

Full Paper

Electrochemical Study of Catechol and Hydroquinone at poly (congo red) Modified Carbon Paste Electrode: A Voltammetric Study

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Abstract- The poly (congo red) film was developed on the surface of carbon paste electrode by electrochemical method. The fabricated poly (congo red) modified carbon paste electrode exhibited excellent electrocatalytic activity towards the oxidation of catechol (CC) and hydroquinone (HQ) in a binary mixture by cyclic voltammetric (CV) and differential pulse voltammetric (DPV) techniques. The scan rate effect was found to be adsorption controlled electrode process. The interference study was done by varying the concentration of one species while other kept constant. Overall a sensitive and selective method was developed for the electroanalysis of CC and HQ.

Keywords- Catechol, Hydroquinone, Electropolymerisation, Electrocatalytic effect, Poly(congo red)

1. INTRODUCTION

Over the past few years, the modification of the carbon paste electrode has achieved much more attention in the electroanalysis of biologically important electroactive molecules [1-2]. Compared to the traditionally used unmodified electrodes, the modified electrodes have merits of excellent electrocatalytic activity, higher sensitivity and selectivity, antifouling

property and reproducibility with lower limit of detection [3-5]. The modification can be carried out by using nano particles [6-7], nano tubes [8-9] ionic liquids [10] and conducting polymer layers [11]. Recently, working electrodes coated with electropolymerised conducting polymer films have been paid great attention due to their improved physiochemical properties and electrocatalysis in the redox phenomenon [12-13]. Electropolymerisation method has certain advantages. Such as, a good approach to immobilize the organic molecule in a uniform manner, film thickness can be easily controlled by adjusting the electrochemical input parameters, the long term operation stability and charge transport characteristics [14]. Many studies have indicated that polymer film modified electrodes showed an enhanced response for the determination of various electroactive molecules. In general, polymerization of dyes can form cross-linked oligomer which leads to the enhancement of its adsorptive ability [15-16].

Catechol (CC, 1,2-dihydroxybenzene) and hydroquinone (HQ, 1,4-dihydroxybenzene) are the two positional isomers of a dihydroxybenzene family [17-18]. They widely exist in industrial effluents. Such as, the oil waste from refineries, coal tar, cosmetics, plastic, leather, paint, steel and pharmaceutical industries [19-20]. Even in a very low concentration itself these isomers are very toxic to animals and human beings and they are very difficult to degrade in biological environment. Because of these factors they are one of the main sources and cause for the environment pollution [21-22]. Therefore, the determination of these phenolic compounds is important in environmental control [23-24]. Furthermore, because of the similar structure and properties both CC and HQ coexist together in the ecological systems. Hence, it is very important to develop simple and rapid electroanalytical methods for the qualitative and quantitative determination of these molecules [25]. There are many varieties of techniques are adopted for the determination of these isomers. Like; spectrophotometry [26], pH based-flow injection analysis [27], high performance liquid chromatography (HPLC) [28-29], synchronous fluorescence [30] and electrochemiluminescence [31]. All the mentioned methods are complicated and require long duration for the analysis.

An overlapped voltammetric response was obtained for the oxidation of CC and HQ at bare working electrodes. Oxidation requires high over potential due to fouling of the electrode surface by the adsorption of oxidized products. To overcome these demerits, modification of the bare working electrodes has been proposed. In continuation of our research work, here in; we demonstrated the modification of the bare carbon paste electrode by electropolymerising the congo red by cyclic voltammetric technique for the determination CC and HQ in a binary mixture. Congo red is a water soluble secondary diazo dye, widely used in biochemistry and histology for staining. The fabricated poly(congo red) modified carbon paste electrode (MCPE) showed enhanced electrocatalytic activity for the

determination of phenolic isomers by both cyclic voltammetric and differential pulse voltammetric techniques.

2. EXPERIMENTAL

2.1. Reagents and instrumentation

Catechol (CC) and hydroquinone (HQ) was purchased from Himedia. Congo red was obtained from Nice Chemicals. The stock solution of 25×10^{-4} mol L⁻¹CC, 25×10^{-4} mol L⁻¹HQ and 25×10^{-3} mol L⁻¹congo red was prepared in double distilled water respectively. Phosphate buffer solution (PBS) of same ionic strength was maintained (0.2 mol L⁻¹) and desired pH was obtained by mixing appropriate ratio of NaH₂PO₄·H₂O and Na₂HPO₄. 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 and used as received without any further purification. The electrochemical experiments were conducted using a model CHI-660c (CH Instrument-660 electrochemical workstation). A traditional three electrode system was employed in a single compartment electrochemical cell with a saturated calomel electrode(SCE) as a reference, a platinum counter electrode, and bare or poly (congo red) modified carbon paste electrode (MCPE) as a working electrode. The oxidation potentials of corresponding analytes were recorded versus SCE.

2.2. Preparation of the bare carbon paste electrode

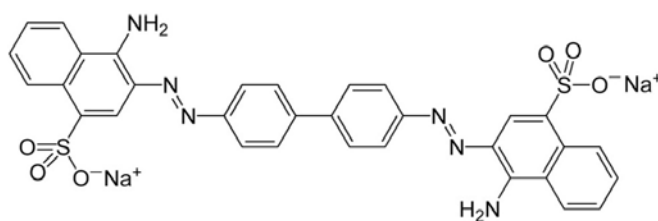
The bare carbon paste electrode (BCPE) was prepared by hand mixing of 70% graphite powder and 30% silicone oil in an agate mortar for about 45 min until a homogeneous paste was obtained. The paste was then packed into a homemade cavity of PVC tube with 3mm internal diameter and smoothed on a tissue paper. The electrical contact was provided by a copper wire connected to the end of the tube [4].

