0.1 mM HQ in ABS pH 5.0 at a scan rate of 100 mV s⁻¹. At the bare electrode, the oxidation and reduction of HQ result in broad waves with the corresponding peak potentials of 222 mV and 92 mV. So it shows irreversible behavior with Δ*E*_p, the difference between the anodic peak potential (*E*_{pa}) and the cathodic peak potential (*E*_{pc}), 130 mV. However, at the *p*-Phe modified electrode, the reversibility of HQ is significantly improved together with the current signal increasing. The oxidation peak potential negatively shifts to 207 mV and the reduction peak positively shifts to 127 mV with Δ*E*_p = 80 mV. The peak current is 7.31-fold larger than the corresponding one at the bare GCE. This indicated that catalytic reaction occurred between the *p*-Phe modified electrode and HQ. The catalytic reaction facilitates electron transfer between hydroquinone and the modified electrode, as a result the redox of hydroquinone becomes easier. *p*-Phe, itself, is electroinactive in the potential range from -0.2 to 0.6 V (Fig. 1b). Due to the high porosity of the *p*-Phe, the real surface area of the modified electrode is far greater than that of bare GCE. So the peak current increases evidently

together with the background voltammetric response at the *p*-Phe coated GCE stronger than that at the bare surface.

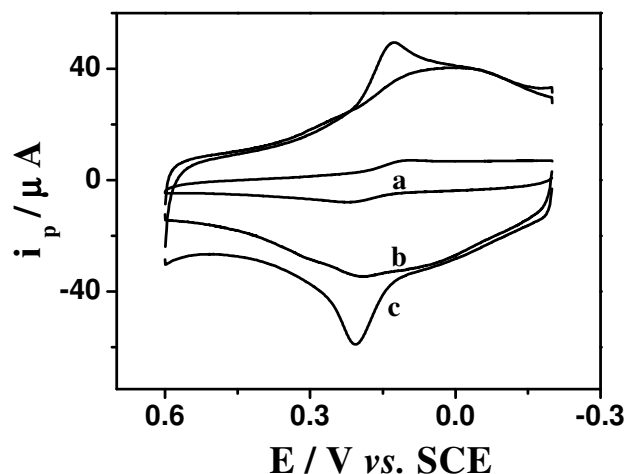


Figure 1. Cyclic voltammograms at bare GCE (a) and *p*-Phe modified electrode (b, c) in presence of 0.1 mM HQ (a, c) and in the absence of HQ (b) in 0.1 M ABS (pH 5.0); scan rate, 100 mV s^{-1} .

Fig. 2 shows the CVs of HQ at the *p*-Phe modified electrode at different scan rates. The reduction peak potential was observed to shift negatively with the increase in scan rate, and in addition, exhibited a linear relation to the square root of the scan rate, $v^{1/2}$, with the linear regression equation $i_{pc} / \mu\text{A} = -8.6437 + 3.4577 v^{1/2} / (\text{mV s}^{-1})^{1/2}$ (correlation coefficient, $r=0.9976$). The result indicates that the oxidation of HQ at the *p*-Phe modified electrode is a diffusion-controlled process.

