

Full Paper

Poly-nile Blue Based Electrochemical Sensor for Catechol and Hydroquinone

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Abstract- An electrochemical sensor was developed for the electroanalysis of catechol (CC) and hydroquinone (HQ) using poly-nile blue (NB) modified glassy carbon electrode (MGCE) i.e., poly-NB/MGCE. The fabricated electrode showed an excellent electrocatalytic activity towards the electrooxidation of CC and HQ in 0.2 M phosphate buffer solution (PBS) of pH 7.4 by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The effect of scan rate suggests the adsorption and diffusion controlled electrode process for CC and HQ respectively. The limit of detection of CC and HQ was found to be 53.2 nM and 31.5 nM by CV techniques. Overall, the sensitivity, selectivity, stability, linearity and reproducibility were obtained at the poly-NB/MGCE.

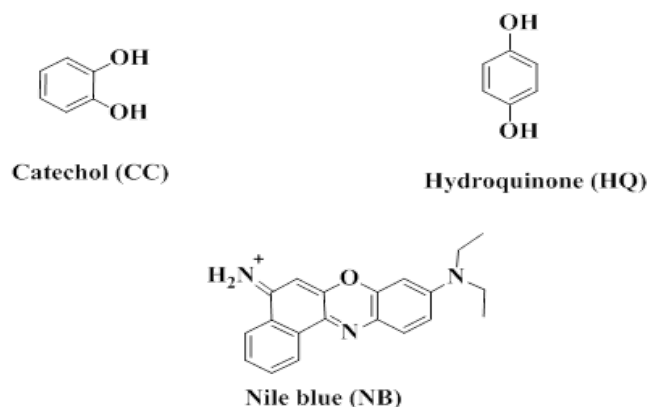
Keywords- Catechol, Hydroquinone, Poly-Nile Blue Modified Glassy Carbon Electrode, Voltammetry

1. INTRODUCTION

Catechol (CC) (1,2-dihydroxybenzene, Scheme 1) and Hydroquinone (HQ) (1,4-dihydroxybenzene, Scheme 1) are the two phenolic polymers having two hydroxyl group bonded to benzene ring which belongs to the class of dihydroxy benzene isomers [1,2]. They are extensively used as raw materials in the production of dyes, plastics, plasticizers, pesticides, paint, cosmetics and some pharmaceuticals industries [3,4]. Even in a very low concentration itself these isomers are highly toxic and can be harmful to animals and plants. Because of these factors they are major cause for environmental pollutions [5-7]. Therefore several analytic methods are proposed for the quantitative and qualitative estimation for these phenolic isomers [8] including HPLC (high performance liquid chromatography) [9,10], synchronous fluorescence [11], electrochemiluminescence [12], pH based flow injection analysis [13] and spectrophotometry [14]. All these techniques require tedious extraction procedure, a requirement of high-priced instruments and relatively time consuming.

On the other hand, during the last few decades electrochemical method has been recognised and attracted in recent years due to their low cost, fast response, sensitivity, accuracy and simple preparation method of analysis. The electroanalytical method involves the use of bare electrodes like bare glassy carbon electrode, graphite, gold and platinum. However, these electrodes show poor response for the detection of electroactive molecules by conventional method due to its low sensitivity, poor selectivity, high overpotential, electrode fouling property. To overcome such problems development of an electro sensor for the electroanalysis of biomolecules via electropolymerisation method with bare electrodes. For example, *J. He et al.*, studied the electropolymerised film of eosin Y modification of the glassy carbon electrode used for the voltammetric separation of CC and HQ [15]. *Wang. L. et al.*, reported the qualitative determination of CC and HQ in a binary mixture by simple amino acids with fabrication of modified glassy carbon electrode [2] and *Suna. W. et al.*, studied simultaneously detection of HQ and CC by a poly(crystal violet) functionalized graphene modified carbon ionic liquid electrode sensor [16].

Nile blue (NB, Scheme 1) is a phenoxazine dye, used for different applications in biological and histological fields for the application of staining and it is a well-known electroactive molecule. It has been extensively used as a mediator of electron transfer with a two electron redox conversion to modify solid electrodes for electrocatalytic oxidation of the reduced form of the nicotinamide coenzymes NADH and NADPH [17-19]. The present work describes a detailed work for the modification of glassy carbon electrode by electropolymerising Nile blue using cyclic voltammetric technique. The fabricated poly-Nile blue modified glassy carbon paste electrode (poly-NB/MGCE) at pH 7.4 was successfully used for the simultaneous determination of phenolic isomers such as CC and HQ by both CV and DPV techniques. The sensitivity, selectivity, stability and reproducibility in the result were obtained at the fabricated poly-NB/MGCE.



