Int. J. Electrochem. Sci., 15 **(2020)** 11509 – 11521, doi: 10.20964/2020.11.53

International Journal of
ELECTROCHEMICAL
SCIENCE
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Electrochemical Sensor for Hydroquinone based on Polyeugenol/PVA-Modified Graphite Electrode

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Received: 21 July 2020 / *Accepted:* 5 September 2020 / *Published:* 30 September 2020

The electrochemical sensor based on polyeugenol/polyvinyl alcohol-modified graphite electrode, i.e., GEPVAEu, was prepared for the determine the hydroquinone (HQ). The electrode was modified through an electropolymerization process. The modified electrode showed excellent performance for the HQ sensor in phosphate buffer solution (PBS) of pH 7.0 by the cyclic voltammetry method. The impact of scan rates confirmeds that the redox electrochemical behavior of HQ was a diffusion-controlled electrochemical process on the GEPVAEu electrode. The cyclic voltammetry results informed that GEPVAEu hads excessive electrocatalytic activity towards HQ oxidation if compared to the unmodified graphite electrode. The GEPVAEu electrode was able to determine the HQ concentration across two linear response stages from 3.67-103.27 and 140.90 - 482.11 μM with the sensitivities of 4.13 and 1.02 μA μM^{-1}, respectively. The LOD and LOQ values were 2.27 μM and 6.87 μM, respectively, which were remarkable. Therefore, the GEPVAEu electrode has the potential to be used as an electrochemical sensor for the HQ.

Keywords: Hydroquinone, Electropolymerization, Polyeugenol, PVA, Graphite

1. INTRODUCTION

Hydroquinone (1,4-dihydroxybenzene, abbreviated as HQ) is the oxidation product of some aromatic compounds. HQ is widely found in cigarette smoke, diesel engine lubricant, and the chemical industry [1]. Moreover, HQ has been used for skin depigmentation purposes since the 1960s [2]. Unfortunately, HQ is carcinogenic; thus, it has been banned since 2001 in a few nations due to the fear of cancer possibility. However, HQ is still found in the skin whitening cream at present [3, 4]; therefore, the HQ sensor is pivotal, primarily in beauty care product.

As for today, there are some methods for the HQ analysis, such as spectrophotometry [4], high-performance liquid chromatography (HPLC) [5], and chemiluminescence [6]. All of these methods are complicated in the sample pre-treatment stage, expensive in terms of the instruments, and time-consuming in the analysis [7]. In contrast, electrochemical methods that lead to an electrochemical sensor for HQ have gained attention due to their quick results, cheap, simple operation, and high sensitivity in recent years [8, 9].

Recently, the development of electrochemical sensors is conducted through the electropolymerization of the surface of working electrodes [10]. Compared to the unmodified electrodes, the altered electrodes show remarkable physicochemical properties like high sensitivity, high selectivity, high reproducibility, high stability, and low limit of detection [9, 11, 12]. Additionally, the points of interest of a chemically modified electrode are the reduce analyte reduction/oxidation potential caused by the speeding up of the electron transfer reaction [13]. Chemically modified electrode prepared by electropolymerization is widely applied using several monomers such as brilliant cresyl blue [11], glutamic acid [14], arginine [15], neutral red [16], o-phenylenediamine [17], benzoguanamine [18] and eugenol [13, 19–21]. All of these monomers have been applied for the determining HQ, except for eugenol.

The polyeugenol modified electrodes by electropolymerization process have been applied to determine the wine antioxidant activity [13], dopamine and ascorbic acid [19], and as well as oxygen [21]. Eugenol has three potential functional groups (allyl, hydroxy, and methoxy) that can be utilized as the main components for the synthesis of polyeugenol. Meanwhile, the hydroxy groups which are high activity could be utilized as a major functional group for electropolymerization of eugenol [22]. In addition, polyeugenol films produced on the surface electrode are known to be porous, and this issue has been explored by several researchers [23]. Polyeugenol films have been performing well for analytes that are detected by oxidation, but these polymer films have not been broadly used with negative potentials, namely for detecting the analytes by reduction [24]. In this report, the HQ that is detected by oxidation using polyeugenol film is reported for the first time.

Eugenol is a simple organic molecule that can be conveniently electropolymerized on the surfaces of the working electrode such as multi-walled carbon nanotubes (MWCNTs) [13], platinum [19], glassy carbon [20], and gold disk [21]. In this work, the eugenol was electropolymerized on a graphite electrode. Graphite is a soft and porous material with adsorption capacity and highly conductive fillers for conducting a polymer composite [25].