3. RESULTS AND DISCUSSION

3.1. Electropolymerisation of congo red on BCPE

Cyclic voltammetry was used for the electropolymerisation of congo red on the surface of BCPE. The poly (congo red) MCPE was prepared by placing 1.0×10^{-3} mol L⁻¹congo red solution with 0.1 mol L⁻¹ NaOH as a supporting electrolyte in an electrochemical cell. The potential window was maintained from -0.5 V to 1.5 V for 25 multiple cycles with the applied scan rate of 0.1Vs⁻¹. During the process of multiple cycles, the voltammogram was gradually descended with increase of cyclic times as showed in Figure1. This indicates that a uniform thin layer of congo red was formed and deposited on the surface of BCPE [1-2,4]. The structure of congo red was shown in scheme 1.

In the electropolymerisation of congo red, the potential was maintained in window of -0.5 V to +1.5 V. If the positive potential is less than the +1.5 V no polymer film would be obtained due to the lack of the monomer free radical concentration. The positive potential is higher than the +1.5 V leads to the over oxidation of the congo red monomer, which declines the polymer film. If the initial potential was negative than the -0.5 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 [2,4]. The electrocatalysis property of the electrode is directly depends upon the thickness of the film, The extent of level of thickness was also calibrated by controlling the number of multiple cycles on the BCPE (from 5 to 35 multiple cycles) and corresponding electrocatalytic activity towards the oxidation of $0.2 \times 10^{-3} \text{ mol L}^{-1}$ CC in 0.2 M PBS of pH 7.4 was investigated as shown in the Figure 2A. From the obtained experimental results, both the anodic and cathodic peak currents were maxima at 25 multiple cycles as shown in the inserted Figure 2B. Therefore, twenty five cycles were chosen as representative for the electropolymerisation of congo red.



Scheme 1. Structure of congo red

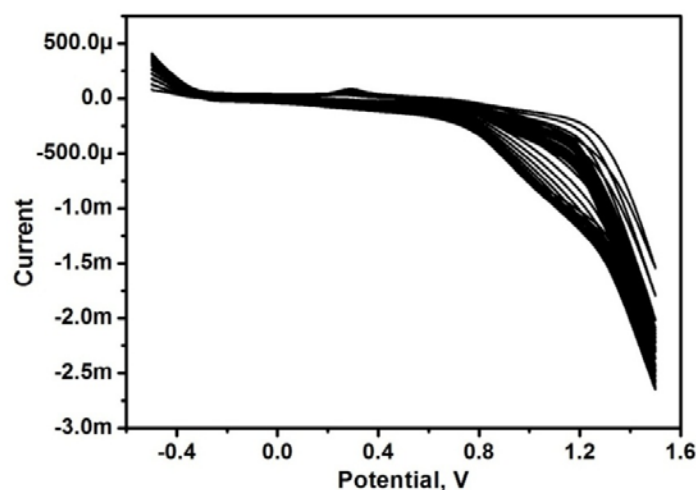


Fig. 1. Cyclic voltammograms of preparation of poly (congo red) MCPE. $1 \times 10^{-3} \text{ mol L}^{-1}$ aqueous solution in 0.1 mol L^{-1} NaOH at 25 cycles with scan rate 0.1 Vs^{-1}