Scheme 1. The structural formula of catechol, hydroquinone and nile blue

2. EXPERIMENTAL SECTION

2.1. Apparatus

All electrochemical experiments were carried out using a model CHI-660c (CH Instrument-660 electrochemical work station). A conventional three electrode system was used in an electrochemical cell with a saturated calomel electrode (SCE) as a reference, a platinum wire counter electrode and bare glassy carbon electrode (BGCE) or poly-nile blue modified glassy carbon electrode (poly-NB/MGCE) as a working electrode. Oxidation potentials of all the analytes were recorded versus SCE at an ambient temperature of 25 ± 0.5 °C.

2.2. Reagents and materials

Catechol, Hydroquinone ($M_{wt}=110.11$ g/mol, purity $\geq 99\%$) and Nile blue ($M_{wt}=353.84$ g/mol) was purchased from Sigma Aldrich Ltd., all chemicals were of analytical grade and used as received without any further purification. All the experiments were carried out at room temperature. The CC and HQ stock solution ($C_{CC}=25 \times 10^{-4}$ M and $C_{HQ}=25 \times 10^{-4}$ M) was prepared by dissolving in double distilled water. Phosphate buffer solution (PBS) of same ionic strength was prepared (0.2 M) and 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 . All the aqueous solutions were prepared with double distilled water.

2.3. Pretreatment of glassy carbon electrode

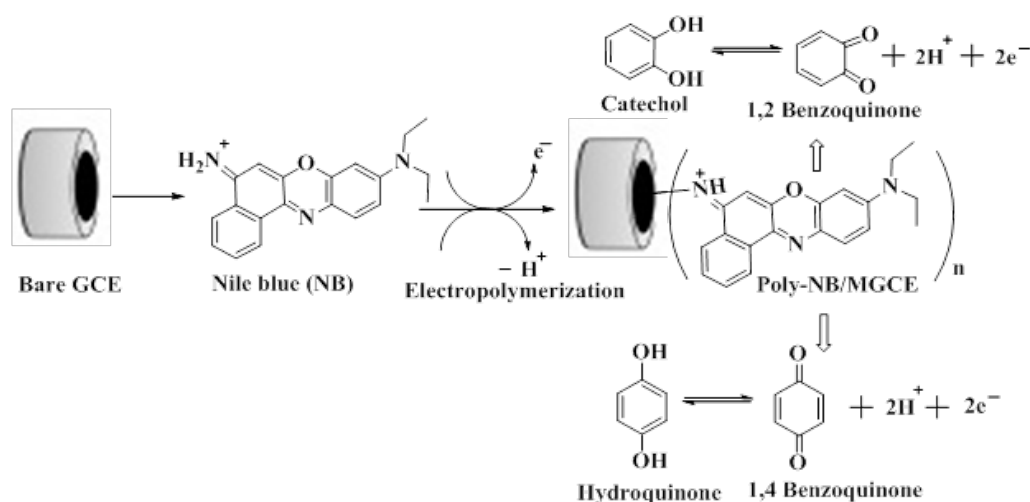
First, the glassy carbon electrode (GCE) was polished on a polishing micro-cloth with 0.5 mM alumina powder and rinsed thoroughly with redistilled water, followed by sonication for 5 min in an ultrasonic bath. The electrode was then transferred to the supporting electrolyte

and applied successive cyclic voltammetric sweep between -0.75 to 1.75 V with the scan rate of 0.1 Vs^{-1} for 10 cycles.

3. RESULT AND DISCUSSION

3.1. Electropolymerization of nile blue on GCE

The electroactive poly-nile blue (1.0 mM) modified glassy carbon sensor electrode was fabricated by cyclic voltammetric technique by multiple potential sweeping the electrode between the potential window of -0.75 to 1.75 V with scan rate 0.1 Vs^{-1} for 10 multiple cycles in 0.2 M PBS of pH 7.4 until a stable cyclic voltammogram was obtained as shown in Fig. 1. After the 10 cycles the increase in the voltammograms tends to be almost constant, suggesting the growth and formation of a polymer film reached the level of saturation [20,21].



