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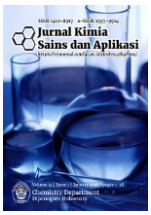

Development of Methyl Methacrylate-Based Molecularly Imprinted Polymer (MIP) Modified Electrodes for the Cyclic Voltametric Analysis of Caffeine in Coffee

Intan Cahya Callista *, Pirim Setiarso

Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Surabaya, Surabaya, Indonesia

* Corresponding author: intancahya.22009@mhs.unesa.ac.id

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Abstract

Caffeine is a type of alkaloid found in coffee, tea, and chocolate. Caffeine consumption is generally safe and offers benefits such as increased alertness and concentration; however, excessive consumption can potentially lead to caffeine poisoning or overdose, which can be harmful to health and even life-threatening. Analytical determination of caffeine is generally performed using conventional techniques such as HPLC and UV-Vis spectrophotometry. An alternative analytical method with potential, but has not yet been widely explored, is cyclic voltammetry. In this study, a cyclic voltammetry method for caffeine analysis was developed using a working electrode modified with a molecularly imprinted polymer to enhance electrode sensitivity. Bulk polymerization was used to produce the molecularly imprinted polymer (MIP), whose characteristics were then analyzed using SEM and FTIR instruments. The optimal electrode composition was obtained at a ratio of 1:2:2 (KCl: agar powder: MIP), which resulted in a cathodic peak current ($I_{p,c}$) of -1.45×10^{-3} A at pH 5. Higher conductivity facilitates easier electron transfer, which in turn results in a higher peak current. The application of this method to the analysis of caffeine in ground coffee types A, B, and C resulted in caffeine contents of 17.46 ppm, 12.87 ppm, and 13.78 ppm, respectively. The voltammetric method showed a limit of detection (LoD) of 2.26 ppm and a limit of quantitation (LoQ) of 7.53 ppm. These results indicate that the molecularly imprinted polymer-modified electrode is an effective tool for analyzing caffeine using the cyclic voltammetry method.

1. Introduction

High coffee consumption has made it a popular beverage in Indonesia, with an average consumption of 1.692 kg per capita per year [1]. Coffee consumption continues to trend upward, in line with the growth of the global coffee market, the expansion of the coffee shop industry, and rising consumer demand for various coffee products. These factors have made coffee one of the beverage commodities with steadily increasing consumption across various countries [2]. Coffee is a beverage brewed from roasted and ground coffee beans. Coffee offers flavor, aroma, and stimulating effects influenced by its primary component, caffeine [3]. Caffeine is a xanthine-derived purine alkaloid that has various physiological effects on humans, including increased alertness, improved physical performance, and diuretic effects [4]. Caffeine consumption is generally safe and offers benefits such as increased alertness and concentration; however, excessive consumption has the potential to cause caffeine poisoning or overdose, which can be harmful to health and even life-threatening [5]. Therefore, accurate quantitative analysis of caffeine in coffee samples is crucial to ensure safe consumption, guarantee product quality, and provide consumers with reliable information about the caffeine content of the beverages they consume.

Conventional methods for measuring caffeine levels still face significant challenges. Research on caffeine analysis in coffee remains limited to instruments such as UV-Vis spectrophotometry and HPLC, which require

expensive sample preparation and involve lengthy testing times [6]. Quantitative analysis of caffeine requires a selective and sensitive approach to detect low concentrations (micromolar) as found in beverages. From a chemical structural perspective, caffeine can undergo oxidation and reduction reactions [7], making it easier to analyze using electrochemical methods. Electrochemical techniques, particularly voltammetry, have proven effective for quantitative testing due to their high sensitivity, short analysis time, low cost, and simple sample preparation process [8]. Voltammetry is an electroanalytical method based on oxidation-reduction reactions at the electrode surface [9]. The principle of voltammetry involves measuring the electric current generated in an electrochemical cell by applying a potential [10]. The current produced is proportional to the concentration of chemical species in the solution.

Bhanjana *et al.* [7] reported that KCl solution was added to the sample during measurement to serve as an electrolyte, enhancing conductivity and system stability. In a voltammetric cell, measurements are performed using three types of electrodes: the working electrode, the reference electrode, and the counter electrode [9]. At the working electrode, oxidation-reduction reactions of the analyte occur. According to Barry *et al.* [11], the use of an unmodified (conventional) working electrode was found to be less selective due to low detection sensitivity, necessitating surface modification to enhance specificity in analyte measurements.

In recent years, polymer-based sensors, particularly Molecularly Imprinted Polymers (MIPs), have emerged as a trend for food and pharmaceutical analysis applications, with selectivity as the key factor. MIPs offer a general solution to selectivity issues in electrochemical sensors, as these polymers are designed with molecular imprints specific to the target analyte, enabling reversible binding and accurate detection [12]. The synthesis of MIPs requires five main components: functional monomers, template molecules, initiators, porogens, and crosslinkers. In this study, the functional monomer was methyl methacrylate (MMA), and the other components were acetonitrile as the porogen solvent, ethylene glycol dimethacrylate (EDGMA) as the crosslinker, and benzoyl peroxide (BPO) as the polymerization initiator.

The selection of MMA as a functional monomer is based on its ability to form stable pre-polymerization complexes with caffeine template molecules through noncovalent interactions, primarily hydrogen bonding and dipole–dipole interactions. These interactions facilitate the formation of specific imprinting sites following the template-release process. Structurally, MMA has a methyl ester group (-$COOCH_3$) that plays a role in forming interactions with caffeine molecules, as well as a vinyl double bond (-$CH=CH_2$) that provides high reactivity during polymerization . For complexation to proceed optimally, the functional groups of the monomer must match those of the template molecule, thereby forming a selective recognition cavity. Therefore, in non-covalent interaction-based MIPs, the monomer is generally used in excess to maximize the formation of monomer–template complexes. Compared with MAA, this monomer was selected because of its better mechanical stability while still being capable of forming recognition sites selective for caffeine molecules [13].

MIP formation begins through interactions between the template molecule and the functional monomer, which can involve covalent, non-covalent, or reversible ligand exchange. These interactions produce a monomer–template complex, which then undergoes polymerization and crosslinking by the crosslinker and initiator, resulting in a three-dimensional polymer matrix. After polymerization is complete, the template molecules are removed or extracted from the matrix, leaving behind specific binding sites with sizes, shapes, and functional-group orientations that correspond to those of the template molecules [14]. This porous structure, with specific binding sites, provides high selectivity for target molecules. Therefore, MIP has the potential to be an effective solution for detecting caffeine in coffee samples, given that conventional methods for caffeine analysis still have several limitations [15].