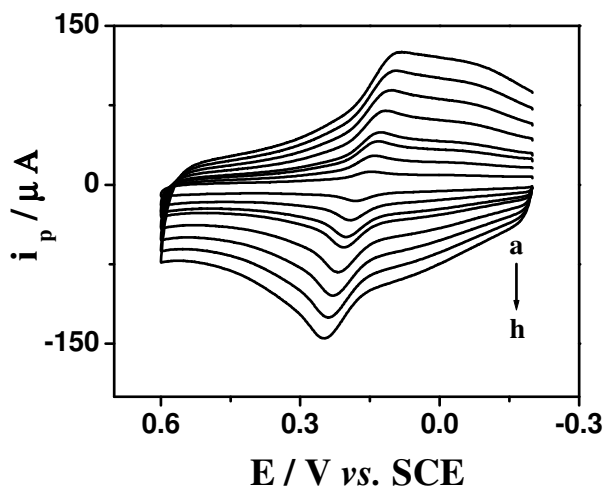


Figure 2. Cyclic voltammograms of 0.1 mM HQ at *p*-Phe modified electrode in 0.1 M ABS (pH 5.0) at different scan rates: (a) 20 mV s^{-1} ; (b) 50 mV s^{-1} ; (c) 80 mV s^{-1} ; (d) 100 mV s^{-1} ; (e) 150 mV s^{-1} ; (f) 200 mV s^{-1} ; (g) 250 mV s^{-1} ; (h) 300 mV s^{-1} .

The effect of the pH value of ABS on the response of HQ was investigated by CV. The response of HQ is well-behaved in ABS, as the solution pH increases, the anodic peak potential shifts to the negative and the potential of E_{pa} vs. pH in ABS has a good linear relation in the range of pH 3.01 – 6.50. The linear regression equation $E_{pa} / \text{V} = 0.5126 - 0.0593 \text{ pH}$ (correlation coefficient, $r = 0.9959$) was obtained, which showed that the uptake of electrons is accompanied by an equal number of protons. In the range of pH 3.01 – 6.50, the oxidative peak current of HQ increased with increasing the pH up to 5.0, after that the peak current decreased.

3.2. Electrochemical Oxidation of CC at the *p*-Phe Modified Electrode

The CVs of CC at *p*-Phe modified electrode is also compared with that at bare GCE. Fig. 3 shows the CVs at bare GCE (Fig. 3a) and *p*-Phe modified electrode (Fig. 3c) in presence of 0.1 mM CC in ABS pH 5.0 at a scan rate of 100 mV s^{-1} . At the bare electrode, the oxidation and reduction of CC result in broad waves with the corresponding peak potentials of 326 mV and 208 mV. So it shows irreversible behavior with ΔE_p , 118 mV. However, at the *p*-Phe modified electrode, the reversibility of CC is significantly improved together with the current signal increasing. The oxidation peak potential negatively shifts to 310 mV and the reduction peak positively shifts to 242 mV with $\Delta E_p = 68 \text{ mV}$. The peak current is 5.68-fold larger than the corresponding one at the bare GCE. These results indicated that *p*-Phe could accelerate the rate of electron transfer of CC in pH 5.0 ABS, and may be called a promoter.

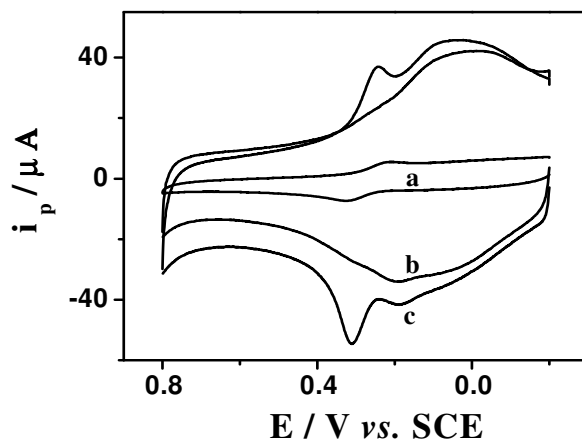


Figure 3. Cyclic voltammograms at bare GCE (a) and *p*-Phe modified electrode (b, c) in presence of 0.1 mM CC (a, c) and in the absence of CC (b) in 0.1 M ABS (pH 5.0); scan rate, 100 mV s^{-1} .

Fig. 4 shows the CVs of CC at the *p*-Phe modified electrode at different scan rates. The reduction peak potential was observed to shift negatively with the increase in scan rate, and in addition, exhibited a linear relation to the square root of the scan rate, $v^{1/2}$, with the linear regression equation $i_{pc} / \mu\text{A} = -10.1150 + 3.2312 v^{1/2} / (\text{mV s}^{-1})^{1/2}$ (correlation coefficient, $r=0.9979$). The result indicates that the oxidation of CC at the *p*-Phe modified electrode is a diffusion-controlled process.

