Lantanida Journal, 13(2): 267-291 e-ISSN: 2548-9062 p-ISSN: 2356-3133

ELECTROCHEMICAL SENSOR FOR THE DETECTION OF HYDROQUINONE USING A CARBON PASTE ELECTRODE MODIFIED WITH MOLECULARLY IMPRINTED POLY(METHYL RED)

Riskia Chandra Widianti[1*], Yussi Pratiwi[1], Feni Mustika Sari[2], Arinda Putri Nurhaliza[1], Riky Afianto[1], Annisa Mulyanah[1]
[1]Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Negeri Jakarta, Rawamangun Muka Road, Jakarta, 13220, Indonesia
[2] Siliwangi University , Jl. Siliwangi No.24, Kahuripan, Tawang District, Tasikmalaya Regency, West Java 46115, Indonesia
[*]Email: riskia.chandra@unj.ac.id

DOI: https://doi.org/10.22373/lj.v13.i2.32610

Article History: *Received: November 3, 2025* *Revised: December 25, 2025*
Accepted: December 26, 2025 *Published: December 31, 2025*

ABSTRACT

Hydroquinone is a toxic compound that is still found in illegal cosmetic products, so the development of sensitive sensors is needed. In this study, an electrochemical sensor based on carbon paste electrode modified with molecularly imprinted poly(methyl red) (CPE–MIP) was developed to detect hydroquinone. Electrode modification was carried out by electropolymerization of methyl red in the presence of hydroquinone using cyclic voltammetry at a potential range of −0.6 to +1.4 V for 15 cycles. The surface morphology was characterized by Scanning Electron Microscope (SEM), while the electrochemical performance was evaluated using Differential Pulse Voltammetry (DPV). Compared with unmodified CPE, CPE–MIP showed an increase in the oxidation peak current and a shift towards lower oxidation potentials. The sensor showed a linear response to hydroquinone concentrations ranging from 20 to 20,000 µM with a coefficient of determination (R^2) of 0.9992, a sensitivity of 0.0018 µA μM^{-1}, a limit of detection of 6.43 µM (3.3σ/slope), and good repeatability with a %RSD of 1.07% (n = 30) using a single. These results indicate that the fabricated CPE–MIP sensor exhibits promising initial analytical performance for hydroquinone detection and provides a basis for further validation.

Keywords: carbon paste electrode, hydroquinone, electrochemical sensor, methyl red, voltammetry

INTRODUCTION

In modern times, appearance has become an essential aspect of both professional and social life, driving many people to try various skincare methods, whether natural or instant. In recent years, a large number of cosmetic and beauty products have emerged, as fair and bright skin is often regarded as the ideal standard of beauty by many individuals (Saraswati &

Perwitasari, 2022). Cosmetics are formulations applied to the epidermal skin, hair, nails, lips, teeth, and oral cavity, with the purpose of cleaning, caring for, and protecting these parts of the body (Zaky & Safitri, 2023). However, cosmetics are often used without considering the chemical ingredients contained in them, which can be harmful to the skin. One of the most widely used cosmetic products is whitening cream.

Whitening creams are popular because they can lighten or reduce dark spots on the skin (Sulaiman et al., 2020). These facial whitening products generally contain active ingredients such as hydroquinone, which functions by inhibiting melanin formation and degrading existing melanin, thus producing a skin-lightening effect (Yuliati, 2023). Hydroquinone is a benzene derivative compound known to be toxic (Suharyani et al., 2021). Due to its hazardous nature, the Indonesian National Agency of Drug and Food Control (BPOM) issued Regulation No. KH.00.01.43.2503 on June 11, 2009, prohibiting the use of hydroquinone in cosmetic formulations, especially in whitening creams, except under medical supervision. This regulation was later updated through the *Head of BPOM Regulation on Technical Requirements for Cosmetic Ingredients* (2019), which emphasizes that hydroquinone use as a whitening agent in cosmetics is strictly prohibited and only allowed in artificial nail formulations at a maximum concentration of 0.02%, applied by professionals (Charismawati, 2021).

Monitoring the presence of hydroquinone in whitening creams is generally conducted by periodically determining its concentration in cosmetic compositions. The method most commonly employed for this purpose is UV–Visible spectrophotometry (Yuliati, 2023). According to a study by Silitonga *et al*., (2024), all ten whitening cream samples tested were found to contain hydroquinone, with the highest concentration detected at 2.11%. Similarly, research by Julan et al. (2023) reported the presence of hydroquinone in all ten samples analyzed, with concentrations reaching up to 6.08%. These findings indicate that hydroquinone to be used in facial whitening creams. However, UV–Vis spectrophotometry has several limitations, including long analysis time, high reagent consumption, and costly instrument maintenance (Ilahi et al., 2021). Consequently, alternative analytical approaches for hydroquinone determination continue to be explored, often involving electrode modification strategies to improve analytical efficiency.

One such modification involves the voltammetric determination of hydroquinone as demonstrated by Harsini et al (2019). Voltammetry represents an innovative analytical technique that offers faster, more efficient, and cost-effective analysis. Being an electrochemical-based method (Harsini et al., 2019), Voltammetry represents an electrochemical analytical technique that offers faster analysis, operational simplicity, and cost effectiveness. As an electrochemical method, voltammetry is particularly suitable for hydroquinone, which is an electroactive compound capable of undergoing oxidation and reduction reactions. Owing to its high sensitivity and low detection limits, voltammetric techniques have been widely applied in hydroquinone analysis through the development of various electrode configurations (Ningrum, 2022). For example, Sidhu et al. (2025) reported a hydroquinone biosensor based on FAD-functionalized fluorapatite/SWCNTs, achieving a linear detection range of 0.005–258.2 μM with a limit of detection (LOD) of 2.70 nM. Other studies, such as that by Ahmed et al. (2024), employed a PEDOT/CNTs-graphene oxide modified electrode, resulting in an LOD of 8.5 nM and a linear range of 0.04–100 μM. Despite their excellent analytical performance, many previously reported hydroquinone sensors involve high material costs and complex fabrication procedures, which may limit their broader application. Therefore, the development of simpler and more cost-effective sensing platforms remains of interest.

In voltammetric techniques, the choice of electrode plays a crucial role, as the electrode facilitates redox reactions from the analyte and generates measurable current responses. One commonly used electrode is the carbon paste electrode (CPE) (Mashhadizadeh et al., 2021). CPEs are widely applied due to their favorable electrochemical properties, ease of preparation, and flexibility in surface modification (Harsini et al., 2019). A study by Harsini et al. (2019) successfully detected hydroquinone levels of 2% in whitening cream samples using a modified CPE. However, their modification involved ferrocene, which is relatively expensive and not environmentally friendly. This highlights the need for alternative electrode modifiers that are both economical and environmentally benign.

Modification of CPE using poly(methyl red) offers potential alternative. Methyl red was selected due to several advantages over ferrocene, including easier biodegradability, lower toxicity, pH responsiveness, and reduced cost (Soraya & Sari, 2024). From a structural perspective, methyl red is an azo dye containing aromatic rings and functional groups such as the azo (–N=N–) linkage and carboxylic acid moiety, which may promote π–π interactions and facilitate electron transfer at the electrode interface, potentially enhancing sensitivity toward phenolic compounds such as hydroquinone (Zahran, 2023). In addition, methyl red has a pK_a of approximately 5.1, allowing it to exist in both ionized and non-ionized forms under typical working conditions, which may support proton-coupled electron transfer processes. Although direct experimental confirmation of these interaction mechanisms remains limited, the role of aromatic systems and acid–base functional groups in improving electrochemical sensor performance has been reported in previous studies (Wu et al., 2024).

