

Full Paper

Electropolymerisation of DL-methionine at Carbon Paste Electrode and its Application to the Determination of Catechol and Hydroquinone

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Abstract- The poly(methionine) modified carbon paste electrode (MCPE) was fabricated for the electroanalysis of catechol (CC) and hydroquinone (HQ) in phosphate buffer solution (PBS) of pH 7.4 by cyclic voltammetric (CV) and differential pulse voltammetric (DPV) techniques. The modified electrode shows selective and sensitive response for the simultaneous determination of CC and HQ in a binary mixture. The peak to peak separation of CC and HQ was 0.115 V and 0.112 V by CV and DPV techniques respectively. The effect of concentration and scan rate reveals the electrode process was controlled by the adsorption of the analytes. This study provides a new method for the modification of working electrode for the voltammetric determination of the CC and HQ.

Keywords- Catechol, Hydroquinone, Electropolymerisation, Electroanalysis, Voltammetry

1. INTRODUCTION

Over the past few decades the modification of working electrodes surface by some special layers has received much more attention in the development of electrochemical sensors [1-2]. Compared to the conventional working electrodes, the modified electrodes shows improved

physicochemical properties such as, high degree of selectivity, sensitivity, reproducibility, stability and antifouling properties [3-5]. The amino acids are the simple molecules which can be easily electropolymerised on the surfaces of the working electrodes [6]. These amino acids based modified electrodes are extensively used as an electrochemical sensor for the qualitative and quantitative determination of important electroactive molecules [7-10]. The electropolymerisation phenomenon is a simple and convenient way of modifying the working electrode surface. Here in, the film thickness and its composition can be altered easily during the electrochemical process by controlling the electrochemical parameters. There are so many literature reports on the fabrication of an electrode by using amino acids as a modifier [6,11-12].

Catechol (CC, 1,2-dihydroxybenzene) and hydroquinone (HQ, 1,4-dihydroxybenzene) are the two positional isomers of a dihydroxybenzene [13-14]. These compounds are considered to be the major harmful contaminants in environment due to their widespread applications in various chemical industries [15-16]. They are extensively used for the various applications like cosmetics, antioxidants, oil refineries, coal tar, plastic, leather, paint, steel and pharmaceutical industries [17-19]. Even in a very low concentration itself these isomers are very toxic to animals and human beings and they are very difficult to degrade. Because of this reason they are the major problem and cause for the environment pollution [20-22]. Owing to this fact the qualitative and quantitative determination of these phenolic isomers is of great importance in the fields like environmental control [23]. There are various research reports for the simultaneous determination of these isomers. Like high performance liquid chromatography (HPLC) [24-25], spectrophotometry [26], electrochemiluminescence [27], pH based-flow injection analysis [28] and synchronous fluorescence [29]. All these methods are complicated and require long duration for the analysis.

Electrochemical techniques based on the anodic oxidation are most widely studied and accepted method for the determination of the various electroactive compounds due to its simple, sensitive, rapid and economical properties [30-31]. However, because of the similar structure and properties both HQ and CC shows overlapped anodic oxidation at bare working electrodes [32]. Also the individual identification of these isomers is a task with high difficulty. Most of all the bare working electrodes suffer from a fouling effect due to the adsorption of the oxidised products on the surface of the electrode. Therefore to resolve this problem the modification of the bare carbon paste electrode was proposed. Therefore, in the present study, methionine was used as the modifier. The DL-methionine is sulphur containing α -amino acid used in the biosynthesis of protein [33]. In this paper the DL-methionine was used to fabricate a modified electrode by electropolymerisation method. The developed poly (methionine) modified carbon paste electrode (MCPE) was used for the sensitive and selective determination of CC and HQ in a binary mixture by cyclic voltammetric (CV) and differential pulse voltammetric (DPV) techniques.

2. EXPERIMENTAL SECTION

2.1. Reagents

Hydroquinone (HQ), catechol (CC) and DL-methionine were purchased from Himedia. The stock solution 25×10^{-4} M HQ, 25×10^{-4} M CC and 25×10^{-3} M DL-methionine was prepared in double distilled water. Phosphate buffer solution (PBS) of same ionic strength was maintained (0.2 M) throughout the experiment. Desired pH was obtained by mixing appropriate ratio of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and Na_2HPO_4 . Graphite powder of 50 μm particle size was purchased from Merck and silicone oil from Himedia was used to prepare carbon paste electrode (CPE). All the chemicals mentioned were all of analytical grade used as received without any further purification.

2.2. Equipment

All electrochemical experiments were performed using a model CHI-660c (CH Instrument-660 electrochemical workstation). A conventional three electrode system was used in a single compartment electrochemical cell with a saturated calomel electrode (SCE) as a reference, a platinum counter electrode, and bare carbon paste electrode (BCPE) or poly (methionine) MCPE as working electrode. All the redox potentials of analytes were recorded versus the SCE at an ambient temperature of 25 ± 0.5 °C.

2.3. Preparation of the working electrode

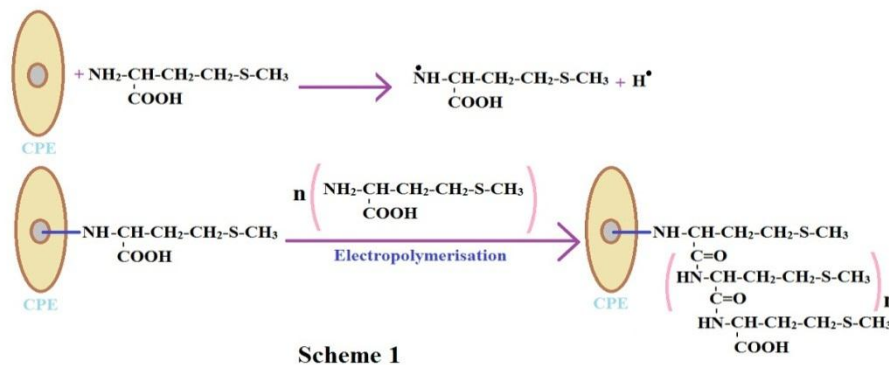
The BCPE was prepared by hand mixing of 70% graphite powder and 30% silicone oil in an agate mortar for about 45 min until a homogeneous paste was obtained. The paste was then packed into a cavity of PVC tube of 3 mm internal diameter and smoothed on a tissue paper. The electrical contact was provided by a copper wire connected to the end of the tube.

