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SIMULTANEOUS DETERMINATION OF HYDROQUINONE AND CATECHOL AT POLY(P-ASA)/MWNTS COMPOSITE FILM MODIFIED GLASSY CARBON ELECTRODE

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ABSTRACT: A poly p-aminosalicylic acid (Poly(p-ASA)) and multiwall carbon nanotubes (MWCNTs) composite modified glassy carbon (GC) electrode was constructed by casting the MWNTs on the GC electrode surface followed by electropolymerization of the p-ASA on the MWCNTs/GCE. The electrochemical behaviours of hydroquinone (HQ) and catechol (CC) were investigated using cyclic voltammetry at the composite-modified GCE. The observed oxidative peak separation for HQ and CC of about 115 mV in phosphate buffer solution (PBS) pH 7.0 made possible the simultaneous determination of HQ and CC in their binary-mixture using the modified electrode. In the presence of 1.0×10^{-4} mol L^{-1} CC, the differential pulse voltammetric (DPV) oxidative peak current responses of HQ were linear in the concentration range 2.0×10^{-5} to 7.0×10^{-4} mol L^{-1}, with a detection limit (based on S/N=3) of 8.35×10^{-7} M. Similarly, in the presence of 1.0×10^{-4} mol L^{-1} HQ, the DPV oxidative peak current responses of CC were linear in concentration range of 2.0×10^{-5} to 6.0×10^{-4} mol L^{-1}, with a detection limit (based on S/N=3) of 3.9×10^{-7} M. The proposed method was tested for the simultaneous determination of HQ and CC in tap water binary mixture. The applicability of the method was shown by the satisfactory recoveries obtained for both isomers.

Key words/phrases: Catechol, hydroquinone, multiwall carbon nanotubes, poly(para-amino-salicylic acid), voltammetry

INTRODUCTION

Phenolic compounds are involved in large-scale manufacturing of resins, plastics, pesticides, explosives, detergents and pharmaceutical products. A large variety of phenolic compounds are also generated in industrial processes, such as paper bleaching, coal mining, oil refinery and production of dyes and appear as environmental pollutants (Bartlett, 2008). 1,4-dihydroxybenzene or hydroquinone (HQ) and 1,2-dihydroxybenzene or catechol (CC) are two isomers of phenolic compounds which are considered as environmental pollutants by the US environmental Protection Agency (EPA) and the European Union (EU) (Xie *et al*., 2006). HQ and CC are also known to be tumour promoters in tobacco (Gopalakrishna *et al*., 1994). They have similar structures and properties and they usually exist together (Scheme 1 b and c). Hence, developing simple and rapid analytical methods for simultaneous determination of HQ and CC in environmental samples is becoming very important.

There is a growing interest to develop simple, sensitive and accurate electrochemical methods for the detection of phenolic compounds in environmental samples. Spectrofluorimetry (Pistonesi *et al*., 2004; Pistonesi *et al*., 2006), spectrophotometry (Sirajuddin *et al*., 2007), high-performance liquid chromatography (HPLC) with different detectors (Penner and Nesterenko, 2000) and gas chromatography-mass spectrometry (GC-MS) (Molnar-Perl *et al*., 1995) methods have been used for the determination of hydroquinone and catechol, most of which are commonly performed after pre-treatment and separation (Pistonesi *et*

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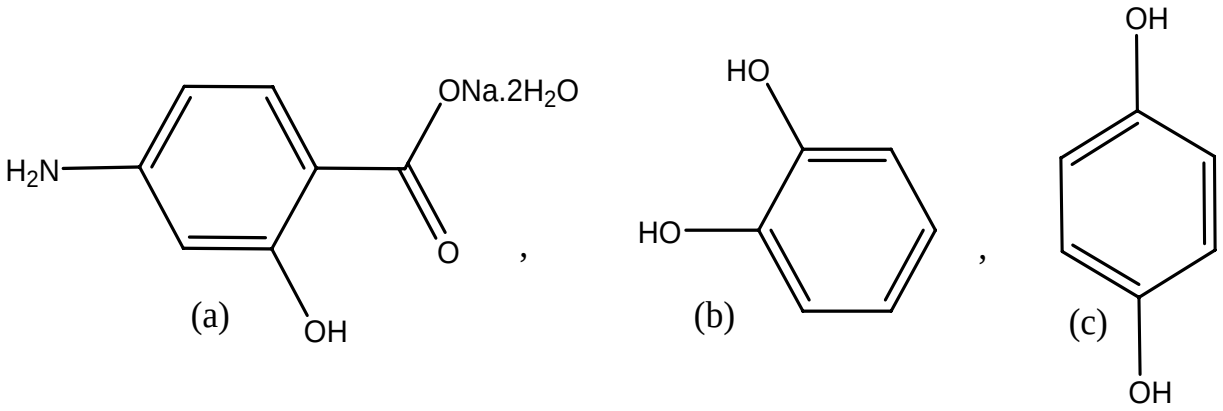
al., 2006). This sample pretreatment and separation, as well as the significant operating complexity, the long times required and the large volumes of reagents consumed by the established techniques, make it important to develop a new method capable of simultaneous determination without the need for prior separation of these isomeric compounds. Electrochemical techniques are becoming important alternatives for such analysis due to certain convenient features including sensitivity, selectivity, and simplicity in experimental procedure, low cost and short duration of analysis. Electrochemical methods also offer the advantage of immobilizing enzymes and synthesize different new organic/-inorganic composite materials. This allows for the possibility of exploiting the synergistic catalytic effect of composite materials. Most of the electrochemical methods used for simultaneous determination of CC and HQ employ chemically modified electrodes (CMEs) to separate the overlapping oxidation peaks of CC and HQ at unmodified electrodes. The CMEs also further improve the selectivity and sensitivity of the electrochemical methods. Some of the methods reported in the literature include multiwall carbon nanotube (MWCNT) (Ding *et al*., 2005; Qi and Zhang, 2005), single wall carbon nanotube (SWCNT) (Wang *et al*., 2007), aspartic acid (Wang *et al*., 2007d), penicillamine (Wang *et al*., 2007a), poly(glutamic acid) (Wang *et al*., 2007c), polyglycine (Wang *et al*., 2007a), poly(*p*-aminobenzoic acid) (Yang *et al*., 2009), poly(3-methylthiophene) (Kelly *et al*., 2006), polypyrrole (Dong and Ding, 1988), polyaniline (Erdogdu and Karagozler, 1997), poly(amidosulfonic acid)/carbon nanotube (Zhao *et al*., 2009), poly(bromophenol blue)/carbon nanotube (Yang *et al*., 2007), poly(phenylalanine) (Wang *et al*., 2006), micelles (Peng and Geo, 2006) and polypyrrole/carbon nanotube horsredish peroxidase (Korkut *et al*., 2008) modified electrodes. There are few reports on polymer/multiwall carbon nanotube composites modified electrodes and to the best of our knowledge, the use of poly(p-aminosalicylic acid)/multiwall-carbon nanotubes modified glassy carbon electrode for the simultaneous determination of CC and HQ has not been reported. Hence, in this contribution, we report a simple preparation method for poly(p-aminosalicylic acid)/-multiwall carbon nanotubes composite modified glassy carbon electrode and its application for simultaneous determination of CC and HQ in water samples.