Furthermore, the integration of molecularly imprinted polymer (MIP) technology with CPE modification has attracted increasing attention due to its ability to introduce recognition sites complementary to target molecules. MIPs are synthetic polymers that contain specific cavities capable of recognizing target analytes based on size, shape, and functional group interactions (Bow et al., 2021). MIPs offer advantages such as chemical stability, low toxicity, reusability, and favorable analytical performance (Sodik, 2024). However, the application of environmentally friendly functional monomers in MIP-based CPE systems for hydroquinone detection remains relatively limited.

Therefore, this study aims to develop and characterize a carbon paste electrode modified with molecularly imprinted poly(methyl red) (CPE–MIP) for the electrochemical detection of hydroquinone. The analytical performance of the proposed sensor was evaluated in terms of linear response range, sensitivity, limit of detection, and repeatability using differential pulse voltammetry. This work provides a preliminary assessment of the feasibility of poly(methyl red)-based MIP modification as a simple and cost-effective approach for hydroquinone sensing.

METHODS

Chemicals and Instrumentations

Graphite powder (≥99.99%, synthetic, Sigma-Aldrich, Cat. No. 282863) was used as the conductive matrix for the carbon paste electrode. Hydroquinone (Himedia), methyl red (Himedia), and phosphate buffer solution pH 7.0 (Himedia) were used as the analyte, functional monomer, and supporting electrolyte, respectively. Potassium ferricyanide ($K_3[Fe(CN)_6]$) and potassium ferrocyanide ($K_4[Fe(CN)_6]$) (Sigma-Aldrich) were employed as redox probes for electrochemical characterization. All reagents were of analytical grade and were used without further purification. Deionized water was used for all solution preparations.

Electrochemical measurements were performed using an EDAQ potentiostat system (eDAQ Pty Ltd., Australia) equipped with a conventional three-electrode configuration. Surface morphology was characterized using a Scanning Electron Microscope (SEM), Hitachi SU3500 (Hitachi High-Tech Corp., Japan).

Preparation of Carbon Paste Electrode (CPE)

Carbon paste electrodes (CPE) are made by mixing graphite powder and liquid paraffin in a 7:3 (w/w) ratio, with a total mass of 1.00 g, consisting of 0.70 g of graphite powder and 0.30 g of liquid paraffin. The two materials are mixed homogeneously using a mortar for approximately 15 minutes to obtain a uniform carbon paste. A copper wire approximately 6 cm long is used as an electrical connector and inserted into the glass electrode body, as shown in Figure 1.

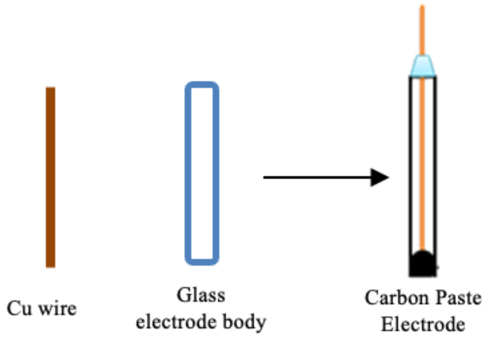

Figure 1. Scheme of Carbon Paste Electrode

The carbon paste is then compacted into the electrode cavity until it is full and there are no air gaps. The electrode surface is leveled using weighing paper before use. The geometric surface area of the electrode is approximately 0.07 cm^2 (diameter ± 3 mm) (Widianti, 2018).

Preparation of Modified CPE

Modification of carbon paste electrodes with molecularly imprinted polymers (MIPs) was performed through electropolymerization using cyclic voltammetry (CV). Methyl red was used as the functional monomer, while hydroquinone served as the template molecule. The electropolymerization process was carried out in a solution containing 1.0 mM methyl red and 1.0 mM hydroquinone, prepared in methanol and phosphate buffer solution (PBS, pH 7) as supporting electrolytes. The schematic diagram of the electrochemical cell used in this study is shown in Figure 2.

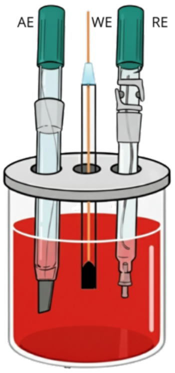

Figure 2. Electrochemical Cell

A three-electrode system was employed, consisting of a carbon paste electrode (CPE) as the working electrode (WE), an Ag/AgCl electrode as the reference electrode (RE), and a platinum wire as the auxiliary (counter) electrode (AE). The CPE was immersed in the polymerization solution during the electropolymerization process. Cyclic voltammetry was performed over a potential range of −0.6 to +1.4 V (vs. Ag/AgCl) at a scan rate of 0.1 V s^{-1}. The number of polymerization cycles was varied during the optimization stage (5–20 cycles).

After the electropolymerization process, the electrodes were rinsed with distilled water to remove physically adsorbed species. This modified electrode is hereinafter referred to as CPE–MIP. For comparison, non-imprinted polymer electrodes (CPE–NIP) were prepared using the same procedure, but without the addition of hydroquinone to the polymerization solution.

Removal of Hydroquinone Molecules from MIP

The removal of hydroquinone molecules from the CPE–MIP surface was carried out using cyclic voltammetry for 10 cycles within a potential range of −0.6 to +1.4 V at a scan rate of 0.1 V s^{-1} in phosphate buffer solution (pH 7), in order to generate recognition cavities on the polymer layer.

Electrochemical Characterization

Electrochemical characterization of the fabricated electrode was carried out using cyclic voltammetry (CV). The voltammetric responses of the modified electrode were recorded and systematically compared with those of the reference electrode to evaluate changes in electrochemical behavior resulting from the surface modification. This characterization aimed to assess the electron transfer properties, surface conductivity, and the successful formation of the modified layer on the electrode surface.

Scanning Electron Microscope (SEM) Characterization

The surface morphology of the carbon paste electrode and the modified electrode was examined using scanning electron microscopy (SEM). SEM analysis was conducted to observe differences in surface texture, polymer layer coverage, and porosity before and after electrode modification. This characterization provided visual evidence of morphological changes associated with the modification process and supported the successful formation of the polymer layer on the electrode surface.

Variation of Monomer and Template Ratios in CPE–MIP Preparation

Optimization was carried out by varying the ratio of analyte (hydroquinone) to monomer (methyl red) from 1:1 to 1:5. The analyte concentration was fixed at 1.0 mM, while the monomer concentration was varied between 0.1 mM and 0.5 mM. Measurements were performed using differential pulse voltammetry (DPV).

Variation in the Number of Polymerization Cycles

Electropolymerization was conducted using cyclic voltammetry within a potential range of −0.6 to 1.4 V. The number of polymerization cycles was varied at 5, 10, 15, and 20 cycles to study the effect of cycle number on the formation of the polymer layer.

Variation of Scan Rate

After optimizing the analyte-to-monomer ratio and the number of polymerization cycles, the modified electrode was employed for electrochemical measurements. Standard hydroquinone at a concentration of 1 mM was analyzed at various scan from 0.02 – 0.2 V/s rates using cyclic voltammetry within a potential range of -0.2 V to +0.3 V.

Performance Evaluation of CPE, CPE–NIP, and CPE–MIP

Following the optimization step, the analytical performance of the unmodified carbon paste electrode (CPE), the non-imprinted polymer-modified electrode (CPE–NIP), and the molecularly imprinted polymer-modified electrode (CPE–MIP) was evaluated. Hydroquinone determination was carried out at a concentration of 1.0 mM using differential pulse voltammetry (DPV).

Validation of Modified Electrode Performance

Repeatability was evaluated by measuring 1.0 mM hydroquinone solution using a single electrode for 30 measurements. The standard deviation was calculated and compared with the acceptable range based on the Horwitz coefficient of variation.