At present, various approaches have been developed for the preparing the modified electrode. The simplest and cheapest method is by using PVA [26]. PVA is one of the water-soluble polymers with high wettability property, high thermal stability, elastic nature, and high swelling in the aqueous solution [26, 27]. Because of its high swelling nature, PVA is often used in a modified electrode to increase the contact area between the analyte and the electrode [28] wich consequently enhances the electrochemical response [26]. In the previous studies, using PVA as a stabilizer in modified electrodes was applied in the eugenol electropolymerization [29] and in determining the ascorbic acid [30].

In this study, eugenol and PVA were used to modify the graphite electrode by using the electropolymerization method. The proposed electrode exhibits a low limit of detection and good sensitivity, stability, and reproducibility towards the HQ determination by cyclic voltammetry. This modification shows very interesting properties which are not observed in the similar compounds, making it potentially useful in the development of a variety of electrochemical sensors.

2. EXPERIMENT

2.1. Apparatus and reagents

All electrochemical observations were conducted using an advanced electrochemistry system (EA 163 Potentiostat, eDaq Pty Ltd, Australia) with the Echem v2.1.0 computer program. The three electrodes cell was utilized in the reaction vial cell with a refillable miniature of Ag/AgCl electrode (saturated KCl) as the reference electrode, an inert wire electrode (titanium rods coating of platinum) as the auxiliary electrode, and bare graphite electrode (GE) or Graphite/PVA electrode (GEPVA) or Graphite/PVA/Polyeugenol electrode (GEPVAEu) as the working electrode. All potentials of the analytes in this experiment were referred to this reference electrode and performed at a room temperature.

Eugenol, Polyvinyl alcohol (PVA), NaOH, graphite powder, and silicone oil were used to prepare the working electrode. Ethanol (70%) was used to prepare the eugenol stock solution and also to prepare the HQ stock solution in a phosphate buffer solution (PBS) of 0.1 M at pH 7.0. Potassium ferrocyanide and KCl were used for working electrode characterization. Double distilled water was used to prepare all aqueous solutions. All of the used materials were purchased from Merck, and they were of analytical reagent grade. Nitrogen obtained from Samator Indonesia was used to deaerate the electrochemical cell. A blank cream as a sample was purchased from Ikapharmindo.

2.2. Preparation of the modified electrodes

The GEPVA electrode was processed by hand blending 70% graphite powder, 30% silicone oil, and 20 mg of PVA in an agate mortar for 30 minutes until a uniform blend was obtained. The GE was prepared without PVA in a similar preparation method. The paste was packed into a teflon cavity cylinder with 3 mm inner diameter and polished up using tissue. Copper as the electrical contact was connected to the quit of the cylinder. The GEPVAEu was fabricated using a 10.0 mM eugenol at GEPVA in 0.1 M NaOH solution using the cyclic voltammetry technique for 15 scan cycles at the scan rate of 0.05 V s^{-1} in the potential range of –0.5 – +0.5 V. Before every experiment, the compartment electrochemical cell was purged using nitrogen for 5 minutes.

2.3. Electrochemical characterization of modified electrodes

All electrodes were characterized electrochemically in 1 mM of potassium ferrocyanide solution containing 1 M KCl by cyclic voltammetry technique in the potential range of –0.5 – +0.5 V at various scan rates (0.010 – 0.125 V s^{-1}). The results of this characterization were attributed to the electroactive surface area of all the electrodes. The quality of the electrodes for the HQ response was evaluated using the cyclic voltammetry technique in a solution containing the HQ (1.0 mM) in BPS of pH 7.0 that was recorded in the potential range of –1.0 – +1.0 V at the scan rate of 0.05 V $s^{–1}$.

The influence of the scan rate for 0.1 mM HQ in PBS of pH 7.0 at GEPVAEu was an important determining factor to support the interaction between the modified electrode and the analyte (HQ). This effect was investigated using the cyclic voltammetry method at the scan rate of 0.025 - 0.250 V $s^{–1}$. The effect of pH PBS on the current response of GEPVAEu for the detection of HQ was observed using the cyclic voltammetry in the pH range of 5-9 at the scan rate of 0.05 V $s^{–1}$. The electrocatalytic oxidation of HQ was performed, varying its concentration at GEPVAEu. This experiment was operated using the cyclic voltammetry technique at the scan rate of 0.05 V $s^{–1}$ and pH optimum. All of these experiments were recorded in the potential range of -1.0 – +1.0 V.