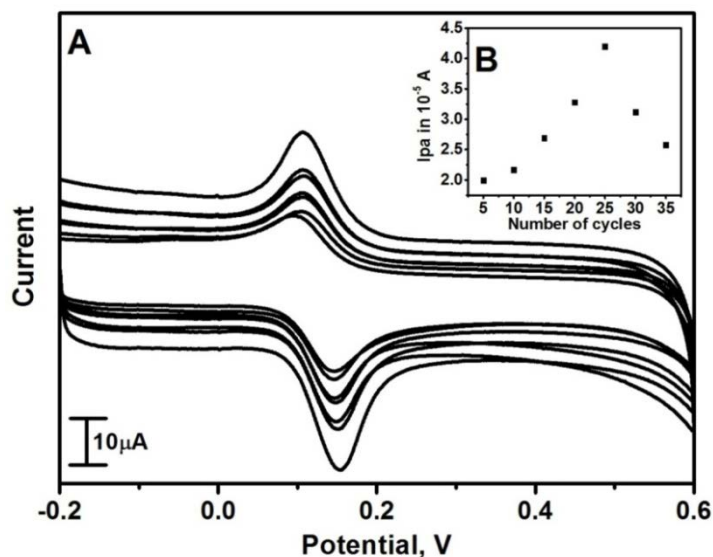


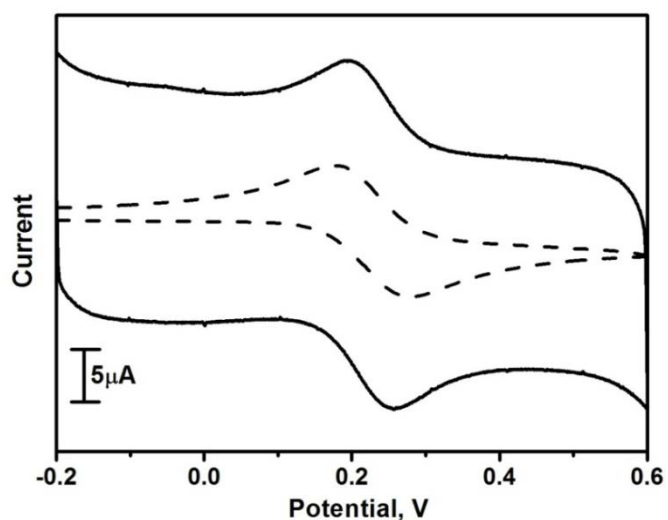
Fig. 2. (A) Cyclic voltammograms recorded for the oxidation of 0.2×10^{-3} mol L⁻¹CC at poly (congo red) MCPE; (B) Graph of anodic peak current versus number of polymerisation cycles

3.2. Electrochemical characterization of poly (congo red) MCPE

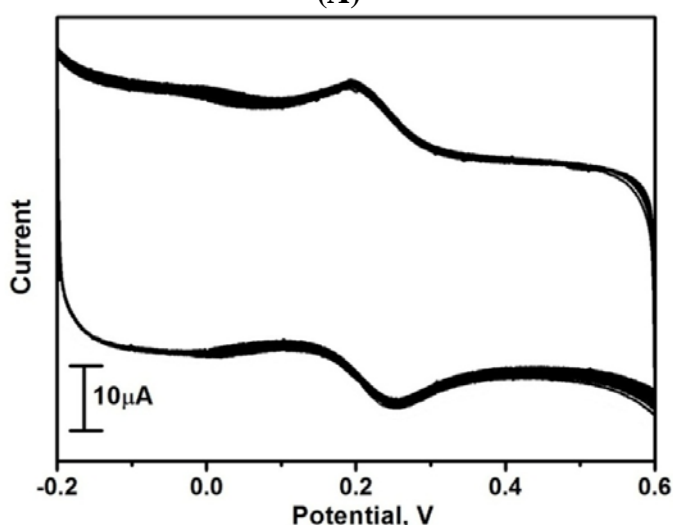
The freshly prepared stock solution of 1×10^{-3} mol L⁻¹ potassium ferrocyanide in 1.0 mol L⁻¹ KCl as a supporting electrolyte was taken in an electrochemical cell. The cyclic voltammograms were recorded for the oxidation of 1×10^{-3} mol L⁻¹ potassium ferrocyanide at both BCPE (dashed line) and poly (congo red) MCPE (solid line) at the scan rate 0.05 Vs⁻¹ as showed in the Figure 3A. The voltammetric response at BCPE was least sensitive due to the slow electron transport phenomenon. The redox peak separation was 0.092 V (versus SCE). However, in the same identical condition the poly (congo red) MCPE exhibited strong enhancement in the redox peak currents and the peak separation was found to be 0.061 V, reflecting the electrocatalytic activity of the fabricated electrode. This refinement in the result is due to improved electron transfer kinetics. Therefore, the surface property of the modified electrode has been changed significantly and also the result confirms the electrocatalytic activity of poly (congo red) MCPE. The surface area available for reaction of species in solution can be calculated by the Randles-Sevick's equation (1) [4,11].

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

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 involved, D is the diffusion coefficient in cm²s⁻¹, ν is the scan rate (Vs⁻¹) and A is the electroactive surface area (cm²). For poly (congo red) MCPE the electroactive surface area is maximum (0.0368 cm²) as compared with BCPE (0.0291 cm²).



(A)



(B)

Fig. 3. (A) Cyclic voltammograms of 0.1×10^{-3} mol L⁻¹ potassium ferrocyanide at BCPE (dashed line) and poly (congo red) MCPE (solid line) at scan rate of 0.05 Vs^{-1} ; (B) Cyclic voltammograms of 0.1×10^{-3} mol L⁻¹ potassium ferrocyanide in 1.0 mol L^{-1} KCl at poly (congo red) MCPE at the scan rate of 0.05 Vs^{-1} for successive 40 cycles

The stability of the poly (congo red) MCPE was checked by recording 40 multiple cycles in 1 M KCl containing 1×10^{-3} mol L⁻¹ potassium ferrocyanide. From the Figure 3B it was observed that, after the first cycle the redox peak currents remains virtually constant, which suggests that the electrode is highly stable. The % degradation of the poly (congo red) MCPE was calculated by using equation (2)[32].

$$\% \text{ Degradation} = \frac{I_{pn}}{I_{p1}} \times 100 \quad (2)$$

Where I_{p1} and I_{pn} are the first and n^{th} anodic peak currents respectively; it was found to be less than 5%, indicating that the modified electrode is stable.

3.3. Electrochemical response of CC at poly (congo red) MCPE

The cyclic voltammograms were recorded for the oxidation of $0.2 \times 10^{-3} \text{ mol L}^{-1}$ CC at BCPE and poly (congo red) MCPE in 0.2 mol L^{-1} PBS of pH 7.4 at the scan rate of 0.05 Vs^{-1} as showed in the Figure 4. At BCPE (dashed line) the CC showed oxidation and reduction potentials in the low current signal with poor voltammetric response and located at 0.212 V versus SCE. The peak potential separation was nearly 0.14 V. However, in the same identical conditions the poly (congo red) MCPE (solid line) showed significant increment in redox current signals and the oxidation potential was observed at 0.154 V. Here the peak to peak separation was found to be 0.041 V. It shows electrocatalytic activity of poly (congo red) MCPE towards the electrochemical oxidation of CC.