Linearity was determined by measuring hydroquinone solutions at range concentrations. The range with a correlation coefficient (r^2) closest to 0.99 was considered the linear working range. The limit of detection (LOD) was calculated based on the standard deviation of blank measurements using the equation LOD = 3.3σ/slope (Marwati et al., 2020).

RESULTS AND DISCUSSION

Study on the Fabrication of Modified Carbon Paste Electrodes (CPEs)

In this study, carbon paste electrodes (CPEs) were modified to produce non-imprinted polymer electrodes (CPE–NIP) and hydroquinone molecularly imprinted polymer electrodes (CPE–MIP). The CPE–NIP was prepared through the electropolymerization of a monomer solution, resulting in the formation of a polymer layer deposited on the surface of the CPE. In contrast, the CPE–MIP was fabricated by electropolymerizing a solution containing both the monomer and hydroquinone (HQ) as the template molecule, leading to the formation of a polymer matrix that incorporates the analyte within its structure.

An additional step was applied during the preparation of CPE–MIP, namely the removal of the template molecule. This step is essential to generate recognition sites or cavities on the polymer surface that are complementary in size and shape to the hydroquinone molecule, which is expected to enhance the selectivity of the modified electrode toward the target analyte. In this system, methyl red was employed as the functional monomer, while hydroquinone functioned both as the template molecule during polymer formation and as the analyte during detection. The presence of the polymer matrix on the electrode surface was anticipated to improve the overall electrochemical response. The cyclic voltammogram of the electropolymerization process of CPE-NIP is presented in Figure 3. Meanwhile, the cyclic voltammograms corresponding to the electropolymerization of CPE–MIP and the subsequent hydroquinone template removal process are shown in Figure 4.

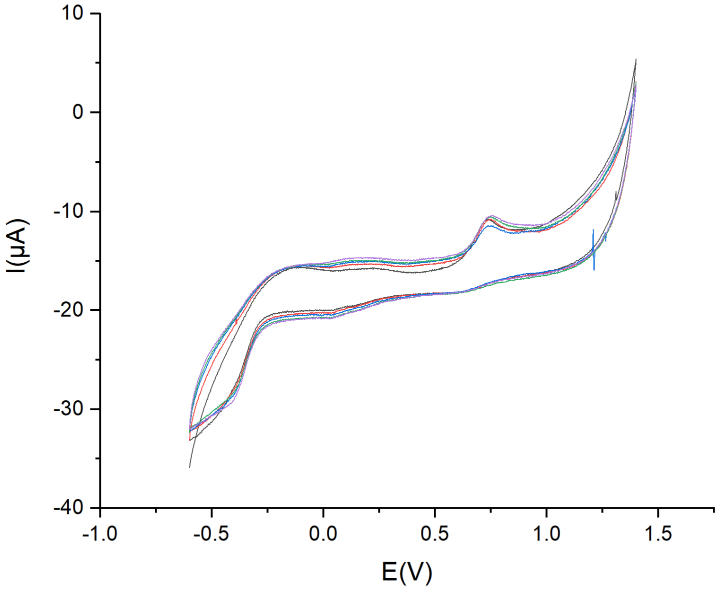

Figure 3. Cyclic Voltammogram of CPE-NIP Electropolymerization

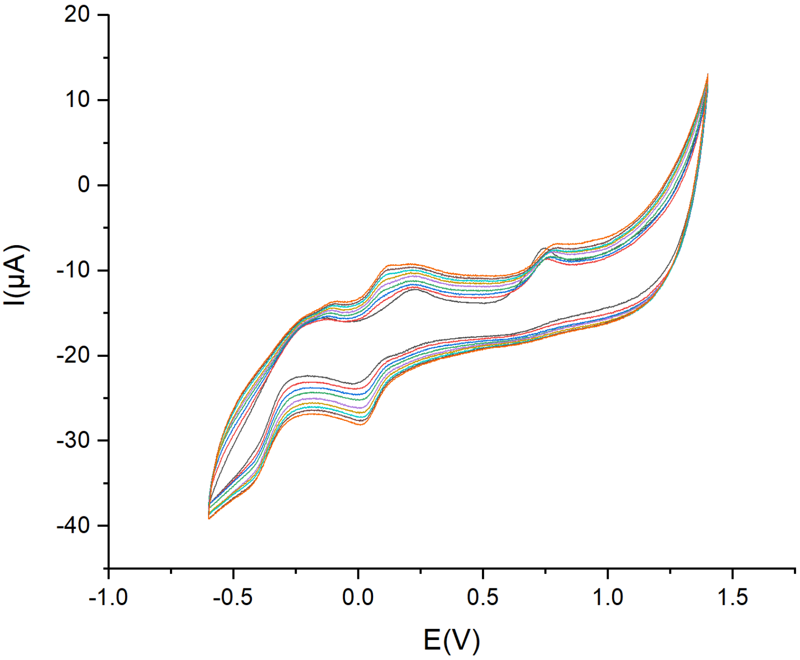

Figure 4. Cyclic Voltammogram of CPE-MIP Electropolymerization

Based on the recorded voltammograms, the CPE–MIP exhibited distinct peaks that were not observed in the CPE–NIP. These peaks are attributed to the oxidation of the hydroquinone template incorporated within the polymer matrix during the electropolymerization process, as illustrated schematically in Figure 5.

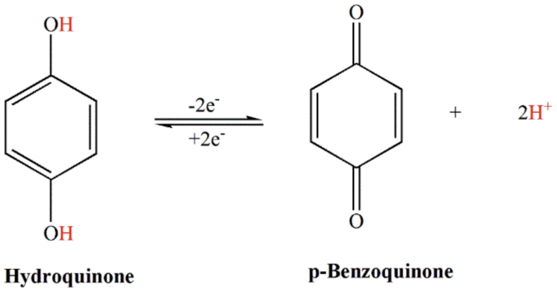

Figure 5. Oxidation Reaction of Hydroquinone (Arfin et al, 2019)

Prior to its application for hydroquinone determination, the template molecules embedded in the CPE–MIP must be removed to create vacant imprinted cavities that are specific to hydroquinone. This leaching process is expected to enhance the sensitivity of the electrode, as the resulting cavities facilitate the selective redox reaction of hydroquinone at the electrode surface. Template removal was carried out using cyclic voltammetry in a phosphate buffer solution at pH 7 by scanning the potential from −0.6 to 1.4 V. The cyclic voltammogram obtained during the template removal process is shown in Figure 6.

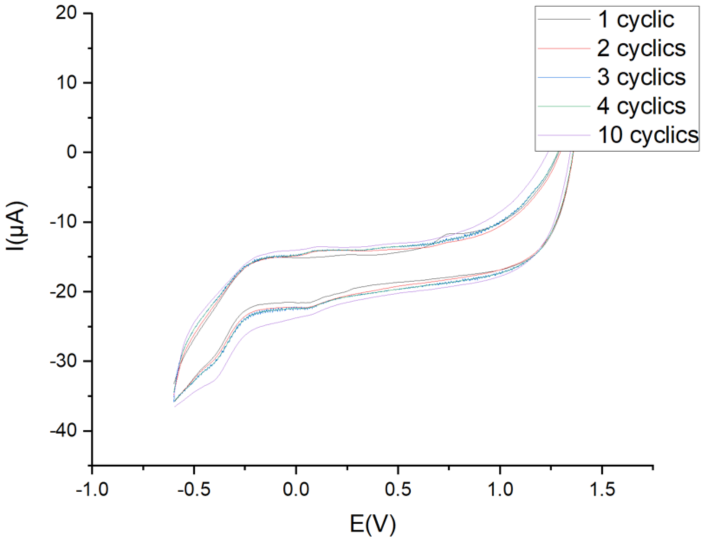

Figure 6. Cyclic Voltammogram of Hydroquinone Template Removal Process on CPE-MIP

Based on the voltammogram, during the first cycle, clear oxidation peaks associated with hydroquinone and methyl red were still observed, indicating that hydroquinone remained present on the electrode surface and was electrochemically active. However, from the second cycle onward up to the tenth cycle, the oxidation peak corresponding to hydroquinone gradually disappeared. This behavior confirms that the hydroquinone template molecules were successfully removed from the CPE–MIP surface. These results indicate that the poly(methyl red) molecularly imprinted with hydroquinone was successfully formed on the electrode surface, and after the template removal process, the CPE–MIP was ready to be used for hydroquinone determination.