EXPERIMENTAL

Para-aminosalicylic acid (p-ASA) (Scheme 1 a), Multi-wall carbon nanotubes (MWCNTs, purity >95%, diameter 30–10 nm, length 5–20 mm), hydroquinone and catechol were purchased from Sigma-Aldrich. Phosphate buffer solutions (PBS) were prepared from KH_2PO_4 and K_2HPO_4, the pH of which was adjusted with KOH and H_3PO_4. The chemicals used were of analytical grade from BDH laboratory supplies, England, and were used without further purification. All experiments were carried out at room temperature and all solutions were prepared from distilled water except the sample for recovery that was prepared with tap water.



Scheme 1. Structural formula of dihydrated sodium salt of p-aminosalicylic acid (p-ASA) (a), catechol (b) and hydroquinone (c).

Multi-wall carbon nanotubes were functionalized and casted on the surface of GCE as previously described (Alexeyeva and Tammeveski, 2008). To prepare the polymer-modified electrodes, Poly(p-ASA)) was grown at the bare GC and MWCNTs/GC electrodes potentiodynamically by scanning the potential between -0.8 and 2.0 V at a scan rate of 100 mV s^{-1} for twelve cycles in a 0.1 M HNO_3 containing 2×10^{-3} M *para*-aminosalicylic acid. After modification, the modified electrode was rinsed repeatedly with distilled water and cycled between -0.5 to 0.5 V at 100 mVs^{-1} in a monomer free 0.1M PBS (pH 7.0) until a stable voltammogram is obtained. The poly(p-ASA)/MWCNTs composite film modified GCE was rinsed with distilled water, then kept in air prior to use.

Jenway 3345 ion meter has been used to measure and adjust the pH of the buffer solutions. All electrochemical measurements were performed with BAS-50W electrochemical analyzer connected to a personal computer. A conventional three-electrode system was employed with a bare GCE (3 mm in diameter), poly(p-ASA)/GCE, MWCNTs/GCE, or poly(p-ASA)/MWCNTs/GCE as a working electrode, saturated silver-silver chloride as a reference electrode and a platinum foil as a counter electrode.

RESULTS AND DISCUSSION

Electropolymerization of (p-ASA) on the MWCNT/GCE surface

Figure 1 shows the successive cyclic voltammograms of MWCNTs/GCE in 0.1 N HNO_3 containing 2.0×10^{-3} mol L^{-1} aminosalicylic acid scanned between −0.8 and +2.0 V for twelve cycles. In the first scan, a weak anodic peak (1) and cathodic peak (2) were observed at potentials of +1.2 and -0.2 V, respectively. In the subsequent scanning, new weak anodic peak (3) appeared at a potential of +0.38 V, and then larger peaks were observed with continuous scanning, indicating the continuous growth of the film. A uniform adhering blue-black film was produced at the surface of the electrode, indicating the p-ASA was electropolymerized on the surface of MWCNTs/-GCE. After eleven cycles, the film thickness hardly grew, so twelve cycles were chosen in the modification process.

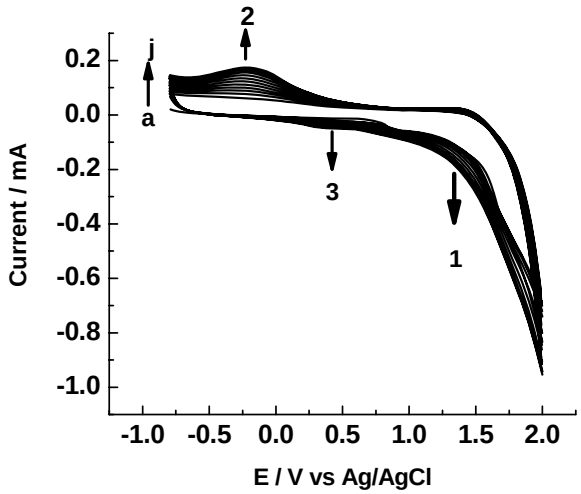


Fig. 1. Repetitive cyclic voltammograms (a–j) of 2.0×10^{-3} mol L^{-1} para-aminosalicylic acid in 0.1M HNO_3 at the MWCNTs/GCE. Scan rate: 100 mV s^{-1}.

