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Simultaneous electroanalysis of hydroquinone and catechol at poly(brilliant blue) modified carbon paste electrode: A voltammetric study

P.S. Ganesh, B.E. Kumara Swamy *

Department of PG Studies and Research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta, 577451 Shimoga, Karnataka, India

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ABSTRACT

A sensitive, selective and reproducible electrochemical method was developed for the electroanalysis of important phenolic isomers such as catechol (CC) and hydroquinone (HQ) using poly(brilliant blue) modified carbon paste electrode. The modified electrode shows excellent electrocatalytic activity towards the oxidation of CC and HQ in phosphate buffer solution of pH 7.4 by cyclic voltammetric (CV) and differential pulse voltammetric (DPV) techniques. The lower limit of detection of CC and HQ was 68.1 nM and 46.4 nM respectively. The peak to peak separation of CC and HQ was about 0.107 V by both CV and DPV techniques. This work provides a simple and easy approach for the simultaneous analysis of CC and HQ.

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1. Introduction

Hydroquinone (HQ, 1,4-dihydroxybenzene) and catechol (CC, 1,2-dihydroxybenzene) are the two positional isomers of a dihydroxybenzene [1,2]. They widely exist in industrial effluents, such as the waste from oil refineries, coal tar, cosmetics, plastic, leather, paint, steel and pharmaceutical industries [3–5]. Even in a very low concentration itself these isomers are toxic to animals and human beings and they are difficult to degrade. Because of these factors they are one of the main sources for the environment pollution [6,7]. The determination of these phenolic compounds is of great importance in environmental control [8]. Furthermore, because of the similar structure and properties both HQ and CC coexist in the eco system. Therefore, it is very important to develop simple and rapid analytical methods for the qualitative and the quantitative estimation of these dihydroxybenzene isomers [9]. So far various methods have been reported for their determination, high performance liquid chromatography (HPLC) [10,11], spectrophotometry [12], electrochemiluminescence [13], pH based-flow injection analysis [14] and synchronous fluorescence [15]. All these methods are generally little bit complicated and tedious.

Electroanalytical techniques are promising methods for the analysis of electroactive molecules based upon the anodic oxidation [16–18]. There are many practical advantages of employing electroanalytical methods for the determination of these electroactive molecules because of the instrumental sensitivity, selectivity, quick response and reproducibility in the result. HQ and CC usually coexist in the raw sample and due to isomorphic nature they possess similar oxidation potentials at bare working electrodes making their individual identification very difficult. Moreover, due to the slow electron transport phenomenon the voltammogram obtained was broad and results in an overlapped response. To overcome this drawback there are so many efforts to modify the working electrodes. For example, boron-doped graphene [19], polyaniline/MnO_2 nanofibers [20], graphitic mesoporous carbon/ionic liquid composite [21], carbon nanocage-reduced graphene oxide composites [22], carbon nanofibers [23], and poly(crystal violet) functionalized graphene [24] are used as a modified electrode for the determination of HQ and CC.

The present work describes the fabrication of stable working electrode by electropolymerizing Coomassie brilliant blue R-250 (brilliant blue) on the surface of carbon paste electrode to achieve the task of simultaneous determination of these isomers. Brilliant blue is the name of triphenylmethane dye widely used for staining proteins in the analytical biochemistry and also used as a food colorant [25,26]. However, no investigations were reported for the analysis of HQ and CC at poly(brilliant blue) film coated carbon paste electrode by cyclic voltammetric and differential pulse voltammetric techniques. We recently reported the modification of carbon paste with different quantities of brilliant blue and its use for the electrochemical determination of dopamine in the presence of ascorbic acid [27]. The present study

* Corresponding author.
E-mail address: kumaraswamy21@yahoo.com (B.E. Kumara Swamy).

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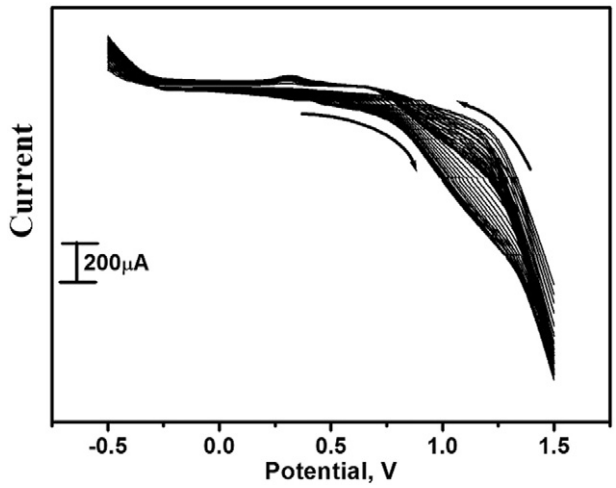


Fig. 1. Cyclic voltammograms of the preparation of poly(brilliant blue) MCPE. 0.5 mM aqueous solution in 0.1 M NaOH at 25 cycles with scan rate of 0.1 V s^{-1}.