Characterization of Carbon Paste Electrode (CPE)

The surface morphology of the unmodified CPE and the CPE–MIP was examined using SEM, and the resulting images are presented in Figure 7. The SEM image of the bare CPE shows closely packed graphite/carbon flakes with a relatively flat and granular surface. Only a limited number of interparticle gaps and minor surface fragments were observed, indicating a compact carbon matrix. In contrast, the CPE–MIP exhibits a noticeably rougher and more heterogeneous surface morphology. The modified electrode is characterized by textured particle aggregates, thin polymer-like film layers covering the carbon grains, and the presence of more pronounced micro-cavities or porous chain-like structures.

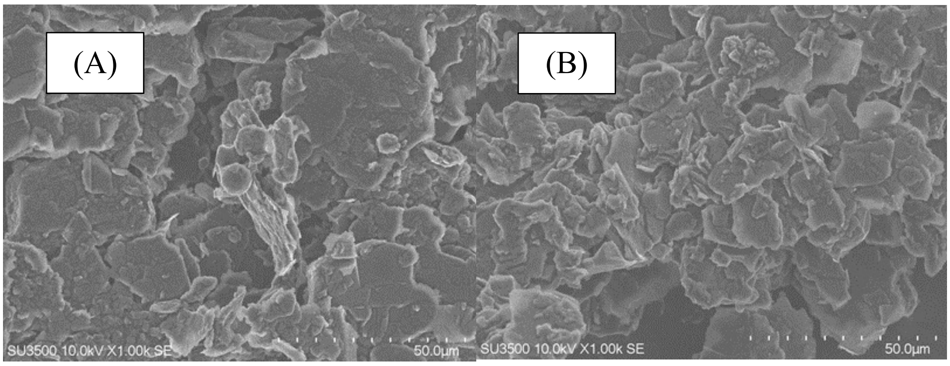

Figure 7. SEM Images of (A) CPE; (B) CPE-MIP

Similar surface features have been reported by Hernández-García et al. (2024), where the formation of molecularly imprinted polymer layers on carbon paste electrodes resulted in increased surface roughness and the appearance of porous structures. According to Hernández-García et al (2024), such porous morphologies can contribute to an increase in the effective surface area and facilitate specific interactions between the target molecule and the modified electrode surface. This structural characteristic is expected to support the electrochemical response observed in subsequent measurements.

Performance of the Electrode Toward Hydroquinone Analysis

In this preliminary study, an important initial step was to evaluate whether methyl red could function effectively as a sensing monomer for hydroquinone detection. For this purpose, the electrochemical responses of the unmodified carbon paste electrode (CPE), non-imprinted polymer electrode (CPE–NIP), and molecularly imprinted polymer electrode (CPE–MIP) were compared in a hydroquinone solution. This comparison was carried out to assess the influence of electrode modification on the detection behavior toward the target analyte. Differential Pulse Voltammetry (DPV) measurements were performed within a potential range of −0.2 to 0.55 V at a scan rate of 0.1 V/s. The resulting DPV voltammograms obtained using CPE, CPE–NIP, and CPE–MIP are shown in Figure 8. A comparison of the oxidation peak currents and peak potentials obtained from the three electrodes is summarized in Table 1.

As shown in Figure 8 and Table 1, all three electrodes were able to detect hydroquinone, indicating that the analyte is electroactive at the carbon paste surface. However, clear differences in electrochemical response were observed after electrode modification. Both CPE–NIP and CPE–MIP exhibited higher peak currents and a noticeable shift of the oxidation potential toward more negative values compared to the bare CPE. The shift in oxidation potential suggests that the modification of the electrode surface facilitates the electron transfer process of hydroquinone. In particular, the CPE–MIP displayed the highest peak current among the tested electrodes, indicating a more pronounced enhancement of the electrochemical response. The increase observed for CPE–NIP can be attributed to the presence of the poly(methyl red) layer, while the significantly higher response of CPE–MIP is associated with the formation of specific recognition sites created through the molecular imprinting process.

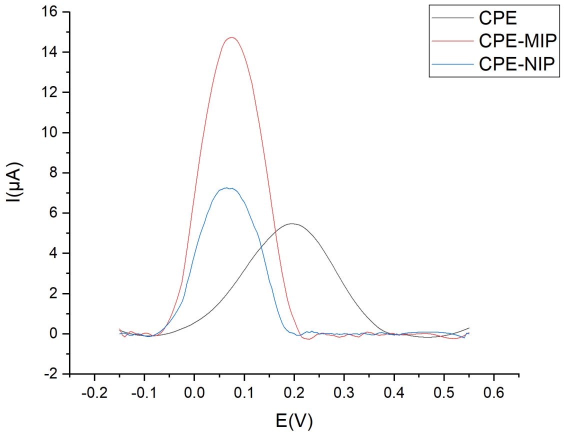

Figure 8. DPV Voltammograms of Hydroquinone Determination using CPE, CPE-NIP, and CPE-MIP

Table 1. Peak Current of Electrodes in 2 mM Hydroquinone Solution

Electrode	I_p (μA)	E_p (V)
CPE	5.47	0.195
CPE-NIP	7.24	0.075
CPE-MIP	14.74	0.075

These observations are consistent with previous reports, where a shift of the oxidation potential toward more negative values was interpreted as an indication of faster electron transfer at modified electrode surfaces (Lu et al., 2020). Mashhadizadeh (2021) also reported that surface modification with electroactive polymers can lower the oxidation potential of hydroquinone and enhance the current response by improving interfacial electron-transfer kinetics. Therefore, the results obtained in this preliminary evaluation confirm that the CPE–MIP provides a more favorable electrochemical environment for hydroquinone detection compared to the unmodified and non-imprinted electrodes.

Optimization of Analyte-to-Monomer Rasio

To obtain optimal performance of the synthesized CPE–MIP, the ratio between the functional monomer and the template molecule was optimized. This step is important because the monomer–template composition strongly influences the formation of imprinted sites within the polymer matrix. In this study, the ratio of methyl red (monomer) to hydroquinone (template) was varied from 1:1 to 5:1. The DPV responses of CPE–MIP prepared at different ratios are presented in the voltammograms shown in Figure 9. The corresponding peak current and peak potential values obtained from these measurements are summarized in Table 2.