2.4. Electrochemical detection of HQ in the real samples

The application of GEPVAEu was evaluated by the detection of the HQ concentration in the beauty care product cream samples. The cream samples were prepared by mixing the blank cream (1 gram) with the HQ solution in different concentrations. These cream samples were dissolved in 25 mL of PBS pH 7.0, heated in a water bath for 10 minutes, stirred for 10 minutes, and then filtered through Whatman 41 filter paper to obtain the supernatant as an extract of the HQ. The HQ extraction from these cream samples was carried out using the cyclic voltammetry technique in the potential range of –1.0 – +1.0 V at the scan rate of 0.05 V $s^{–1}$.

3. RESULTS AND DISCUSSION

3.1. Electropolymerization of Eugenol at GEPVA

Eugenol was electropolymerized at the GEPVA electrode's surface using the cyclic voltammetry technique in an electrochemical cell over the potential sweep of -0.5 V to +1.0 V with a scan rate of 0.05 V $s^{–1}$ for 15 successive cycles. The cyclic voltammograms of eugenol electropolymerization are displayed in Figure 1 in which the oxidation peak of the eugenol was located at 0.34 V and discovered on the primary scan. Afterwards, it is reduced gradually during continuous potential scanning. On the other hand, the oxidation peak is moved towards more positive value and reaches a constant form. This behavior demonstrates a fast deposition of polymer on the GEPVA electrode’s surface, as previously reported [13, 19, 20].

The number of cycles and the charges under the oxidation peak were attributed to the polymer's amount (thickness) deposited on the electrode [13]. This thickness can be arranged by changing the number of different cycles [12]. According to Figure 1, after ten cycles were performed, there was no change in the cyclic voltammograms. The less number of cycles resulted in electropolymerization completeness. In contrast, the number of cycles distorted the uniformity of polymer arrangement and increased the thickness of the polymeric film; thus, the electron transfer in the modified electrode could be prevented [31].

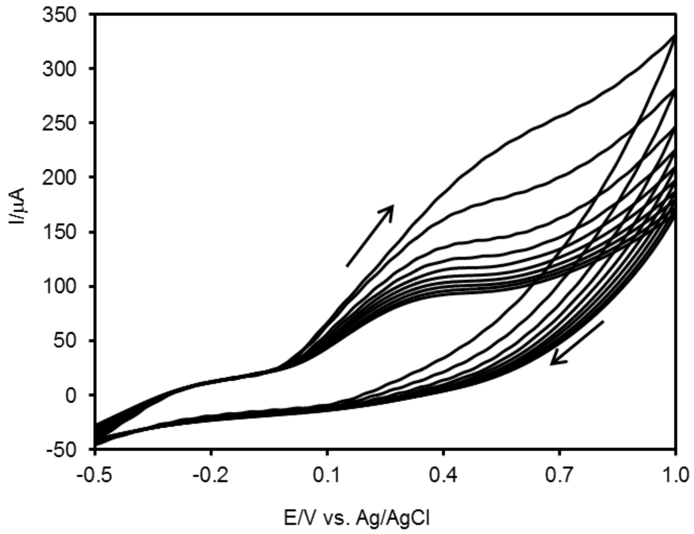
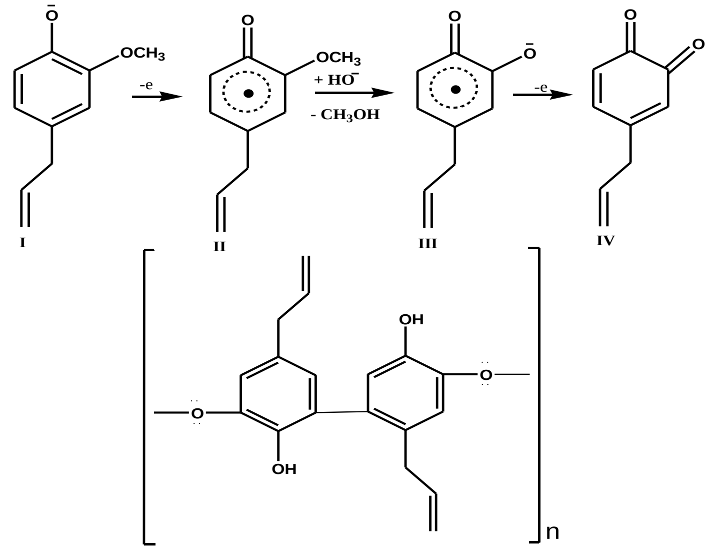
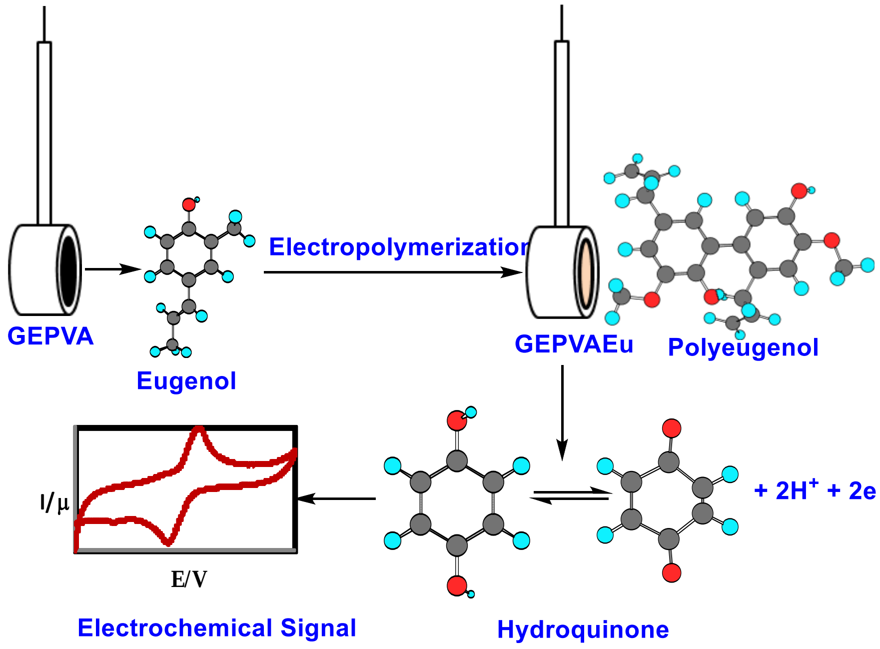


