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Polyeugenol-modified graphite electrode for determination of hydroquinone in cosmetic

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Abstract. Graphite electrode was modified by electropolymerization of eugenol in alkaline medium by cyclic voltammetry. The polyeugenol-graphite modified electrode (GEEU) was than used for the determination of hydroquinone (HQ) at phosphatbuffer solution (PBS) of pH 7.0 by cyclic voltammetry technique. The performance of this modified has shown excellent electrocatalytic activity toward HQ than an unmodified electrode (GE). The oxidation and reduction peak separation (ΔE) has been decreased from 0.309 V to 0.228 V. In addition, the effect of scanratesindicate that redox electrochemical behaviour of HQ is diffusion controlled electrochemical process on GEEU. Under experimental, the oxidation peak current (I_p) increases linearly with concentration (C) of HQ ranged from 1.42 -101.07µMat the linear regression equation of $I_p = 3.86C + 355.20$ (μ A, $\mathbb{R}^2 = 0.9989$). On the other hand, the oxidation peak current also increases linearly at ranged from $136.67 - 480.50 \mu$ M at the linear regression equation of $I_p = 1.69C + 559.72$ (µA, $R^2 = 0.9956$). The LOD and LOQ were measured at a lower concentration of HQ,1.44µM and 4.37µM, respectively. Moreover, the proposed modified has been successfully applied to the determination of HQ in the cosmetic sample with satisfactory recoveries.

1. Introduction

Cosmetics are part of human needs, especially for care and aesthetics nowadays. HQ (1,4dihydroxybenzene) is one of the organic compounds used in cosmetics and medical preparation as a topical application in skinwhitening to reduce the colour of the skin[1].HQ is carcinogenic ithas been baned since 2008 in some countries because of fears of cancer risk, but is still found skinwhitening cream containing HQcurrently [1], [2]. Owing to this fact the quantitative determination of HQ is great importance in cosmetics. There are various determination of HQ like high performance liquid chromatography (HPLC) [3], spectrophotometry [1] and electrochemical methods[2], [4]. Among all these techniques, HPLC has the potential for detection of HQ but it time-consuming pretreatment steps and expensive in the instrument.Spectrophotometry suffers from easy interference by related compounds but it needs complicated pre-separation steps[5]. Electrochemical methods are most widely studied for the determination of the various electroactive compounds due to their simple, sensitive, rapid and cheap equipment [6]. To raise the electrocatalytic activity of the electrode in electrochemical methods, the modification was explored by using a different type. One of the

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electrode modifications iselectropolymerization on bare electrodes like carbon paste electrode [7], glassy carbon electrode[4], [5]and multi-walled carbon nanotubes (MWCNT)[8]for voltammetric determination of HQ.

Chemically modified electrode using electropolymerization methode use one of the approaches for electrode surface modification by the formation of the polymeric film. The examples of monomers undergoing oxidative polymerization are DL-methionine[7], nile blue[9] and eugenol[10].Eugenol can be used as a starting material of synthesis of polymer compounds due to the presence of three functional groups on eugenol namely hydroxy, methoxy and allyl group. Through allyl groups, polyeugenol can be synthesized from eugenol. On the other hand, the presence of hydroxy groups can be synthesized by functional groups with higher activity[11]. This paper describes the preparation and properties of the polymeric coating derived from eugenol. The formulated polyeugenol-modified graphite electrode (GEEU) was succesfully for the determination of HQ in cosmetic.

2. Experimental section

2.1. Materials

Eugenol, hydroquinone (HQ), graphite powder, silicone oil for the preparation of electrodes. Ethanol (70%) for preparation of eugenol stock solution and phosphat buffer solution (PBS) 0.1 M at pH 7.0 for preparation of HQ stock solution. Potassium ferrocyanide andKCl for electrochemical characterization and nitrogen for deaerated. Cosmetic cream as a sample and double disstilled water for preparation of all aquaeous solution. All of the materials were purchased from Merck. All of the chemicals recognized were all of the analytical grade used as obtained without any further purification.

2.2. Apparatus

All electrochemical experiments were operated using a Quadstat electrochemical workstation (eDaq Pty. Ltd., Australia) controlled by Echem v2.1.0 software. A conventional three electrode system was used in a single compartment electrochemical cell with a silver/silver chloride (Ag/AgCl) as a reference electrode, a platinum wire as a counter electrode, and graphite electrode (GE) and polyeugenol-modified graphite electrode (GEEU) as a working electrode. All the redox potentials of analytes were recorded versus Ag/AgCl at an ambient temperature of 25 ± 0.5 °C. In addition, another apparatus were magnetic stirrer, the cavity ofteflon, copper wire, tissue paper, digital scales and laboratory glassware.