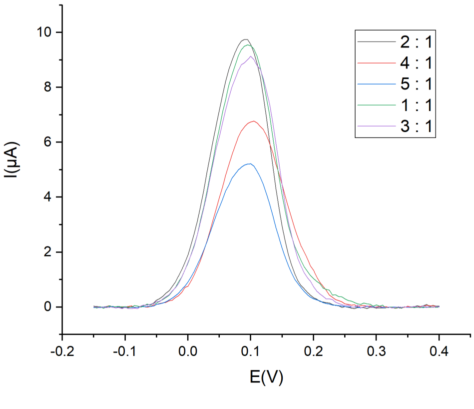

Figure 9. DPV Voltammograms of Hydroquinone Measured using CPE–MIP Prepared at Various Methyl Red to Hydroquinone Ratios (1:1 to 5:1)

Table 2. Peak Current and Peak Potential of CPE–MIP Prepared at Different Monomer-To-Template Ratios

Methyl Red:Hidrokuinon	DPV		n
	$\overline{I_p}$ (μA) ± SD	$\overline{E_p}$ (mV) ± SD	
1:1	9.52 ± 0.035	0.095 ± 0.000	2
2:1	9.82 ± 0.098	0.092 ± 0.003	2
3:1	9.04 ± 0.127	0.100 ± 0.000	2
4:1	6.79 ± 0.021	0.100 ± 0.007	2
5:1	5.06 ± 0.212	0.097 ±0.003	2

Based on the peak current and potential values, the CPE-MIP prepared with a 2:1 ratio (methyl red : hydroquinone) exhibited the highest peak current. These results indicate that this composition gives the best electrochemical response to hydroquinone and is therefore selected as the optimum ratio for further experiments.

In molecularly templated polymer-based electrode systems, the monomer-to-template ratio plays a critical role in determining the number and accessibility of specific recognition sites formed during polymerization. At lower monomer contents, the number of functional groups available to interact with the template may be insufficient, while excessive monomer concentrations can lead to the formation of a thicker polymer layer and hinder analyte mass transfer. The best response at a 2:1 ratio indicates a balance between effective template site formation and adequate polymer permeability, allowing hydroquinone to efficiently access the electrode surface after template removal.

Similar results have been reported by Setiyanto (2020) in the development of polyglutamate-modified carbon paste electrodes for Rhodamine B detection. An optimal monomer-to-template ratio resulted in optimal current response, while higher monomer ratios resulted in decreased sensitivity due to diffusion limitations. These findings support the selection of a 2:1 ratio as the optimal composition for CPE–MIP preparation in this study.

Optimization of Polymerization Cycles

To evaluate the influence of poly(methyl red) film thickness on the electrode response, the number of electropolymerization cycles was optimized. CPE–MIP electrodes were prepared using different numbers of cycles (5–25 cycles) and subsequently evaluated for hydroquinone determination under the optimized experimental conditions. The DPV responses obtained from CPE–MIP prepared at different numbers of electropolymerization cycles are presented in Figure 10. A comparison of the peak current and peak potential values corresponding to each number of cycles is summarized in Table 3.

Based on the data, the optimal number of electropolymerization cycles is 15 cycles, because it produces the highest average peak current ($\overline{I_p}$) value. An increase in peak current was observed as the number of cycles increased from 5 to 15, indicating progressive growth of a poly(methyl red) film on the carbon paste electrode surface. This trend suggests that the formation of a sufficiently thin and conductive polymer layer enhances electron transfer and facilitates access of hydroquinone to the electrode surface.

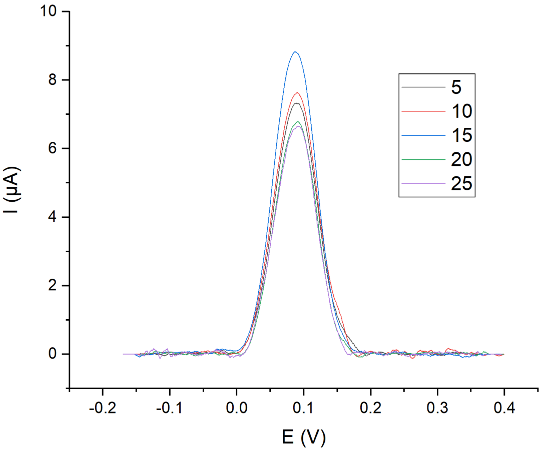

Figure 10. DPV Voltammograms of Electropolymerization Cycles

Table 3. Peak Current and Potential Values Obtained From The Optimization of Electropolymerization Cycle Numbers

Electropolymerization Cyclic	DPV		n
	$\overline{I_p}$ (μA) ± SD	$\overline{E_p}$ (mV) ± SD	
5	7.32 ± 0.014	0.088 ± 0.001	2
10	7.59 ± 0.094	0.090 ± 0.003	2
15	8.81 ± 0.007	0.088 ± 0.000	2
20	6.81 ± 0.028	0.091 ± 0.000	2
25	6.62 ± 0.035	0.090 ± 0.001	2

When the number of cycles exceeded 15, the peak current decrease, suggesting that a thicker poly(methyl red) film hindered charge migration and electron transfer processes. Therefore, the optimal number of electropolymerization cycles was determined to be 15 cycles.

In addition to the influence of film thickness, the formation of molecular template cavities within the poly(methyl red) matrix contributes to the analytical performance of the modified electrodes. During electropolymerization in the presence of hydroquinone as a template, recognition sites with complementary sizes and shapes are formed within the polymer layer. After template removal, these sites can facilitate selective rebinding of hydroquinone through non-covalent interactions, such as hydrogen bonds and π–π interactions, as suggested in previous MIP-based electrochemical studies (Cheng et al., 2025).

Overall, the number of electropolymerization cycles directly affects the thickness, compactness, and permeability of the polymer layer, which in turn affects the kinetics of electron transfer and analyte diffusion. The optimal response obtained at 15 cycles reflects a balance between the formation of sufficient imprinted sites and the maintenance of effective electrical conductivity, while higher cycle numbers result in polymer layers that limit mass and charge transfer (Ait Lahcen et al., 2025).

Effect of Scan Rate on Measurement

The influence of scan rate on the electrochemical response of 1 mM hydroquinone at the CPE–MIP electrode was evaluated in the range of -0.02 to +0.2 V/s. The corresponding cyclic voltammograms are shown in Figure 11.

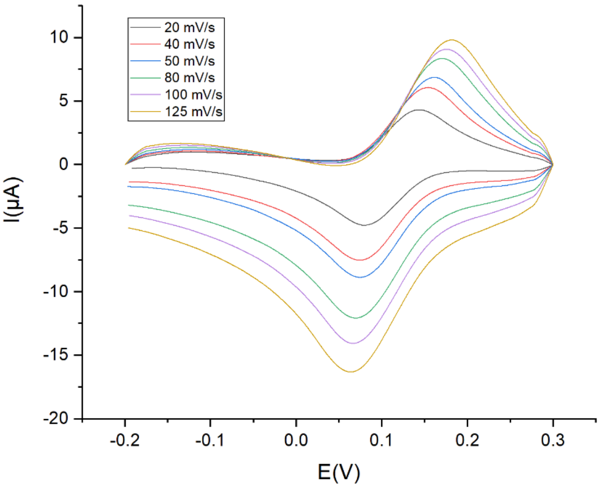

Figure 11. Cyclic Voltammogram on The Study of The Effect of Scan Rate Variation

To elucidate the electrochemical mechanism, the peak current (Ipa) was analyzed as a function of both the scan rate (ν) and the square root of the scan rate ($\nu^{1/2}$). This analysis was performed based on the Randles–Sevcik equation for a diffusion-controlled process at 25 °C, as reported by Bard and Faulkner et al., (2001).

$$I_p=(2.69\times10^5)n^{3/2}AD^{1/2}C\nu^{1/2}$$

where n is the number of transferred electrons, A is the electrode area, D is the diffusion coefficient, C is the analyte concentration, and v is the scan rate. The plots of Ipa versus scan rate and Ipa versus the square root of scan rate ($v^{1/2}$) are presented in Figure 12.