Figure 1. Cyclic voltammograms of the electropolymerization of 10 mM eugenol in 0.1 M NaOH at GEPVA (scan rate: 0.05 V s^{-1}; number of scans: 15)

The possible primary reaction of eugenol electropolymerization in the alkaline medium has been reported previously [13, 19, 20]. Similar with phenols in a strong alkaline solution, it is presented as a phenolic anion (I), which is easily oxidized to o-quinone via a one-electron transfer to phenolate radicals (II). The existence of the methoxy group in eugenol makes further reactions available. At first, anionic radicals (III) are formed from the elimination of the methanol molecule in the radical (II) using the alkaline hydrolysis. In contrast, the highly reactive o-quinone was formed via the other one-electron reaction. The plausible mechanism of eugenol electropolymerization is displayed in Scheme 1. Meanwhile, the possible electropolymerization process of GEPVAEu and electrocatalytic interaction are illustrated in Scheme 2.



Scheme 1. The hypothesized mechanism of eugenol electropolymerization in alkaline medium



Scheme 2. Schematic of eugenol electropolymerized at GEPVA and HQ interaction with GEPVAEu

3.2. Electrochemical characterization of GEPVAEu

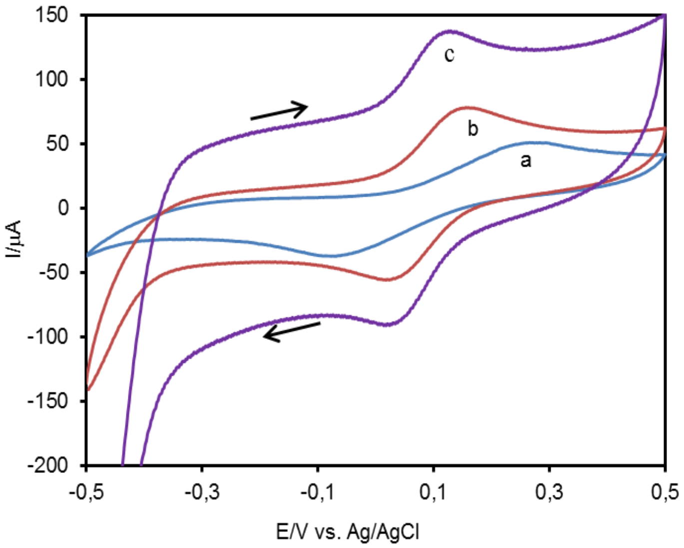


Figure 2. Cyclic voltammograms of unmodified GE (a), GEPVA (b), and GEPVAEu (c) in 1.0 mM potassium ferrocyanide redox system and 1.0 M KCl at the scan rate of 0.025 V s^{-1}