The combination of cyclic voltammetry and a MIP-modified working electrode using methyl methacrylate as the monomer promises accurate linear calibration for quantitative testing, and this success is highly dependent on optimizing three parameters: the optimal pH range, the optimal scan rate, and the optimal deposition time. pH optimization determines the speciation of the analyte and the stability of interactions at the electrode; thus, an optimal pH is required for effective redox reactions. The scan rate influences the magnitude of the peak current through changes in the electron-transfer rate, while the deposition time controls the amount of analyte accumulated on the electrode prior to measurement. These three parameters must be optimized to obtain a sensitive, stable, and reproducible electrochemical response.

In this study, the preparation of MIP via bulk polymerization was chosen due to its relative simplicity [16]. This study aims to develop a methyl methacrylate-based MIP-modified electrode for quantitative caffeine analysis in coffee by cyclic voltammetry, targeting an accuracy of over 95% and a response time of less than 5 minutes. The electrode composition was varied during the analysis to determine the optimal composition and optimal pH that produced the highest current response in caffeine concentration measurements. This development not only addresses the limitations of caffeine analysis in coffee but also contributes to the advancement of electrochemical sensors in general, supporting sustainable applications in food monitoring and public health in the Industry 4.0 era.

2. Experimental

2.1. Tools and Materials

The equipment used included a UV-Vis 1800 spectrophotometer, a 797 VA voltameter, a PerkinElmer Two Spectrum FTIR spectrometer, a Hitachi FlexSEM 1000 SEM, a Thermo Scientific Precision oven, an Ohaus balance, a LabNet vortex mixer, an Eppendorf 5810 centrifuge, a pH meter, and an Ag/AgCl electrode.

The materials used included methyl methacrylate (MMA; 99%, Sigma-Aldrich, USA), ethylene glycol dimethacrylate (EGDMA; 98%, Sigma-Aldrich, USA), caffeine (99%, Sigma-Aldrich, USA), polyethylene glycol (PEG 1000; Sigma-Aldrich, USA), benzoyl peroxide (BPO; 98%, Labotiq), acetonitrile (HPLC grade), potassium chloride (KCl), disodium hydrogen phosphate (Na_2HPO_4, 99%, SAP Chemicals), sodium dihydrogen phosphate (NaH_2PO_4, 99%, SAP Chemicals), ethanol (96%), glacial acetic acid, agar powder, and nitrogen gas. All materials were used without further purification.

2.2. Synthesis of Molecularly Imprinted Polymers (MIPs)

The MIP was synthesized by dissolving 0.155 g of caffeine (0.8 mmol) in acetonitrile, followed by the addition of 0.4 g of methyl methacrylate (4 mmol). The mixture was allowed to stand for 30 minutes. Separately, 2.376 g of EGDMA (12 mmol) was mixed with 6.75 g of PEG and 18 mL of acetonitrile and allowed to stand for 5 minutes. The two mixtures were then combined and vortexed for 5 minutes, followed by purging with nitrogen gas for 5 minutes.

Subsequently, 0.2422 g of BPO (1 mmol) was added, and the mixture was vortexed until the initiator was completely dissolved and then purged with nitrogen gas for an additional 5 minutes. The mixture was polymerized in a water bath at 65°C until a paste was formed. The resulting product was washed with acetonitrile, filtered, and dried at 60°C to constant weight to obtain the unleached polymer. Template extraction was subsequently performed using an ethanol–acetic acid mixture (8:2) with sonication for 120 minutes at 60°C, followed by centrifugation at 3500 rpm for 30 minutes. The residue was washed with distilled water, filtered, and dried at 60°C to obtain the dry MIP. The MIP recovery percentage was then calculated using Equation 1.

$$Polymer\ recovery\ (\%) = \frac{mass\ after\ polymerization\ (g)}{mass\ before\ polymerization\ (g)} \times 100\% \quad (1)$$

2.3. Synthesis of Non-Molecularly Imprinted Polymers (NIP)

The synthesis of NIP was carried out in the same manner as that of MIP, but without a caffeine template. A total of 0.4 g of methyl methacrylate (4 mmol) and 2.376 g of EDGMA (12 mmol) were mixed, followed by the addition of 6.75 g of PEG and 24 mL of acetonitrile, and the mixture was allowed to stand for 5 minutes. The mixture was vortexed for 5 minutes and purged with nitrogen gas for 5 minutes. Subsequently, 0.2422 g of BPO (1 mmol) was added, and the mixture was vortexed until the initiator was completely dissolved, followed by purging with nitrogen gas for an additional 5 minutes. The mixture was weighed and polymerized in a water bath at 65°C until a paste was formed. The resulting product was washed with acetonitrile and then with distilled water, followed by vacuum filtration. The residue was dried at 60°C to constant weight to obtain NIP, which was subsequently weighed. The NIP recovery percentage was calculated using Equation 1.

2.4. Characterization Analysis of NIP, Unleached Polymer, and MIP

The characterization of NIP, unleached polymer, and MIP compounds using bulk polymerization and precipitation polymerization methods was performed using a Fourier transform infrared spectroscopy (FTIR) instrument in the wavelength range of 500–4000 cm^{-1}, and morphological analysis was conducted using Scanning Electron Microscopy (SEM) at a magnification of 5,000×.

2.5. Preparation of Molecularly Imprinted Polymer Modified Electrode

The MIP-modified electrodes were prepared by weighing 0.1 g each of KCl, agar powder, and MIP and mixing them in a beaker. Then, 2 mL of distilled water was added. The mixture was heated to 60°C and stirred with a spatula until homogeneous, forming a paste with a 1:1:1 (w/w) composition. The same procedure was applied to other compositions, namely 1:2:1, 1:2:2, and 2:1:2 (w/w), to determine the optimal electrode composition. For the control electrode, KCl and agar powder were mixed at a 2:1 (w/w) ratio.