Scheme 2. Electropolymerisation of poly-NB/MGCE and Mechanism of CC and HQ with poly-NB/MGCE

In the oxidation mechanism step the poly-nile blue developed an electrocatalytic layer on the surface of bare glassy carbon electrode. The thickness of the polymeric film can be controlled by varying the number of multiple cycles. The probable electropolymerisation mechanism i.e., poly-NB/MGCE sensor and electrocatalysis interaction with CC and HQ was described in Scheme 2. Such types of mechanisms have been proposed in earlier report [7,22].

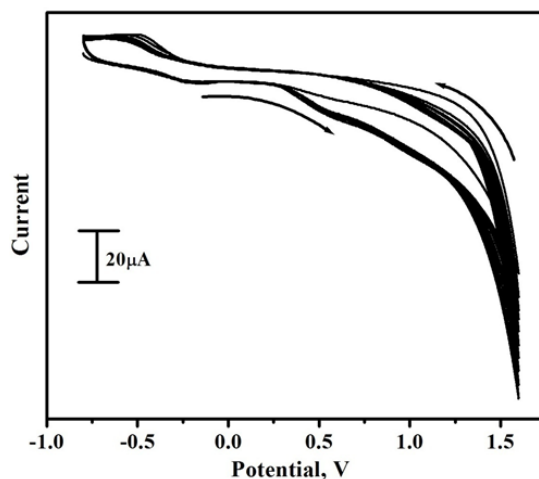


Fig. 1. Cyclic voltammograms of preparation of poly-NB/MGCE in 1.0 mM aqueous solution of Nile blue in 0.2 M PBS of pH 7.4 at 10 cycles with scan rate of 0.1 Vs^{-1}

3.2. Characterization of poly-NB/MGCE sensor using standard potassium ferrocyanide system

The cyclic voltammetric response was recorded for the electro-oxidation of 1.0 mM potassium ferrocyanide with 1.0 M KCl as a supporting electrolyte with the scan rate 0.05 Vs^{-1} . The voltammograms obtained at bare GCE (dashed line) were with less sensitivity. However, in the same identical condition, poly-NB/MGCE (solid line) shows remarkable improvement in the electro-transfer process as well as reproducibility of the poly-NB/MGCE as shown in Fig. 2. The improved result obtained for the voltammetric response of potassium ferrocyanide at poly-NB/MGCE confirms that the surface property was significantly changed and also results prove electrocatalytic activity of the poly-NB/MGCE. The total active surface area available for reaction of species in solution can be estimated by the Randles-Sevcik equation (1) [23,24].

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

where, I_p refers to 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). For poly-NB/MGCE the electroactive surface area is maximum (0.02946 cm^2) as compared with bare GCE (0.02089 cm^2).

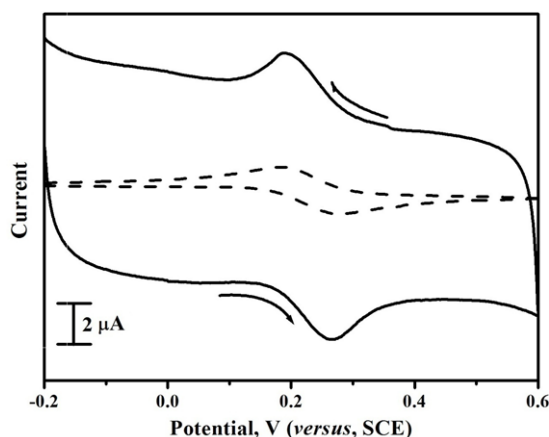


Fig. 2. Cyclic voltammograms of 1.0 mM potassium ferrocyanide at BGCE (dashed line) and poly-NB/MGCE (solid line) at scan rate of 0.05 Vs^{-1}

3.3. Electrochemical response of CC at poly-NB/MGCE

Fig. 3 shows the cyclic voltammetric responses recorded for 0.1 mM CC at BGCE and poly-NB/MGCE in 0.2 M PBS of pH 7.4 with the scan rate 0.05 Vs^{-1} . The electrochemical behaviour of CC at BGCE (dashed line) showed a poor voltammetric response due to slow electron transfer phenomenon and the oxidation peak potential occurred at 0.1659 V versus SCE. But, in the same identical condition poly-NB/MGCE (solid line) showed significant increment in current signals and the oxidation peak potential was observed at 0.2642 V. It can be observed that there is a slight positive shift in the oxidation potential [7]. Hence, this study reveals the excellent electrocatalytic activity and reproducibility of poly-NB/MGCE towards the electrochemical oxidation of CC. The mechanism of oxidation of both CC and HQ was shown in Scheme 2.