The characteristics of the modified electrode (GEPVAEu) were investigated by using the 1.0 mM potassium ferrocyanide stock solution in 1.0 M KCl as the supporting electrolyte in the electrochemical cell. Figure 2 shows the cyclic voltammograms for the 1.0 mM potassium ferrocyanide at an unmodified GE compared with both GEPVA and GEPVAEu at the constant scan rate of 0.025 V s^{-1}. As can be seen in Figure 2, GE has the lowest redox peak currents response while the redox peak current response for GEPVA is higher than GE. The presence of PVA on the GEPVA electrode could generate electrostatic repulsion with the –OH groups that were available from PVA. As a results, the voltammetric response was increased [30]. In the same condition, the GEPVAEu showed stable enhancement of redox peak current. These results indicated a substantial improvement in the voltammetric responses of potassium ferrocyanide at GEPVAEu, which was remarkable.

The peak to peak separation (ΔE_p) was calculated at 0.336 V for GE. In a similar condition, both GEPVA and GEPVAEu exhibited stronger electron transfer kinetics of 0.138 and 0.112 V, respectively. The electroactive surface area for GEPVAEu was 1.92 cm^2, which was larger than that of GE (0.43 cm^2) and GEPVA (0.79 cm^2). A high accessibility surface area was achieved for GEPVAEu, and the confirmation of the GEPVAEu showed that the morphology hads improved considerably.

3.3. The electrochemical response of HQ at GEPVAEu

The electrochemical response of HQ was evaluated at the GEPVAEu and was compared to both GEPVA and GE. Figure 3 displays the response for 0.1 mM of HQ in PBS pH 7.0 at each electrode which was operated at the scan rate of 0.05 V s^{-1}. The GE was given a poor response, which was indicated at -0.018 V. The oxidation peak current of HQ at GEPVA was higher than GE, which was found at 0.030 V. The presence of PVA, which has a high swelling ability in aqueous solution, caused an increase in response to HQ [30]. However, in the same condition, the GEPVAEu showed significant enhancement in the peak current of HQ, wich was shown at 0.252 V. The effect of the eugenol electropolymerization at GEPVAEu caused enhancement in the electroactive surface area. Additionally, eugenol electropolymerization at GEPVAEu caused an increasing amount of –OH groups at polymer, which was used to interact with HQ by hydrogen bonding.

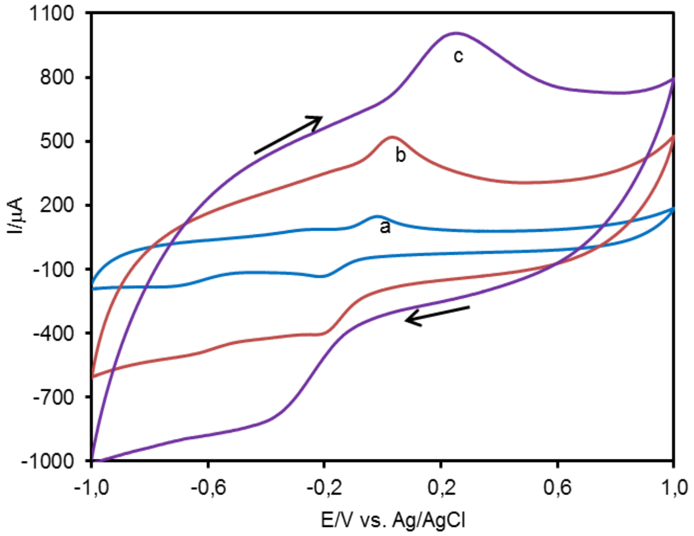


Figure 3. Cyclic voltammograms of 0.1 mM HQ in PBS of pH 7.0 at GE (a), GEPVA (b) and GEPVAEu (c) at the scan rate of 0.05 V s^{-1}

