Full Paper

Electrochemical Investigation of Catechol and Hydroquinone at Poly(o-Phenylenediamine) Modified Carbon Paste Electrode: A Voltammetric Study

K. Chetankumar and B. E. Kumara Swamy[*]

Department of P.G studies and Research in Industrial chemistry, kuvempu university, Jnanasahyadri, Shankaraghatta -577451, Shivamogga (D), Karnataka, India

[*]Corresponding Author, Tel.: +918282256225; Fax: +918282256255

E-Mail: kumaraswamy21@yahoo.com

Abstract- A simple and highly selective electrochemical method for the investigation of catechol (CC) and hydroquinone (HQ) was developed on the surface bare carbon paste electrode (BCPE) modified with electropolymerized thin film of o-Phenylenediamine (o-PD) by using cyclic voltammetric technique. Electrochemical measurements were carried by using both cyclic voltammetric (CV) and differential pulse voltammetric (DPV) techniques at poly(o-PD) modified carbon paste electrode (MCPE). The proposed modified electrode shows adsorption-controlled process and exhibited a good limit of detection for CC and HQ was 1.1 and 2.1 µM respectively. In order to study the selectivity of the electrode, interference study was carried out by using DPV technique. Therefore, poly(o-PD)/MCPE showed excellent electrocatalytic behavior for the simultaneous electrochemical investigation of CC and HQ.

Keywords- o-Phenylenediamine, Catechol, Electropolymerization, Cyclic voltammetry, Hydroquinone

1. INTRODUCTION

Electrochemical method has been recognized as a fast, cost-effective and simple method of analysis. In the recent year's design and construction of electrochemical sensors gained more

attention towards in the field of electroanalytical chemistry and the developed sensor is purely based on the construction of a working electrode [1,2].

The two phenolic compounds catechol (1, 2-dihydroxybenzene) and hydroquinone (1,4-dihydroxybenzene) are ubiquitous in nature and they have been widely exploited in cosmetics, medicines, and so forth [3,4]. These dihydroxybenzene isomer compounds are considered environmental pollutants by the CONAMA [5], due to their high toxicity and low degradability in the environment [6]. However, the excessive intake of CC and HQ may lead to different diseases including but not limited to fatigue, headache, and liver function lesion [7,8]. The simultaneously sensing CC and HQ is quite difficult because of their redox peak potentials largely overlap using conventional electrodes [9,10]. Several methods to detect CC and HQ, including voltammetry [11], fluorescence [12], gas chromatography-mass spectrum [13], calorimetry [14] etc. Among these methods, electrochemical methods having much more attention because of due to their advantages of low cost, high sensitivity, good selectivity, time-saving [15]. Therefore, in the electrochemical methods more focus on the simultaneous investigation of CC and HQ [16,17].

In recent decade, polymer-modified electrodes (PMEs) have received more attention [18,19] due to because of their good stability, homogeneity, and reproducibility in electrochemical deposition and strong adherence to electrode surface [20]. o-Phenylenediamine (1.2-Diaminobenzene) was an organic compound with the molecular formula $C_6H_4(NH_2)_2$. It is isomeric with p-phenylenediamine and m-phenylenediamine. This aromatic diamine is an important precursor to many heterocyclic compounds [21,22]. The films of poly(o-PD) electropolymerized on carbon paste electrodes (CPE) show very high electrocatalytic activity [23].

The main aim of this study was to design a selective and sensitive sensor for the simultaneous investigation of CC and HQ at physiological pH by using electropolymerized film of o-Phenylenediamine (o-PD) by using both CV and DPV techniques.

2. EXPERIMENTAL

2.1. Instrumentation and chemicals

All Electrochemical experiments was performed by using CHI-660c model (CH Instrument-660 electrochemical workstation). A conventional three-electrode system was used. Where a poly(o-PD)/MCPE as a working electrode, a platinum wire as counter electrode and saturated calomel electrode (SCE) as a reference electrode.

o-Phenylenediamine and silicone oil was obtained from Himedia chemicals. The stock solution of o-PD were prepared in double distilled water. CC and HQ obtained from Merck chemical, the stock solution (25×10^{-4} M) was prepared in double distilled water. Disodium hydrogen phosphate and sodium dihydrogen phosphate purchased from Himedia chemicals.

Graphite powder purchased from Merck chemicals and all reagent were of extra pure analytical grade.

2.2. Preparation of bare and poly(o-PD)/MCPE

The BCPE was done by hand mixing of graphite powder and silicone oil (70: 30%) in a mortar for about 40 min obtain a homogeneous mixture. The paste was packed into the homemade Teflon cavity (3 mm internal diameter) and electrical contact was established with copper wire.

The MCPE was constructed by, electropolymerization of o-PD on the surface of CPE was carried out by placing of 1.0 mM (o-PD) solution along with 0.1 M NaOH as a supporting electrolyte in the electrochemical cell. The potential sweeping was maintained b/w -0.4 to +1.0 V at sweep rate 0.1 Vs^{-1} for 20 cycles, later the electrode rinsed with double distilled water because to remove unreacted o-PD and the modified electrode was used for further electrochemical investigations.