3. RESULTS AND DISCUSSION

3.1. Electrochemical polymerization of DL-methionine on BCPE

The poly (methionine) MCPE was prepared by placing 1.0 mM solution of DL-methionine monomer in 0.2 M PBS of pH 7.4 in an electrochemical cell over the potential sweep of -0.8 V to +1.6 V with scan rate 0.1 Vs^{-1} for 10 successive cycles. It is observed from the Figure 1, the anodic peak currents enhanced gradually in the cyclic voltammograms which is the indication of growth and formation of an electroactive layer on the surface of BCPE. After the few cycles (5cycle), the increase of this peak current becomes virtually constant and becomes more stable; suggesting that growth of polymerization was reached the level of saturation [6,34].

The potential window of -0.8 V to +1.6 V was chosen in electropolymerisation of methionine. If the positive potential is less than the +1.6 V no polymer film would be obtained due to the paucity of the monomer free radical concentration. The positive potential is higher than the +1.6 V leads to the over oxidation of the methionine monomer, which leads to decline in the polymer film. If the initial potential was negative than the -0.8 V will causes the distortion in the uniform arrangement of the polymer film. Also increase in thickness of the film would prevent the electron transfer process [6]. Therefore, the 10 multiple cycles was chosen as a representative for the fabrication of poly (methionine) MCPE. These optimum conditions play a key role in fabricating a stable working electrode. The poly (methionine) film was formed due to the condensation between the one carboxyl group of DL- methionine with one amino group of another DL- methionine [35]. The probable electropolymerisation mechanism of DL-methionine is described in scheme 1.



Scheme 1. Electropolymerisation of DL-methionine on the surface of carbon paste electrode

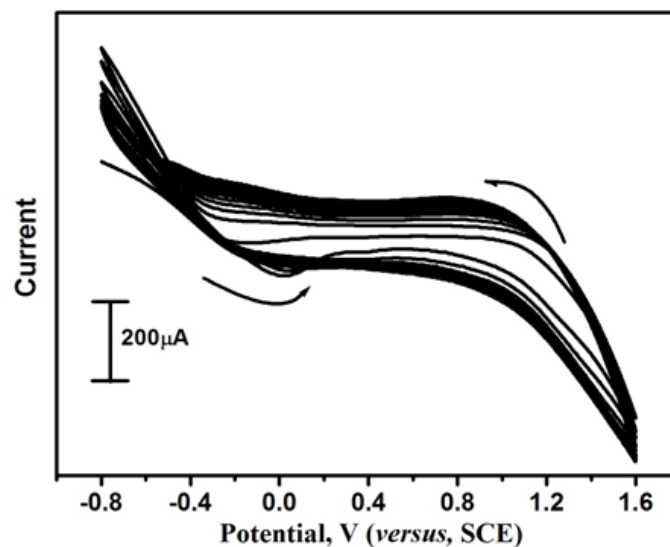


Fig. 1. Cyclic voltammograms of preparation of poly (methionine) MCPE. 1.0 mM aqueous solution in 0.2 M PBS of pH 7.4 at 10cycles with scan rate 0.1 Vs^{-1}

3.2. Characterization of poly (methionine) MCPE

The Figure 2a shows the cyclic voltammograms recorded for the redox couple of 1mM $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ in 1 M KCl at both BCPE (dashed line) and poly (methionine) MCPE (solid line) with the applied scan rate of 0.025 Vs^{-1} . The low redox peak currents response was obtained at BCPE. The peak to peak separation (ΔE_p) was found to be 0.089 V. However, in the same identical condition poly (methionine) MCPE evince a stable enhancement of redox peak currents and also showed faster electron transfer kinetics with the ΔE_p of 0.060V. This voltammetric refinement at poly (methionine) MCPE reveals the surface morphology was changed remarkably, and also result demonstrates the electrocatalytic activity of the poly (methionine) MCPE. The total active surface area available for reaction of species in solution can be estimated by the Randles-Sevcik equation (1) [6].

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_0 \nu^{1/2} \quad (1)$$

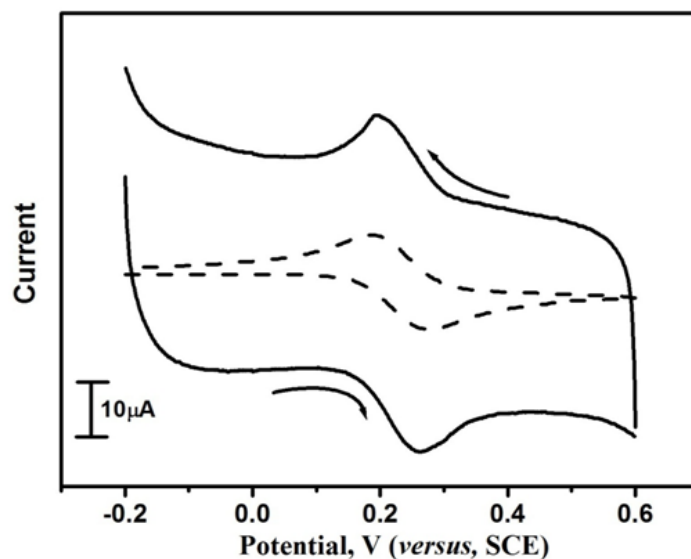
Where, I_p is the peak current in A. C_0 is the concentration of the electroactive species (mol cm^{-3}), n is the number of electrons exchanged, D is the diffusion-coefficient (cm^2s^{-1}), and ν is the scan rate (Vs^{-1}), A is the electroactive surface area (cm^2). A high accessible surface area was obtained for poly (methionine) MCPE (0.0464 cm^2) as compared with BCPE (0.0282 cm^2).