2.3. Preparation of the working electrodes

The GE was prepared by hand mixing of 70% graphite powder and 30% silicone oil in an agat mortar for about 30 minutes until uniform wetted was obtained. The paste was packed into a cavity of a teflon 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. The GEEU was prepared by electropoymerization of eugenol (10 mM) and NaOH (0.1 M) which was previously deaerated with nitrogen for 5 minutes. Electropolymerization of eugenol on the GE was conducted by cyclic the potential between -0.5 – 1.0 V at a scan rate of 0.05 Vs⁻¹ in ten cycles. After modification, the modified electrode was electrochemically characterized by cyclic scaning from -0.5 to 0.5 V at different scan rates in the redox couple of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ in 1 MKCl. Then the electrode was ready for use after washing with double disstilled water. Hereafter the modified electrode will be referred to as the GEEU.

2.4. Preparation of cosmetic cream sample

An accurate amount ranging from 1.0 - 2.0 g of cosmetic cream samples containing 0.02 g of HQ was dissolved in 20 mL of 0.1 M PBS pH 7.0 with magnetic setirrer for 10 minutes and then filtered. The filtrat (250 μ L) was adjusted with this solvent in a 25 mL volumetric flask. The determination of the

hydroquinone content in the samples was performed after the successive addition of reference HQsolutions in the same solvent. After each aliquot addition, cyclic voltammograms were reported by cycling the potential between -0.5 - 0.5 V at a scan rate of 0.05 Vs⁻¹.

3. Result and discussion

3.1. Electropolymerization of eugenol on GE

Electropolymerization of eugenol on the surface of GE has been observed from eugenol solution in alkaline medium by cyclic voltammetry technique. It is exposed in Figure 1, the anodic peak at 0.032 V observed on the first scan is raised gradually on the second scan which is the suggestion of growth and formation of an electroactive layer on the surface of GE. After a few cycles, the increase of this peak current tends to be almost constant indicating that the growth of polymerization was reached level saturation[9].According to Figure 1, the oxidation peak potential is shifted toward more positive value, reaching a steady shape after ten scans. This behaviour indicates the rapid deposition of polymer thin film on the electrode surface and has been discovered earlier for eugenol on MWNT[10],Pt[12],GE[13].



Figure 1. Cyclic voltammograms of eugenol polymerization on GE at ten cycle scans with a scan rate of 0.05 Vs^{-1}

Electropolymerization of eugenol in alkalin medium, it presents as phenolat ion (I) and easily oxidized to o-quinone via radical and anion radical. It is well documented [12]that the presence of the methoxy group in the monomer makes many follow up reactions possible. Firstly, the methanol molecule can be eliminated from radical (II) presenting an anion radical (III), which via the other one-electron reaction is coverted to highly reactive o-quinone (IV). The electropolymerization mechanism of eugenol is described in Scheme 1.



Figure 2.Hypothesized mechanism of the polyeugenol formation during elextrooxidation in alkaline medium

On the electropolymerization process, the thicknes of the polymeric film can be controlled by varying the number of multiple cycles. The probable electropolymerization mechanism of GEEU and electrocatalysis interaction with HQ is described in Scheme 2. Such types of mechanism have been proposed in earlier reports[7].



Figure 3. Illustration of eugenol electropolymerization at GE and interaction of HQ with GEEU

3.2. Characteristics of the modified electrode

The electrochemical performance of GEEU was investigated by using the redox couple of 1 mM $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$ in 1 M KCl. As Figure 2, shows the voltammogram of the GE, compared with GEEU at the scan rate 0,025 V s⁻¹, it could be seen that the redox peak currents response at GE was lower than at GEEU. The peak of peak separation (ΔE_p) of GE was found to be 0.336 V. On the other hand, in the same identical condition of GEEU indicates a stable enhancement of redox peak currents and also showed faster electron transfer kinetics with the ΔE_p of 0.120 V.





According to Figure 2A, these voltammograms clarification at modified electrodes inform the morphology was changed significantly and also resultindicate the electrocatalytic activity of modified electrodes. The total active surface area available for the reaction of species in solution can be estimated by the Randles-Sevcik equation (1) [6], [9]. $I_p = 2.69 \times 105 \ n^{3/2} A \ D^{1/2} \ C_0^{-1/2}$

(1)

 $I_p = 2.09 \times 100 \text{ m}^{-1} \text{ A D}^{-1} \text{ C}_0^{-1}$ Where I_p , n, A, C_0 , D and $\hat{}$ the peak current, the number of involved (n = 1 in the [Fe(CN)_6]^{3-1} /[Fe(CN)_6]⁴⁻ redox system, the electroactive surface area, the concentration of reactant, the diffusion coefficient of the [Fe(CN)_6]^{3-1}/[Fe(CN)_6]^{4-1} (7.6 \times 10^{-4} \text{ cm}^2 \text{s}^{-1}) and the scan rate, respectively. According to Figure 2B, the slopes were 0.32×10^{-3} and 1.00×10^{-3} in two lines at GE and GEEU respectively. The value of A for GEEU was 1.35 cm², which was larger than that of GE (0.43 cm²). These results were attributable to the particular porous of graphite.