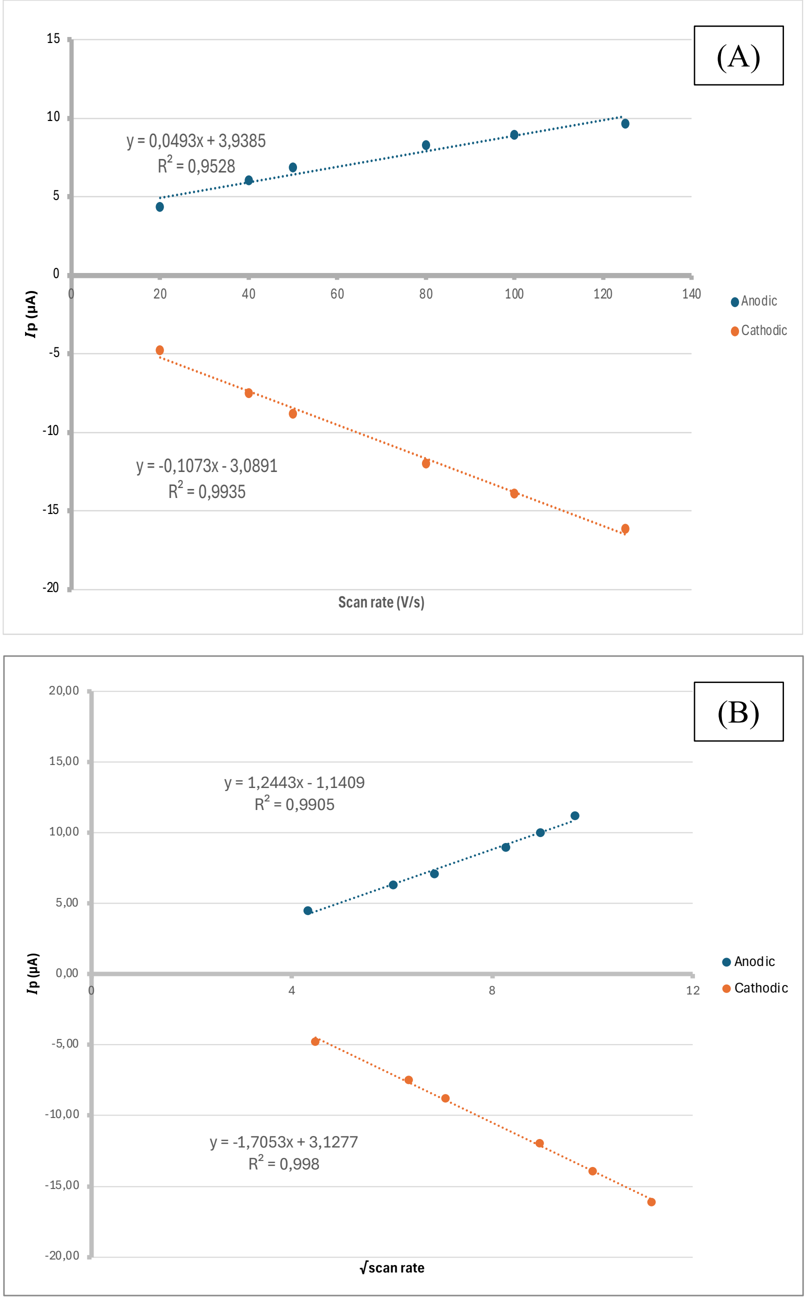

Figure 12. Randles–Sevcik Plots Of Peak Current Versus Scan Rate (A) and Square Root (B)

Based on the voltammograms, an increase in scan rate resulted in higher anodic (Ipa) and cathodic (Ipc) peak currents, both exhibiting a linear relationship. This behavior aligns with the principle that faster scan rates enhance electron transfer kinetics at the electrode surface, thereby generating greater current responses. According to to Aoki (2020), increasing the scan rate enhances the peak current due to faster electron-transfer kinetics at the electrode interface, while the redox potential remains relatively unchanged under reversible conditions.

Then from the data plot it is also known that the linear relationship between Ipa and the square root of the scan rate ($R^2 = 0.9905$) is higher than the relationship between Ipa and the scan rate ($R^2 = 0.9528$), which indicates that the electrochemical process on the modified electrode is dominated by a diffusion mechanism according to the Randles–Sevcik theory. This behavior is consistent with diffusion-controlled electrochemical systems, where charge transport is dominated by the diffusion of electroactive species from the bulk solution to the electrode surface under semi-infinite linear diffusion conditions, as described in recent theoretical and modeling studies of electrochemical diffusion processes (El-Latif et al., 2025).

Repeatability Test of a Single Electrode

The repeatability test was performed using the Differential Pulse Voltammetry (DPV) technique under optimized electrode conditions. The modified electrode was used to measure 1 mM hydroquinone in PBS buffer (pH 7) over a potential range of –0.2 to +0.4 V for 30 measurements. The peak current responses and statistical analysis are summarized in Figure 13 and Table 4.

Tabel 4. Repeatability Test Calculation

Number of Repetition	Hidrokuinon 1 mM (ΔIp, μA)	Number of Repetition	Hidrokuinon 1 mM (ΔIp, μA)
1	2.86	16	2.85
2	2.85	17	2.96
3	2.88	18	2.90
4	2.88	19	2.86
5	2.86	20	2.86
6	2.90	21	2.84
7	2.88	22	2.88
8	2.94	23	2.85
9	2.88	24	2.89
10	2.91	25	2.92
11	2.92	26	2.86
12	2.96	27	2.91
13	2.90	28	2.88
14	2.87	29	2.87
15	2.88	30	2.88
Mean			2.88
Standard Deviation			0.03

%RSD	1.07
%RSD Horwitz	7.90
95% confidence interval (μA)	2.88 ± 0.01

The results showed a mean peak current of 2.88 μA, with a standard deviation of 0.03 μA, and a %RSD of 1.07%. This %RSD is well below the acceptable limit according to the Horwitz coefficient of variation (7.90%), which was calculated using a hydroquinone concentration of 1 mM. The Horwitz %RSD is commonly used as a benchmark to assess the repeatability of analytical methods across different laboratories and concentration levels (Horwitz, 1982; Thompson, 2000). The 95% confidence interval (2.88 ± 0.01 μA) further confirms the consistency of the measurements.

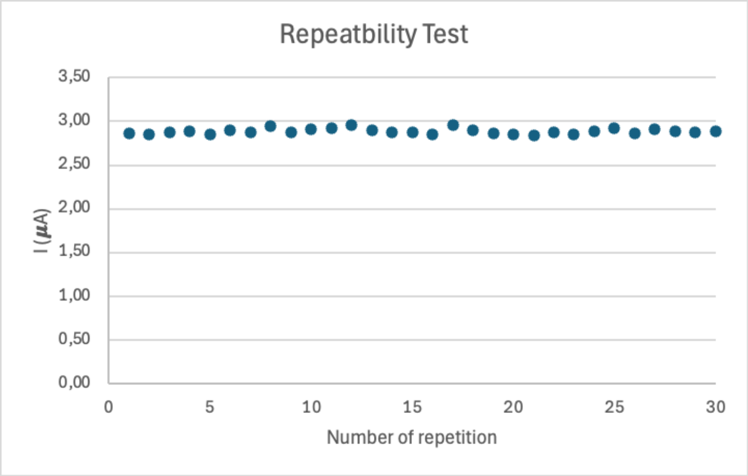

Figure 13. Repeatability of One Electrode

These results indicate that the polymer film templated with poly(methyl red) molecules adhered strongly to the electrode surface, maintained its integrity during repeated measurements, and retained selective binding sites for hydroquinone. The uniform surface morphology and optimized template dissolution procedure contributed to the observed stability, preventing degradation during repeated use.