The effect of the pH value of ABS on the response of CC was investigated by CV. The response of CC is well-behaved in ABS, as the solution pH increases, the anodic peak potential shifts to the negative and the potential of E_{pa} vs. pH in ABS has a good linear relation in the range of pH 3.01 – 6.50. The linear regression equation $E_{pa} / \text{V} = 0.5631 - 0.0492 \text{ pH}$ (correlation coefficient, $r = 0.9955$) was obtained, which showed that the uptake of electrons is accompanied by an equal number of protons. In the range of pH 3.01 – 6.50, the oxidative peak current of CC increased with increasing the pH up to 5.0, after that the peak current decreased.

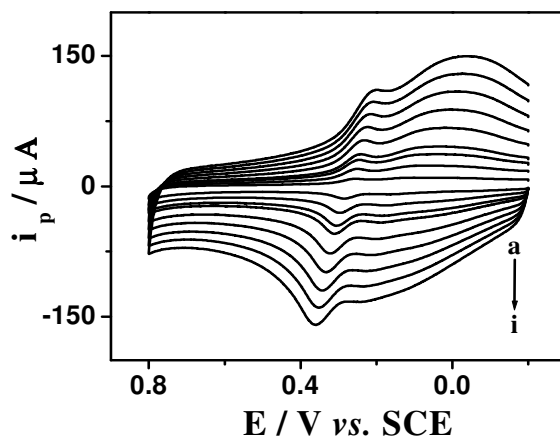


Figure 4. Cyclic voltammograms of 0.1 mM CC at *p*-Phe modified electrode in 0.1 M ABS (pH 5.0) at different scan rates: (a) 20 mV s^{-1} ; (b) 50 mV s^{-1} ; (c) 80 mV s^{-1} ; (d) 100 mV s^{-1} ; (e) 150 mV s^{-1} ; (f) 200 mV s^{-1} ; (g) 250 mV s^{-1} ; (h) 300 mV s^{-1} ; (i) 350 mV s^{-1} .

3.3. Effect of the *p*-Phe film thickness on the electrochemical response of HQ and CC

The thickness of the *p*-Phe film could be controlled by the cyclic number of voltammetric scans during the electrochemical modification. The effect of the thickness of *p*-Phe film on the electrode surface on the electrochemical response of HQ and CC was investigated by CV. The peak currents of HQ and CC were strongly dependent on the thickness of *p*-Phe film. The oxidation peak current and reduction peak current increased with increasing thickness of *p*-Phe film, meantime, the oxidation peak potential is positively shifted and the reduction peak potential is negatively shifted, indicating that the redox reversibility of HQ and CC was impaired with increasing thickness of *p*-Phe. In order to obtain better redox reversibility and higher sensitivity of the electrochemical response of HQ and CC, 8 scans were chosen to control the thickness of the *p*-Phe film.

3.4. Simultaneous Determination HQ and CC

In order to evaluate the sensitivity and selectivity of the *p*-Phe modified electrode for the quantification of HQ and CC, the electrochemical behavior of binary mixtures of 0.1 mM HQ and 0.1 mM CC at the *p*-Phe modified electrode was investigated using CV and differential pulse voltammetry

(DPV). For the binary mixtures containing of HQ and CC, 0.1 M ABS was used to control the pH of mixtures and the pH 5.0 was chosen, at this pH the oxidations of the two compounds have high electrochemical response.

Fig. 5 shows the CV and DPV voltammograms obtained for HQ and CC coexisting at bare GCE and *p*-Phe modified electrode. As shown in Fig. 5, the bare electrode cannot separate the voltammetric signals of HQ and CC. Only one broad voltammetric signal was observed for both analytes. The fouling of the electrode surface by the oxidation products results in a single voltammetric peak for HQ and CC. Therefore it is impossible to use the bare electrode for the voltammetric determination of CC in the presence of HQ.