3.3. Electrochemical respon for HQ at GEEU

The electrochemical response of HQ was studied at the GEEU and GE in 0.1 M phosphate buffer solution (pH 7.0) with the scan rate of 0.05 V s⁻¹. Figure3 shows the cyclic voltammograms for 0.1 mM of HQ at different electrodes. The voltammetric responses of HQ at GE werelower than at GEEU because of the slow electron transfer phenomenon. The oxidation potential was located at -0.012 V. The peak currentofHQ atGEEUwas more sensitive than GE and the anodicpeakpotentiallocated at -0.072 V. However, in the same identical condition the GEEU demonstrated the oxidation peak potential was shifted toward the positive side with the advancement in current signals.



Figure 5. Cyclic voltammograms of 0.1 mM HQ in PBS pH 7.0 at GEEU and GE



Figure 6. (A) Cyclic voltammograms of 0.1 mM of HQ in 0.1 M PBS of pH 7.0 at GEEU at different scan rate (a-f; $0.025 - 0.225 \text{ V s}^{-1}$); (B) Plots of peak current (anode and cathode)versus square root of scan rate

3.4. Effect of scan rateon the peak current of HQ

The effect of scan rate gives information on the electrode interaction with HQ. The cyclic voltammograms for the redox of 0.1 mMHQ in PBS of pH 7.0 at GEEU with different scan rates were shown in Figure4A. According to Figure 4B, the GEEU obeys Randles-Sevcik equation and showed peak current (I_p) increased linearly with the square root of scan rate ($v^{1/2}$)in the range from 0.025–0.220V s⁻¹with the regression equation of $I_{pa} = 3.17^{-1/2}$ -0.39 (A, (V s⁻¹)^{1/2}, R² = 0.9955) an $I_{pc} = -2.02^{-1/2} - 0.16$ (A, (V s⁻¹)^{1/2}, R² = 0.9934). As the obtained correlation coefficient was linier with I_p versus $v^{1/2}$ suggesting electrode phenomenon was diffusion controlled electrochemical process.

3.5. Determination of HQ

The determination of HQ at GEEU was performed by cyclic voltammetry. Figure5A presented cyclic voltammogram responses of different concentrations of HQ from 1.2 μ M to 490 μ M in 0.1 M of PBS (pH 7.0). The result show that the anodic peak current (I_p) was linear to the concentration(C) of HQ (Figure 5B) with the linear regression equation as follows $I_p = 3.86C+355.20$ (μ A, R² = 0.9989) in the concentration range of 1.42 – 101.7 μ M. On the other hand, the oxidation peak current of HQ also was proportional tothe linear regression equation of $I_p = 1.693C + 559.72$ (μ A, R² = 0.9956) in the concentration range of 136.67 – 480.50 μ M. The LOD and LOQ were measured in the lower concentration range for HQ, 1.44 μ M and 4.37 μ M, respectively.The reproducibility was estimated at ten different electrodes, which were formulated independently under the same condition. The RSD was 2.66%.



Figure 7. (A) Cyclic voltammogram of GEEU in 0.1 M PBS pH 7.0 at different concentration (a-x : $1.2 - 490.0 \ \mu$ M) at scan rate 0.05 V s⁻¹; (B) Calibration plots of HQ in the concentration range of $1.42 - 101.70 \ \mu$ M and $136.67 - 480.50 \ \mu$ M

3.6. Analytical application

Table1. Determination of HQ in cosmetic cream sample (n = 3)

$[HQ]_{added}$ (μM)	$[HQ]_{found} (\mu M)$	Recovery (%)
10	9.97	99.74±0.15
20	20.41	102.03±0.29
30	29.91	99.70±0.21
40	40.35	100.88±0.16

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To established the proposed sensor for HQ at GEEU, the cosmetic cream sample was tested. Into cosmetic cream was added to HQ and was than extracted by PBS pH 7.0. The experiments were performed by cyclic voltammetry to get the responses of samples solution of cosmetic cream. The recovery experiments were than determined by the calibration method and the result was demonstrated in Table 1. According to Table 1, the recoveries were from $(99.70\pm0.21)\%$ to $(102.03\pm0.29)\%$, which suggested that the applicability of the sensor proposed.

4. Conclusion

In summary, the GEEU as a kind of polyeugenol-graphite modified alectrode was prepared for the determination of HQ in cosmetic cream sampel by cyclic voltammetry. This modified showed an electrocatalytic activity toward the electrochemical response of HQ with the increase of the peak oxidation of HQ compared with the unmodified electrode. This method presented a wide linear range, low detection limit and good reproducibility for the determination of HQ. Moreover, the result indicated that the modified electrodewas applied to the determination of HQ in the cosmetic cream sample with satisfactory recoveries, which recommended that the applicability of the sensor proposed.

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