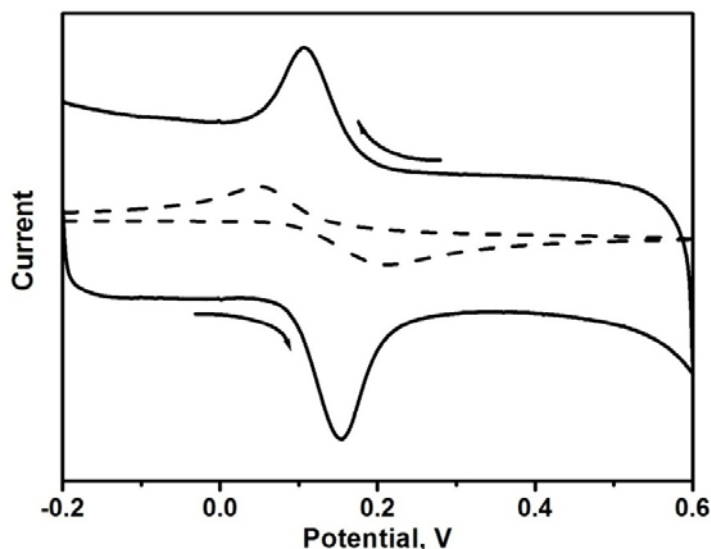


Fig. 4. Cyclic voltammograms of $0.2 \times 10^{-3} \text{ mol L}^{-1}$ CC in 0.2 mol L^{-1} PBS solution of pH 7.4 at BCPE (dashed line) and poly (congo red) MCPE (solid line) at scan rate of 0.05 Vs^{-1}

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

The variation of scan rate was conducted for the oxidation of $50 \times 10^{-6} \text{ mol L}^{-1}$ CC in 0.2 mol L^{-1} PBS of pH 7.4 was studied by CV technique at poly (congo red) MCPE as shown in Figure 5A. Poly (congo red) MCPE obeys Randles-Sevcik's equation and showed increase in the redox peak currents with increase in the scan rate with the small shifting of the redox peak potentials. A linear relationship was observed for the graph of logarithm of anodic peak current ($\log I_{pa}$) versus logarithm of scan rate ($\log \nu$) as shown in the Figure 5B, with the

linear regression equation of $\log I_{pa}(\mu A)=0.8843(\log v \text{ mVs}^{-1})-0.1185$, $r^2=0.9998$. The slope of 0.8843 suggests the electrode phenomenon is an adsorption controlled [4,33].

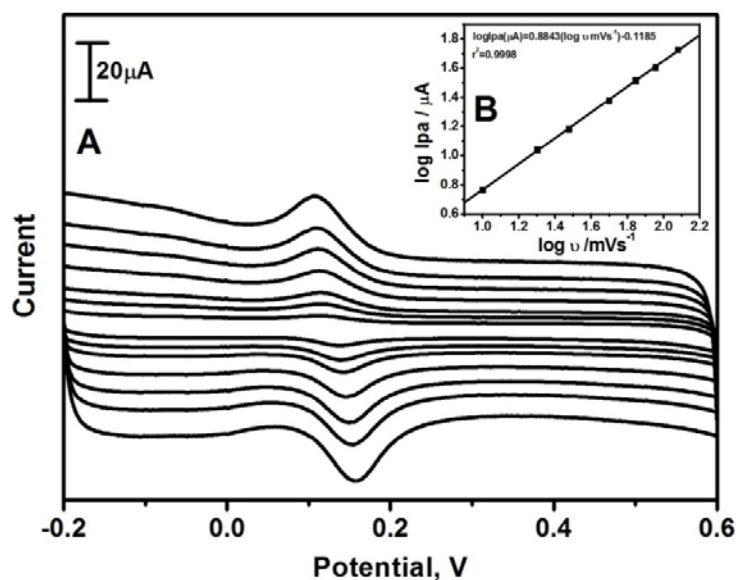


Fig. 5. (A) Cyclic voltammograms of $50 \times 10^{-6} \text{ mol L}^{-1}$ CC in 0.2 mol L^{-1} PBS solution of pH 7.4 at poly (congo red) MCPE at different scan rate (a-k; 0.01 Vs^{-1} to 0.12 Vs^{-1}); (B) Graph of $\log I_{pa}$ versus $\log v$

3.5. Effect of pH value on the determination of CC

The pH of the buffer solution has a significant contribution on the electrocatalytic oxidation of CC at the poly (congo red) MCPE by affecting both peak currents and peak potentials. The influence of the 0.2 mol L^{-1} PBS pH value on the determination of CC at poly (congo red) MCPE was carefully investigated in the pH range of 5.5–8.0. The Figure 6A shows cyclic voltammograms recorded for the oxidation of $1.25 \times 10^{-4} \text{ mol L}^{-1}$ CC at poly (congo red) MCPE. The oxidation peak potential (E_{pa}) shifts to a more negative potential with increasing pH. A linear graph was established between the E_{pa} versus pH, this clearly indicated that the E_{pa} depends linearly on the pH value in the range of 5.5–8.0 with a slope of 0.0583 V/pH ($r^2=0.9986$) as shown in inset Figure 6B and suggesting there is an equal number of electrons and protons are involved in the redox mechanism. This is consistent with that reported in literature [4].