Cyclic voltammetry was used to study the electrochemical behaviour of poly(p-ASA) at the MWCNTs/GCE in pH 7.0 PBS by scanning the potential between -0.80 and +0.60 V. Curve b of Figure 2A shows the cyclic voltammogram of the poly(p-ASA)/MWCNTs/GCE in pH 7 PBS after stabilization. In the scanning potential, the polymer film exhibited a reductive and oxidative couple centred at -0.110 and 0.040 mV, respectively, which are absent at the bare GCE (curve a of Fig. 2A) treated under the same conditions substantiating the deposition of an electroactive polymer film at the electrode surface. The cyclic voltammograms of poly(p-ASA)/MWCNTs modified GCE at different scan rates are shown in Figure 2B.

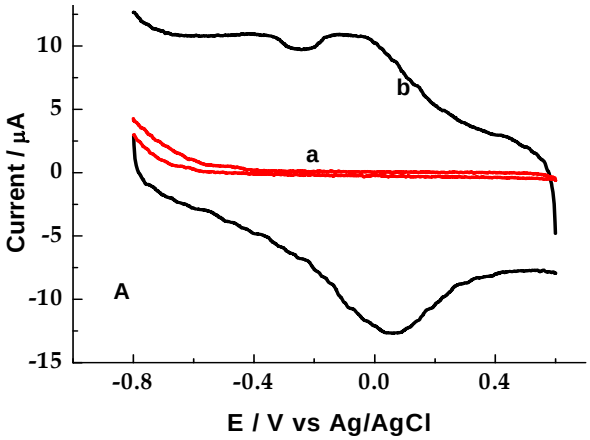


Fig. 2A. Cyclic voltammogram of bare GCE (a) and stabilized poly(p-ASA)/MWCNTS/GCE (b) in pH 7 PBS at a scan rate of 0.1 V s-1.

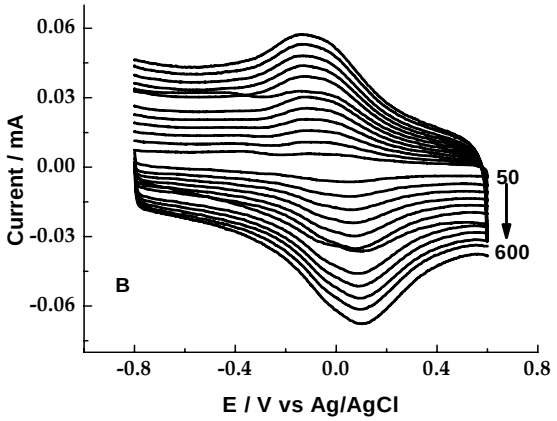


Fig. 2B. Cyclic voltammograms of poly(p-ASA)/ MWCNTs/ GCE in pH 7 PBS at different scan rates (from inner to outer waves: 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550 and 600 mV s^{-1}).

A reductive and an oxidative redox peaks were observed with peak current directly proportional to the scan rate, v, in the range 50 to 600 mV s^{-1} with a correlation coefficient of 0.99886 and 0.99657, respectively (Fig. 2C) indicating that these peaks correspond to redox processes involving a surface-confined species. In the case of such a surface-confined redox process, the peak current (Ipa) and the electrical charge (Q) consumed during the electrolysis are given by equations 1 and 2, respectively (Bard and Faulkner, 2001).

$$Q = nFA\Gamma \quad \text{.....(1)}$$

$$I_{pa} = (n^2F^2 / 4RT)\ \Gamma\ Av \quad \text{.....(2)}$$

where, n is the number of electrons transferred, F is Faraday's constant, R is the gas constant, T is the temperature (K), A is the electrode area (cm^2) and Γ is the surface coverage of the species (mol cm^{-2}).

By rearranging the above two equations and integrating the anodic peak area of the voltammogram in Figure 2A at 100 mV s^{-1} scan rate, the number of electrons transferred n and thereby the surface coverage Γ were calculated to be 2.17 and 8.42 × 10^{-8} mol cm^{-2}, respectively.

From the appearance of three peaks during its polymerization (Fig. 1), peak separation and calculated n value, the electropolymerization reaction mechanism of p-ASA at the MWCNTs modified GCE is most likely similar to that of the reaction mechanism proposed for para-aminobenzene sulfonic acid (Scheme 2) (Jin *et al.*, 2005).