3. RESULTS AND DISCUSSIONS

3.1. Electropolymerization of o-PD on the surface of CPE

Electropolymerization of o-PD was carried out on the surface of CPE (scheme 1) by using CV technique in the presence of 0.1 M NaOH as supporting electrolyte. The electrode was treated with cyclic scanning between -0.4 to +1.0 V at the scan rate of 0.1 Vs^{-1}, for 20 multiple cycles as shown in Fig. 1a. The peak current goes on increases with increase in cycle indicates the growth of thin polymeric film on the surface of the CPE [24]. The thickness of polymeric film affects the electrocatalytic activity of CPE. The coating of o-PD was done by varying the number cycles on the surface of the CPE (from 5-25 multiple cycles) and electrocatalytic activity towards the oxidation of CC (10 µM) at phosphate buffer solution (PBS) of pH 7.4. Fig. 1b shows the number of varying polymerization cycles, in that twenty cycles shows good current enhancement for both anodic and cathodic peak current [25-27]. Therefore, 20 cycles chosen for the optimum for the polymerization of o-Phenylenediamine.
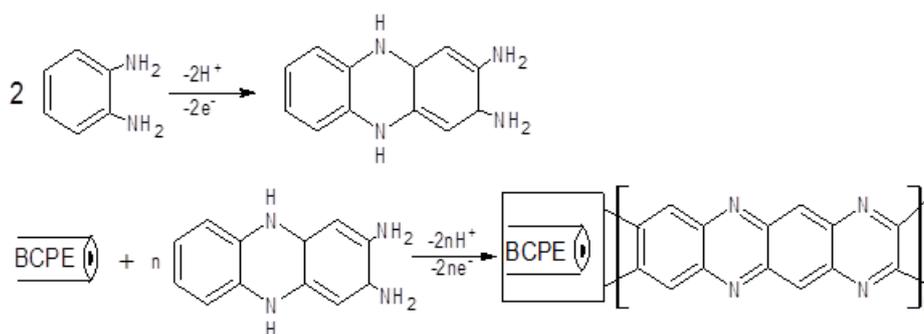
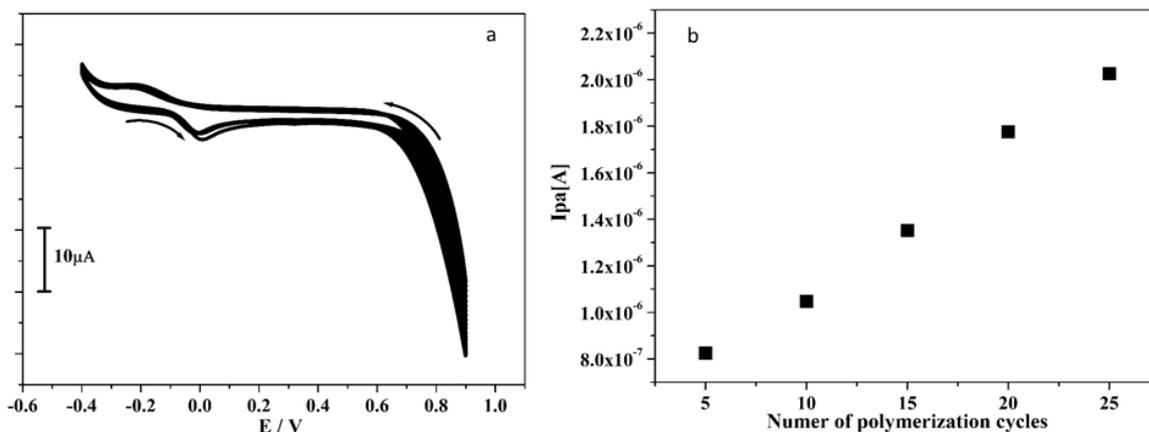**Scheme 1.** Schematic Electropolymerization of o-PD

Fig. 1. a) Electropolymerization of 1.0 mM o-PD on the surface of CPE in presence of 0.1 M NaOH with scan rate 0.1 Vs^{-1} at 20 multiple cycles; **b)** Graph of Ipa versus a number of varying polymerizartion cycles

3.2. Electrochemical behaviour of CC at poly (o-PD)/MCPE

Fig. 2 shows the recorded cyclic voltammograms (CVs) for the 10 µM CC for BCPE (dashed line) and poly(o-PD)/MCPE (solid line) in 0.2 M PBS at pH 7.4 with sweep rate 0.05 Vs^{-1} by CV technique.