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

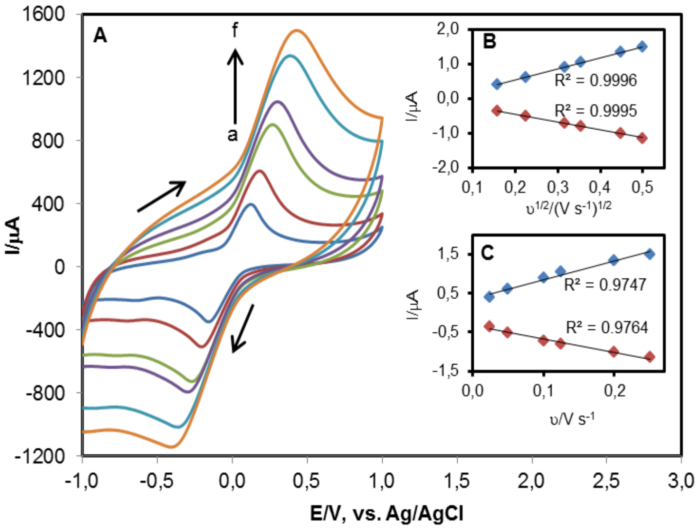


Figure 4. (A) Cyclic voltammograms of 0.1 mM of HQ in 0.1 M PBS, pH 7.0 at GEPVAEu at varying scan rate (a-f; 0.025 V s^{-1} to 0.225 V s^{-1}); (B) Curve of current signal versus scan rate; (C) Curve of current signal versus square root of scan rate

The interaction between the electrode and the HQ was explored through the influence of the scan rate. The cyclic voltammetry of 0.1 mM HQ in pH 7.0 PBS media using GEPVAEu was evaluated for the variance of the scan rate as seen in Figure 4(A). According to Figure 4(B), the experimental results obtained at GEPVAEu followed the Randles-Sevcik equation [9, 31]. The peak current was shown to rise linearly with the square root of the scan rate in the range of 0.025 to 0.250 V s^{-1} with the regression equation of $I_{pa} = 3.243\upsilon^{1/2} - 0.114$ (A, V s^{-1}, R^2 = 0.9996) and $I_{pc} = -2.305\upsilon^{1/2} + 0.013$ (A, (V s^{-1})$^{1/2}$, R^2 = 0.9995). In addition, in order to validate the electrode process, the graph of the peak current (I_p) versus the scan rate (υ) was also plotted and the obtained graph was in line with the correlation equation of $I_{pa} = 4.798\upsilon + 0.367$ (A, V s^{-1}, R^2 = 0.9747) and $I_{pc} = -3.413\upsilon - 0.328$ (A, V s^{-1}, R^2 = 0.9764) (see Figure 4(C)). As the coefficient of correlation obtained was more linear with I_p versus $\upsilon^{1/2}$, the electrode phenomenon was indicated by a diffusion controlled electrochemical process [9, 31].

3.5. Effect of pH on determining the HQ

The influence of the PBS pH value on the HQ responses at GEPVAEu was studied in a range of pH of 5.5 – 9.0. The variation of pH value influenced the electrocatalytic oxidation of HQ (55.0 µM) at GEPVAEu by influencing both peak current and redox peak potential, which could be confirmed in Figure (5A). Figure (5B) shows that the oxidation peak current of HQ increased significantly at the varying pH from 5.5 to 7.0. The peak current gradually decreased from 7.0 to 8.0 at varying pH levels, and the peak current significantly decreased from 8.0 to 9.0 at varying pH levels. At the higher pH value, the proton in solution was decreased; therefore, figuring out the electrochemical reaction was more difficult. As a result, pH 7.0 was selected to detect the HQ concentration.