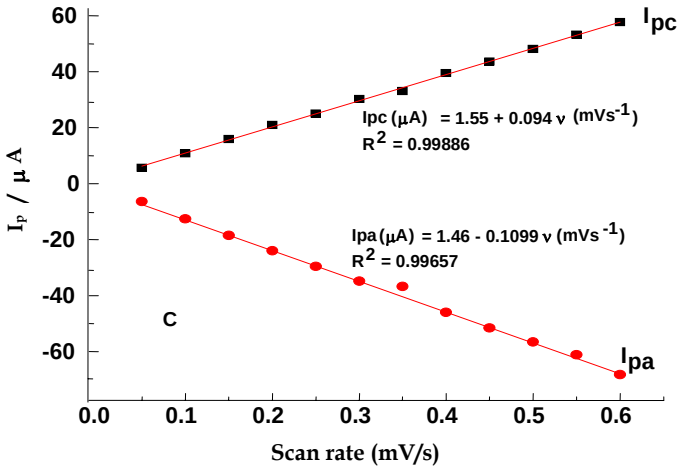
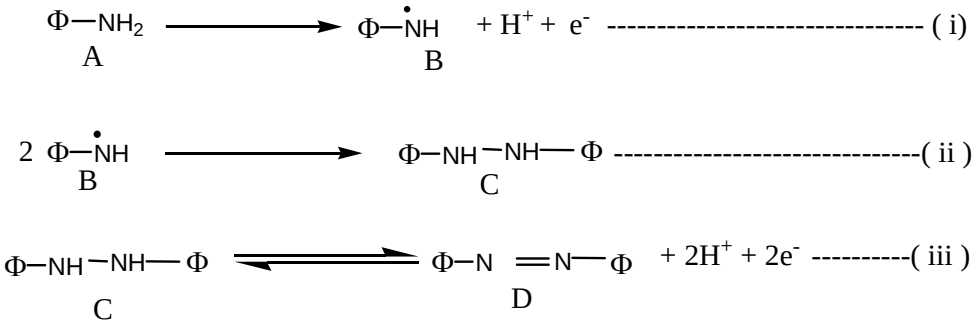


Fig. 2C. Plot of peak currents (Ipc and Ipa) vs scan rate (v).



Scheme 2. Proposed reaction mechanism.

In short, p-ASA (A) is first irreversibly oxidized to free radical (B) (peak 1); two free radicals (B) are combined rapidly to hydrazobenzene salicylic acid (C); then the hydrazobenzene salicylic acid (C) is oxidized to azobenzene salicylic acid (D) (peak 2), and the azobenzene salicylic acid (D) is reduced back to hydrazobenzene salicylic acid (C) (peak 3).

Electrochemical behaviour of HQ and CC at poly(p-ASA)/MWCNTs modified GCE

Figure 3A (curve a) shows that, at the bare GC electrode, the oxidation and reduction of HQ and CC resulted in one broad oxidation peak at about +0.430 V and two weakly separated reduction peaks at -0.131 V and +0.25 V, respectively. Table 1 summarizes the redox couples of HQ and CC give overlapping peaks with irreversible behaviour and hence their simultaneous determination using a bare glassy carbon electrode is impossible. On the other hand, the reversibility of the redox couples of each species, the oxidative peak potential separation between HQ and CC, and the oxidation peak current responses are remarkably improved at the modified GC electrodes (Fig. 3A, curves (b-d)); maximum improvement being observed at the Poly(p-ASA)/MWCNT/GCE. At the composite modified GCE, an oxidative peak separation of 114.73 mV and more than twofold current as compared to the bare GCE has been achieved. From this observation, it can be concluded that the catalytic activity of the composite modifier could be used for the simultaneous determination of HQ and CC with a remarkable selectivity and sensitivity from their binary mixture.

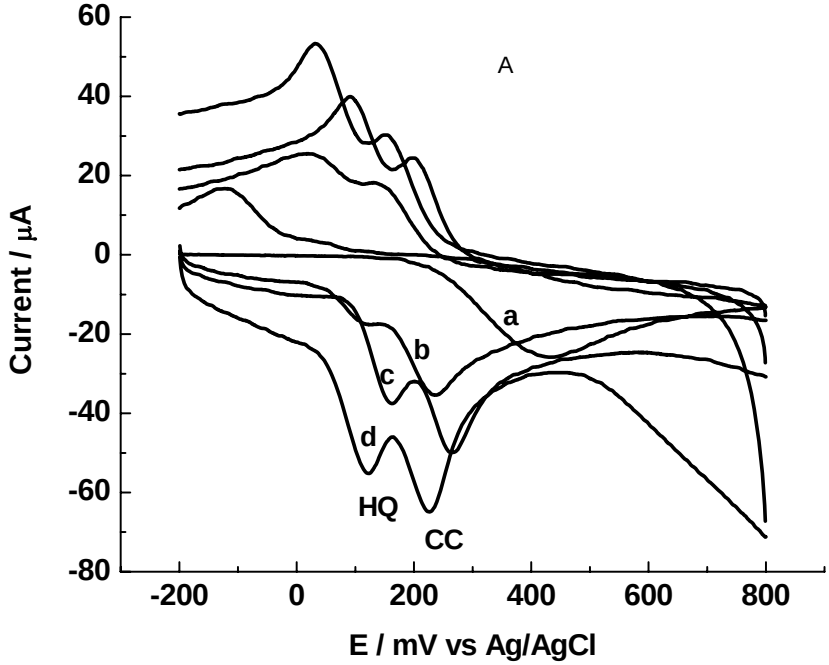


Fig. 3A. Cyclic voltammograms of 1 × 10^{-3} mol L^{-1} HQ and CC in PBS (pH 7.0) at different electrodes: bare GCE (a), poly(p-ASA)/GCE (b), MWCNTs/GCE (c) and poly(p-ASA)/ MWCNTs/GCE (d). Scan rate: 20 mV s^{-1}.

Table 1. Summary of the effect of electrode used on the reversibility of the redox couple, oxidative peak current response and oxidative peak separation of HQ and CC in PBS (pH 7).