Catechol   1,2 Benzoquinone
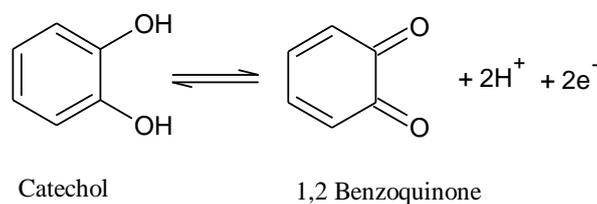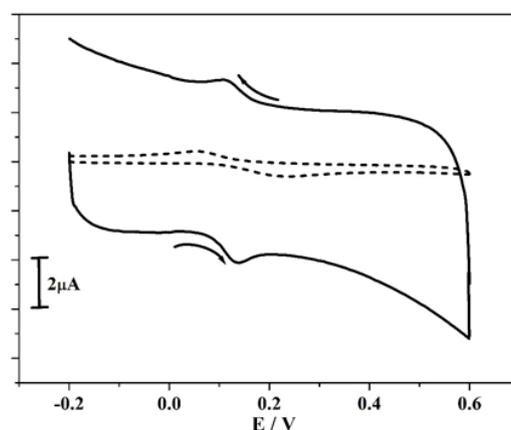
Scheme 2. Oxidation mechanism of CC

Fig. 2. Voltammograms recorded at 10 µM CC at BCPE (dashed line) and poly (o-PD)/MCPE (solid line) at scan rate of 50 mVs^{-1} using 0.2 M PBS (pH 7.4)

At BCPE (dashed line) the CC shows redox peak potentials with poor response of anodic and cathodic peak potential, the ΔE_p for BCPE is 0.176. In the same condition, the poly(o-PD)/MCPE (solid line) shows magnificent enhancement in peak current signals and the oxidation potential was observed at 0.041 V. Therefore, difference between ΔE_p for BCPE was greater than ΔE_p value for MCPE, lower the ΔE_p value higher will be the electron transfer rate [28]. Therefore, the poly(o-PD)/MCPE gives proof for the electrocatalytic effect of the proposed electrode. Scheme-2 gives the oxidation mechanism for CC.

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

In order to study the kinetics of the electrode process by varying the scan rate (ν) at poly(o-PD)/MCPE by using a CV technique. Fig. 3a shows the CVs recorded for 10 µM CC at varied scan rates (0.07 to 0.16 Vs^{-1}) in presence of 0.2 M PBS (pH 7.4). It can be seen that the peak currents of CC goes on increases linearly with increasing the scan rates. The anodic peak potential (E_{pa}) of CC shifted positively and cathodic peak potential (E_{pc}) small shifted towards negative side. Fig. 3b shows the graph of anodic peak current (I_{pa}) versus scan rate (ν) was plotted and inset the Fig. 3b shows the plot of I_{pa} versus square root of scan rate ($\nu^{1/2}$). The obtained graph gives good linearity and the correlation coefficient value was found at $R^2=0.9983$ and $R^2=0.9964$. Therefore, the modified electrode indicates the more adsorption-controlled process [29].
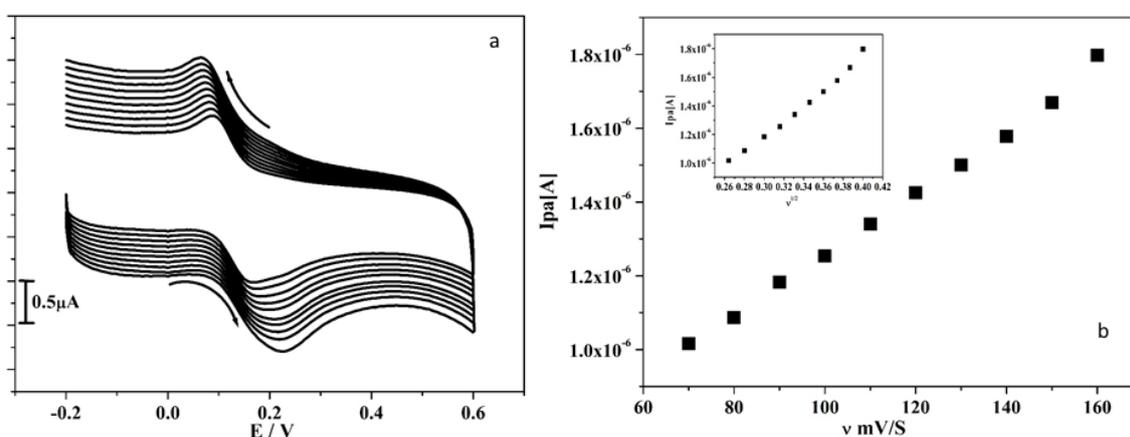

Fig. 3. a) Cyclic voltammograms of 10 µM CC at poly(o-PD)/MCPE with different scan rates (70-160 mVs^{-1}) using 0.2 M PBS (pH 7.4); **b)** Graph of I_{pa} *vs.* scan rate (ν). Inset the figure is graph of I_{pa} *vs.* square root of scan rate ($\nu^{1/2}$) of 10 µM CC in 0.2 M PBS (pH 7.4)

3.4. Effect of concentration on CC

The effect of concentration on CC recorded at poly(o-PD)/MCPE in 0.2 M PBS of pH 7.4 by using CV technique. Fig. 4a depicts the increasing concentration of CC from 10-90 µM at poly(o-PD)/MCPE in 0.2 M PBS of pH 7.4 with sweep rate 0.05 Vs^{-1}. The cathodic and anodic

peak current goes on increasing with increase in the concentration of CC and the E_{pc} and E_{pa} shifts slightly towards the negative and positive side. Fig. 4b shows the plot of I_{pa} versus concentration of CC, it shows the good linearity with correlation coefficient value R^2=0.9989. The limit of detection (LOD) and limit of quantification (LOQ) were calculated by using equation (1) and (2) [30]. Moreover, the poly(o-PD)/MCPE exhibited good LOD and LOQ for CC 1.1 µM and 4.6 µM respectively. Comparison of different modified electrode for the investigation of CC were depicted in table 1.