It should be noted that this repeatability assessment was performed using a single electrode. Although preliminary, the results provide strong evidence for the intraday stability of the electrodes. Further studies involving multiple independently prepared electrodes are recommended to fully assess interelectrode reproducibility. These findings are consistent with previous reports showing that well-controlled electrode surface morphology and a homogeneous polymer film are critical for achieving high repeatability in MIP-based carbon paste electrodes (Tajik et al., 2020).

Electrode Linearity

Linearity measurements were performed from 0 μM - 20000 μM. The linear range of the electrode measurement is shown in Figure 14. The calibration curve for hydroquinone exhibited a linear response in the concentration range of 20–20000 µM (n = 12). The regression equation was $I_p = 0.0018 \pm 0.0000155) C + (0.5529 \pm 0.158)$ with correlation coefficient (R^2) of 0.9992. The limit of detection (LOD), calculated using the as 3.3σ/slope criterion based on blank measurements (n = 3, SD_{blank} = 0.00351), was determined to be 6.43 µM. To further evaluate the analytical performance of the developed sensor, a comparison with a recently reported electrochemical sensor is presented in Table 5.

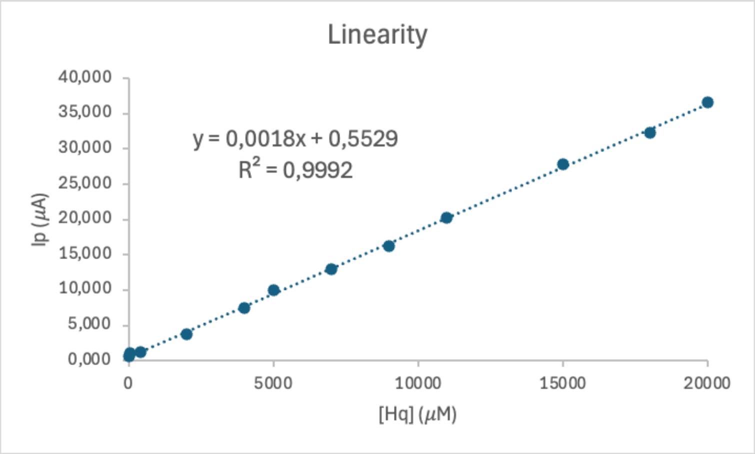

Figure 14. Linearity of Hydroquinone Detection Using The Modified CPE

Table 5. Comparative Studies of Electrochemical Sensors For Hydroquinone Detection

Electrode Modification	Detection Technique	Linear Range (µM)	LOD (µM)	Ref.
CPE–MIP poly(methyl red)	DPV	20–20000	6.43	This work
CNT/ERGO-modified CPE	DPV	0.4–400	0.028	(Chen et al., 2024)
MnO_2 NRs/GO–GCE	DPV	0.5-300	0.012	(Karami-Kolmoti et al., 2023)
SPCE	DPV	1-100	23.4	(Safitri et al., 2015)

Comparison of analytical performance with previously reported electrochemical sensors (Table 5) shows that nanomaterial-based sensors, such as CNT/ERGO-modified CPE and MnO_2 NRs/GO–GCE, have lower LOD, reflecting higher sensitivity (Chen et al., 2024; Karami-Kolmoti et al., 2023). However, these sensors generally have a relatively narrow linear range. This finding is in line with previous reports showing that molecularly imprinted polymers (MIPs) are known to have good stability and can be applied to a wide range of working conditions, while conductivity and diffusion limitations in the polymer matrix often pose challenges in achieving very high sensitivity without the integration of additional conductive materials (Liu et al., 2021).

CONCLUSION

This study successfully developed an electrochemical sensor based on carbon paste electrode imprinted with poly(methyl red) (CPE–MIP) for hydroquinone detection. The modification process resulted in specific recognition sites that significantly enhanced the electrochemical response. Under optimum conditions (monomer–template ratio of 2:1 and 15 cycles), CPE–MIP exhibited a significantly higher peak current ($\Delta Ip = 14.74\ \mu A$) compared to CPE and CPE–NIP, indicating the success of the imprinting process. The sensor exhibited good linearity in the range of 20–20000 µM ($R^2 = 0.9992$), with a LOD of approximately 6.43 µM and good repeatability (%RSD = 1.07%). Although interference tests and validation on real samples have not been conducted, this CPE–MIP shows potential as a selective sensor for the initial screening of hydroquinone in cosmetic products.

ACKNOWLEDGMENT

The authors would like to express their sincere gratitude to the Rector and the Head of the Research and Community Service Institute (LPPM) of UNJ for facilitating this research through the Faculty Basic Research Scheme (D-FP), funded under Rector's Decree Number 329/UN.39/HK.02/2025 and Contract Agreement Number 46/SPK PENELITIAN/FMIPA/2025. The authors also gratefully acknowledge the support of the Chemistry Study Program for providing the facilities that enabled this research to be carried out successfully.

REFERENCES

Ahmed, Y. M., Eldin, M. A., Galal, A., & Atta, N. F. (2024). Electrochemical sensor based on PEDOT/CNTs-graphene oxide for simultaneous determination of hazardous hydroquinone, catechol, and nitrite in real water samples. *Scientific Reports*, *14*(1).

Ait Lahcen, A., Saidi, K., & Amine, A. (2025). A critical review of electrosynthesized molecularly imprinted polymers in electrochemical sensing: Pros and cons. *Current Opinion in Electrochemistry*, *54*, 101752.

Aoki, K. J., Chen, J., Liu, Y., & Jia, B. (2020). Peak potential shift of fast cyclic voltammograms owing to capacitance of redox reactions. *Journal of Electroanalytical Chemistry*, *856*, 113609.

Arfin, T., & Sonawane ;Arshiya Tarannum, K. (2019). Review on Detection of Phenol in Water . *Advanced Materials Letters*, *10*(11), 753–785.

Bard, A. J., & Faulkner, L. R. (2001). Electrochemical methods: Fundamentals and applications (2nd ed.). John Wiley & Sons.

Bow, Y., Syakdani, A., Purnamasari, I., & Rusdianasari, R. (2021). Uji Kinerja Sensor Molecularly Imprinted Polymer (MIP) Simazin secara Potensiometri. *Jurnal Teknik Kimia Dan Lingkungan*, *5*(2), 145–154.

Charismawati, N., Erikania, S., & Ayuwardani, N. (2021). Analisis kadar hidrokuinon pada krim pemutih yang beredar online dengan metode kromatografi lapis tipis (Klt) dan spektrofotometri UV-Vis. *Jurnal Kartika Kimia*, *4*(2), 58-65.

Chen, T., Liu, C., Liu, X., Zhu, C., & Zheng, D. (2024). Simultaneous electrochemical detection of catechol and hydroquinone based on a carbon nanotube paste electrode modified with electro-reduced graphene oxide. *International Journal of Molecular Sciences*, *25*(18), 9829.

Cheng, C., Zhu, X., Qin, X., Zhang, J., Liu, M., & Wang, Y. (2025). An ultra-low fouling electrochemical mocularly imprinted sensor based on size exclusion effect for highly selective pentachlorophenol detection. *Sensors and Actuators B: Chemical*, *425*, 136974.

El-Latif, E. I. A., Kebede, M. A., Sekar, K., Hameed, T. A., Yahia, I. S., Gao, H., & Sheha, E. (2025). Modeling the Diffusion Coefficient of Charge Carriers in Metal Ion Batteries using the Randles-Sevcik Equation. *Advanced Theory and Simulations*, 2500346.

Harsini, M., Untari, U., Fitriany, E., Farida, A. N., Fahmi, M. Z., Sakti, S. C. W., & Pari, G. (2019). Voltammetric analysis of hydroquinone in skin whitening cosmetic using ferrocene modified carbon paste electrode. *Rasayan Journal of Chemistry*, *12*(4), 2296–2305.