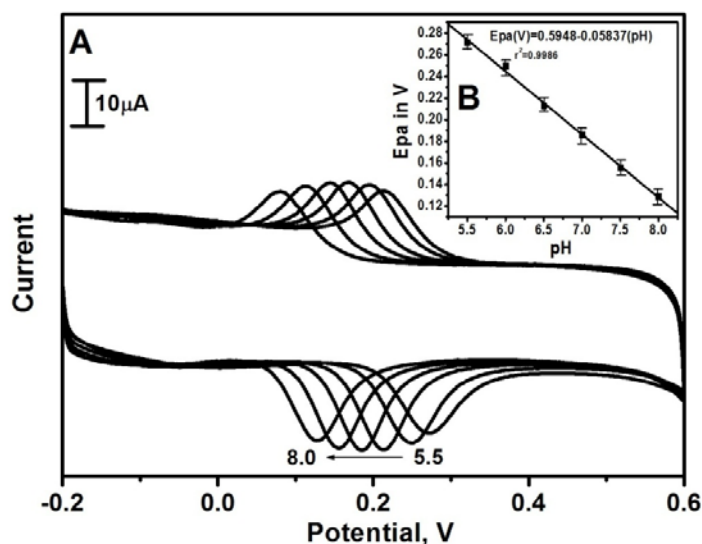


Fig. 6. (A) Cyclic voltammograms of the poly (congo red) MCPE in 0.2 mol L⁻¹ PBS solution at different pH (a-f: 5.5 to 8.0) at scan rate of 0.05 Vs⁻¹; (B) The effect of pH on the peak current response of 1.25×10⁻⁴ mol L⁻¹ CC in 0.2 M PBS solution

3.6. Electrocatalytic oxidation of HQ at poly (congo red) MCPE

The Figure 7 shows the oxidation of 0.2×10⁻³ mol L⁻¹ HQ at BCPE and poly (congo red) MCPE in 0.2 mol L⁻¹ PBS of pH 7.4 at the scan rate of 0.05 Vs⁻¹. From the Figure 7, it was observed that the voltammetric response for the oxidation of HQ at BCPE was broad and least sensitive (dashed line) the anodic peak potential was located at around 0.14 V. The redox peak potential separation was 0.21 V. However, at poly (congo red) MCPE the oxidation peak potential was shifted towards more negative side by minimizing the over potential with enhancement in peak current, the anodic peak potential was located at 0.046 V. The redox peak potential separation was 0.038 V at modified electrode. This shifting of oxidation peak potential and enhancement of peak current signal confirms the electrocatalytic activity of poly (congo red) MCPE towards the favorable oxidation of HQ.

To evaluate the electrode phenomenon, the effect of scan rate variation was conducted at poly (congo red) MCPE. The cyclic voltammograms were recorded for the oxidation of 50 μM HQ in 0.2 mol L⁻¹ PBS of pH 7.4 by varying the applied scan rates as shown in the Figure 8A. The redox peak currents were increased with increase in the scan rates in accordance with the Randles-Sevick's equation. To know the mechanism of the electrode process, the graph of log I_{pa} versus log ν was constructed (Figure 8B). A linear relationship was obtained in the range 0.01 Vs⁻¹ to 0.12 Vs⁻¹ with the linear regression equation of log I_{pa}(μA)=0.8343(log ν mVs⁻¹)-0.0084, r²=0.9989. The obtained slope value of 0.8343 confirms the electrode process have some adsorption complications.

The anodic peak potential for the oxidation of 1.25×10⁻⁴ mol L⁻¹ HQ was shifted to less positive side with increasing in the pH of 0.2 mol L⁻¹ PBS at poly (congo red) MCPE. The

anodic peak potential of HQ was shifted from 0.168 to 0.026 V with reference to the pH from 5.5 to 8.0 as shown in the Figure 9A. From inset Figure 9B the anodic peak potential and pH of the solution shows a good linearity with a slope of 0.0563 V/pH. This behaviour is nearly obeyed the Nernst equation for equal number of electron and proton transfer reaction [4].

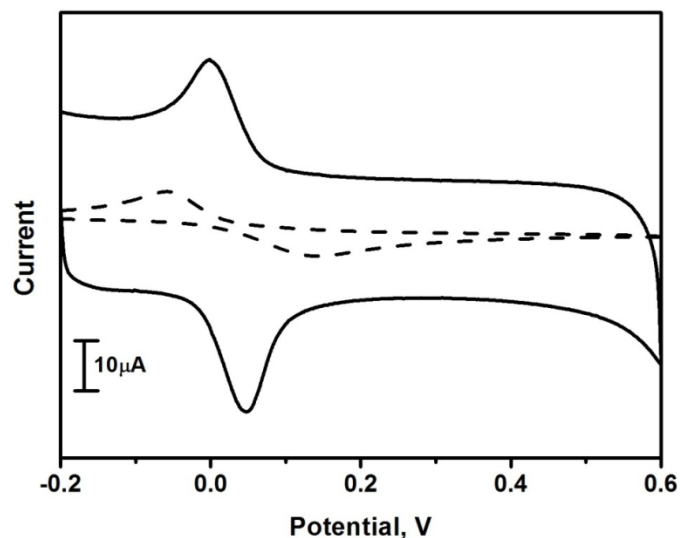


Fig. 7. Cyclic voltammograms of $0.2 \times 10^{-3} \text{ mol L}^{-1}$ HQ in 0.2 mol L^{-1} PBS solution of pH 7.4 at BCPE (dashed line) and poly (congo red) MCPE (solid line) at scan rate of 0.05 Vs^{-1}