LOD=3S/M   (1)

LOQ=10S/M   (2)

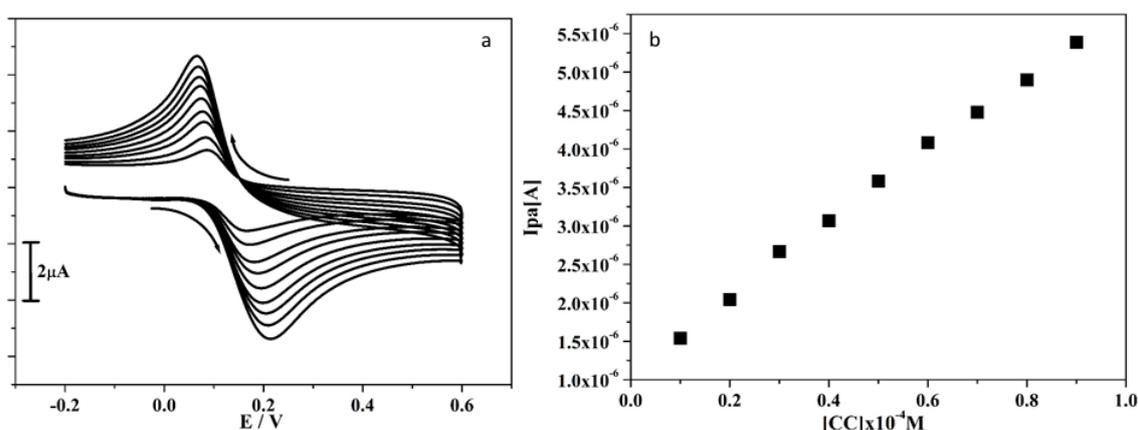where M is the slope and S is the standard deviation.

Fig. 4. a) Cyclic voltammograms of CC at poly(o-PD)/MCPE with different concentrations (10-90 µM) using 0.2 M PBS (pH 7.4); **b)** Graph of I_{pa} *vs.* concentration of CC at poly(o-PD)/MCPE in 0.2 M PBS (pH 7.4)

Table 1. Comparison of the poly(o-PD)/MCPE electrode with other modified electrodes

Working electrode	LOD (µM)		Method	Ref.
	CC	HQ		
PNR/MCPE	6.4	4.9	CV	[16]
RGO-MWCNTs/GC	1.8	2.6	CV	[33]
Poly(calmagite) MCPE	1.75	2.75	CV	[34]
Poly(BGA)/MCPE	2.55	3.84	CV	[36]
Poly(oPD)/MCPE	1.1	2.1	CV	This work

3.5. Influence of pH on the oxidation CC and HQ

The influence of pH (6.2-7.8) on the peak potential of CC and HQ at poly (o-PD) was also investigated by CV technique. Fig. 5a and Fig. 5b depict the CVs recorded for 10 µM CC and 10 µM HQ in presence of 0.2 M PBS with sweep rate 0.05 Vs^{-1}. It can be seen that as pH increases the peak potential shifts negative side, this indicates that proton was directly involving in the electrochemical redox process [31]. Inset Fig. 5a and Fig. 5b show the relationship between E_{pa} and pH value of both CC and HQ. By considering the sensitivity and selectivity, pH 7.4 was chosen for further electrochemical investigations of both CC and HQ.
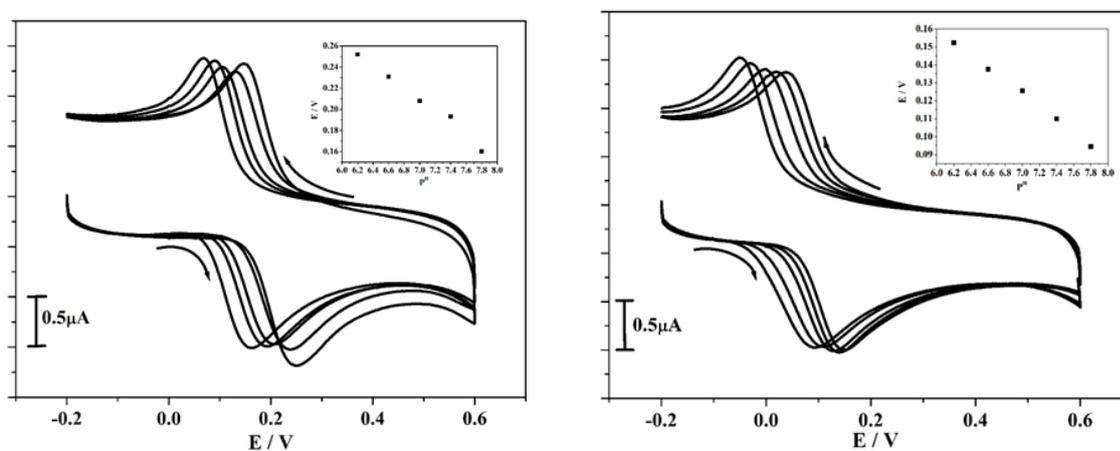