Electrode type	HQ		CC		$E_{pa\,(CC)} - E_{pa\,(HQ)}$
	ΔE_p (mV)	i_{pa} (μA)	ΔE_p (mV)	i_{pa} (μA)	ΔE_{pa} (mV)
Bare GCE	561.75	25.25	405.81	25.25	(Overlapped)
Poly(p-ASA)/GCE	111.17	26.89	90.91	35.08	91.87
MWNT/GCE	69.40	37.50	81.23	49.84	101.30
Poly(p-ASA)/MWCNT/GCE	57.82	54.75	55.09	64.59	114.73

Effect of scan rate on the peak current of HQ and CC

The CV curves of 1.0×10^{-3} mol L^{-1} CC and HQ at the poly(p-ASA)/MWCNTs composite modified GCE were recorded in pH 7 PBS at different scan rates (Fig. 3B). The anodic and cathodic peaks of both CC and HQ showed a shift to more positive and more negative potentials, respectively showing the quasi-reversiblity of the electron transfer.

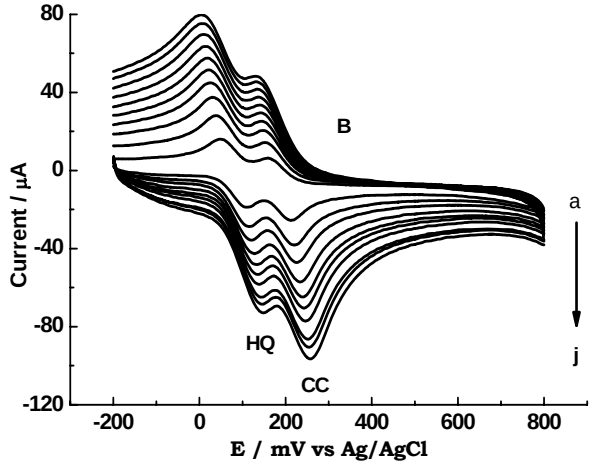


Fig. 3B Cyclic voltammograms of 1 × 10^{-3} mol L^{-1} HQ and CC in pH 7.0 PBS at Poly(p-ASA)/MWCNTS/GCE at different scan rates (a → j: 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s^{-1}).

Figure 4 showed the linear dependence of oxidative peak current of CC and HQ on the square root of scan rate in the range 10 to 100 (mV s^{-1}) with a common correlation coefficient R^2=0.998, indicating that the electrode reactions are both diffusion-controlled.

Effect of pH on the peak potential and peak current of HQ and CC

The effect of the pH of the solution on the response of poly(p-ASA)/MWCNTs/GCE for CC and HQ in 0.1 M PBS was investigated and the results are shown in Figure 5. As can be seen from Figure 5, the peak current and peak potential response of the composite-modified GCE in CC and HQ showed a strong dependence on the pH of the buffer solution. Both the cathodic and anodic peak potentials of HQ and CC shifted to more negative potential with increasing pH, in the pH range 4.0 to 9.0.

The effect of solution pH on the peak potentials of the two bis-phenols is depicted in Figure 5B. The shift in peak potentials towards more negative values with increasing pH indicates the participation of protons in the reaction of both HQ and CC at the poly(p-ASA)/MWCNT/GC electrode. Both oxidative and reductive peak potentials of HQ showed linear dependence on the pH of the solution in the range 4.0–9.0 with regression equations and correlation coefficients of E_{pa} (mV)=559.53–59.8pH, E_{pc}=435.70–56.05pH, R^2=0.9975 and R^2=0.9978, respectively. In the same manner, the responses for CC showed a linear dependence on the pH with regression equations and correlation coefficient of E_{pa}(mV)=688.4–62.64 pH, E_{pc}(mV)=560.21–56.31 pH, R^2 =0.9990 and R^2=0.9967, respectively. The slopes of the linear regression equations, which are in the range 56.05–62.64, are in agreement with two protons taking part in a two-electron redox reaction mechanism already proposed for HQ and CC (DuVall and McCreery, 1999).

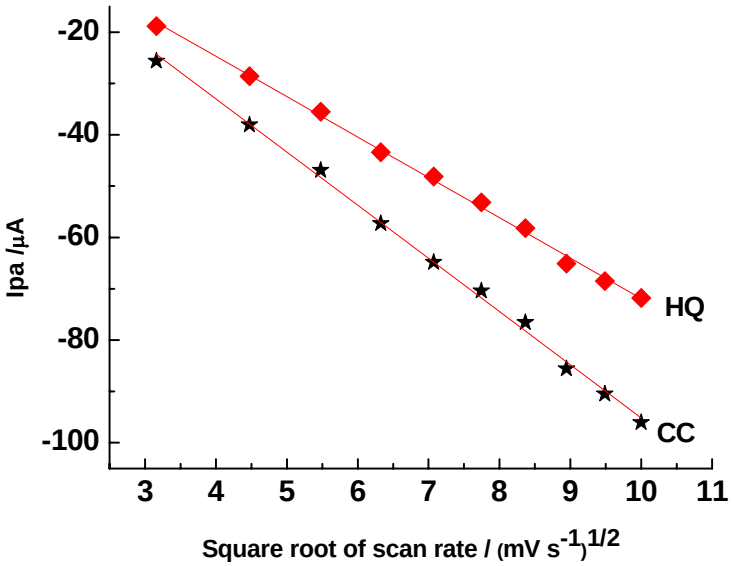


Fig. 4. Oxidative peak current vs square root of scan rate curve of 1 × 10^{-3} mol L^{-1} CC and HQ in the range of 10 to 100 mV s^{-1}.