The electrode body was prepared using a 15-cm-long copper wire. The insulation was stripped from the wire, and the exposed surface was sanded until smooth. The wire was then marked at 2 cm and 0.5 cm from the electrode tip to define the electrode dimensions. A small piece of plastic tubing was attached to the bottom of the electrode as a protective cover to prevent leakage of the MIP paste. The homogenized MIP paste was manually inserted into the electrode body using a spatula. The same procedure was followed to fabricate electrodes containing the unleached polymer and NIP.

2.6. Measurement of Optimal Electrode Composition and pH

Electrodes with various compositions were tested using KCl electrolyte, phosphate buffer at pH 5, and standard caffeine solutions in a voltammetric cell at a scan rate of 0.1 V/s, a potential range from -0.2 V to 1.5 V, and a deposition time of 10 seconds. The optimal electrode was then further tested to determine its optimal pH by varying it to 4, 5, 6, 7, and 8. The resulting voltammograms were analyzed in Origin and compared to determine the optimal composition and pH.

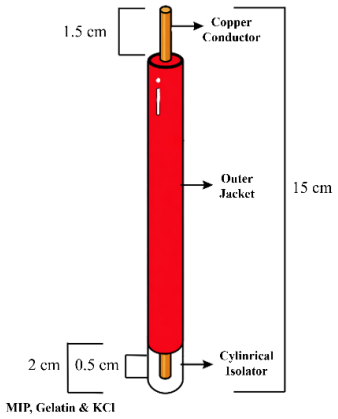

Figure 1. Illustration of the MIP modified electrode

2.7. Measurement of Caffeine Standard Linearity

The linearity of various standard caffeine concentrations was measured using an electrode with optimal composition and conditions to generate a caffeine standard curve at concentrations of 10, 20, 30, 40, and 50 ppm. The resulting voltammograms were used to generate the caffeine standard curve.

2.8. Caffeine Analysis in Coffee Samples

A 1-g coffee sample was added to distilled water in a beaker, and the volume was adjusted to 50 mL. The mixture was sonicated at 80°C for 30 minutes. The resulting solution was separated into filtrate and residue by vacuum filtration. Subsequently, 1 mL of the filtrate was transferred to a 100-mL volumetric flask and diluted to volume with distilled water. This procedure was repeated for all three coffee sample types. The coffee samples were analyzed by cyclic voltammetry using an electrode with the optimal composition of 1:2:2 (w/w) under the optimal conditions. A 2500-ppm KCl solution was used as the supporting electrolyte at the optimal pH of 5. The measurements were performed over a potential range of -2.0 to 1.5 V, with a dwell time of 20 s and a scan rate of 0.15 V/ms.

3. Results and Discussion

3.1. Synthesis of Molecularly Imprinted Polymers (MIPs)

MIPs are highly selective polymers formed through three main stages: template–monomer complex formation, polymerization and cross-linking, and template extraction, producing specific cavities [14, 17]. In this study, the bulk polymerization method was used because it is simple, easy to operate, and capable of producing polymers with good adsorption capacity and selectivity [16].

During the prepolymerization stage, caffeine, as the template molecule, interacts with MMA via non-covalent interactions. The carbonyl group (C=O) on caffeine acts as a hydrogen-bonding acceptor for hydrogen from the methyl group or the polar environment of MMA. Additionally, dipole–dipole interactions occur between the caffeine carbonyl group and the MMA ester group, as well as hydrophobic interactions between the nonpolar regions. These interactions result in an organized and reversible caffeine–MMA complex, enabling the formation of a precise molecular template.

The polymerization stage begins with the decomposition of BPO as an initiator at 65°C, producing the benzoyloxy free radical ($C_6H_5COO\cdot$), which then undergoes decarboxylation to form the phenyl radical ($C_6H_5\cdot$). This radical attacks the double bond (C=C) in MMA, breaking the π bond and forming a new radical on the monomer. This reaction continues into the propagation stage, where MMA units continue to add, forming a polymer chain with C–C main chains. Simultaneously, EDGMA, which has two vinyl groups, acts as a crosslinker, forming covalent bonds between polymer chains to create a rigid, stable three-dimensional network. This structure traps caffeine molecules within the matrix through a combination of covalent bonds in the polymer backbone and non-covalent interactions between caffeine and the polymer's functional groups. This process results in an unleached polymer.

The synthesis results showed that the mass of the mixture decreased from 16.3779 g before polymerization to 13.7715 g after polymerization, which may be attributed to the loss of solvent or other volatile components during the polymerization process. After washing and drying, 4.5701 g of unleached polymer was obtained. Based on Equation 1, the recovery percentage of the unleached polymer was calculated to be 84.1%.

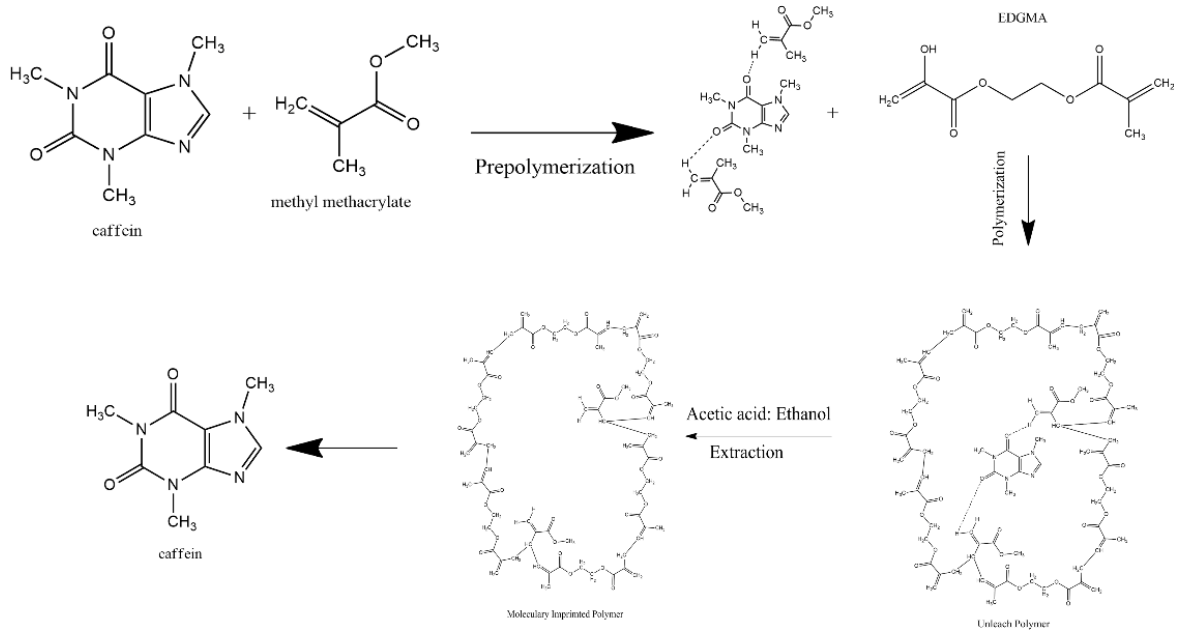

Figure 2. Illustration of the synthesis of caffeine-molecularly imprinted polymer