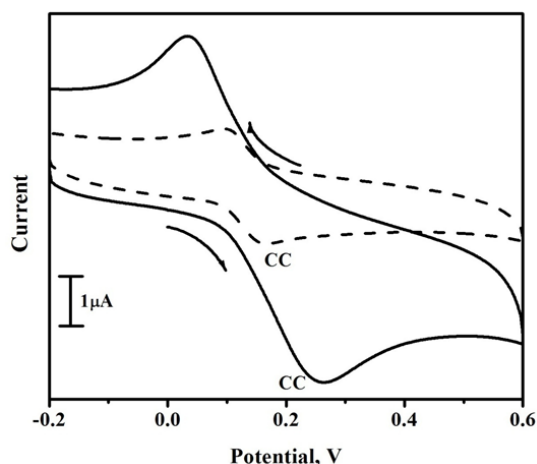


Fig. 3. Cyclic voltammograms for 0.1 mM CC at BGCE (dashed line) and poly-NB/MGCE (solid line) in 0.2 M PBS of pH 7.4 at scan rate 0.05 Vs^{-1}

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

The effect of scan rate for 0.1 mM CC in 0.2 M PBS of pH 7.4 was studied by CV technique at poly-NB/MGCE as shown in Fig. 4a. Poly-NB/MGCE obeys Randles–Sevcik equation and showed increase in the redox peak currents with increase in the scan rate with the small shifting of 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 0.02 to 0.1 Vs^{-1} as shown in Fig. 4b with the correlation coefficient (r^2) 0.9975 and 0.9995. The I_p versus square root scan rate ($\nu^{1/2}$) was plotted as shown in Fig. 4c with the correlation coefficient (r^2) 0.9987 and 0.9934. This result suggests that the electrode process is adsorption-controlled [25-27].

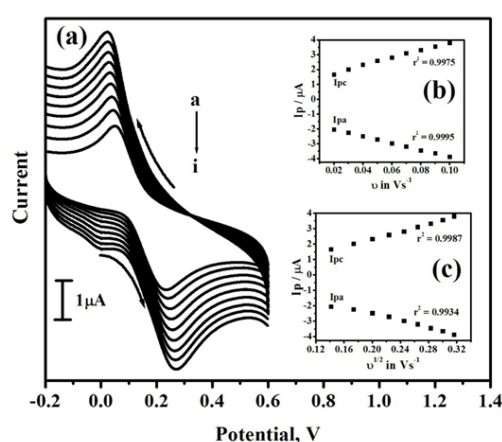


Fig. 4. (a) Cyclic voltammograms for 0.1 mM CC at poly-NB/MGCE in 0.2 M PBS of pH 7.4 at different scan rate (a-i; 0.02 Vs^{-1} , 0.03 Vs^{-1} , 0.04 Vs^{-1} , 0.05 Vs^{-1} , 0.06 Vs^{-1} , 0.07 Vs^{-1} , 0.08 Vs^{-1} , 0.09 Vs^{-1} and 0.1 Vs^{-1}); (b) Graph of peak current (I_p) versus scan rate (ν); (c) Graph of peak current (I_p) versus square root of scan rate ($\nu^{1/2}$)

3.5. Effect of CC concentration

The cyclic voltammograms were recorded for the electrocatalytic oxidation of CC with varying concentration in the range of 0.10 mM to 0.55 mM in 0.2 M PBS of pH 7.4 at scan rate 0.05 Vs^{-1} at poly-NB/MGCE as show in Fig. 5a. By increasing the concentration of catechol I_{pa} goes on increasing with shifting E_{pa} towards less positive side. The graph of I_{pa} versus concentration of CC justifies the reason of increase in anodic peak current, which is due to increase in the concentration of CC as shown in Fig. 5b. The graph showed almost straight line with good linearity with the linear regression equation $I_{pa}(\mu\text{A})=1.5759(C_{\text{omM/L})+1.442$, ($r^2=0.9986$). The LOD were calculated using the following equations, $\text{LOD}=3S/M$. Where, S is the standard deviation of the six blank measurements and M is the slope of the calibration curve [7-20]. The calculated detection limit of catechol at poly-NB/MGCE was found to be 53.2 nM.