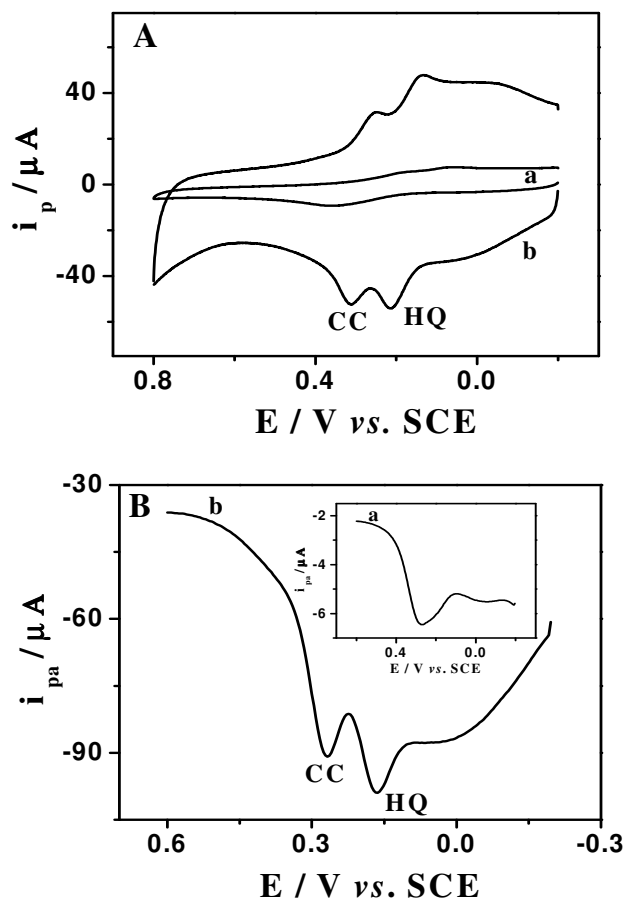


Figure 5. CVs (A) and DPVs (B) for the binary mixtures of 0.1 mM HQ and 0.1 mM CC at bare (a) and *p*-Phe modified electrode (b) in 0.1 M ABS (pH 5.0). (A) Scan rate, 100 mV s⁻¹; (B) scan rate: 4 mV s⁻¹; pulse amplitude: 50 mV; pulse width: 50 ms; pulse time: 200 ms.

Moreover, the *p*-Phe modified electrode resolved the mixed voltammetric signals into two well-defined voltammetric peaks. The *p*-Phe modified electrode shows good selectivity and excellent sensitivity in the simultaneous determination of HQ and CC. The peaks observed at 268 and 164 mV

in DPV recording is corresponding to the oxidation of CC and HQ, respectively (Fig. 5B). In theory, the density of the electron cloud is lower from HQ to CC, therefore their electroactivity is decreasing and the oxidation of the HQ is easier than that of CC, which shows that the potentials of their oxidation peaks increase [3]. The experimental results accord with this theory. As the oxidation potential of HQ is shifted to the less positive side, the anodic current of CC has no contribution from HQ, because HQ is readily oxidized well before the oxidation potential of CC reached. Thus elimination of the fouling of the electrode surface by the oxidation products could be achieved and the precise determination of CC in the presence of HQ is possible at the *p*-Phe modified electrode. The voltammetric signals of HQ and CC remained unchanged in the subsequent sweeps, indicating that the *p*-Phe modified electrode does not undergo surface fouling. Furthermore, the separation between the DPV oxidative peaks of HQ and CC is large (-104 mV) and thus the simultaneous determination of HQ and CC or the selective determination of CC in the presence of HQ is feasible at the *p*-Phe modified electrode.