The next step was template extraction, which aimed to disrupt the non-covalent interactions between caffeine and the polymer matrix. Template extraction was performed using an ethanol–acetic acid mixture (8:2). The solvent mixture was expected to weaken the interactions between caffeine and the polymer matrix, while ethanol facilitated the dissolution and diffusion of caffeine from the polymer matrix. Since the extraction process does not involve breaking covalent bonds in the polymer backbone, the three-dimensional polymer network was expected to remain structurally stable. After sonication and centrifugation, the MIP was obtained with a final mass of 2.0821 g. Based on Equation 1, the MIP recovery percentage was calculated to be 78.2%.

The decrease in mass from the unleached polymer to the MIP may be attributed to the removal of the caffeine template and formation of specific recognition cavities. These cavities have the appropriate size, shape, and orientation of functional groups for caffeine, allowing it to selectively rebind through the same mechanisms as in the prepolymerization stage, including hydrogen bonding, dipole–dipole interactions, and hydrophobic forces.

3.2. Synthesis of Non-Molecularly Imprinted Polymers (NIP)

The synthesis of NIP was carried out via bulk polymerization using a 1:3 ratio of MMA monomer to EDGMA crosslinker to produce a rigid and mechanically stable polymer structure. The addition of porogens in the form of acetonitrile and PEG aims to form a porous structure with a high surface area. The mixture was homogenized and purged with nitrogen gas to remove oxygen, which can inhibit the free-radical polymerization reaction. The reaction was initiated by adding BPO as a source of free radicals. The initial weight of the mixture before the reaction was recorded as 13.5122 g.

The polymerization process took place at 65°C until a paste formed, following a free-radical reaction mechanism consisting of three main stages. In the initiation stage, BPO undergoes thermal decomposition to produce benzoyloxy radicals, which then undergo decarboxylation to form phenyl radicals. This radical attacks the double bond (C=C) on the MMA vinyl group, thereby forming an active radical at the end of the monomer chain.

In the propagation stage, this active radical reacts in a chain reaction with other MMA monomers by opening the π bond on the vinyl group, forming carbon–carbon (C–C) covalent bonds that constitute the polymer backbone. Simultaneously, EDGMA, which has two vinyl groups, plays a role in cross-linking by connecting two different polymer chains via a free-radical reaction, thereby forming a rigid, insoluble three-dimensional network. The dominant bonds formed in this process are the C–C covalent bonds in the main chain and the cross-links from EDGMA, which reinforce the polymer structure.

The termination stage occurs when two active radicals meet and form a stable covalent bond, thereby halting polymer chain growth. After polymerization, the mixture's weight decreased to 12.6732 g, indicating the formation of the polymer network and the loss of volatile components. Thus, the MIP recovery percentage, calculated using Equation 1, is 93.7%. The NIP recovery percentage is higher than that of the unleached polymer and the MIP because NIP lacks a caffeine template, allowing polymerization to proceed without a template-release step; consequently, the mass of the final product is nearly identical to the theoretical mass, resulting in a higher recovery percentage. The polymer product was then washed with acetonitrile and distilled water to remove residual monomers, porogens, and unreacted initiators, and then dried at 60°C until a dry polymer was obtained. The resulting polymer is referred to as a NIP.

3.2.1. Characterization of Morphological Using a Scanning Electron Microscope (SEM)

The morphology of the NIP and MIP was characterized using SEM to examine their particle size and surface morphology. The SEM analysis showed that the NIP had an average particle size ranging from 1.5 to 2.5 µm, whereas the MIP exhibited a particle size range of 1.2–2.0 µm. The surface morphology was further examined at a magnification of 5000×, as shown in Figure 3. The SEM images showed that the NIP exhibited a relatively denser surface with coarser particles and a broader particle size distribution. In contrast, the MIP exhibited smaller and relatively more uniform particles, with a smoother surface and more visible interparticle spaces, suggesting a relatively more uniform particle size distribution.

3.2.2. Characterization of Functional Groups Using Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to identify the functional groups formed during bulk polymerization, with measurements taken in the 500–4000 cm^{-1} range. As shown in Figure 4, the synthesis of the MIP was successful. This is indicated by the formation of characteristic polymer groups in the form of C=O esters (~1724–1726 cm^{-1}) and C–O–C (~1094–1149 cm^{-1}) in all polymer samples.

The presence of caffeine in the unwashed polymer was indicated by the appearance of C=O (~1642 cm^{-1}) and C–N (~1351 cm^{-1}) groups, which subsequently disappear in the MIP after the compression process, indicating successful template removal because during the MIP extraction process, caffeine molecules are removed through repeated washing with acetonitrile, which aims to dissolve the caffeine while maintaining the integrity of the cross-linked polymer network. Furthermore, shifts in the wavenumbers of the O–H and C–O–C groups indicate interactions between caffeine and the monomers during molding. Meanwhile, the characteristic absorption bands of the carbonyl ester (C=O) and C–O–C groups remain unchanged, confirming that the polymer backbone is preserved during the extraction process.