To characterize the surface morphology of the electrodes scanning electron microscopy (SEM) images were taken. The SEM images for BCPE and poly (methionine) MCPE has shown in Figure 2b. The surface of BCPE is of irregular shape (A). After the electropolymerisation (B) methionine forms a uniform film with number of aligned ridges and valleys on the surface, which is entirely different from the BCPE. This morphological feature is having more advantages due to the exposure of large surface area. This will enable as an active platform for the electroanalysis of the targeted molecule [6,32].

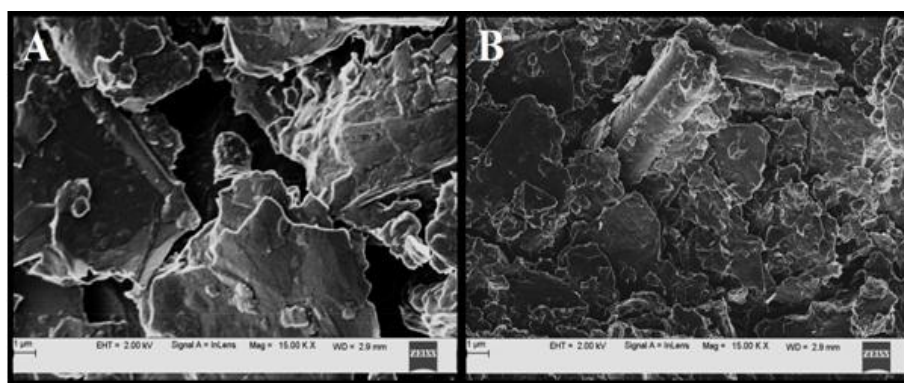
An approximate estimation on the amount of incorporated methionine monomer was calculated by the amount of surface coverage of the electroactive species on the working electrode, and is given by the following equation (2) [36].

$$I_p = n^2 F^2 A \Gamma \nu / 4RT \quad (2)$$

Where, Γ (M/cm^2) represents the surface coverage concentration which is proportional to peak current (I_p), ν is the scan rate, A is the geometric surface area of the electrode (0.028 cm^2), n is the number of electrons involved in the reaction and R , F , T have their usual significance. The surface concentration of poly (methionine) film adhered on the surface of CPE was determined to be $0.3589 \times 10^{-10} \text{ M/cm}^2$.



(a)

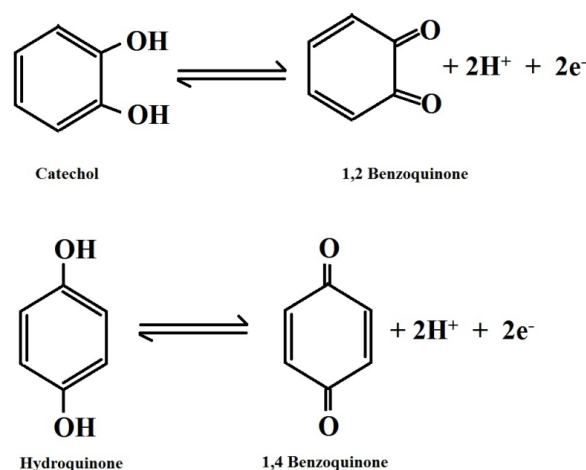


(b)

Fig. 2. (a) Cyclic voltammograms of 1.0 mM potassium ferrocyanide at BCPE (dashed line) and poly (methionine) MCPE (solid line) at scan rate of 0.025 Vs^{-1} ; (b) SEM image of BCPE (A) and poly(methionine)MCPE (B)

3.3. Electrochemical response of CC at poly (methionine) MCPE

Figure 3 shows the cyclic voltammograms recorded for 0.2 mM CC at BCPE and poly (methionine) MCPE in 0.2 M PBS of pH 7.4 with the scan rate of 0.05 Vs^{-1} . The voltammetric response of CC at BCPE (dashed line) is with low current response due to the slow electron transfer phenomenon. The oxidation potential was located at 0.214 V versus SCE. However, in the same identical condition the poly (methionine) MCPE (solid line) shows significant increment in current signals. This result shows favourable oxidation of CC at poly (methionine) MCPE. The mechanism of oxidation of both CC and HQ was shown in scheme 2.



Scheme 2. Oxidation mechanism of catechol (CC) and hydroquinone (HQ)

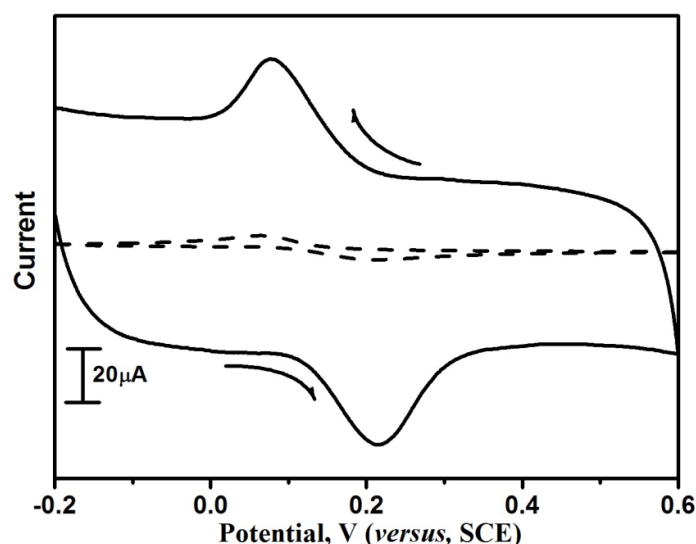


Fig. 3. Cyclic voltammograms of 0.2 mM CC in 0.2 M PBS solution of pH 7.4 at BCPE (dashed line) and poly (methionine) MCPE (solid line) at scan rate of 0.05 Vs⁻¹

3.4. Effect of scan rate on the peak current of CC

The influence of applied scan rate gives useful information on the electrode phenomenon. The scan rate effect was studied for 0.2 mM CC in 0.2 M PBS of pH 7.4 by CV technique at poly (methionine) MCPE as shown in Figure 4A. The poly (methionine) MCPE obeys Randles-Sevcik equation and showed increase in the redox peak currents with increase in the scan rate, with a small shifting in the redox peak potentials. In order to confirm the electrode process, the graph of peak current (I_p) versus scan rate (ν) was plotted and the obtained graph is a straight line with good linearity in the range from 0.04-0.12 Vs⁻¹ as shown in Figure 4B, with the correlation coefficient (r^2) 0.9991 and 0.9987. The I_p versus square root scan rate

($v^{1/2}$) were plotted as shown in Figure 4C with the correlation coefficient (r^2) 0.9989 and 0.9994. This result suggests the electrode kinetics involves adsorption controlled phenomenon [37-38].