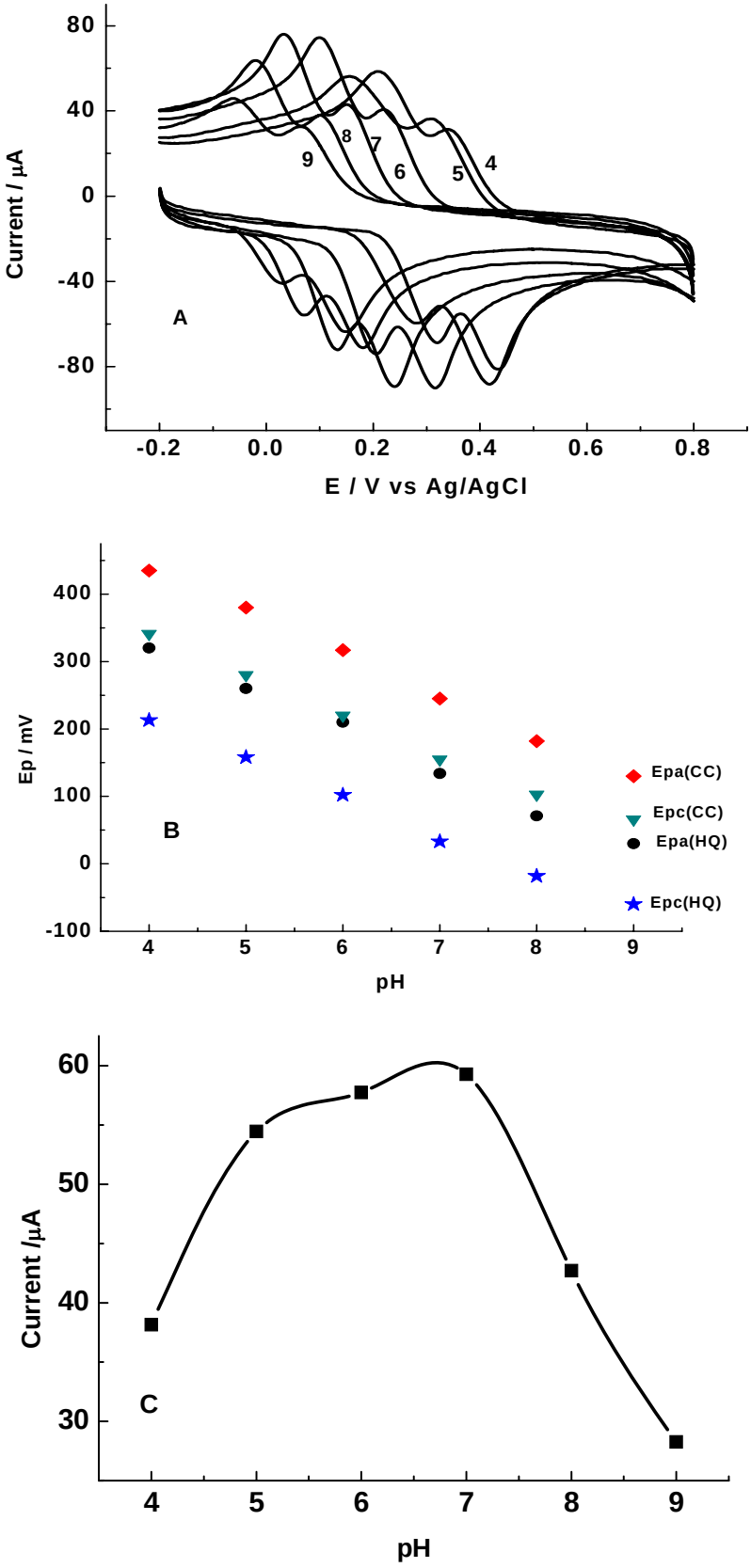


Fig. 5. (A) Cyclic voltammograms of poly(p-ASA)/MWCNTs/GCE in different pHs of 0.1 M PBS containing binary mixture of CC and HQ (each 1×10^{-3} mol L^{-1}); (B) Plot of Ep vs pH of buffer solution; (C) The effect of pH of the solution on the anodic peak current of CC in a binary mixture of CC and HQ. pH range 4.0–9.0; scan rate: 0.1 Vs^{-1}; sensitivity: 100 µA V^{-1}.

The effect of solution pH on the current response of Poly(p-ASA)/MWNT/GC electrode for HQ and CC was examined using cyclic voltammetry. Figure 5C illustrates the dependence of the oxidation peak current of catechol on the pH of the supporting electrolyte solution. It can be seen that the oxidation peak current of catechol increased with increasing pH in the range 4.0 – 7.0 and then decreased from pH 7.0 to 9.0. This trend could be explained taking the nature of the polymer and analyte in acidic and alkaline media. At low pH, both the carboxylic acid functional group of polymer and the hydroxyl functional group of CC (HQ) are positively charged. This affects the ease of oxidation and mass transport of the catechol (hydroquinone) to the electrode surface due to the repulsive interaction between the positively charged electrode surface and analytes. This is improved with increasing pH until it reaches its maximum at pH 7.0. After pH 7.0, the current begins to decrease which may be due to the repulsive interaction between the negatively charged electrode surfaces and CC (HQ). Thus, the physiological pH of 7.0 at which a relatively maximum current response was obtained for both isomers is taken as the optimum pH.