Fig. 5. a) Series of voltammograms recorded for CC at poly(o-PD)/MCPE in presence of different pH. Inset the figure is graph of E_{pa} *vs.* pH, **b)** Series of voltammograms obtained for HQ at poly(o-PD)/MCPE in presence of different pH. Inset the figure is Graph of E_{pa} *vs.* pH

3.6. Electrochemical behavior of HQ at poly (o-PD) MCPE

The electrochemical behavior of HQ at BCPE and poly(o-PD)/MCPE was studied by CV technique. Fig. 6 reveals the obtained CVs obtained for 10 µM HQ for both BCPE (dashed line) and poly(o-PD)/MCPE (solid line) in presence of 0.2 M PBS at pH 7.4 with sweep rate 0.05 Vs^{-1}. At BCPE, HQ was observed with low peak current signal and for MCPE HQ shows good enhancement in peak current signals compared to BCPE. The ΔE_p for BCPE is 0.075 and ΔE_p for MCPE is 0.056, the difference between ΔE_p for MCPE is less than ΔE_p for BCPE. When ΔE_p is lower electron transfer rate is higher. Therefore, enhancement in current signal gives the evidence for the electrocatalytic effect of poly(o-PD)/MCPE. Scheme 3 shows the oxidation mechanism of HQ.
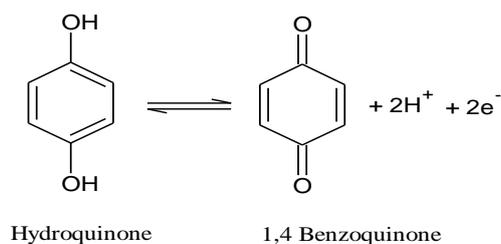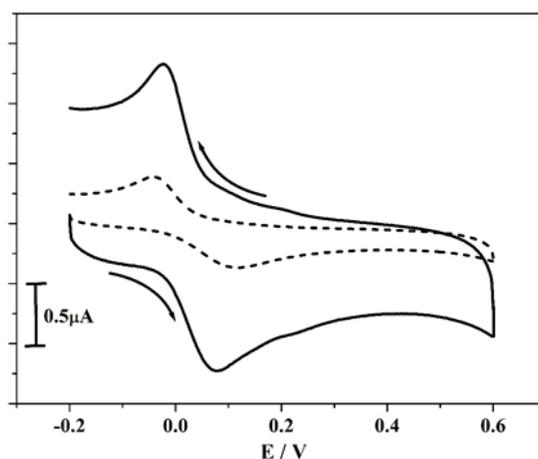
Scheme 3. Oxidation mechanism of HQ

Fig. 6. Cyclic voltammograms of 10 μM HQ at BCPE (dashed line) and poly(o-PD)/MCPE (solid line) at scan rate of 50 mVs^{-1} using 0.2 M PBS (pH 7.4)

3.7. Effect of sweep rate on the peak current of HQ

Fig. 7a reveals the CVs recorded for the 10 μM HQ at varied scan rates (50 mVs^{-1} to 150 mVs^{-1}) in presence of 0.2 M PBS pH 7.4. The peak current goes on increases with increasing the sweep rates and E_{pa} and E_{pc} of HQ slightly shifted towards opposite side (negative and positive side).
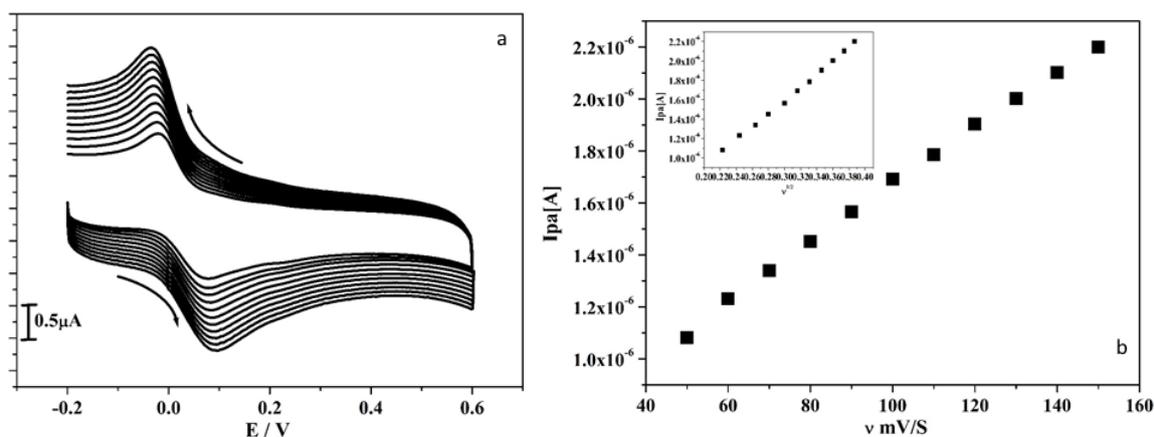

Fig. 7. a) Cyclic voltammograms of 10 μM HQ at poly(o-PD)/MCPE with different scan rates (50-150 mVs^{-1}) using 0.2 M PBS (pH 7.4); **b)** Graph of I_{pa} *vs.* scan rate (ν). Inset the figure is I_{pa} *vs.* square root of scan rate (ν$^{1/2}$)

In order to investigate the electrode kinetics by plotting the graph of I_{pa} *vs.* sweep rate (v) shown in Fig. 7b. Inset the Fig.7b shows the graph of I_{pa} versus square root of the sweep rate ($v^{1/2}$) and obtained graph gives good linearity with coefficient value $R^2=0.9994$ and $R^2=0.9987$ so poly(o-PD)/MCPE shows the adsorption-controlled process.