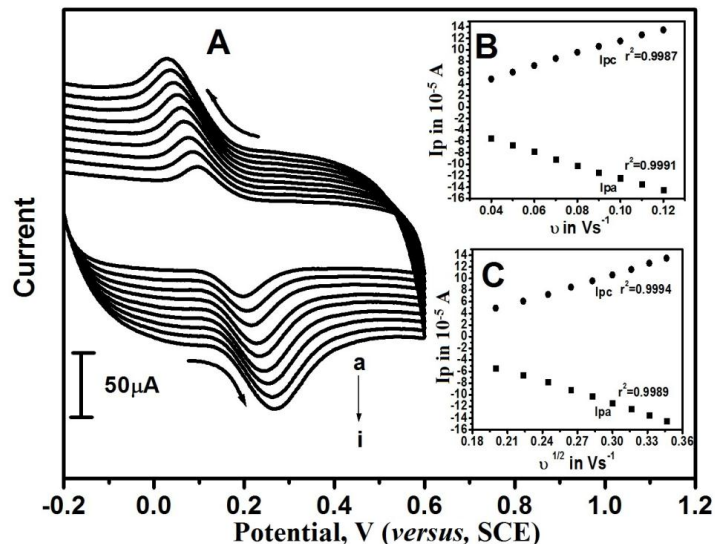


Fig. 4. (A) Cyclic voltammograms of 0.2 mM CC in 0.2 M PBS solution of pH 7.4 at poly(methionine) MCPE at different scan rate (a–i; 0.04 Vs⁻¹ to 0.12 Vs⁻¹); (B) Graph of peak current versus scan rate; (C) Graph of peak current versus square root of scan rate.

Table 1. Variation of the voltammetric parameters gathered from the plots shown in Figure 4 and Figure 8 as a function of the potential scan rate

v/Vs^{-1}	$\Delta E_p/V$		k^0/s^{-1}	
	Catechol (CC)	Hydroquinone (HQ)	Catechol (CC)	Hydroquinone (HQ)
0.04	0.1004	0.1191	0.4028	0.3253
0.05	0.1172	0.1426	0.4155	0.3108
0.06	0.1378	0.1604	0.3940	0.3042
0.07	0.1604	0.1691	0.3549	0.3213
0.08	0.1752	0.1939	0.3425	0.2766
0.09	0.1929	0.1987	0.3147	0.2945
0.10	0.2076	0.2145	0.2955	0.2732
0.11	0.2263	0.2352	0.2626	0.2374
0.12	0.2420	0.2519	0.2394	0.2137

The heterogeneous rate constant (k^0) values was determined from the experimental peak potential difference (ΔE_p) data's, equation (3) was used for such voltammograms whose ΔE_p values are greater than 10 mV [6].

$$\Delta E_p = 201.39 \log(v/k^0) - 301.78 \quad (3)$$

From the experimental ΔE_p values as shown in the Table 1 and equation (3); the values of k^0 for the CC and HQ oxidation was determined. The values of k^0 obtained at the scan rate of 0.05 Vs^{-1} for the poly (methionine) MCPE exhibits larger heterogeneous rate constant compared with those determined in other scan rate variation studies. All the parameters are tabulated in Table 1.

3.5. Effect of CC concentration

The electrochemical oxidation of CC was carried out by varying its concentration at poly (methionine) MCPE.

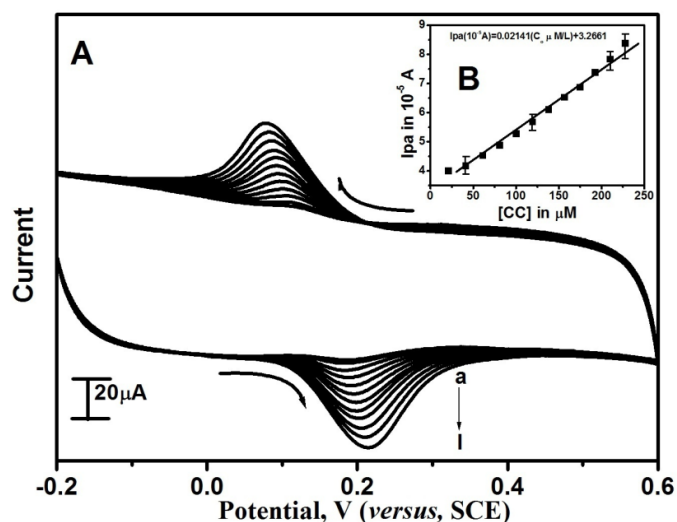


Fig. 5. (A) Cyclic voltammograms of CC in 0.2 M PBS solution of pH 7.4 at poly (methionine) MCPE at scan rate of 0.05 Vs^{-1} with different concentration (a–l; $20.66 \mu\text{M}$, $40.98 \mu\text{M}$, $60.97 \mu\text{M}$, $80.64 \mu\text{M}$, $100.00 \mu\text{M}$, $119.04 \mu\text{M}$, $137.79 \mu\text{M}$, $156.25 \mu\text{M}$, $174.41 \mu\text{M}$, $192.30 \mu\text{M}$, $209.92 \mu\text{M}$); (B) Graph of anodic peak current versus concentration

The Figure 5A shows by increasing the concentration of CC from $20.66 \mu\text{M}$ to $209.92 \mu\text{M}$ the I_{pa} and I_{pc} goes on increasing with a small shifting in the redox peak potentials. The graph of I_{pa} versus concentration of CC (Inset Figure 5B) reveals an almost straight line with good linearity with the linear regression equation of $I_{pa}(10^{-5} \text{ A}) = 0.02141(C_0 \mu\text{M/L}) + 3.2660$, ($r^2 = 0.9992$). The limit of detection (LOD) and limit of quantification (LOQ) was calculated according to the equation (4) and (5).

$$\text{LOD}=3 \text{ S/M} \quad (4)$$

$$\text{LOQ}=10 \text{ S/M} \quad (5)$$

Where, S is the standard deviation of six blank-solution measurements. M is the slope of the calibration graph [6]. The LOD and LOQ were calculated in the lower concentration range for CC is found to be 55.66 μM and 185.5 μM respectively.