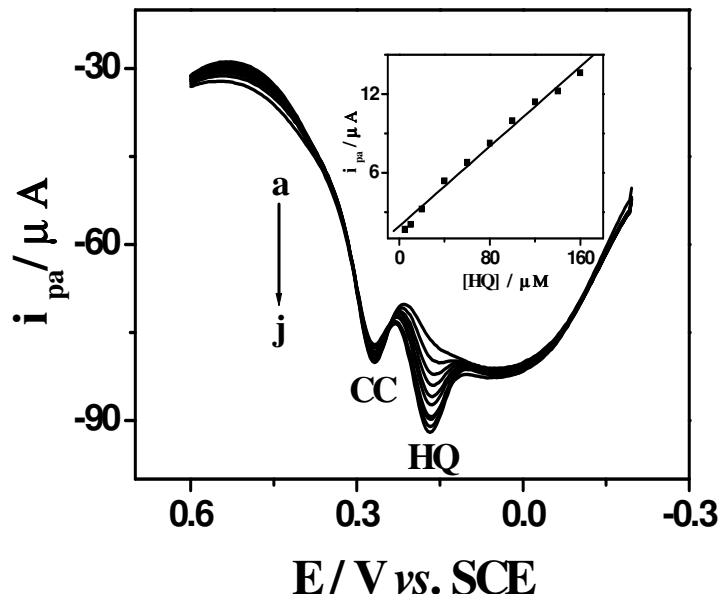


Figure 6. DPVs of HQ and CC at *p*-Phe modified electrode in 0.1 M ABS (pH 5.0), [CC] was kept constant and [HQ] was changed (i.e., [CC]=0.1 mM, [HQ]: (a) 5, (b) 10, (c) 20, (d) 40, (e) 60, (f) 80, (g) 100, (h) 120, (i) 140, (h) 160 μ M). The inset shows the relationship between the anodic peak current and the concentration of HQ. Scan rate: 4 mV s⁻¹; pulse amplitude: 50 mV; pulse width: 50 ms; pulse time: 200 ms.

The next attempt was taken to determine HQ and CC simultaneously by using the *p*-Phe modified electrode. In order to obtain a better sensitivity, DPV has been employed. Fig. 6 represents the DPV recordings at different concentrations of HQ where the concentration of CC was kept constant. The oxidative peak current for HQ was increased linearly with the increase in HQ concentration. Furthermore, while HQ peak current increased with the increase in HQ concentration, the peak current

of CC kept almost constant. Thus, it is confirmed that the responses of HQ and CC at the *p*-Phe modified electrode are independent. The determination limit of HQ in the presence of 0.1 mM CC was found to be 1.0×10^{-6} M.