3.8. Effect of HQ concentration at poly(o-PD)/MCPE

The effect of HQ concentration was recorded at poly(o-PD)/MCPE in presence of 0.2 M PBS (pH 7.4) with sweep rate 0.05 Vs^{-1} by using CV technique and the concentration of HQ was varied from 10-90 µM. Fig. 8a reveals the CVs obtained for HQ at varied concentrations. As a result, the concentration of HQ is varied peak current goes on increases and the E_{pa} and E_{pc} considerably shift towards the positive and negative side. Fig. 8b shows the relationship between I_{pa} and concentration of HQ and it shows good linearity with correlation coefficient value found to be $R^2=0.9991$. The LOD and LOQ for HQ in the lower range was found at 2.1 and 10.5 µM at poly(o-PD)/MCPE and comparison of other different electrochemical sensors for the investigation of HQ were shown in Table 1.
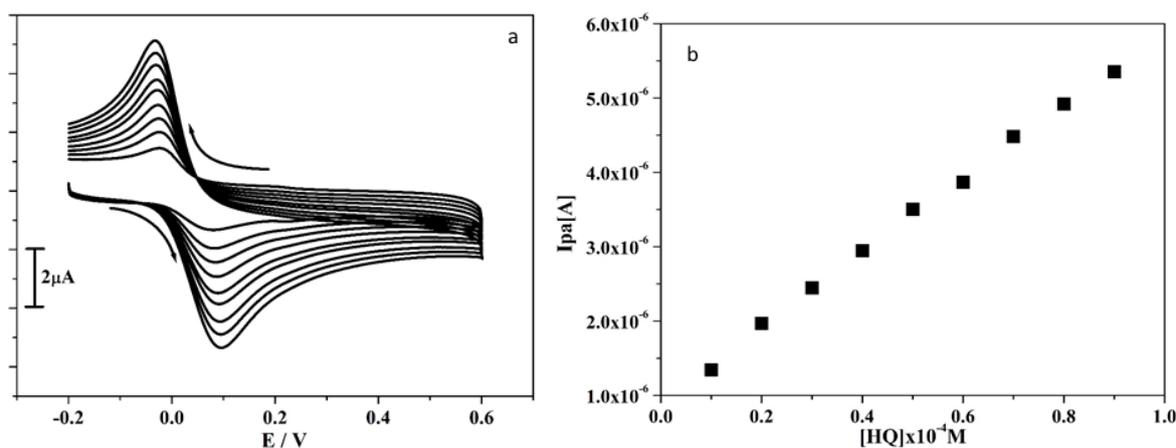

Fig. 8. a) Voltammograms recorded at poly(o-PD)/MCPE with varied concentration of HQ (10-90 µM) using 0.2 M PBS (pH 7.4); **b)** Graph of I_{pa} *vs.* concentration of HQ

3.9. Simultaneous investigation of binary mixture CC and HQ at poly(o-PD) MCPE

The main aim of our present work is simultaneous investigation CC and HQ at poly(o-PD)/MCPE. In the binary mixture CC and HQ have nearly the same oxidation potentials. Therefore, the simultaneous determination of these dihydroxybenzene isomers gives a voltammetric response with lower sensitivity and less selectivity at BCPE. Fig. 9 gives the CVs recorded for binary mixture of CC and HQ (10 µM) in 0.2 M PBS with scan rate 0.05 Vs^{-1} at both BCPE (dashed line) and poly(oPD)/MCPE (solid line). Inset the Fig. 9 shows the simultaneous investigation of CC and HQ by using DPV technique. By both CV and DPV technique BCPE is failed to demonstrate the peaks for CC and HQ, whereas the modified

electrode showed a well distinct anodic peak of CC is 0.15 V and HQ at 0.059 V with great enhancement in redox peak current compared to BCPE. Therefore, the poly(oPD)/MCPE act as a good sensor for the simultaneous investigation CC and HQ.
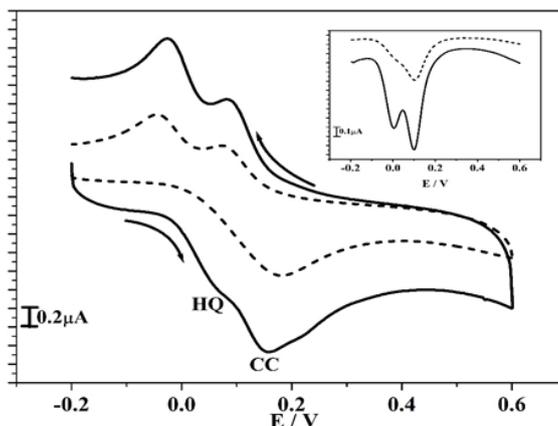