Hernández-García, F., Cruz-Navarro, J. A., García-Serrano, J., Franco-Guzmán, M., Islas, G., & Alvarez-Romero, G. A. (2024). Development of a Voltammetric Methodology Based on a Methacrylic Molecularly Imprinted Polymer-Modified Carbon-Paste Electrode for the Determination of Aflatoxin B1. *Separations*, *11*(8), 246.

Horwitz, William. (1982). Evaluation of analytical methods used for regulation of foods and drugs. *Analytical Chemistry*, *54*(1), 67–76.

Ilahi, R. A., Firdaus, M. L., & Amir, H. (2021). Pemanfaatan Nanopartikel Emas (NPE) Sebagai Pendeteksi Kadar Asam Urat Pada Urine dengan Metode Citra Digital. *ALOTROP*, *5*(2), 135–140.

Jajang Japar Sodik. (2024). Peran Molecularly Imprinted Polymers (Mips) Dalam Aplikasi Farmasi: Tinjauan Literatur. *An-Najat*, *2*(2), 71–91.

Julan, M., Febria Leswana, N., & Linden, S. (2023). Identification Of Hydroquinone Content In Whitening Cream Circulated In Segiri Market Samarinda City Using Uv-Visible Spectrophotometry Method Identifikasi Kandungan Hidrokuinon Dalam Krim Pemutih Yang Beredar Di Pasar Segiri Kota Samarinda Dengan Metode Spektrofotometri Uv-Visible. *Pharmacon*, *12*(2), 244–250.

Karami-Kolmoti, P., Beitollahi, H., & Modiri, S. (2023). Electrochemical sensor for simple and sensitive determination of hydroquinone in water samples using modified glassy carbon electrode. *Biomedicines*, *11*(7), 1869.

Liu, Z., Xu, Z., Wang, D., Yang, Y., Duan, Y., Ma, L., ... & Liu, H. (2021). A review on molecularly imprinted polymers preparation by computational simulation-aided methods. *Polymers*, *13*(16), 2657.

Lu, Y., Wu, D., Li, Z., Lin, Q., Ma, X., Zhang, Z., & Xiang, S. (2019). MOFs-derived nano-CuO modified electrode as a sensor for determination of hydrazine hydrate in aqueous medium. *Sensors*, *20*(1), 140.

Marwati, S., Siwanta, D., Trisunaryanti, W., & Louise, I. S. Y. (2020, March). Polyeugenol-modified graphite electrode for determination of hydroquinone in cosmetic. In *Journal of Physics: Conference Series* (Vol. 1485, No. 1, p. 012034). IOP Publishing.

Mashhadizadeh, M. H., Kalantarian, S. M., & Azhdeh, A. (2021). A Novel Electrochemical Sensor for Simultaneous Determination of Hydroquinone, Catechol, and Resorcinol Using a Carbon Paste Electrode Modified by Zn-MOF, Nitrogen-doped Graphite, and AuNPs. *Electroanalysis*, *33*(1), 160–169.

Ningrum, I. R. W. (2022). *Sintesis Nanopartikel Emas Menggunakan Kulit Jeruk Sunkist (Citrus sinensis) dan Aplikasinya untuk Elektroda Sensor Hidrokuinon dalam Krim Kosmetik*. Universitas Islam Indonesia.

Safitri, A., Mulyasuryani, A., & Triandi Tjahjanto, R. (2015). Determination of Hydroquinone in a Square Wave Voltammetry based on Screen Printed Carbon Electrode. *The Journal of Pure and Applied Chemistry Research*, *4*(1), 1–4.

Saraswati, S. N. P., & Perwitasari, M. (2022). KANDUNGAN HIDROKUINON PADA KRIM PEMUTIH WAJAH YANG DIJUAL DI KOTA BEKASI DENGAN METODE SPEKTROFOTOMETRI UV-Visible. *Jurnal Mitra Kesehatan*, *4*(2), 71–79.

Setiyanto, H., Ferizal, M. Y. A., Zulfikar, M. A., Saraswaty, V., & Mufti, N. (2020, July). Modification of Carbon Paste Electrode with Molecularly Imprinted Poly (Gluthamic Acid) for Determination of Rhodamine: A Preliminary Study. In *MSCEIS 2019: Proceedings of the 7th Mathematics, Science, and Computer Science Education International Seminar, MSCEIS 2019, 12 October 2019, Bandung, West Java, Indonesia* (p. 474). European Alliance for Innovation.

Sidhu, M. S., Sridharan, G., Ganapathy, D., Atchudan, R., Arya, S., Mahadevegowda, S. H., & Sundramoorthy, A. K. (2025). Development of highly sensitive electrochemical biosensor for the detection of hydroquinone using a FAD functionalized fluorapatite/SWCNT hybrid composite modified electrode. *RSC Advances*, *15*(23), 17829–17842.

Silitonga, D., & Gunawan, M. (2024). ANALYSIS OF THE HYDROQUINONE CONTENT OF WHITENING CREAM IN BEAUTY PRODUCTS BY UV-VIS SPECTROPHOTOMETRY. *Journal of Pharmaceutical and Medicine*, *1*(2), 47-55.

Soraya, & Sari, R. (2024). Penyisihan Warna Metil Merah dengan Metode Elektrolisis Menggunakan Elektroda Aluminium. *Jurnal Teknologi*, *24*(2), 136–140.

Suharyani, I., Karlina, N., Rahmi, N., Zahra Salsabila, D., Annisa, N., Sadira, A., ... & Rahmasari, Y. Tinggi Farmasi Muhammadiyah Cirebon, S., Cideng Indah No, J., & Barat, J.(2021). Review: Analisis Kualitatif Dan Kuantitatif Hidrokuinon Dalam Sediaan Kosmetika. *Journal of Pharmacopolium*, *4*(3), 162-173.

Sulaiman, R., Umboh, J. M., & Maddusa, S. S. (2020). Analisis kandungan merkuri pada kosmetik pemutih wajah di Pasar Karombasan Kota Manado. *KESMAS: Jurnal Kesehatan Masyarakat Universitas Sam Ratulangi*, *9*(5).

ajik, S., Beitollahi, H., Nejad, F. G., Safaei, M., Zhang, K., Van Le, Q., ... & Shokouhimehr, M. (2020). Developments and applications of nanomaterial-based carbon paste electrodes. *RSC advances*, *10*(36), 21561-21581.

Thompson, M. (2000). Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing. *The Analyst*, *125*(3), 385–386.

Widianti, R. (2018). *Penentuan simultan kafein dan parasetamol secara voltammetri menggunakan elektroda pasta karbon termodifikasi poli(xylenol orange) bercetakan molekul kafein*. Institut Teknologi Bandung.

Wu, D., Zhu, J., Zheng, Y., & Fu, L. (2024). Electrochemical Sensing Strategies for Synthetic Orange Dyes. *Molecules*, *29*(21), 5026.

Yuliati, E. N. D. (2023). Analisis Kadar Hidrokuinon Dalam Krim Pemutih Yang Tidak Memiliki Izin Bpom Yang Beredar Di Kecamatan Ajibarang. *Jurnal Mahasiswa Ilmu Farmasi dan Kesehatan*, *1*(1), 56–76.

Zahran, M. (2023). Conducting dyes as electro-active monomers and polymers for detecting analytes in biological and environmental samples. *Heliyon*, *9*(9).

Zaky M, Safitri M. (2023). Sosialisasi Dalam Upaya Peningkatan Pengetahuan Masyarakat Terhadap Penggunaan Bahan-bahan Alami yang Bermanfaat Dalam Produk Kosmetik dan Cara Pemilihan Produk Kosmetik yang Aman di Pasaran. *J Pengabdian Kefarmasian*,4(1). 1-6.