3.6. Effect of pH on the determination of CC

The effect of the PBS pH value on the determination of CC at poly (methionine) MCPE was carefully examined in the pH range of 5.5–8.0. The change in the pH values has a significant contribution on the electrocatalytic oxidation of CC at poly (methionine) MCPE by affecting both peak current and redox peak potentials. The Figure 6A shows cyclic voltammograms recorded for 2.27×10^{-4} M CC at poly (methionine) MCPE with different pH solutions with scan rate 0.05Vs^{-1} . The oxidation peak potential shifts to a more negative potential with increasing pH. The E_{pa} versus pH graph clearly suggested that the E_{pa} depends linearly on the pH value in the range of 5.5–8.0 (Figure 6B). The linear regression can be expressed as $E_{\text{pa}}(\text{V})=0.6119-0.0535(\text{pH})$, ($r^2=0.9924$). The obtained slope of 0.0535 V/pH suggests an equal number of protons and electrons are involved in the redox mechanism. This was consistent with the reported literature [32,39].

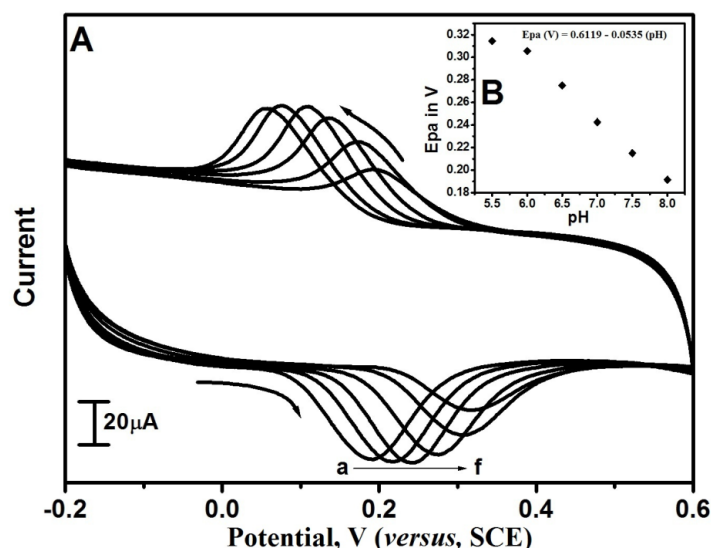


Fig. 6. (A) Cyclic voltammograms of the poly (methionine) MCPE in 0.2 M PBS solution at different pH (a-f: 5.5 to 8.0) at scan rate of 0.05Vs^{-1} ; (B) The effect of pH on the peak current response of 2.27×10^{-4} M CC in 0.2 M PBS solution

3.7. Electrocatalytic oxidation of HQ at poly (methionine) MCPE

The Figure 7 shows the oxidation of 0.2 mM HQ at BCPE and poly (methionine) MCPE in 0.2 M PBS of pH 7.4 with the scan rate of 0.05 Vs^{-1} . From the Figure 7 it is observed that the oxidation potential of HQ at BCPE was seldom broad and poor in sensitivity (dashed line), the anodic peak potential was located at around 0.144 V. However, for the poly (methionine) MCPE the enhancement in peak current was observed with a negative shifting of oxidation potential and was located at 0.101 V. This minimization of over potential and enhancement of peak current signal confirms the electrocatalytic activity of poly (methionine) MCPE towards the favourable oxidation of HQ.

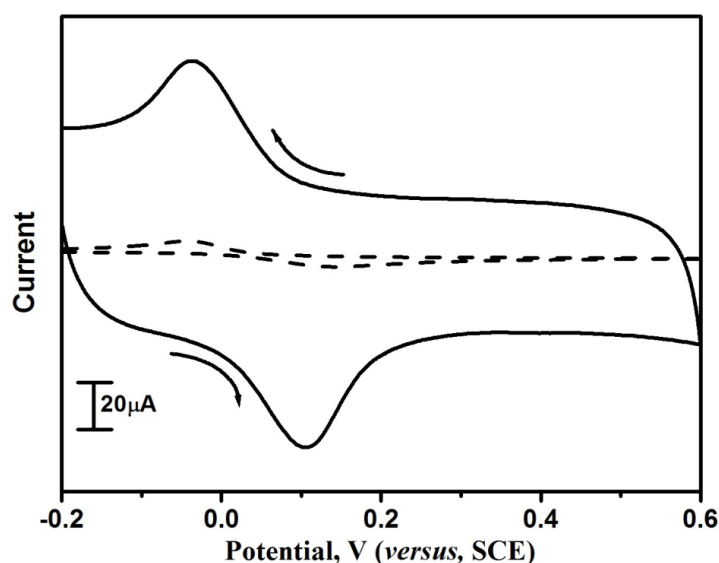


Fig. 7. Cyclic voltammograms of 0.2 mM HQ in 0.2 M PBS solution of pH 7.4 at BCPE (dashed line) and poly (methionine) MCPE (solid line) at scan rate of 0.05 Vs^{-1}

3.8. Effect of scan rate on the peak current of HQ

The Figure 8A shows the cyclic voltammograms recorded for 0.2 mM HQ in 0.2 M PBS of pH 7.4 with different scan rates at poly (methionine) MCPE. The redox peak currents were increased with increase in the scan rate from 0.04 Vs^{-1} to 0.12 Vs^{-1} for poly (methionine) MCPE. To evaluate the kinetics of the electrode process, the graph of peak I_p versus v was plotted in the range from 0.04 - 0.12 Vs^{-1} as shown in Figure 8B with the correlation coefficient (r^2) 0.9990 and 0.9992. The I_p versus $v^{1/2}$ were plotted as shown in Figure 8C with the correlation coefficient (r^2) 0.9977 and 0.9962. This result suggests the electrode process was controlled by adsorption of analytes on the electrode surface [37-38].