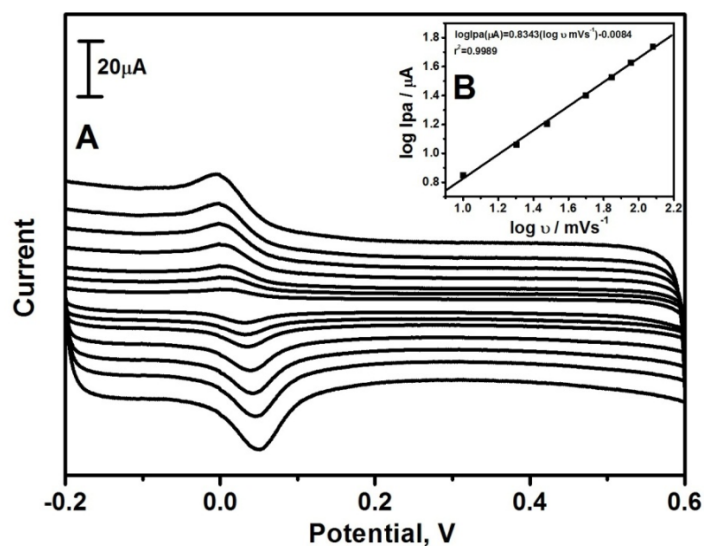


Fig. 8. (A) Cyclic voltammograms of $50 \times 10^{-6} \text{ mol L}^{-1}$ HQ in 0.2 mol L^{-1} PBS solution of pH 7.4 at poly (congo red) MCPE at different scan rate (a –k; 0.01 Vs^{-1} to 0.12 Vs^{-1}); (B) Graph of $\log I_{pa}$ versus $\log \nu$

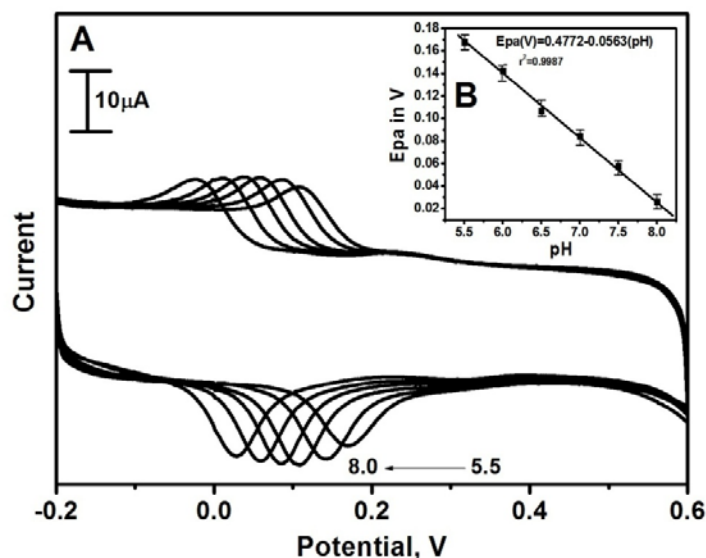


Fig. 9. (A) Cyclic voltammograms of the poly (congo red) MCPE in 0.2 mol L^{-1} PBS solution at different pH (a-f: 5.5 to 8.0) at scan rate of 0.05 Vs^{-1} ; (B) The effect of pH on the peak current response of $1.25 \times 10^{-4} \text{ mol L}^{-1}$ HQ in 0.2 M PBS solution

3.7. Simultaneous electroanalysis of CC and HQ

The binary mixtures of CC and HQ have nearly similar oxidation potentials. Therefore, the simultaneous analysis of these isomers gives an overlapped voltammetric response with least sensitivity and selectivity at BCPE. This makes the individual identification of these molecules very difficult. The Figure 10 shows the cyclic voltammograms recorded for the oxidation of CC and HQ ($30 \times 10^{-6} \text{ mol L}^{-1}$) in 0.2 mol L^{-1} PBS of pH 7.4 at BCPE (dashed line) and poly (congo red) MCPE (solid line). The voltammetric response obtained at BCPE is indistinguishable and least selective; the overlapped oxidation was occurred at 0.186 V . However, in the same identical condition the poly (congo red) MCPE has resolved the voltammetric peaks of CC and HQ and are located at 0.141 V and 0.031 V respectively. The peak to peak separation was 0.11 V and this result good enough for the simultaneous determination of CC and HQ in a binary mixture.

