



Research Article

Electrochemical detection of dimethyl phthalate using an electropolymerised pyrrole-based molecularly imprinted polymer sensor on screen-printed carbon electrode

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Abstract

Dimethyl phthalate (DMP) is an emerging contaminant commonly found in cosmetics, personal care products, and polyvinyl chloride (PVC) materials, requiring reliable electrochemical detection methods for selective analysis. Conventional DMP detection methods are often expensive, labor-intensive, and require complex instrumentation. This study presents an electropolymerised molecularly imprinted polymer (e-MIP) sensor based on a screen-printed carbon electrode (SPCE) for selective and cost-effective DMP detection. Pyrrole was employed as the monomer, while non-imprinted polymers (e-NIPs) served as controls. Template removal using ethanolic hydrochloric acid created specific recognition sites within the polymer matrix. Characterization of the polymers was performed by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Optimal sensor performance was achieved with five electropolymerisation cycles, 15-minute incubation time, and pH 7. The sensor exhibited a linear response to DMP concentrations ranging from 5 to 25 mM ($R^2 = 0.9943$), with a limit of detection (LOD) of 1.796 mM and a limit of quantification (LOQ) of 5.44 mM. The developed e-MIP-SPCE sensor offers a promising, disposable, and low-cost platform for rapid DMP detection.

Keywords: dimethyl phthalate, electropolymerisation, molecularly imprinted polymer, pyrrole, screen printed carbon electrode

Introduction

Dimethyl phthalate (DMP) is a low molecular weight phthalate ester (**Figure 1**) produced by esterifying methanol with phthalic acid [1]. It is commonly used as a solvent, plasticiser, and additive in cosmetics, personal care products, pesticides, and insect repellents [1]. In manufacturing, DMP improves the flow properties of binder systems, particularly in injection moulding, due to its ring structure, which reduces molecular friction [2, 3]. DMP is not chemically bound to plastics, making it prone to

leaching under environmental stressors such as radiation, pH shifts, temperature, or product content [4]. Its widespread use in plastics, pesticides, and personal care products has led to environmental contamination and disruption of marine ecosystems [5, 6]. Low molecular weight phthalates like DMP readily migrate into water, air, soil, and sediments [7]. DMP concentrations in cosmetic products have been reported to be between 0.00004% and 34% [1]. To provide a clear benchmark for environmental safety and public health, the United States Environmental

Protection Agency (US EPA) has established an ambient water quality criterion for DMP at 313 mg/L for the protection of human health from ingestion through both water and contaminated aquatic organisms [8]. In aquatic organisms such as zebrafish, DMP exposure has been linked to endocrine disruption, oxidative stress, and immunotoxicity [9]. It can also disrupt reproductive processes and pose risks to humans via the trophic chain. As endocrine disruptors, phthalates mimic or interfere with hormone activity, resulting in various physiological disorders [10, 11]. In primary producers such as duckweed, DMP exhibits genotoxic and physiotoxic effects, underscoring its ecological threat [12].

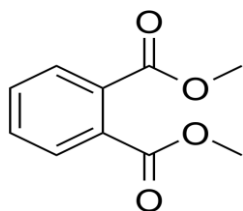


Figure 1. Structure of dimethyl phthalate (DMP)

The detection of DMP at trace levels in environmental and biological samples remains challenging due to its low concentration, complex sample matrices, and potential interference from structurally similar compounds [13]. Traditional techniques like high-performance liquid chromatography (HPLC), gas chromatography (GC), and mass spectrometry (MS) offer high sensitivity and selectivity but are expensive, time-consuming, and require extensive sample preparation [14].

Molecularly imprinted polymers (MIPs) have attracted attention as synthetic receptors capable of selectively recognising target molecules through a lock-and-key mechanism, similar to natural antibodies or enzymes [15]. MIPs are chemically stable, have long shelf lives, and can be integrated with various transduction systems such as optical, gravimetric, or electrochemical for analyte detection [15, 16]. Their selectivity arises from template-shaped cavities in the polymer matrix, enabling precise detection even in complex matrices such as food and water [17]. Electrochemical sensors based on MIPs offer low cost, rapid response, portability, and compatibility with miniaturised platforms [18]. Furthermore, electropolymerised MIPs (e-MIPs), formed directly on electrode surfaces without chemical initiators, offer precise control over film thickness and improved reproducibility [19, 20]. Their chemical stability and robustness make them well-suited for environmental monitoring [21].