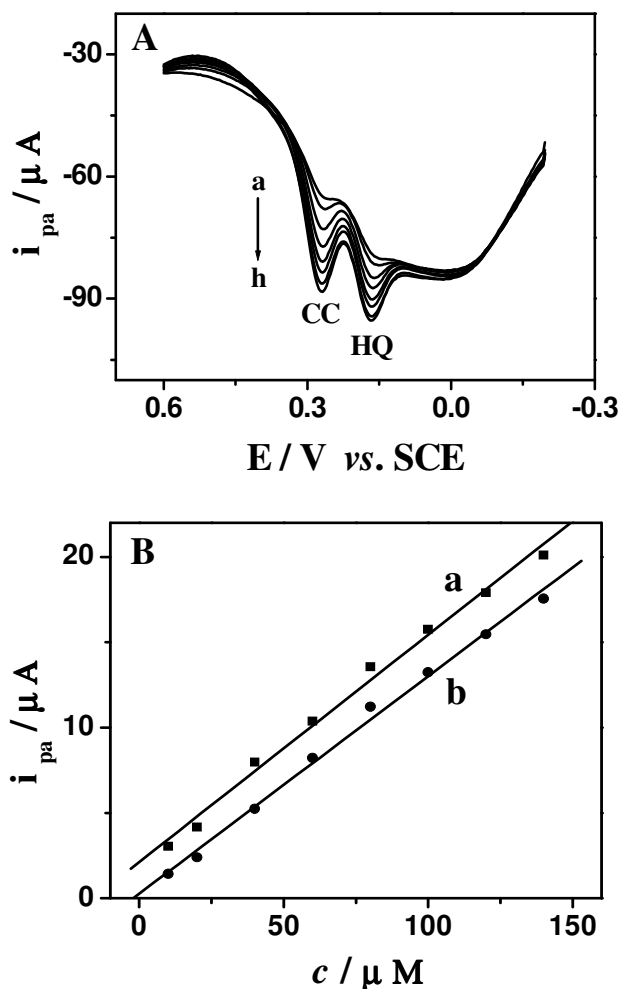


Figure 7. (A) DPVs for HQ and CC at *p*-Phe modified electrode in 0.1 M ABS (pH 5.0) while simultaneously changing their concentration (i.e., [CC]=[HQ]: (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100, (g) 120, (h) 140 μM). Scan rate: 4 mV s^{-1} ; pulse amplitude: 50 mV; pulse width: 50 ms; pulse time: 200 ms. (B) Corresponding calibration plots for CC (a) and HQ (b).

Overall facility of the *p*-Phe modified electrode for simultaneous determination of HQ and CC was demonstrated by simultaneously changing the concentration of HQ and CC. Fig. 7 illustrates the DPV responses of the *p*-Phe modified electrode while simultaneously varying the concentrations of both HQ and CC. The calibration curves for HQ and CC were linear for a wide range of concentrations (10 – 140 μM for both HQ and CC), with correlation coefficients 0.9975 and 0.9962, respectively. The

determination limits for HQ and CC were found to be 1.0×10^{-6} M and 7.0×10^{-7} M, respectively. The slopes ($\Delta I / \Delta C$) of the linear calibration curves were estimated to be 0.1274 and 0.1331 $\mu\text{A} / \mu\text{M}$ for HQ and CC, respectively. This suggests that the fouling of the electrode surface by the oxidation products has been eliminated at the *p*-Phe modified electrode. Thus, the simultaneously selective and sensitive determination of HQ and CC was achieved at the *p*-Phe modified electrode.

To ascertain further the reproducibility of the results, three different GCE was modified with *p*-Phe and their responses towards the oxidation of HQ and CC were tested. The separation between the voltammetric signals of HQ and CC and the sensitivities remained the same at all three modified electrode, confirming that the results are reproducible. The stability of the *p*-Phe modified electrode was also investigated. Its electrocatalytic effect on the electrochemical response of HQ and CC, respectively, or the binary mixtures of HQ and CC, did not change after storage in air for at least one week.

Analytical utility of the *p*-Phe modified electrode in simultaneous determination of HQ and CC has been examined using synthetic samples consisting of HQ and CC in local tap water. The determination of HQ or CC in the samples was carried out using DPV at the modified electrode and 0.1 mM ABS (pH 5.0) was used to control the pH. When known amount of HQ were added to the water control samples containing CC, quantitative recoveries of 96.4% - 103.1% were obtained. When known amounts of CC were added to the water control samples containing HQ, quantitative recoveries of 98.1% -104.2% were obtained. A feasibility of the *p*-Phe modified electrode in the simultaneous determination of HQ and CC is evident.

4. CONCLUSIONS

The present study demonstrates an excellent approach for the development of a novel voltammetric sensor of HQ and CC based on *p*-Phe coating. Fast electron transfer, high selectivity and excellent sensitivity for the oxidation of HQ and CC are achieved at the *p*-Phe modified electrode. The present modified electrode showed excellent sensitivity, selectivity and antifouling properties and can separated oxidation peaks towards HQ and CC, which are indistinguishable at the bare electrode. As the voltammetric signals of HQ and CC are well separated at the *p*-Phe modified electrode, the sensitive determination HQ in the presence of CC or the simultaneous determination of HQ and CC can be achieved. Chemically modified electrode modified with *p*-Phe is a promising approach to determination of isomers.

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