Because of the higher current sensitivity and absence of the background current differential pulse voltammetry (DPV) was employed for the simultaneous analysis of CC and HQ in 0.2 mol L^{-1} PBS of pH 7.4 at both BCPE (dotted line) and poly (congo red) MCPE (solid line) as shown in the Figure 11. Distinct separation was not observed at BCPE and overlapped anodic oxidation was located at 0.103 V . For poly (congo red) MCPE the selective oxidation was observed at 0.10 V for CC and -0.012 V for HQ, the peak separation was 0.112 V . Therefore this result was sufficient for the electroanalysis of CC and HQ in a mixture by DPV technique.

The interference investigation was performed in the mixture of samples containing both CC and HQ at the poly (congo red) MCPE.

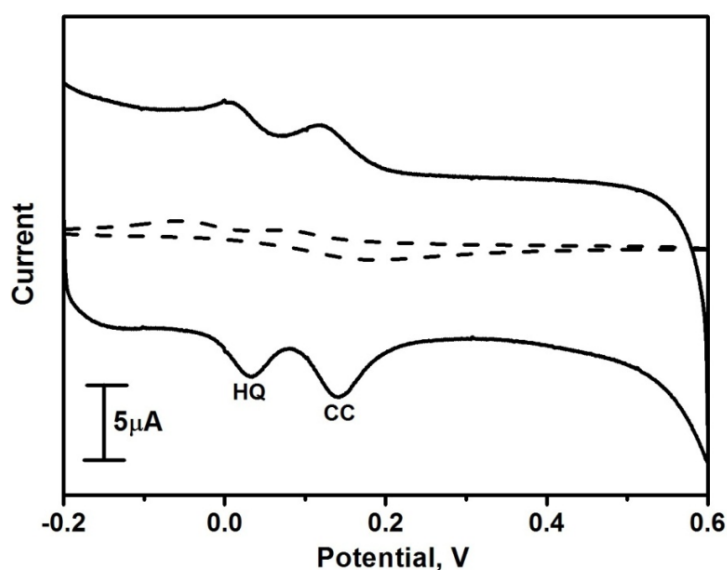


Fig. 10. Cyclic voltammograms of binary mixture of CC and HQ ($30 \times 10^{-6} \text{ mol L}^{-1}$) at BCPE (dashed line) and poly (congo red) MCPE (solid line) at scan rate of 0.05 Vs^{-1}

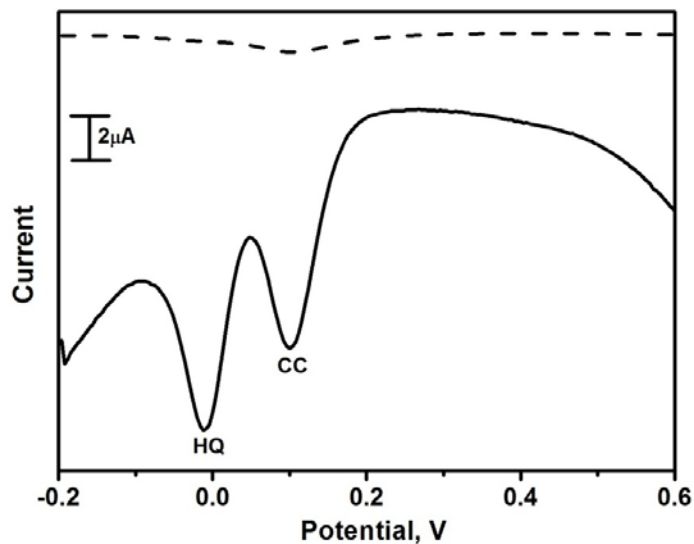


Fig. 11 . Differential pulse voltammogram obtained for $30 \times 10^{-6} \text{ mol L}^{-1}$ CC and $30 \times 10^{-6} \text{ mol L}^{-1}$ HQ in 0.2 mol L^{-1} PBS solution of pH 7.4 at BCPE (dashed line) and poly (congo red) MCPE (solid line)

The concentration of one analyte is changed by keeping the concentration of the other analyte constant..