Compared to sol-gel methods, electropolymerisation is faster, simpler, and more controllable [22, 25].

Conducting polymers like polypyrrole are commonly used in e-MIP sensors. Incorporating polypyrrole-based e-MIPs on screen-printed carbon electrodes (SPCEs) is hypothesised to enable selective and sensitive detection of dimethyl phthalate (DMP) with high reproducibility and low detection limits [26]. Surface imprinting further enhances sensitivity by facilitating thin-film deposition and efficient analyte recognition [22].

Therefore, this study was conducted to develop a screen-printed carbon electrode (SPCE) sensor incorporating polypyrrole-based e-MIPs for the selective detection of DMP. This approach combines the advantages of molecular imprinting and electrochemical transduction, offering a robust, eco-friendly, and cost-effective solution for environmental monitoring.

Materials and Methods

The chemicals used in this study were Dimethyl phthalate ($\geq 99\%$), pyrrole ($\geq 99\%$), which were purchased from Sigma-Aldrich, Lithium Perchlorate, potassium ferrocyanide, potassium chloride, hydrochloric acid, and absolute ethanol solution, which were purchased from R&M Chemical and deionised water.

Preparation of stock solution of molecularly imprinted polymers (e-MIPs) and non-imprinted polymers (e-NIPs)

Stocks of 10 mM of DMP as a template by dissolving 0.0163 mL of DMP in 6 mL of absolute ethanol and 4 mL of deionised water were prepared. 100 mM of pyrrole as a monomer was prepared by dissolving 0.0694 mL of pyrrole in 6 mL of ethanol and 4 mL of deionised water, and 2 M lithium perchlorate, which acts as an electrolyte, was prepared by diluting 2.1278 g in 10 mL of deionised water. These steps were repeated for the non-imprinted polymer without adding DMP as a template.

Preparation of Electropolymerised Molecularly Imprinted Polymers (e-MIPs) and Electropolymerised Non-Imprinted Polymers (e-NIPs)

A 5 mM ferrocyanide solution in 0.1 M KCl was used to characterise the screen-printed carbon electrode (SPCE). To enable the rearrangement of the template and monomer on the SPCE working electrode surface, 0.05 mL of each of the prepared solutions of molecularly imprinted polymer was added to the corresponding SPCE surface and incubated for several minutes (5 to 10 minutes). The monomer film on the SPCE surface was then electropolymerised using cyclic voltammetry scans performed at a 50 mV/s scan rate between -0.3 V and 0.9 V. Electropolymerisation of the polymer was conducted using Metrohm Autolab

PGSTAT302N and NOVA2.1.4 software. The molecularly imprinted polymer modified carbon electrode was submerged in 0.1 M ethanolic hydrochloric acid (HCl) for ten minutes to remove the template.

Characterisation

Electrochemical characterisation using cyclic voltammetry

After template leaching, the electrode was characterised at a scan rate of 50 mV/s using the ferrocyanide solution, scan rate -0.4 V to 0.8 V with a step potential of 0.002 V. The modulation amplitude was 0.05 V, whereas 0.05 s was the modulation duration, and the interval time was 0.1 s. The baseline e-MIP and e-NIP were ascertained after completing this step. All experiments were conducted using Metrohm Autolab PGSTAT302N and NOVA2.1.4 software. The target containing a certain concentration of DMP (0.005 mL) was incubated on the electrode surface for several minutes, and the electrode was rinsed with deionised water. After the incubation and drying process, ferrocyanide was used to characterise the electrode and determine the peak height for the signal obtained. The signal from the baseline was subtracted from the signal after incubation to get the corrected signal.

Fourier transform infrared spectroscopy

The instruments used were OPUS software and a Bruker Invenio-S FTIR Spectrometer connected to a PC laptop. Fourier Transform Infrared Spectroscopy (FTIR) elucidates the structure of DMP. The spectrum was observed using an ATR platinum diamond spectroscopy technique at the range of 450-3600 cm^{-1} and with 17 scans by scanning an ATR crystal without the background noise template for the device and determining the baseline spectrum. A sample was applied to the ATR crystal. Next, DMP, e-MIP, and e-NIP absorption spectra were recorded by the FTIR measurement. The resulting spectrum pattern undergoes examination and comparison with recognised substances for identification purposes [27].