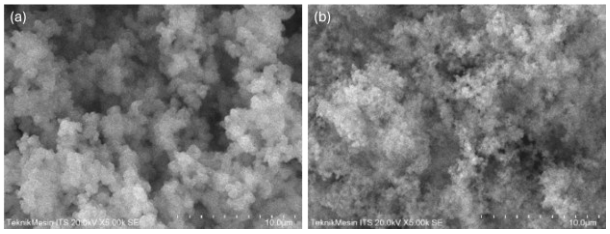

Figure 3. SEM images of the surface morphology at 5000× magnification: (a) NIP and (b) MIP

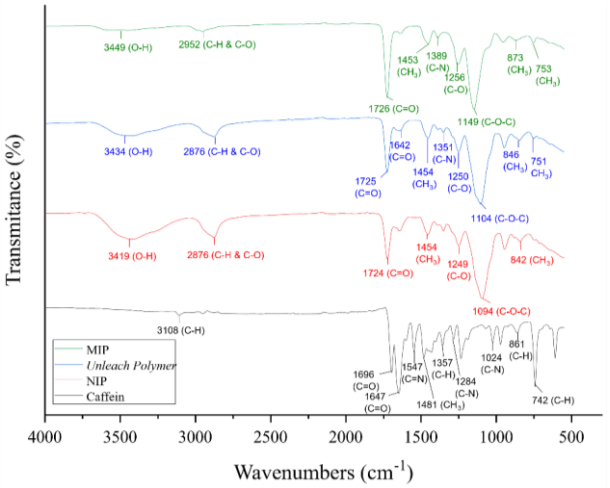

Figure 4. FTIR spectra of the materials

3.3. Determination of the Composition of the Molecularly Imprinted Polymer-Modified Electrode

The peak current generated by each modified working electrode composition was measured with a 50 ppm caffeine standard solution at pH 5 via cyclic voltammetry over a potential range of -2 V to +1.5 V to identify the optimal formulation. The tested composition ratios for KCl: agar powder: MIP were 1:1:1; 1:2:1; 1:2:2; and 2:1:2 (weight/weight). The MIP functions to bind the target molecule, namely the caffeine compound, thereby enhancing the electrode's sensitivity by accumulating or concentrating the analyte molecules on the electrode surface. Agar powder acts as a natural adsorbent capable of absorbing compounds and maintaining the mechanical stability of the electrode, supporting the diffusion of ions and analytes toward the active site [18]. Agar functions as a porous hydrogel matrix that immobilizes the MIP particles while allowing caffeine molecules to diffuse through its interconnected pores toward the recognition sites. This porous structure facilitates analyte transport without significantly restricting mass transfer, thereby maintaining the electrochemical response of the modified electrode. The KCl solution serves as an electrolyte supporting the conductivity and stability of the system [7].

Table 1. FTIR bands and corresponding functional groups of caffeine, NIP, unleached polymer, and MIP

Functional group	Wavenumbers (cm^{-1})				
	Caffeine	NIP	Unleached polymer	MIP	Reference
O-H	-	3419	3434	3449	3400–3450 [19]
C-H and C-O	-	2876	2876	2952	2940–1727 [20]
C=O ester	-	1724	1725	1726	1720–1730 [19]
C=O caffeine	1696	-	-	-	1700–1660 [21]
Stretching vibration C=O	1647	-	1642	-	1650–1600 [21]
C=N	1547	-	-	-	1675–1500 [22]
Deformation CH_3	1481	1454	1454	1453	1450-1370 [13]
C-N	1357	-	1351	1389	1380–1239 [23]
C-O-C	1284	1249	1250	1256	1256–1200 [24]
C-O-C ester bond	1024	1094	1104	1149	1250–1144 [20]
C-H	861/742	842	846/751	873/753	900–700 [25]

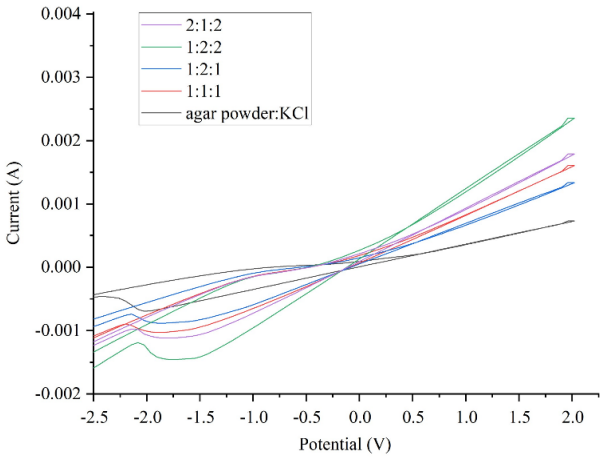

Figure 5. Cyclic voltammograms of the MIP-modified electrodes with different compositions

Table 2. Peak current of the MIP-modified electrodes with different compositions

Composition (w/w)	$I_{p,c}$ (A)
Agar powder:KCl	-0.68×10^{-3}
1:1:1	-1.05×10^{-3}
1:2:1	-0.88×10^{-3}
1:2:2	-1.45×10^{-3}
2:1:2	-1.07×10^{-3}

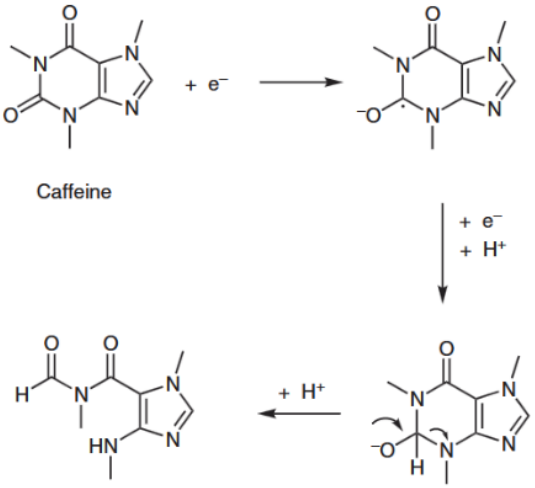

Figure 6. Caffeine reduction reaction

Based on Figure 5, the voltamogram results show that the caffeine compound produces only one current peak, namely the reduction peak ($I_{p,c}$), without the appearance of an oxidation peak ($I_{p,a}$) during the irreversible reverse scan. This is likely due to the instability of the reduction product, the occurrence of subsequent chemical reactions, or the adsorption of the reduction product onto the electrode surface, thereby making it unavailable for the oxidation process. In the cyclic voltammetry process, the reaction mechanism for the reduction of caffeine can occur in an electrolyte solution with the addition of water. In the initial stage, the caffeine molecule accepts one electron, causing the carbonyl group (C=O) to transform into an anionic radical with a negative charge on the oxygen (C-O-). This reaction is highly unstable. Subsequently, the system accepts additional electrons and protons (H^+) derived from water, resulting in the protonation of the oxygen atom and the formation of a hydroxyl group (–OH). Furthermore, the nitrogen atom in the ring can also undergo protonation, leading to the formation of an –NH group. After that, structural rearrangement occurs through tautomerization or the shifting of double bonds to produce a stable product, resulting in N-Formyl-N,1-dimethyl-4-(methylamino)-1H-imidaz-ole-5-carboxamide. Under certain conditions, further structural changes may occur, but generally the reaction stops at a simple reduced product without the formation of complex compounds, as shown in Figure 6. Table 2 shows the optimal composition to be KCl:agar powder:MIP at a ratio of 1:2:2 (w/w), resulting in a peak current of -1.45×10^{-3} A.