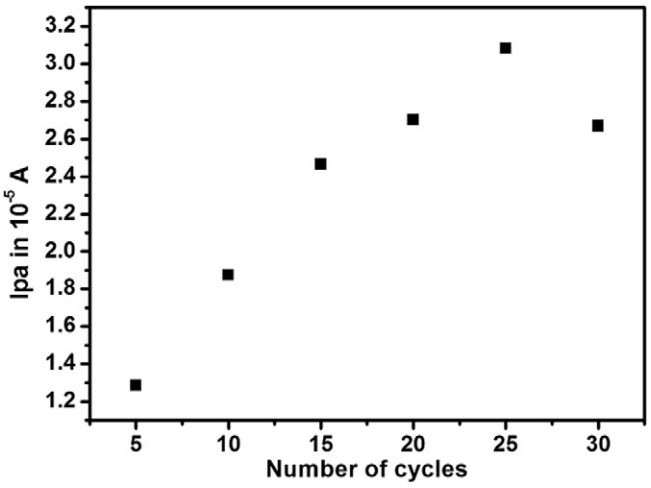


Fig. 2. Graph of anodic peak current of oxidation of 0.2 mM CC in 0.2 M PBS of pH 7.4 versus number of polymerization cycles.

mainly reports the electropolymerization of brilliant blue on the bare carbon paste electrode and its use for the simultaneous determination of hydroquinone and catechol. This modified carbon paste electrode shows very good enhancement when compared to bare carbon paste electrode. This work reports about sensitivity, selectivity, stability and reproducibility of HQ and CC at poly(brilliant blue) film coated carbon paste electrode.

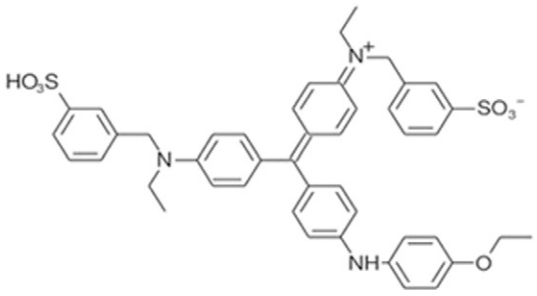
2. Experimental section

2.1. Reagents

Hydroquinone (HQ), catechol (CC) and Coomassie brilliant blue R-250 (brilliant blue) were purchased from Himedia. The stock solution 25×10^{-4} M HQ and 25×10^{-4} M CC was prepared in double distilled water. Phosphate buffer solution (PBS) of same ionic strength was prepared (0.2 M) by mixing appropriate ratio of $NaH_2PO_4 \cdot H_2O$ and Na_2HPO_4. Graphite powder of 50 μm particle size purchased from Merck and silicone oil from Himedia was used to prepare carbon paste electrode (CPE). All the chemicals mentioned were of analytical grade and used as received without any further purification.

2.2. Apparatus

The electrochemical experiments were carried out using a model CHI-660c (CH Instrument-660 electrochemical workstation). A traditional three electrode system was employed in an electrochemical cell with a saturated calomel electrode(SCE) as a reference, a platinum counter electrode, and a bare or poly(brilliant blue) modified carbon paste electrode (MCPE) as working electrode. The corresponding oxidation potential of analytes was recorded versus SCE.



Scheme 1. Structure of brilliant blue.

2.3. Preparation of bare carbon paste electrode

The bare CPE 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 smoothened on a tissue paper. The electrical contact was provided by a copper wire connected to the end of the tube.

3. Result and discussion

3.1. Electrochemical polymerization of brilliant blue on CPE

Cyclic voltammetry is a simple and convenient method to immobilize an organic dye on the surface of CPE. The poly(brilliant blue)-modified carbon paste electrode (MCPE) was prepared by placing 0.5 mM brilliant blue with 0.1 M NaOH in an electrochemical cell. The potential window was maintained from −0.5 V to 1.5 V with scan rate 0.1 V s^{-1} for 25 multiple cycles. During the process of multiple cycles, the voltammogram has gradually descended with increase of cyclic times as shown in Fig. 1. This indicates that the brilliant blue film was formed and deposited on the surface of BCPE [28–30]. The structure of brilliant blue was shown in Scheme 1.

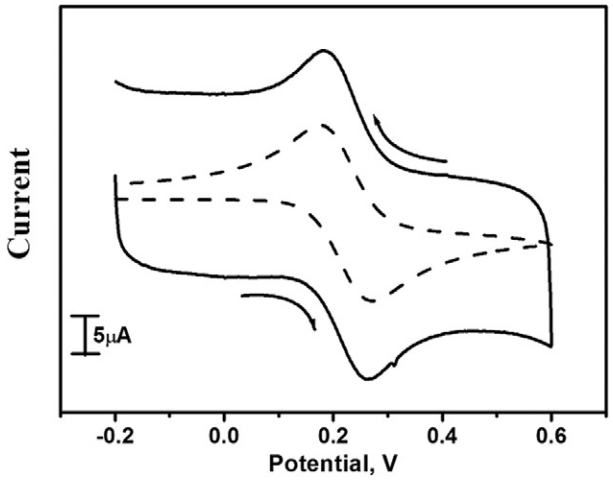


Fig. 3. Cyclic voltammograms of 1 mM potassium ferrocyanide at BCPE (dashed line) and poly(brilliant blue) MCPE (solid line) at scan rate of 0.05 V s^{-1}.

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