Fig. 9. Cyclic voltammograms obtained for mixture of CC (10 µM) and HQ (10 µM) at bare (dashed line) and poly(o-PD)/MCPE (solid line) and inset the figure DPVs obtained for mixture of CC and HQ (10 µM) at bare (dashed line) and poly(o-PD)/MCPE (solid line) with the scan rate of 50 mVs^{-1} using 0.2 M PBS (pH 7.4)

3.10. Interference study

The interference study was carried out by DPV technique at poly(oPD)/MCPE in presence of 0.2 M PBS with the sweep rate of 0.05 Vs^{-1}. In that concentration of one analyte was changed and while keeping the other analyte is constant.
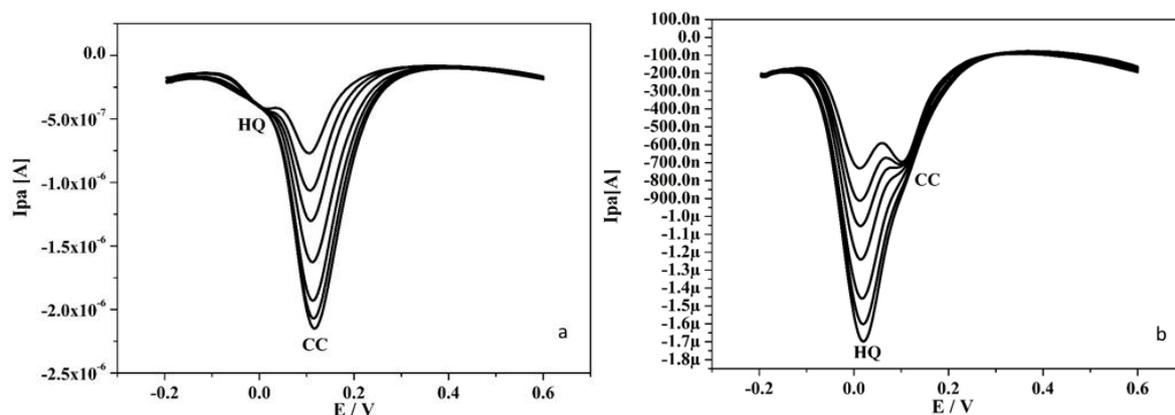

Fig. 10. a) DPVs of CC with varied concentration (50-350 µM) in presence of HQ (50 µM) at poly(o-PD)/MCPE in 0.2 M PBS (pH 7.4); **b)** DPVs of HQ with different concentration (50-350 µM) in presence of CC (500 µM) at poly(o-PD)/MCPE in 0.2 M PBS (pH 7.4)

From Fig. 10a it can be seen that HQ was kept constant (50 µM) and peak current of CC increases because of the increase in the concentration of CC (50-350 µM). Similarly, by

varying the HQ concentration (50-350 µM) peak current goes on increases with constant CC (50 µM) shown in Fig. 10b. Therefore, the modified electrode exhibited good selectivity and sensitivity for the determination of CC and HQ.

3.11. Practical sample analysis

In order to evaluate the proposed method in the practical analysis were investigated by CV technique and local tap water was used for the analysis. The standard addition method [32,33] was followed and obtained results are listed in Table 2. This results indicated that the proposed modified electrode could be efficient for the investigation of CC and HQ.

Table 2. Recoveries of CC and HQ in local tap water sample at the poly(o-PD)/MCPE

Sample	Compound	Added (µM)	Founded (µM)	Recovery (%)
Tap water	CC	20	20.07	103.93
		30	27.85	92.19
		40	39.8	99.55
		50	52.5	105
	HQ	20	19	95.41
		30	27.4	91.33
		40	35	87.5
		50	42	84.01

4. CONCLUSION

This present study exhibits a good approach for the development of a novel voltammetric sensor for CC and HQ at poly(o-PD) coating. The modified electrode showed good selectivity, sensitivity, fast electron transfers and separated oxidation peaks towards CC and HQ which are undistinguishable at BCPE and the electrode process was found to be adsorption-controlled. In addition, compared to other modified electrodes poly(o-PD)/MCPE shows good LOD and LOQ were obtained for catechol and hydroquinone. Therefore, proposed poly(o-PD)/MCPE exhibited good electrocatalytic response and it can be applied for the investigation of other biomolecules.

REFERENCES

[1]　O. Saglam, D. G. Dilgin, B. Ertek, and Y. Dilgin, Mater. Sci. Eng. C 60 (2016) 156.

[2]　T. S. Sunil Kumar Naik, and B. E. Kumara Swamy, J. Anal. Bioanal. Electrochem. 9 (2017) 424.

[3]　Q. H. Guo, M. Zhang, G. Y. Zhou, L. Zhu, Y. Feng, H. D. Wang, B. Y. Zhong, and H. Q. Hou, J. Electroanal. Chem. 760 (2016) 15.

[4]　A. Anil Kumar, B. E. Kumara Swamy, P. S. Ganesh, T. Shobha Rani, and G. Venkata Reddy, J. Electroanal. Chem. 799 (2017) 505.