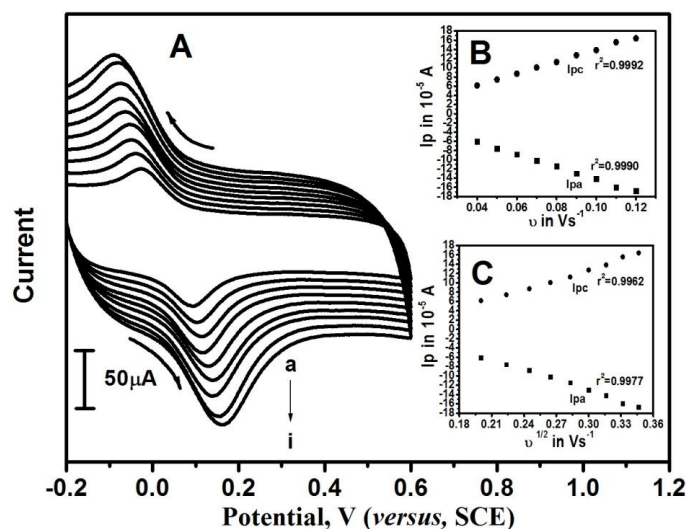


Fig. 8. (A) Cyclic voltammograms of 0.2 mM HQ in 0.2 M PBS solution of pH 7.4 at poly (methionine) MCPE at different scan rate (a–i; 0.04 Vs^{-1} to 0.12 Vs^{-1}); (B) Graph of peak current versus scan rate; (C) Graph of peak current versus square root of scan rate

3.9. Effect of HQ concentration

The effect of concentration on the peak current response of HQ was established at poly (methionine) MCPE.

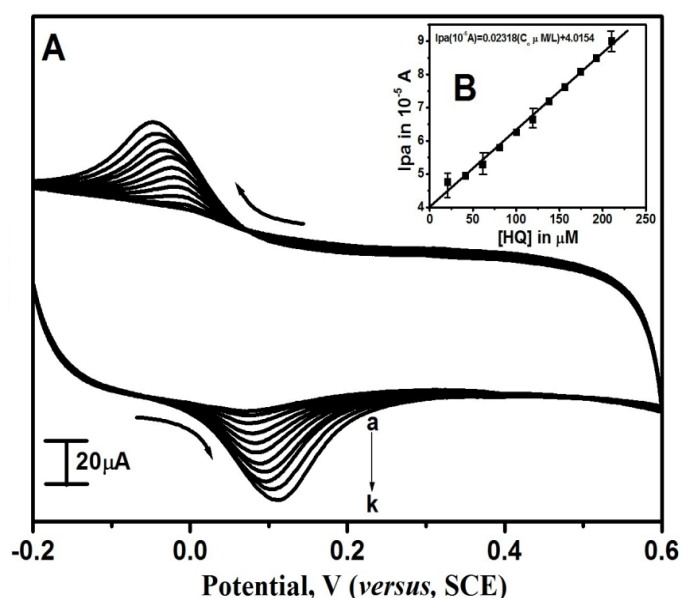


Fig. 9. (A) Cyclic voltammograms of CC in 0.2 M PBS solution of pH 7.4 at poly (methionine) MCPE at scan rate of 0.05 Vs^{-1} with different concentration (a–l; $20.66 \mu\text{M}$, $40.98 \mu\text{M}$, $60.97 \mu\text{M}$, $80.64 \mu\text{M}$, $100.00 \mu\text{M}$, $119.04 \mu\text{M}$, $137.79 \mu\text{M}$, $156.25 \mu\text{M}$, $174.41 \mu\text{M}$, $192.30 \mu\text{M}$); (B) Graph of anodic peak current versus concentration

The Figure 9A demonstrates by increasing the concentration of HQ from 20.66 μM to 192.30 μM the I_{pa} and I_{pc} goes on increasing with a small shifting in the oxidation potentials. The linear establishment was observed between the graph of I_{pa} versus concentration of HQ (Inset Figure 9B) with a linear regression equation of $I_{\text{pa}} (10^{-5}\text{A}) = 0.02318 (C_0 \mu\text{M/L}) + 4.0154$, ($r^2=0.9969$). The LOD and LOQ were calculated in the lower concentration range for HQ, and are 45.8 μM and 152.7 μM respectively.

The oxidation peak potential was shifted to a less positive potential with increasing the pH values for the oxidation of 2.27×10^{-4} M HQ at poly (methionine) MCPE. The anodic peak potential of HQ was shifted from 0.2150 V to 0.0783 V with reference to the pH from 5.5 to 8.0 as shown in the Figure 10A. From the inset Figure 10B the anodic peak potential and pH of the solution are having a good linear relationship with a linear regression equation of $E_{\text{pa}}(\text{V}) = 0.5354 - 0.0573(\text{pH})$, ($r^2=0.9969$). The determined slope value 0.0573 V/pH is in accordance with the theoretical value of 0.059 V/pH. This suggests redox mechanism involves equal number of electron and proton according to Nernst equation [32,39].