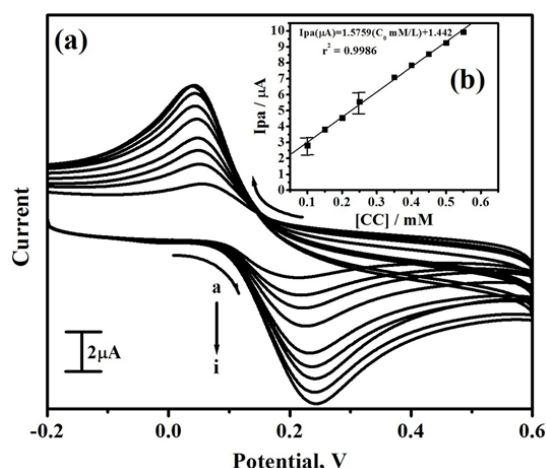


Fig. 5. (a) Cyclic voltammograms of CC in 0.2 M PBS solution of pH 7.4 at poly-NB/MGCE with different concentrations (a-i: 0.10 mM, 0.15 mM, 0.20 mM, 0.25 mM, 0.35 mM, 0.40 mM, 0.45 mM, 0.50 mM and 0.55 mM) at scan rate of 0.05 Vs⁻¹; (b) Graph of anodic peak current versus concentration of CC

3.6. Effect of pH value on the determination of CC at poly-NB/MGCE

Cyclic voltammetry was used to investigate the effect of solution pH value in the electrochemical oxidation behaviour of CC at poly-NB/MGCE. The Fig. 6a illustrates the peak current response of 0.1 mM CC at poly-NB/MGCE in the pH range of 5.5 to 8.0. The result shows, by increasing the pH of 0.2 M phosphate buffer the oxidation potential was shifted to more positive side.

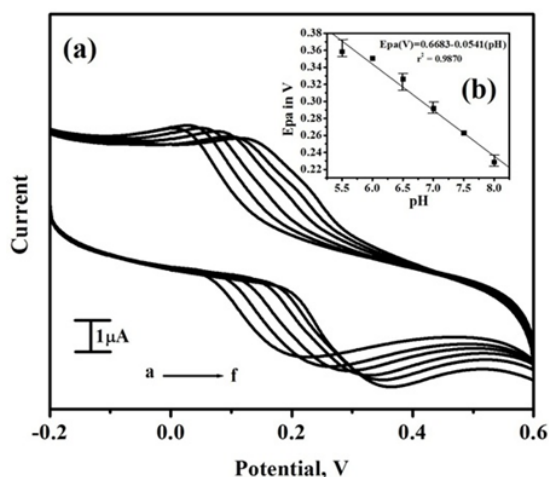


Fig. 6. (a) Cyclic voltammograms obtained for the oxidation of 0.1 mM CC at poly-NB/MGCE in 0.2 M PBS solution of different pH values (a-f: 5.5 to 8.0) at scan rate of 0.05 Vs⁻¹; (b) The effect of pH on the peak potential response of CC

The anodic peak potential (E_{pa}) vs. pH graph clearly indicates that the catalytic oxidation potential depends linearly on the pH with slope of $E_{pa}(V)=0.6683-0.0541(pH)$ ($r^2=0.9870$) as shown in Fig. 6b and signifying that there are an equal number of protons and electrons involved in the mechanism. This is consistent with that reported in literature [28,29].

3.7. Electrocatalytic oxidation of HQ at poly-NB/MGCE

The cyclic voltammograms were recorded for the oxidation of 0.1 mM HQ at BGCE (dashed line) and poly-NB/MGCE (solid line) in 0.2 M PBS of pH 7.4 with the scan rate 0.05 Vs^{-1} as shown in the Fig.7 respectively. At BGCE the HQ showed the oxidation peak potential i.e., broad voltammetric response and less sensitive the anodic peak potential located at 0.1196 V. However, in the same identical condition the poly-NB/MGCE showed the oxidation peak potential was shifted towards positive side with increment in current signals and the anodic peak potential of HQ was observed at 0.1452 V.

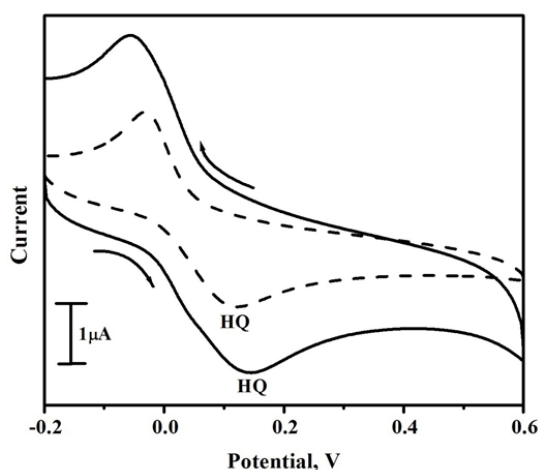


Fig. 7. Cyclic voltammograms for 0.1 mM HQ at BGCE (dashed line) and poly-NB/MGCE in 0.2 M PBS of pH 7.4 at scan rate 0.05 Vs^{-1}

This enhancement of current response reflects the electrocatalytic activity of the fabricated poly-NB/MGCE towards the electrochemical oxidation of HQ.