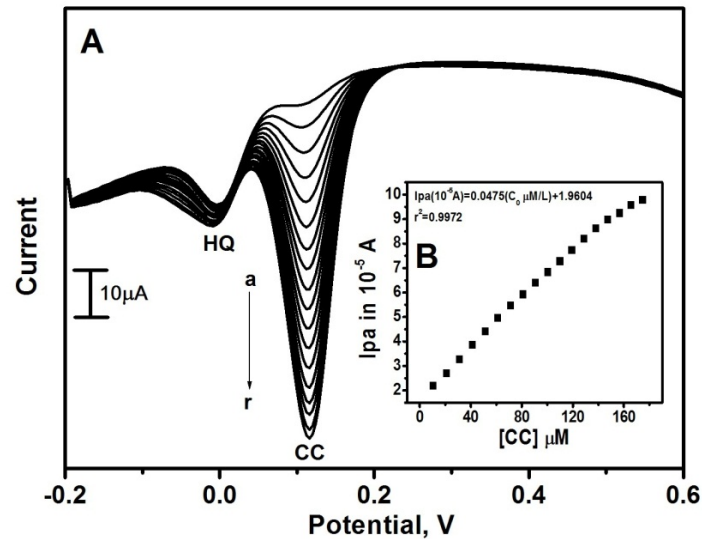


Fig. 12. Differential pulse voltammograms of (a) 10.3×10^{-6} mol L $^{-1}$, (b) 20.6×10^{-6} mol L $^{-1}$, (c) 30.8×10^{-6} mol L $^{-1}$, (d) 40.9×10^{-6} mol L $^{-1}$, (e) 51.0×10^{-6} mol L $^{-1}$, (f) 60.9×10^{-6} mol L $^{-1}$, (g) 70.8×10^{-6} mol L $^{-1}$, (h) 80.6×10^{-6} mol L $^{-1}$, (i) 90.36×10^{-6} mol L $^{-1}$, (j) 100.0×10^{-6} mol L $^{-1}$, (k) 109.5×10^{-6} mol L $^{-1}$, (l) 119.1×10^{-6} mol L $^{-1}$, (m) 128.4×10^{-6} mol L $^{-1}$, (n) 137.7×10^{-6} mol L $^{-1}$, (o) 147.1×10^{-6} mol L $^{-1}$, (p) 156.2×10^{-6} mol L $^{-1}$, (q) 165.4×10^{-6} mol L $^{-1}$, (r) 174.4×10^{-6} mol L $^{-1}$ CC in presence of 30.0×10^{-6} mol L $^{-1}$ HQ at poly (congo red) MCPE

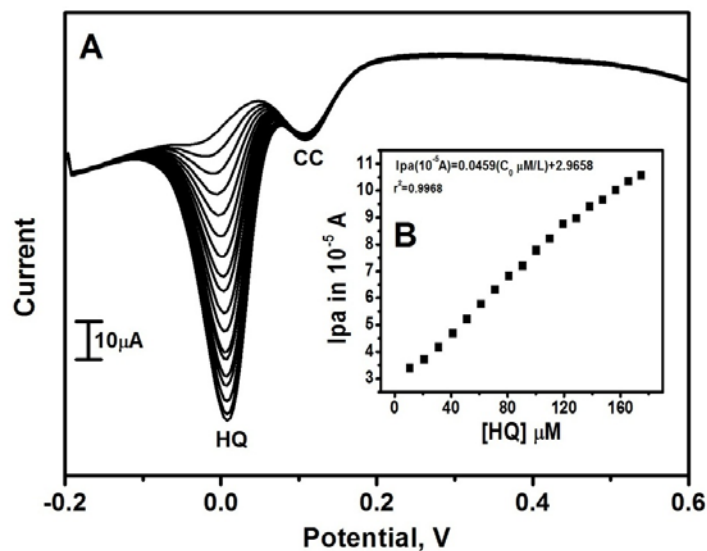


Fig. 13. Differential pulse voltammograms of (a) 10.3×10^{-6} mol L $^{-1}$, (b) 20.6×10^{-6} mol L $^{-1}$, (c) 30.8×10^{-6} mol L $^{-1}$, (d) 40.9×10^{-6} mol L $^{-1}$, (e) 51.0×10^{-6} mol L $^{-1}$, (f) 60.9×10^{-6} mol L $^{-1}$, (g) 70.8×10^{-6} mol L $^{-1}$, (h) 80.6×10^{-6} mol L $^{-1}$, (i) 90.36×10^{-6} mol L $^{-1}$, (j) 100.0×10^{-6} mol L $^{-1}$, (k) 109.5×10^{-6} mol L $^{-1}$, (l) 119.1×10^{-6} mol L $^{-1}$, (m) 128.4×10^{-6} mol L $^{-1}$, (n) 137.7×10^{-6} mol L $^{-1}$, (o) 147.1×10^{-6} mol L $^{-1}$, (p) 156.2×10^{-6} mol L $^{-1}$, (q) 165.4×10^{-6} mol L $^{-1}$, (r) 174.4×10^{-6} mol L $^{-1}$ HQ in presence of 30.0×10^{-6} mol L $^{-1}$ CC at poly (congo red) MCPE

From the Figure 12A it can be seen that the peak current of CC was increased, because of the increased concentration from 10.3 to 174.4×10^{-6} mol L⁻¹ by keeping the concentration of HQ (30.0×10^{-6} mol L⁻¹) constant. The graph of I_{pa} versus concentration of CC gives almost a straight line with good linearity as in Figure 12B. The linear regression equation was I_{pa} (10^{-5} A) = $0.0475(C_0 \mu\text{M/L}) + 1.9604$, ($r^2 = 0.9972$). Similarly by varying the concentration of HQ from 10.3 to 174.4×10^{-6} mol L⁻¹ the peak current of HQ was increased at a constant concentration of CC (30.0×10^{-6} mol L⁻¹) as shown in the Figure 13A. The I_{pa} and concentration of HQ was constructed in Figure 13B the linear regression was expressed as I_{pa} (10^{-5} A) = $0.0459(C_0 \mu\text{M/L}) + 2.9658$, ($r^2 = 0.9968$). This result shows the oxidation of both the molecules was independent of each other

4. CONCLUSION

Poly (congo red) modified carbon paste electrode has been fabricated followed by the electrochemical characterization. This study was indicated that the modified electrode acts as a good analytical sensor, exhibited strong promoting effect and stability towards the electrochemical oxidation of catechol and hydroquinone. The electrochemical parameters are strongly depends on the pH of the solution. The voltammetric separation of CC and HQ was achieved in a binary mixture at modified electrode by CV and DPV techniques. The easy preparation with surface regeneration made the modified electrode as promising working electrode for the determination of CC and HQ. This method can also be applied for the analysis of some other important electroactive molecules

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