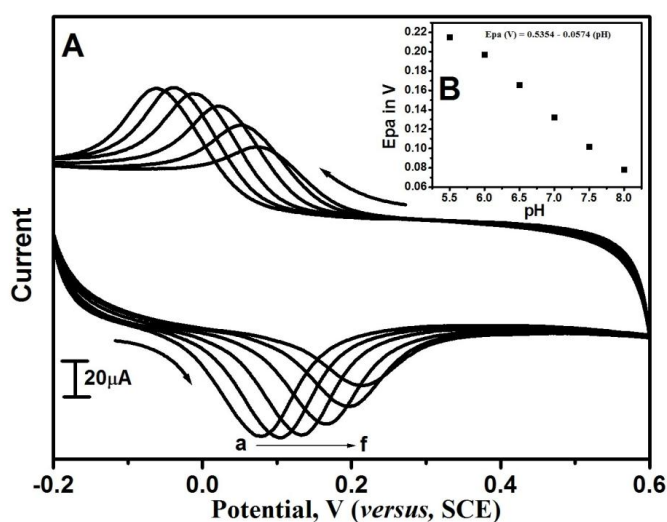


Fig. 10. (A) Cyclic voltammograms of the poly (methionine) MCPE in 0.2 M PBS solution at different pH (a-f: 5.5 to 8.0) at scan rate of 0.05 Vs^{-1} ; (B) The effect of pH on the peak current response of 2.27×10^{-4} M CC in 0.2 M PBS solution

3.10. Simultaneous determination of CC and HQ

The voltammetric response of binary mixtures of two phenolic isomers namely, CC and HQ at BCPE is with least selective and less sensitive. Moreover, due to the fouling of the electrode surface and similar oxidation potential of these isomers the voltammogram obtained was generally broad and overlapped. Therefore, the selective and simultaneous determination of these isomers is of prime concern in modern electroanalytical research. The Figure 11 shows the cyclic voltammograms recorded for the equimolar mixture of CC and HQ (0.2

mM) in 0.2 M PBS of pH 7.4 at BCPE (dashed line) and poly (methionine) MCPE (solid line). The voltammetric response at BCPE is indistinguishable and least selective the overlapped anodic oxidation was occurred at 0.222 V. However, in the same condition the poly (methionine) MCPE has resolved the voltammetric peaks of CC and HQ, were located at 0.216 V and 0.101 V respectively. The peak to peak separation was 0.115 V and this result was well enough for the simultaneous determination of CC and HQ in a binary mixture. As the electron cloud density is lower from HQ to CC, which leads to decrease in their electroactivity and the oxidation of the HQ becomes easier than that of CC [12,16]. Since, the oxidation potential of HQ is shifted to the less positive side at poly (methionine) MCPE; the anodic peak current of CC has no contribution from the oxidation of HQ; because HQ is readily oxidized well before the oxidation potential of CC reached. This prevents the overlapped voltammetric response of the isomers.

Differential pulse voltammetry (DPV) was employed, due to its higher current sensitivity and absence of background current. The Figure 12 shows simultaneous analysis of CC and HQ (0.2 mM) in 0.2 M PBS of pH 7.4 at both BCPE (dashed line) and poly (methionine) MCPE (solid line). Distinct separation was not observed at BCPE and overlapped anodic oxidation was located at 0.132 V. For poly (methionine) MCPE the selective oxidation was observed at 0.127 V for CC and 0.015 V for HQ, the peak separation was 0.112 V. Therefore, this result confirms the CC and HQ were identified simultaneously in a binary mixture.

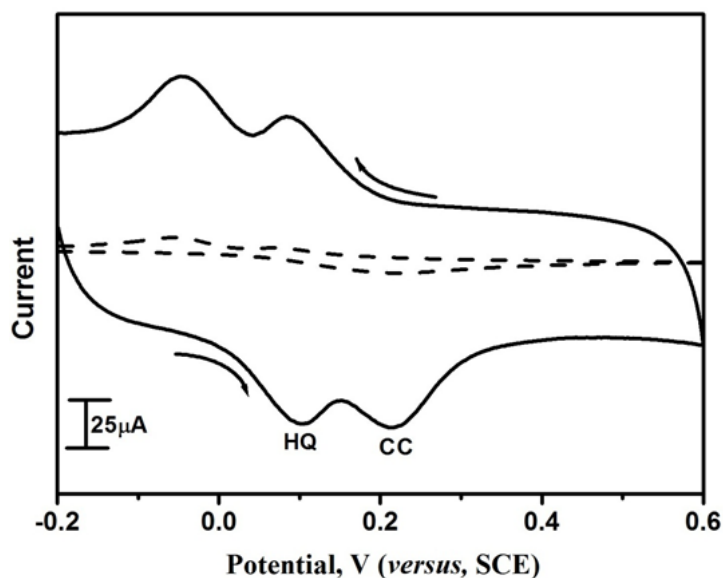


Fig. 11. Cyclic voltammograms for simultaneous determination of 0.2 mM CC and 0.2 mM HQ at BCPE (dashed line) and poly (methionine) MCPE (solid line) at scan rate of 0.05 Vs^{-1}

The study of interference is a major concern in the analysis of these isomers. The investigation was performed at poly (methionine) MCPE. The concentration of one of the analyte is changed by keeping the concentration of the other analyte constant. From the

Figure 13A it can be seen that the peak current of CC was increased due to the increase in concentration from 0.0 to 109.5 μM by keeping the concentration of HQ (30.86 μM) constant.

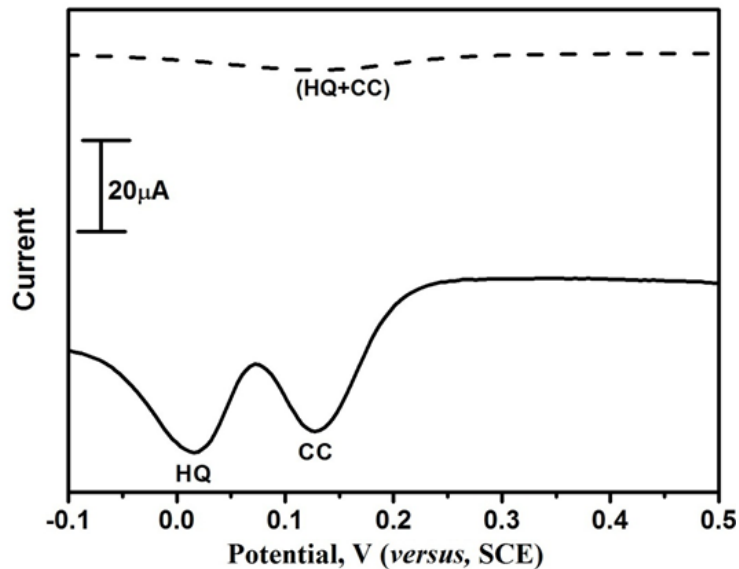


Fig. 12. Differential pulse voltammogram obtained for 0.2 mM CC and 0.2 mM HQ in 0.2 M PBS solution of pH 7.4 at BCPE (dashed line) and poly (methionine) MCPE (solid line)