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

The effect of applied potential scan rate for 0.1 mM HQ in 0.2 M PBS of pH 7.4 was examined by CV technique at poly-NB/MGCE as shown in Fig. 8a. The applied scan rate was proportional to the redox peak current, with a small shift in the anodic peak potential (E_{pa}) towards more positive side and cathodic peak potential (E_{pc}) to the less negative side. The graph I_p versus v (correlation coefficient (r^2) 0.9951 and 0.9979) and I_p versus $v^{1/2}$ (correlation coefficient (r^2) 0.9992 and 0.9982) was plotted in the range from 0.02 Vs^{-1} to 0.1 Vs^{-1} as shown

in Fig. 8b and Fig. 8c. As the obtained correlation coefficient is more linear with I_p versus $v^{1/2}$ suggesting electrode phenomenon was diffusion-controlled [25].

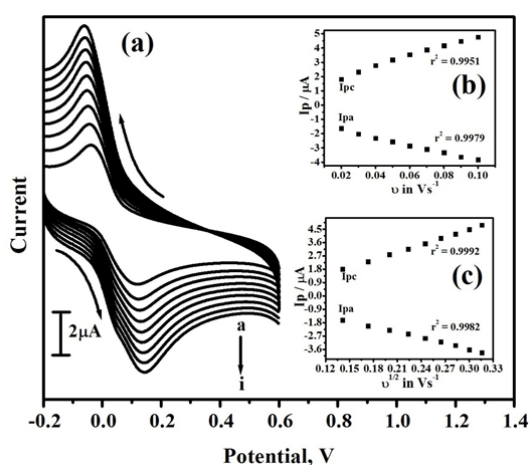


Fig. 8. (a) Cyclic voltammograms for 0.1 mM HQ at poly-NB/MGCE in 0.2 M PBS of pH 7.4 at different scan rate (a-i; 0.02 Vs^{-1} , 0.03 Vs^{-1} , 0.04 Vs^{-1} , 0.05 Vs^{-1} , 0.06 Vs^{-1} , 0.07 Vs^{-1} , 0.08 Vs^{-1} , 0.09 Vs^{-1} and 0.1 Vs^{-1}); (b) Graph of peak current (I_p) versus scan rate (v); (c) Graph of peak current (I_p) versus square root of scan rate ($v^{1/2}$)

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

$v/V s^{-1}$	Catechol (CC)		Hydroquinone (HQ)	
	$\Delta E_p/mV$	k^0/s^{-1}	$\Delta E_p/mV$	k^0/s^{-1}
20	185.1	0.076	157.4	0.104
30	199.7	0.097	163.4	0.146
40	209.6	0.115	174.1	0.173
50	220.4	0.127	177.2	0.209
60	225.4	0.144	183.0	0.234
70	231.2	0.157	187.0	0.261
80	236.1	0.170	194.8	0.273
90	242.2	0.179	198.8	0.294
100	247.7	0.186	204.7	0.305

The heterogeneous rate constant (k^0) values was determined from the experimental peak potential difference (ΔE_p) data's, eq. (2) was used for such voltammograms whose ΔE_p values are greater than 10 mV [30,26].

$$\Delta E_p = 201.39 \log(v/k^0) - 301.78 \quad (2)$$

From the experimental ΔE_p values as shown in Table 1 and eq. (2); the values of the k^0 for the CC and HQ oxidation was determined. All the parameters are tabulated in Table 1.

3.9. Effect of HQ concentration

Fig. 9a shown the electrocatalytic oxidation of HQ was conducted by varying its concentration in the range 0.15 mM to 0.45 mM at poly-NB/MGCE. A linear relationship was established between the I_{pa} and concentration of HQ as shown in the Fig. 9b, with a linear regression equation of $I_{pa}(\mu A)=17.5121(C_0\text{mM/L})+1.2457$, ($r^2=0.9987$).