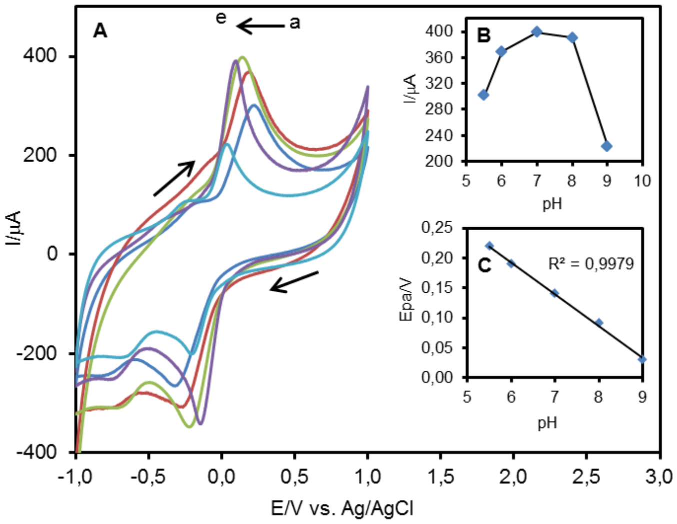


Figure 5. (A) Cyclic voltammograms of GEPVAEu in 0.1 M PBS at varying pH levels (a-e: 5.5 to 9.0) at the scan rate of 0.05 V s^{-1}; (B) The impact of pH on the peak current response of 55.0 µM HQ in 0.1 PBS; (C) The impact of pH on the potential response peak of HQ.

In addition, the pH value influences the redox peak potential shift. Figure 5(C) shows that the peak potential of oxidation moved to a more negative potential with increased pH from 5.5 to 9.0. The E_{pa} versus pH curve clearly expressed that the E_{pa} refers to pH value linearly from 5.5-9.0 at varying pH levels, and the linear regression equation was E_{pa} = -0.0539pH + 0.05196 (V, R^2 = 0.996). The slope value (-0.0539 V/pH) was close to the theoretical value of -0.0590 V/pH, suggesting that the number of protons and electrons was included in the redox process. It was consistent with the results from the previous studies [9, 12].

3.6. Effect of HQ concentration

The effect of HQ concentration was studied using the cyclic voltammetry technique. Figure 6(A) presents the cyclic voltammetry responses at various HQ concentrations from 1.2 µM to 490.0 µM. The results showed that the oxidation peak current (I) was proportional to the HQ concentration (C) (insets Figure. 6(B) and 6(C)) and the given equation as follows $I = 4.129C + 582.900$ (µA, R^2 = 0.9950) in the concentration range of 3.67 – 103.27 µM. Additionally, the oxidation peak current of HQ was linear to the concentration and the given equation of $I = 1.020C + 894.520$ (µA, R^2 = 0.9983) in the concentration range of 140.93 – 482.11 µM. It was found that the LOD and LOQ values were 2.27 µM and 6.85 µM, respectively.

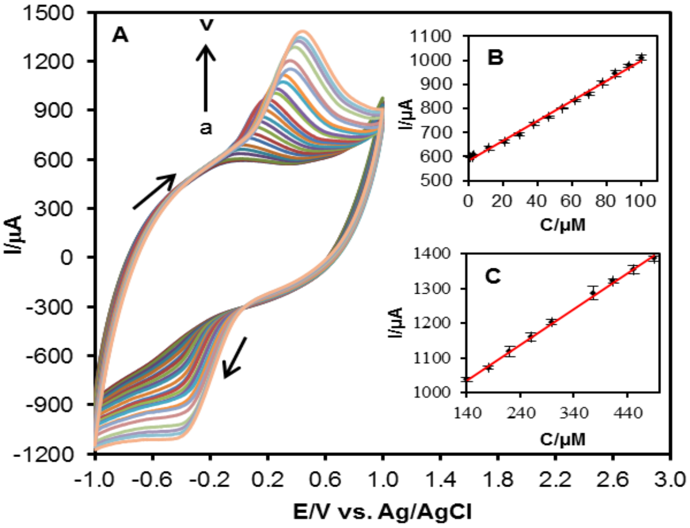


Figure 6. (A) Cyclic voltammograms of GEPVAEu in PBS pH 7.0 at varying concentration (a-v: 1.2 – 490.0 μM) at the scan rate of 0.05 V s^{-1}; (B) insets: The corresponding curve of current response versus HQ concentration at the range of 3.67 – 103.27 μM and; (C) 140.93 – 482.11 μM.

Table 1. The performance of the modified electrodes for detecting the HQ in earlier reports

Working electrodes	Linear range (μM)	LOD (μM)	Methods	Refs:
PGCE[a]	10 – 300/350 -1000	3.57	CV[e]	[32]
PNR/MCPE[b]	20-120	4.90	CV	[16]
Poly(oPD)/MCPE[c]	10-90	3.84	CV	[17]
Poly(BGA)/CPE[d]	10-90	2.10	CV	[18]
GEPVAEu	3.67 – 103.67/ 140.93 – 482.11	2.27	CV	This work

[a] Cathode Polarized Glassy Carbon Electrode

[b] Poly(Neutral Red)/Modified Carbon Paste Electrode

[c] Poly(o-Phenylenediamine)/Modified Carbon Paste Electrode

[d] Poly(Benzoguanamine)/Carbon Paste Electrode

[e] Cyclic Voltammetry

The performance comparison of HQ sensing using GEPVAEu with the other working electrodes was listed in Table 1. GEPVAEu exhibited encouraging sensor performance in terms of a large linear range and low limit of detection over other modified electrodes, suggesting that the proposed sensor was appropriate for HQ detection.