[5]　Conselho Nacional do Meio Ambiente (CONAMA, Brasil). Resolução nº 20, de 18 de Junho de 1986, Dispõe sobre a classificação das águas doces, salobras e salinas do Território Nacional Diário Oficial da União de 30 de Junho de (1986).

[6]　G. H. Ribeiro, L. M. Vilarinho, T. S. Ramos, A. L. Bogado, and L. R. Dinelli, Electrochim. Acta 176 (2015) 394.

[7]　L. Zhao, J. Yu, S. Yue, L. Zhang, Z. Wang, P. Guo, and Q. Liu, J. Electroanal. Chem. 808 (2018) 245.

[8]　G. Mo, X. He, C. Zhou, D. Ya, J. Feng, C. Yu, and B. Deng, Sens. Actuators B 266 (2018) 784.

[9]　M. S. Tsai, C. J. Lu, and P. G. Su, J. Mater. Chem. Phys. 215 (2018) 293.

[10]　H. Jiang, S. Wang, W. Deng, Y. Zhang, Y. Tan, Q. Xie, and M. Ma, Talanta 164 (2017) 300.

[11]　P. Yang, Q. Zhu, Y. Chen, and F. Wang, J. Appl. Polym. Sci. 213 (2009) 2881.

[12]　L. Zhu, H. Wu, L. Xie, H. Fang, S. Xiang, Y. Hu, Z. Liu, T. Wang, and R. Yu, Anal. Methods 8 (2016) 4941.

[13]　C. M. Serban, and K. Melissa, J. Chromatogr. A 1141 (2007) 90.

[14]　 M. Su, P. Chen, Y. Dong, and H. Sun, J. Lumin. 177 (2016) 204.

[15]　H. Yin, Q. Zhang, Y. Zhou, Q. Ma, T. Liu, L. Zhu, and S. Ai, Electrochim. Acta 56 (2011) 2748.

[16]　T. S. Sunil Kumar Naik, and B. E. Kumara Swamy, J. Electroana. Chem. 804 (2017) 78.

[17]　T. S. Sunil Kumar Naik, and B. E. Kumara Swamy, J. Electroanal. Chem. 826 (2018) 23.

[18]　B. Fang, H. Liu, G. Wang, Y. Zhou, and S. Jiao, J. Appl. Polym. Sci. 207 (2007) 3864.

[19]　A. Z. Ernst, S. Zoladek, K. Wiaderek, J. A. Cox, A. Kolary-Zurowska, K. Miecznikowski, and P. Kulesza, Electrochim. Acta 53 (2008) 3924.

[20]　Y. Ohnuki, H. Matsuda, T. Ohsaka, and N. Oyama, J. Electroana. Chemi. Interf. Electrochem. 158 (1983) 55.

[21]　S. Samanta, P. Roy, and P. Kar, Mater. Today: Proceed. 2 (2015) 1301.

[22]　L. Kong, X. Jiang, Y. Zeng, T. Zhou, and G. Shi, Sens. Actuators B l 185 (2013) 424.

[23]　M. J. Lobo-Castakh, A. J. Miranda-Ordieres, and P. Tukh-Blanco, Anal. Chim. Acta 346 (1997) 165.

[24] U. Chandra, B. E. Kumara Swamy, K. R. Mahanthesha, C. C. Vishwanath, and B. S. Sherigara, Chem. Sensors 3 (2013) 1.

[25] P.S. Ganesh, and B.E. Kumara Swamy, J. Electroanal. Chem. 756 (2015) 193.

[26] K. V. Harisha, B. E. Kumara Swamy, and E. E. Ebenso, J. Electroanal. Chem. 823 (2018) 730.

[27] C. M. Kuskur, B. E. Kumara Swamy, and H. Jayadevappa, J. Electroanal. Chem. 804 (2017) 99.

[28] S. B. Tanuja, B. E Kumara Swamy, and K. Vasantakumar Pai, Insights Anal. Electrochem. 2 (2016) 2.

[29] M. Pacios, M. D. Valle, J. Bartroli, and M. J. Esplandiu, J. Electroanal. Chem. 619 (2008) 117.

[30] S. Chitravathi, B. E. Kumara Swamy, G. P. Mamatha, and B. S. Sherigara, Chem. Sensors 3 (2013) 1.

[31] D. Nematollahi, H. Shayani-Jam, M. Alimoradi, and S. Niroomand, Electrochim. Acta 54 (2009) 7407.

[32] Q. Chen, X. Li, X. Min, D. Cheng, J. Zhou, Y. Li, Z. Xie, P. Liua, W. Cai, and C. Zhang, J. Electro. Anal. Chem. 789 (2017) 114.

[33] Y. Umasankar, A. P. Periasamy, and S. M. Chen, Anal. Biochem. 411 (2011) 71.

[34] F. Hu, S. Chen, C. Wang, R. Yuan, D. Yuan, and C. Wang, Anal. Chim. Acta 724 (2012) 40.

[35] P. S. Ganesh, B. E. Kumaraswamy, and Rekha, Sci. Lett. J. 5 (2016) 236.

[36] K. Chetankumar, B. E. K. Swamy, S.C. Sharma, J. Electroanal. Chem., 849 (2019) 113365.