Simultaneous determination of HQ and CC

It has been observed that the P(p-ASA)/MWCNTs/GCE, shows an excellent electrocatalytic behaviour for the oxidation of HQ and CC. It gives sharp, well- separated peaks with enhanced peak current responses as compared to the bare GCE. The oxidation peak potential difference, ΔE_{pa} = 114.17 mV, obtained using the composite-modified GC electrode is large enough to determine the isomers selectively in the presence of one another. Thus a more sensitive method, differential pulse voltammetry (DPV) was employed to determine HQ and CC simultaneously, using the composite-modified GCE.

Figure 6A depicts the DPVs at different concentrations of HQ while the concentration of CC kept constant at 1×10^{-4} mol L^{-1}. For this constant concentration of CC, the oxidation peak current for HQ increased linearly with increasing HQ concentration in the range of 2.0×10^{-5}–7.0×10^{-4} mol L^{-1} with a correlation coefficient and detection limit (S/N=3 for n=4) of R^2=0.99982 and LoD = 8.35×10^{-7} M, respectively (Fig. 6B).

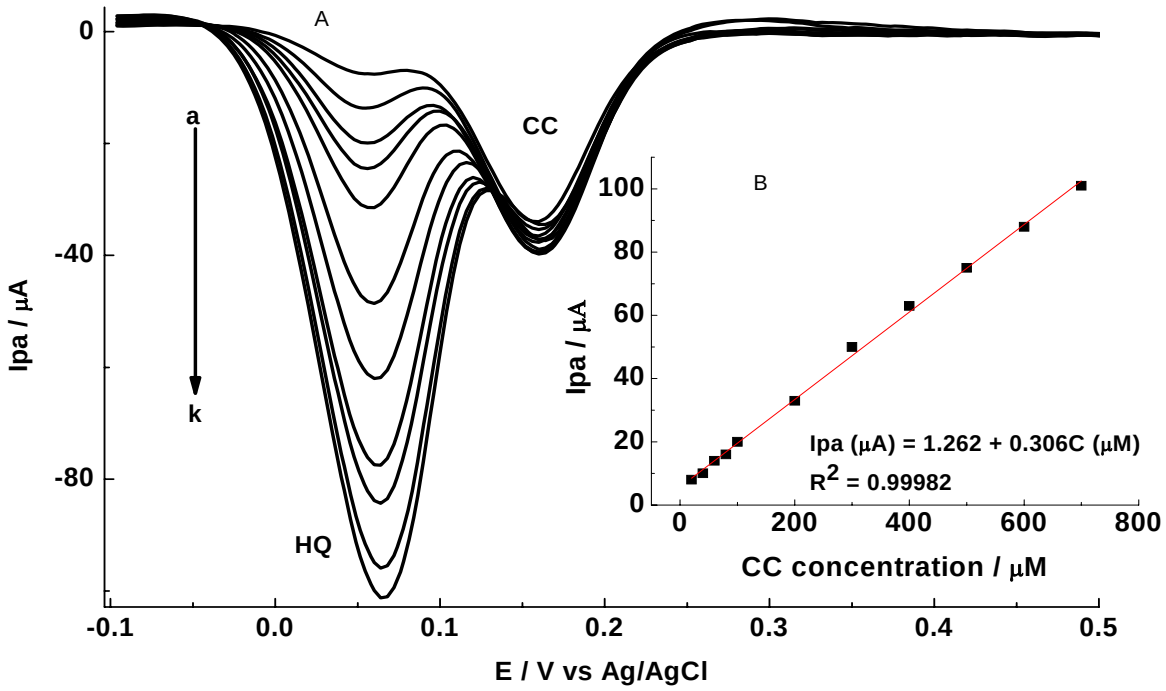


Fig. 6. (A) DPVs of poly(p-ASA)/MWCNTS/GCE in a binary mixture of variable concentration of HQ and constant concentration of CC in pH 7.0 PBS (a → k: 20, 40, 60, 80, 100, 200, 300, 400, 500, 600 and 700×10^{-6} mol L^{-1} of HQ and 1×10^{-4} mol L^{-1} CC); (B) plot of anodic peak current of HQ at the modified electrode vs concentration. Scan rate: 50 mV $s^{-1;}$ pulse amplitude: 20 mV.

Figure 7A shows the DPVs of a binary mixture of variable concentration of CC and constant HQ concentration. As shown in the Figure 7B, in the presence of 1×10^{-4} Mol L^{-1} of HQ, the oxidative peak current of CC increased linearly with increasing CC concentration in the range of 2.0×10^{-5}–6.0×10^{-4} M with a correlation coefficient and detection limit (S/N=3 for n=4) of R^2=0.99985 and LoD=3.9×10^{-7} mol L^{-1}, respectively.

While the peak current for CC was observed to increase with increasing concentration of CC, the peak current for HQ remained almost constant in the same manner as described for HQ in the previous paragraph. This suggests that the oxidized product of HQ does not cause electrode fouling to affect the response of the composite-modified electrode for CC and vice versa and hence the simultaneous determination of HQ and CC was achieved selectively with an improved sensitivity using the composite-modified electrode.