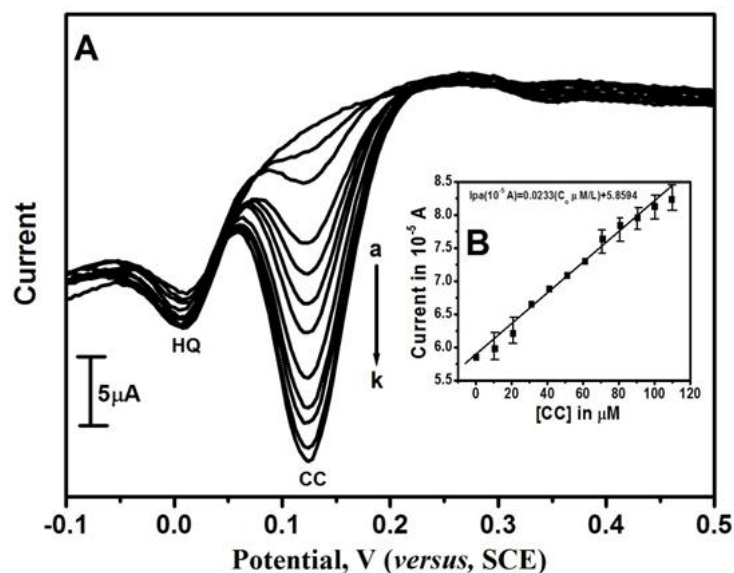


Fig. 13. (A) Differential pulse voltammograms of (a) 0.0 μM (b) 10.37 μM (c) 20.66 μM (d) 30.86 μM (e) 40.98 μM (f) 51.02 μM (g) 60.97 μM (h) 70.85 μM (i) 80.64 μM (j) 90.36 μM (k) 100.00 μM (l) 109.5 μM CC in 0.2 M PBS of pH 7.4 in presence of 30.86 μM HQ at poly (methionine) MCPE; (B) Graph of peak current versus concentration of CC

From the inset Figure 13B it is observed that a linear relationship is obtained between the I_p and concentration CC with a linear regression equation of $I_{pa} (10^{-5}A)=0.0233 (C_0 \mu M/L)+5.8594$, ($r^2=0.9934$) in the range 0.0 to 109.5 μM . The LOD and LOQ were found to be 38.8 μM and 129.6 μM respectively. Similarly by varying the concentration of HQ from 0.0 μM to 80.64 μM only the peak current of HQ increased at a constant concentration of CC (30.86 μM) as shown in the Figure 14A. A linear relationship between I_p and concentration of HQ was established in Figure 14B with a linear regression of $I_{pa} (10^{-5}A)=0.01534 (C_0 \mu M/L)+6.6021$, ($r^2=0.9934$) in the range 0.0 μM to 80.64 μM . the determined LOD and LOQ was 57.85 μM and 192.86 μM respectively. This ultimately leads to the precise electroanalysis of CC and HQ at poly (methionine) MCPE.

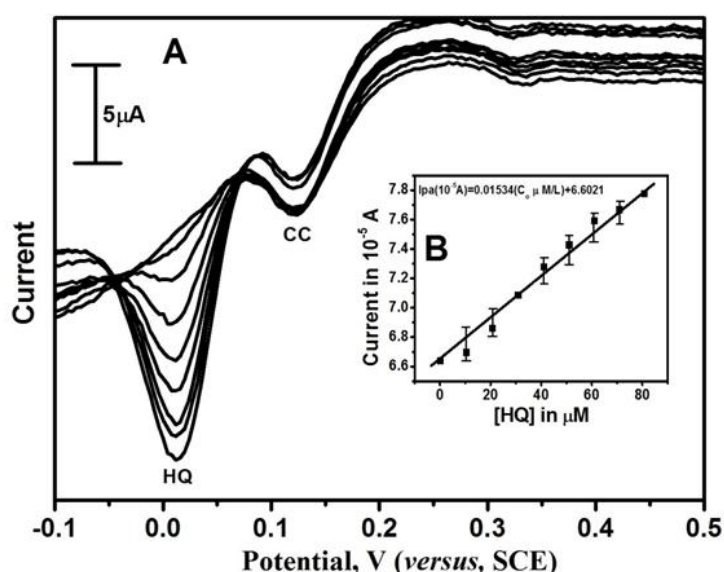


Fig. 14. (A) Differential pulse voltammograms of (a) 0.0 μM (b) 10.37 μM (c) 20.66 μM (d) 30.86 μM (e) 40.98 μM (f) 51.02 μM (g) 60.97 μM (h) 70.85 μM (i) 80.64 μM HQ in 0.2 M PBS of pH 7.4 in presence of 30.86 μM CC at poly (methionine) MCPE; (B) Graph of peak current versus concentration of CC

4. CONCLUSION

In the present work, the electropolymerisation of DL-methionine on the surface of carbon paste electrode produced a stable polymeric film. This study has shown that the poly (methionine) MCPE not only exhibited strong electrocatalytic activity towards the oxidation of CC and HQ but also resolved the overlapping anodic peak potential of CC and HQ into two well resolved peaks. The high sensitivity, selectivity, easy method of preparation with surface regeneration of the modified electrode has great applicability in the simultaneous determination of CC in presence of HQ. The interference study shows the oxidation of CC and HQ was independent of each other.

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