3.3.1. Determining the Best Analysis Method of NIP, Unleached Polymer, and MIP

After determining the optimal electrode composition, the next step was to determine which polymer provided the best analytical performance among the NIP, unleached polymer, and MIP. Figure 7 shows the voltammograms obtained using the three polymer types under the optimal analytical conditions, while Table 3 presents the corresponding peak currents. Based on Figure 7 and Table 3, the $I_{p,c}$ was obtained from the voltammograms of the performance tests on electrodes modified using NIP, unleached polymer, and MIP. Based on the measurement results, the highest peak current value was obtained from the MIP-modified electrode, at -1.56×10^{-3} A.

The higher response of the MIP can be attributed to the formation of complementary cavities after template removal, whereas non-imprinted materials lack these specific binding sites [26]. This indicates that the leaching process successfully removed the template from the polymer matrix, resulting in the formation of specific cavities that match the shape and size of the analyte. The more porous, open structure of the MIP increases the active surface area and facilitates diffusion of the analyte to the binding sites. More specific interactions between the analyte and the MIP also enhance electron transfer efficiency, resulting in a larger current.

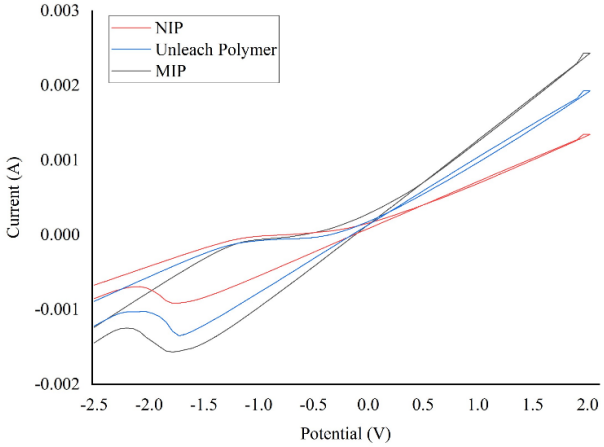

Figure 7. Voltammogram of the best-performing polymer under the optimal analytical conditions

Table 3. Peak current of the NIP, unleached polymer, and MIP electrodes

Polymer	$I_{p,c}$ (A)
NIP	-0.92×10^{-3}
Unleached Polymer	-1.34×10^{-3}
MIP	-1.56×10^{-3}

3.3.2. Determination of the Optimum pH

After selecting the best-performing polymer, the next step was to determine the optimum pH to obtain a stable and reproducible electrochemical response. Because the redox behavior of electroactive species can be affected by pH, a pH range of 4–8 was investigated using a 0.1 M phosphate buffer solution to maintain a stable pH during the measurements. This pH range was selected based on the stability of caffeine under the tested conditions. Figure 8 shows the voltammograms obtained at different pH values, while Table 4 presents the corresponding cathodic peak currents.

Based on Figure 8, the $I_{p,c}$ varied across the tested pH range, although the differences were relatively small; however, pH still influenced the increase in the $I_{p,c}$ value. The use of phosphate buffer can affect the test solution, as it can increase the solution's conductivity and maintain a constant ionic strength. Based on Table 4, the highest cathodic peak current magnitude was obtained at pH 5, with an $I_{p,c}$ value of -2.04×10^{-3} A. Therefore, pH 5 was selected as the optimum pH under the investigated conditions. The variation in peak current with pH indicates that the electrochemical response of caffeine was affected by the solution pH. As the peak current increases, the concentration of the test solution can be analyzed, since the measured concentration is linearly related to the measured current.

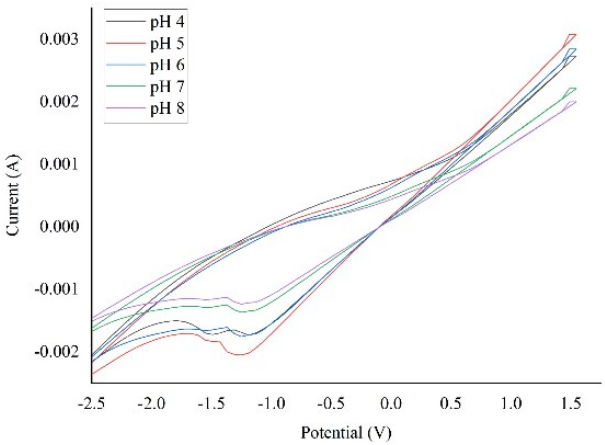

Figure 8. Voltammogram of MIP-modified electrode with pH variations

Table 4. Peak current of the electrode pH variations

pH	$I_{p,c}$ (A)
4	-1.71×10^{-3}
5	-2.04×10^{-3}
6	-1.76×10^{-3}
7	-1.36×10^{-3}
8	-1.24×10^{-3}

3.3.3. Determination of the Optimal Deposition Time

After determining the optimal pH range, the next step was to determine the optimal deposition time to prevent electrode surface saturation while increasing the amount of analoge accumulated during this process. The deposition time was limited to the range of 5–25 seconds to achieve optimal caffeine accumulation on the electrode surface. This range was selected based on a previous study [27], which investigated deposition times ranging from 0 to 300 seconds.

Based on the voltammograms shown in Figure 9, the largest cathodic peak current magnitude was observed at a deposition time of 20 s. As shown in Table 5, the cathodic peak current magnitude increased as the deposition time increased from 5 to 20 s. This increase may be attributed to the greater accumulation of caffeine at the electrode surface with increasing deposition time, resulting in a higher current response [28]. However, the cathodic peak current magnitude decreased at 25 s, which may indicate that prolonged deposition does not further improve analyte accumulation and may lead to saturation of the available binding sites or electrode surface. The highest cathodic peak current magnitude was obtained at 20 s, with an $I_{p,c}$ of -1.45×10^{-3} A. Therefore, a deposition time of 20 s was selected as the optimum condition for caffeine analysis.