The repeatability was measured at ten different electrodes, which were evaluated separately in a similar condition. It was expressed as the RSD that was found to be 0.76% for GEPVAEu, which was lower than GEPVA (2.14%). Furthermore, the stability of GEPVAEu was explored, which is described in Figure 7. After twenty days, only a small decrease in HQ's oxidation peak current was observed with the signal change of 2.42% for GEPVAEu. On the contrary, the signal change after twenty days for

GEPVA was 6.16%. These results informed that the GEPVAEu was better than GEPVA in terms of reproducibility and stability. The reproducibility of the HQ quantification method using GEPVAEu was satisfying as indicated by the low value of RSD and the signal change.

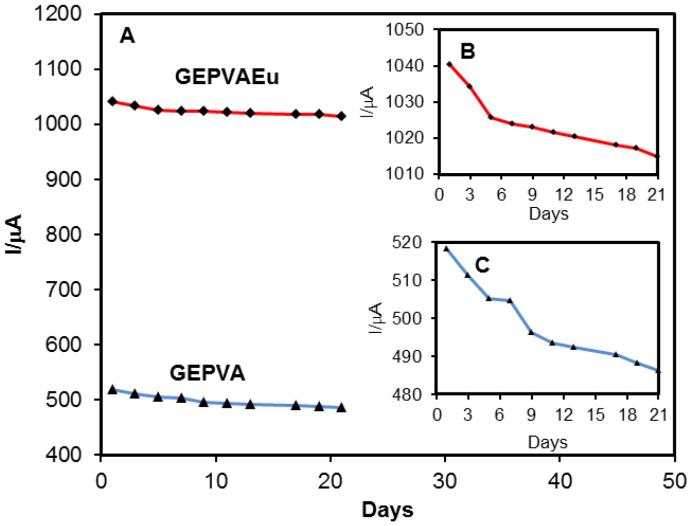


Figure 7. (A) The results of 10 successive repetitive measurements for detecting 100 μM HQ using the cyclic voltammetry technique at the scan rate of 0.05 V s^{-1} in twenty days using GEPVAEu and GEPVA, (B) enlarged curve for GEPVAEu, and (C) enlarged curve for GEPVA.

3.7. Analytical application

Table 2. Determination and output recovery results of the HQ addition in the beauty care product cream sample using the GEPVAEu (n = 3)

HQ added (μM)	HQ detected (μM)	Recovery (%)
20.00	22.79	113.97 ± 0.60
30.00	31.42	104.75 ± 1.57
40.00	39.82	99.55 ± 0.34
50.00	48.72	97.44± 0.38

In this work, the GEPVAEu was also applied as an electrochemical sensor for HQ quantification, particularly in the beauty care product cream sample. The HQ was applied to the sample and then extracted by PBS at a pH of 7.0. The observations were conducted using the cyclic voltammetry to get the responses of real samples solution. The accuracy of the method was determined by its recovery percentages on the addition of standard HQ. The recovery results were measured by the calibration curve in Figure 6B, and they were demonstrated in Table 2. The recoveries were from 97.44 ± 0.38 to 113.97 ± 0.60 μM, showing that this method was applicable and reliable.

4. CONCLUSIONS

In conclusion, the eugenol electropolymerization on the surface of the graphite electrode, and the PVA presence produced a stable GEPVAEu working electrode. This modification raised the current response, enhanced the electroactive surface area, and showed remarkable analytical performance towards HQ's electrochemical sensor. This sensor had an excellent sensing range, high sensitivity, low limit of detection, and high reproducibility in electrochemical detection. The results showed that the GEPVAEu can be directly applied for HQ quantification in the beauty care product cream sample with adequate recovery percentages, which was remarkable.

ACKNOWLEDGMENTS
The Authors would like to thank the Indonesian Education Scholarship (LPDP) for the financial support and the assistance for the electrochemical research instruments in the Analytical Chemistry Laboratory, Yogyakarta State University, Indonesia

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