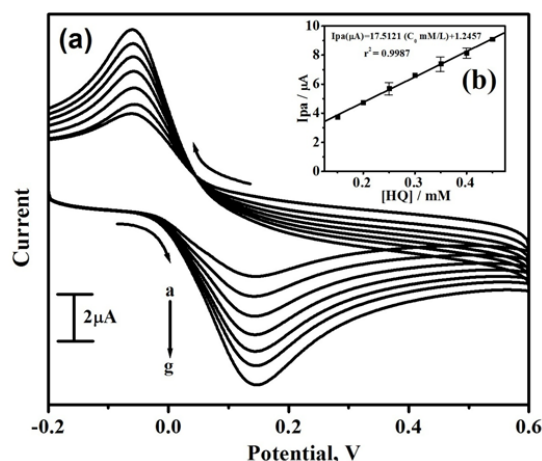


Fig. 9. (a) Cyclic voltammograms of HQ in 0.2 M PBS solution of pH 7.4 at poly-NB/MGCE with different concentrations (a-g: 0.15 mM, 0.20 mM, 0.25 mM, 0.30 mM, 0.35 mM, 0.40 mM and 0.45 mM) at scan rate of 0.05 Vs⁻¹; (b) Graph of anodic peak current versus concentration of HQ

Table 2. Comparison of detection limits for CC and HQ with different classical methods and electrodes

Working electrodes	Limit of detection		Methods	Refs.
	CC	HQ		
Poly(brilliant blue) MCPE	0.068 μM	0.046 μM	CV	[7]
Poly(phenylalanine)	0.7 μM	1 μM	DPV	[29]
Boron-doped graphene	0.2 μM	0.3 μM	DPV	[31]
PANI/MnO ₂ -GCE	0.15 μM	0.12 μM	DPV	[32]
SPC electrode	0.05 μM	0.05 μM	SWV	[33]
LRG/GCE	0.8 μM	0.5 μM	DPV	[34]
Poly(brilliant cresyl blue)/GCE	0.05 μM	0.06 μM	DPV	[35]
MWNT/GCE	0.20 μM	0.75 μM	DPV	[36]
(LDHf/GCE)	1.2 μM	9 μM	DPV	[37]
Co ₃ O ₄ /MWCNTs /GCE	8.5 μM	5.6 μM	DPV	[39]
rGO-Fe ₃ O ₄ -Au /GCE	0.02 μM	0.17 μM	DPV	[40]
AuPd/rGO/GCE	0.1 μM	0.01 μM	DPV	[41]
AuNPs/CNCs/GCE	0.0986 μM	0.0254 μM	DPV	[42]
[Cu(Sal-β-Ala) (3,5-DMPz) ₂]/ GCE	3.5 μM	1.46 μM	DPV	[43]
poly-NB/MGCE	53.2 nM	31.5 nM	CV	Present work

The limit of detection for HQ at poly-NB/MGCE was calculated in the lower concentration range was found to be 31.5 nM by CV technique. The detection limits reported for different classical methods and electrodes are tabulated in Table 2. This method was better compared to other reported methods [7,29,31-37,39-43].

3.10. Effect of solution pH on the oxidation of HQ

The Fig. 10a illustrate the effect of phosphate buffer pH value on the cyclic voltammetric determination of 0.1 mM HQ at poly-NB/MGCE. The oxidation peak potential shifts to a more negative potential with increasing pH. The E_{pa} vs. pH graph clearly indicated the depends of E_{pa} with pH in the range of 5.5-8.0 with a slope of $E_{pa}(V)=0.5053-0.0510(pH)$ ($r^2=0.9962$) as shown in Fig. 10b. This involves an equal number of electron and proton transfer reaction [38,17].

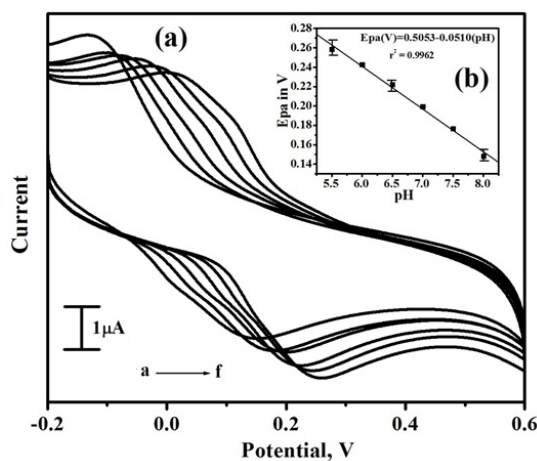


Fig. 10. (a) Cyclic voltammograms obtained for the oxidation of 0.1 mM HQ at poly-NB/MGCE in 0.2 M PBS solution of different pH values (a-f: 5.5 to 8.0) at scan rate of 0.05 Vs^{-1} ; (b) The effect of pH on the peak potential response of HQ