3.3.4. Determination of the Optimal Scan Rate

The scan rate was optimized to obtain the highest cathodic peak current and a stable electrochemical response. Five scan rates, namely 0.05, 0.10, 0.15, 0.20, and 0.25 V/s, were evaluated, and the corresponding peak currents were compared to determine the optimal scan rate [29].

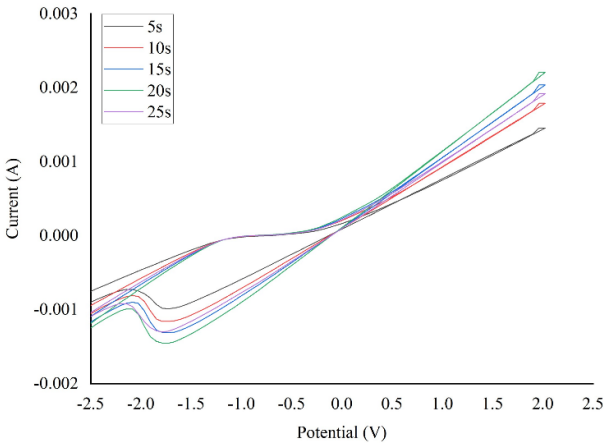

Figure 9. Voltammogram of MIP-modified electrode with different deposition times

Table 5. Peak currents of the MIP-modified electrode at different deposition times

Deposition time (s)	$I_{p,c}$ (A)
5	-0.99×10^{-3}
10	-1.15×10^{-3}
15	-1.30×10^{-3}
20	-1.45×10^{-3}
25	-1.29×10^{-3}

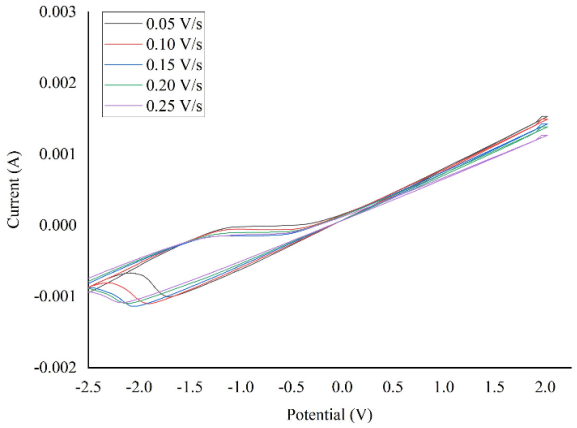

Figure 10. Voltammograms of the MIP-modified electrode at different scan rates

Table 6. Peak current of the electrode scan rate variations

Scan rate (V/s)	$I_{p,c}$ (A)
0.05	-0.99×10^{-3}
0.10	-1.11×10^{-3}
0.15	-1.13×10^{-3}
0.20	-1.10×10^{-3}
0.25	-1.08×10^{-3}

Based on the voltammogram results in Figure 10, the highest peak current across the scan rate variations occurs at 0.15 V/s. Table 6 and Figure 10 show an increase in current with increasing scan rate from 0.05 V/s to 0.15 V/s. This occurs because the diffusion layer forms more rapidly, resulting in faster electron transfer at the working electrode surface and a corresponding increase in the generated current [28]. However, a decrease in current occurs at scan rates of 0.20 V/s and 0.25 V/s due to saturation at the working electrode surface, as shown in Figure 10. The highest current peak across the scan-rate variations for the caffeine analysis occurs at 0.15 V/s with an $I_{p,c}$ value of -1.13×10^{-3} A.

3.3.5. Measurement of Standard Caffeine Linearity

The purpose of measuring the linearity of a caffeine standard solution is to ensure the instruments or methods ability to produce consistent and linear responses within a specific concentration range. In particular, cyclic voltammetry can provide reliable, accurate results for determining caffeine concentrations, especially within a predetermined linear concentration range. The experiment was conducted with the electrode composition and pH set to their optimal values. The voltammogram data for various concentrations of the retinol standard solution are shown in Figure 11.

Table 7. Peak current of a caffeine standard solution

Concentration (ppm)	$I_{p,c}$ (A)
10	-3.18×10^{-3}
20	-3.28×10^{-3}
30	-3.40×10^{-3}
40	-3.51×10^{-3}
50	-3.61×10^{-3}

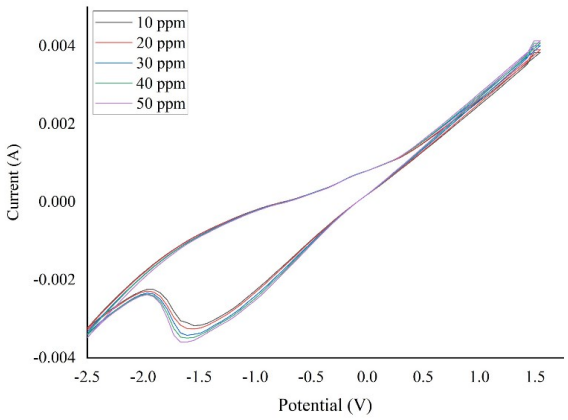

Figure 11. Voltammogram of a caffeine standard solution

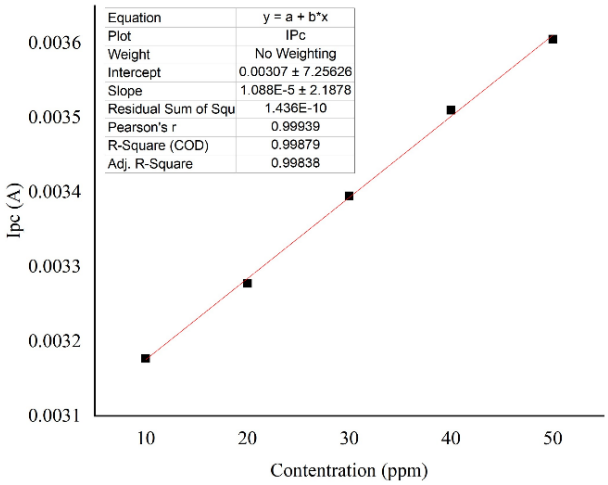

Figure 12. Linear calibration curve of caffeine standard solution

As shown in Figure 11, the standard voltammogram of caffeine exhibits a linear trend, indicating a direct correlation between the concentration of the standard solution and the peak current, with higher concentrations yielding higher peak currents. Table 7 shows the $I_{p,c}$ values for caffeine standard solutions at various concentrations. The calibration curve was constructed using the absolute values of the cathodic peak current ($|I_{p,c}|$). The negative sign of the measured current indicates the cathodic reduction process and was omitted from the regression analysis because only the current magnitude was considered. Figure 12 shows a clear linear relationship between caffeine concentration and its reduction peak current, described by the equation y = 0.00001088x + 0.00307, where the slope (a) is 0.00001088, and the y- intercept (b) is 0.00307. The fit quality is high, with an adjusted R^2 of 0.99879. This equation is used to determine the unknown caffeine concentration via cyclic voltammetry.