Analytical applications

In order to assess the possible applications of the proposed method for the simultaneous determination of HQ and CC, synthetic samples containing HQ and CC in tap water were tested. The determination of HQ and CC in the samples was carried out using DPV at the poly(p-ASA)/MWCNT/GCE in 0.1 mol L^{-1} PBS (pH 7.0) prepared using tap water. The results are given in Tables 2 and 3. When known amounts of CC were added to the tap water samples containing constant amount of HQ (Table 2), quantitative recoveries of 92.79–99.05% were obtained. When in the same manner known amounts of HQ were added to the tap water samples containing constant amount of CC, quantitative recoveries of 94.45–107.5% were obtained (Table 3). The feasibility of the application of poly(p-ASA)/-MWCNT/GCE for the simultaneous determination of HQ and CC is thus strong.

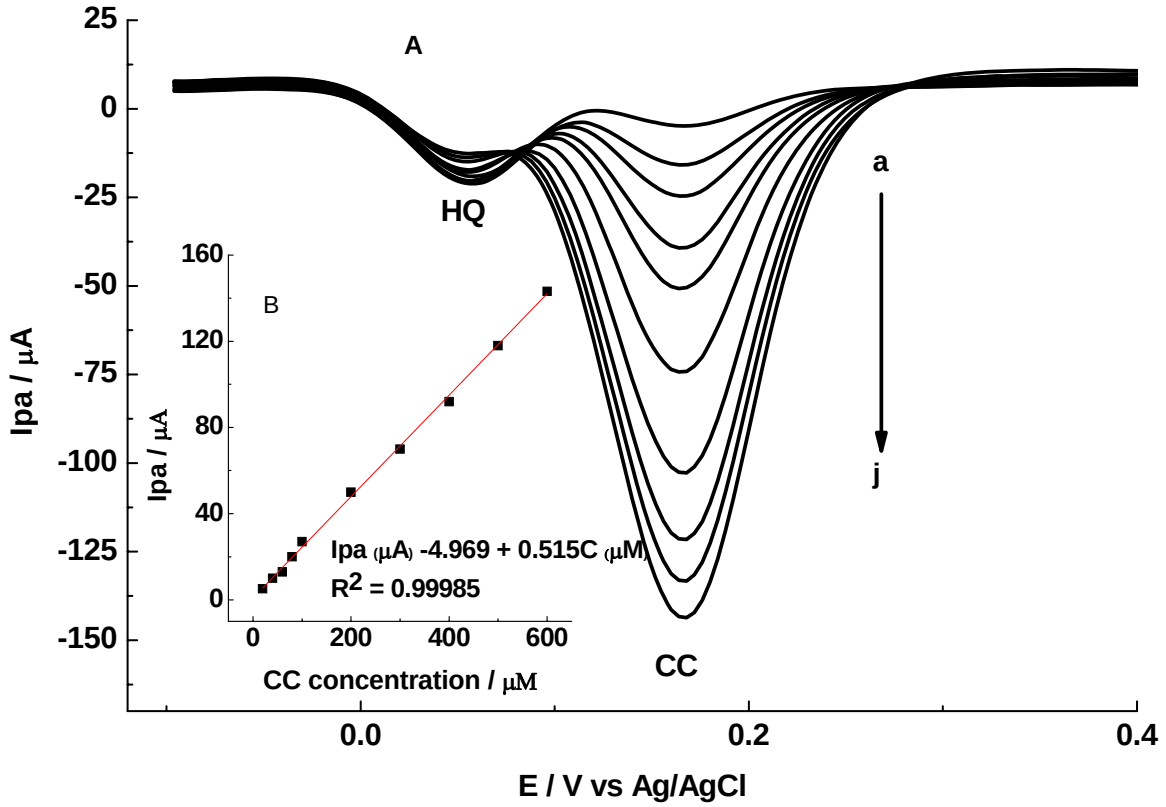


Fig. 7. (A) DPVs of poly(p-ASA)/MWCNTs/GCE in a binary mixture of variable concentration of CC and constant concentration of HQ in pH 7.0 PBS (a → j: 20, 40, 60, 80, 100, 200, 300, 400, 500 and 600 × 10^{-6} mol L^{-1} of CC and 1 × 10^{-4} mol L^{-1} HQ); (B) plot of anodic peak current of CC at the modified GCE vs concentration. Scan rate: 50 mV s^{-1}; pulse amplitude: 20 mV.

Table 2. Simultaneous determination of CC in tap water containing HQ.

Sample No.	HQ (µM)	CC added (µM)	CC found (µM)[a]	Recovery (%)[a]
1	100	40	39.62	99.05
2	100	80	74.23	92.79
3	100	100	88.85	88.85

[a], Average of three determinations

Table 3. Simultaneous determination of HQ in tap water containing CC.

Sample No.	CC (µM)	HQ added (µM)	HQ found (µM)[a]	Recovery (%)[a]
1	100	40	43.0	107.50
2	100	80	84.19	105.24
3	100	100	94.45	94.45

[a], Average of three determinations

CONCLUSION

This study demonstrated an excellent and novel approach for the simultaneous determination of HQ and CC by using differential pulse voltammetry at the Poly(p-ASA)/MWCNTs composite film modified glassy carbon electrode. The significant increase in peak current, well defined peaks with sufficient peak separation, the wider linear range and low detection limits clearly proved that the Poly(p-ASA)/MWCNTs composite film acts as an efficient electrocatalyst enhancing the kinetics of the electrochemical reactions of HQ and CC. DPV results indicated two anodic peaks at potentials of +48 and +160 mV, corresponding to the oxidation of HQ and CC, respectively. The results obtained allow us to conclude that the modified electrode can be used with some advantages for the selective and quantitative determination of HQ and CC, alone or mixed as commonly found in water samples.

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