3.11. Simultaneous determination of CC and HQ

The cyclic voltammograms recorded for the simultaneous investigation of 0.1 mM of CC and HQ in 0.2 M PBS of pH 7.4 at scan rate of 0.05 Vs^{-1} . The Fig. 11 showed at BGCE (dashed line) the voltammetric response of the oxidation of these two molecules is with a low current signal and exhibited the poor sensitivity. The oxidation of CC and HQ was appeared at 0.1629 V (E_{pa}) and 0.0655 V (E_{pa}) respectively. However, in the same identical condition the voltammogram obtained for the poly-NB/MGCE is with a higher current signal with improved sensitivity and showing well separated anodic peaks. The electroanalytical anodic peak of CC was obtained at 0.1649 V (E_{pa}) and HQ was found to be at 0.0615 V (E_{pa}). The distance between two peak of CC and HQ was about 0.1034 V by cyclic voltammetry technique. This result was

more than enough to make out and resolve CC in the presence of high concentration of HQ at poly-NB/MGCE.

The differential pulse voltammetry (DPV) was used due to its high sensitivity and nonappearance of background current. The Fig. 12 shows the DPV curve obtained for the mixture of 0.1 mM of CC and HQ in 0.2 M PBS of pH 7.4. For poly-NB/MGCE the selective oxidation was observed at 0.0291 for CC and 0.1097 V for HQ, the peak separation were 0.0806 V. So, the poly-NB/MGCE shows sensitive and simultaneous separation for the oxidation of CC and HQ. This result was good enough to make out and resolve oxidation peak of CC in the presence of HQ at poly-NB/MGCE.

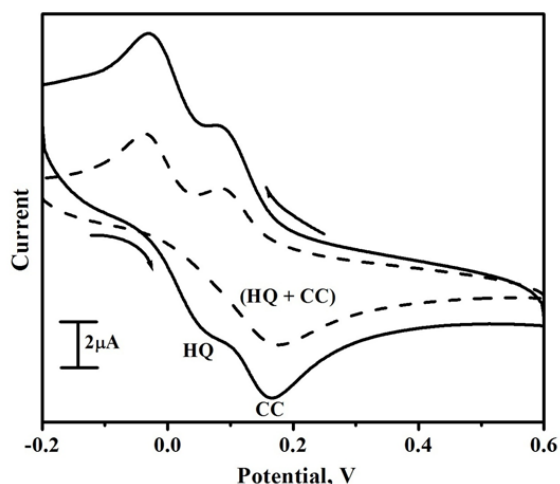


Fig. 11. Cyclic voltammograms for simultaneous determination of 0.1 mM CC and 0.1 mM HQ at BGCE (dashed line) and poly-NB/MGCE (solid line) at scan rate of 0.05 Vs^{-1}

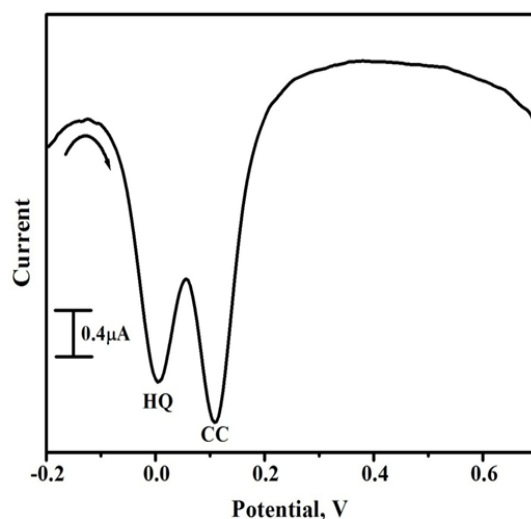


Fig. 12. Differential pulse voltammogram obtained for 0.1 mM CC and 0.1 mM HQ in 0.2 M PBS solution of pH 7.4 at poly-NB/MGCE

4. CONCLUSION

In the present work poly-NB/MGCE was used to study the electrochemical oxidation of both CC and HQ individually and simultaneously in 0.2 M phosphate buffer solution (PBS) of pH 7.4 by using CV and DPV techniques. The lower limit of detection of CC and HQ was found to be 53.2 nM and 31.5 nM by both CV and DPV techniques respectively. In the overall, the fabricated electrode showed good sensitivity, selectivity, linearity and reproducibility for the determination biomolecules.

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