Table 8. Peak current of the caffeine solution in the product

Sample	$I_{p,c}$ (A)	Concentration (ppm)
A	-3.26×10^{-3}	17.46
B	-3.21×10^{-3}	12.87
C	-3.22×10^{-3}	13.78

Table 9. Determination of the standard deviation of a caffeine standard solution by the cyclic voltammetry method

Concentration (ppm)	$I_{p,c}$ (Yi)	Ŷ	(Ŷ-Yi)²
10	3.177×10^{-3}	3.178×10^{-3}	3.24×10^{-12}
20	3.278×10^{-3}	3.287×10^{-3}	9.21×10^{-11}
30	3.395×10^{-3}	3.396×10^{-3}	1.96×10^{-12}
40	3.510×10^{-3}	3.505×10^{-3}	2.30×10^{-11}
50	3.605×10^{-3}	3.614×10^{-3}	8.10×10^{-11}
$\Sigma(\hat{Y} - Yi)^2$			2.01×10^{-10}
S(y/x)			8.19×10^{-6}
slope			1.088×10^{-5}
LoD			2.48 ppm
LoQ			7.53 ppm

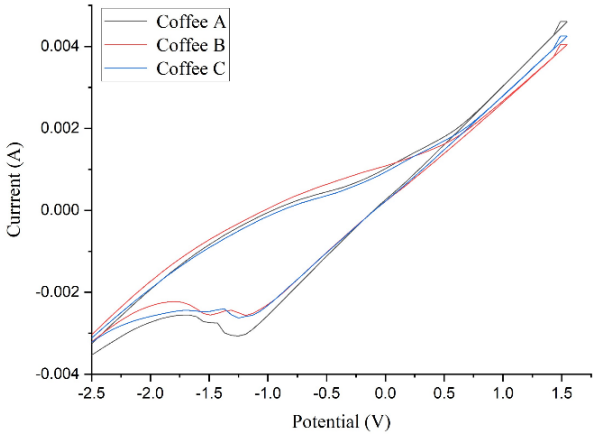

Figure 13. Voltammogram of the caffeine solution in the product

3.3.6. Limit of Detection and Limit of Quantification

LoD is the lowest concentration of an analyte that can be reliably detected by an analytical method but cannot necessarily be quantified with acceptable accuracy and precision. In contrast, the LoQ is the lowest concentration of an analyte that can be quantitatively determined with acceptable accuracy and precision. Therefore, lower LoD and LoQ values generally indicate higher analytical sensitivity. The LoD and LoQ were calculated using Equations 2 and 3.

$$\text{LoD} = \frac{3.3 \times S\left(\frac{y}{x}\right)}{slope} \quad (2)$$

$$\text{LoQ} = \frac{10 \times S\left(\frac{y}{x}\right)}{slope} \quad (3)$$

Where, S(y/x) is the standard deviation. Standard deviation describes the extent to which the data values deviate from the mean. It can be calculated using Equation 4.

$$S\left(\frac{y}{x}\right) = \sqrt{\frac{\Sigma(y-yi)^2}{n-2}} \quad (4)$$

Where, n is the number of data. The standard deviation, LoD, and LoQ values were calculated using the cyclic voltammetry method, as shown in Table 9.

LoD and LoQ were determined from the calibration curve using the standard deviation of the response and the slope of the calibration line [30]. Figure 12 shows the relationship between $I_{p,c}$ and the standard caffeine concentration, yielding a linear regression equation of y = 0.00001088x + 0.00307, with an R^2 of 0.99879. As shown in Table 9, the standard deviation obtained using the cyclic voltammetry method was 8.19×10^{-6}. This value was used to calculate the LoD and LoQ according to Equations (2) and (3), respectively. The calculated LoD and LoQ values were 2.48 and 7.53 ppm, respectively.

3.3.7. Testing of Caffeine in Coffee Samples

Caffeine concentrations were determined in three commercially available coffee samples. The voltammograms obtained from the coffee sample solutions are presented in Figure 13. The caffeine concentration in each sample was calculated by substituting the $I_{p,c}$ values obtained from the cyclic voltammetry measurements into the calibration equation, y = 0.00001088x + 0.00307, with an R^2 value of 0.99879. The three coffee samples exhibited similar voltammogram profiles, with minor differences in peak current, which may be associated with differences in caffeine concentration or interactions between caffeine and other components of the coffee matrix. As shown in Table 8, the caffeine concentrations of the three samples ranged from 12.87 to 17.46 ppm. These results indicate that the caffeine concentrations among the tested coffee samples were within a relatively similar range. The cyclic voltammetry method demonstrated its applicability for the determination of caffeine in coffee samples and showed potential for use in food analysis.

4. Conclusion

Modifying the working electrode with a 1:2:2 composition (KCl:agar powder:MIP) resulted in the best peak current for identifying caffeine solutions. The best measurement conditions for caffeine analysis using cyclic voltammetry are at pH 5, with an $I_{p,c}$ value of -2.04×10^{-3} A, an optimal deposition time of 20 s, and an optimal scan rate of 0.15 V/s. The caffeine content of coffee beverages from brands A, B, and C, measured by cyclic voltammetry, was 17.46 ppm, 12.87 ppm, and 13.78 ppm, respectively. The voltammetric method showed a LoD of 2.26 ppm and a LoQ of 7.53 ppm. These results indicate that a MIP-modified working electrode, combined with cyclic voltammetry, can be used effectively for caffeine analysis.

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