Scanning electron microscope

The instruments used were a ZEISS Supra55VP scanning electron microscope connected to a PC laptop. The surface modifications were microscopically examined using scanning electron microscopy (SEM). A lower voltage should be set for better surface imaging, and the sample must be dry, clean, and correctly mounted on a substrate that is compatible with the SEM. The magnification was increased to focus on particular areas. After taking pictures, quantitative analysis can be used to gauge depth profiles, surface roughness, and particle sizes. The morphology of the polymers can be ascertained

using the zoom levels of 10000X and 20000X. DMP imprinted on SPCE, which was treated with pyrrole, can be observed by techniques [28].

Binding capacity of molecularly imprinted and non-imprinted polymers

To evaluate the sensor's binding capacity and establish the optimal functional conditions for the e-MIP sensor, this study utilized the direct empirical optimization of physical and electrochemical parameters. The binding efficiency was assessed practically by measuring the resulting peak current differences under varying conditions (electropolymerisation cycles, incubation time, and pH). This approach ensures the analytical performance of the developed sensor is directly maximized under its intended operating conditions.

Effect of the electropolymerisation cycle

The sensor's response is related to the thickness of e-MIP on the electrode surface. The polymeric film must neither be too thick nor too thin. Therefore, optimising the number of electropolymerisation cycles is necessary to obtain the optimal film thickness for DMP detection [29]. Cyclic Voltammetry was used to measure this parameter, with various polymerisation cycles tested (1, 3, 5, 7, and 10).

Effect of incubation time

Electropolymerisation experiments with different incubation times, such as 5, 10, 15, 20, 25 minutes, were conducted. The template was removed by rinsing with a suitable solvent (ethanolic HCl solution). This can remove some unreacted compounds. Potential or current is important to initiate the electropolymerisation process. The changes in current are related to the changes in incubation times [21].

Effect of pH

The experiments with the target, which is DMP with different pH values such as pH 5, pH 6, pH 7, pH 8 and pH 9 were conducted. The target was incubated in the developed sensor in the optimum incubation time. The structure of DMP and the stability of the imprinted film are altered by pH values. To effectively detect DMP, the pH must be optimised. This parameter was measured using cyclic voltammetry. The highest peak current of the cyclic voltammograms indicates the redox behaviour of DMP.

Performance of the modified sensor

Analytical curve

The experiments with the DMP with different concentrations: 5, 10, 15, 20 and 25 mM were conducted. After rebinding the target with varying concentrations using imprinting cavities on the SPCE, it was incubated on the electrode surface for 15 minutes. After 15 minutes, deionised water was used to rinse the SPCE. Cyclic voltammetry was utilised to

perform electrochemical measurements using by ferrocyanide solution. Cyclic voltammetry was used for electrochemical tests with a scan rate of 50 mV/s in a potential range of -0.4 V to 0.8 V. The limits of detection (LOD) and quantification (LOQ) for the approach suggested in this study were determined using the following formulas:

$$\text{LOD} = \frac{3.3\sigma}{m} \quad (1)$$

$$\text{LOQ} = \frac{10\sigma}{m} \quad (2)$$

where σ and m stand for the analytical curve's standard deviation and slope, respectively ($n = 5$) [30].

Calculation of imprinting factor (IF)

In this study, the electrochemical detection of DMP was carried out on both e-MIP and e-NIP electrodes using cyclic voltammetry. The template removal was performed using an ethanolic HCl solution. A 10 mM DMP solution and a blank solution were used to evaluate peak currents during a 15-minute incubation period. Peak current was collected from both e-NIP and e-MIP electrodes before or after being incubated with the DMP solution and the blank solution [31]. The imprinting factor was determined using the following formula:

$$\text{IF} = \frac{\Delta I (\text{MIP})}{\Delta I (\text{NIP})} \quad (3)$$

where ΔI (MIP) and ΔI (NIP) represent the change in peak current for the molecularly imprinted polymer (e-MIP) and non-imprinted polymer (e-NIP) electrodes, respectively. These values are calculated as the difference between the voltammetric signals recorded in a blank solution and the signals recorded after incubation with the dimethyl phthalate (DMP) solution.

Repeatability of the sensor

To examine intra-day repeatability, the DMP molecule in solution (10 mM) was detected using the same electrode in three times. Cyclic voltammetry was carried out to perform electrochemical tests with a scan rate of 50 mV/s in a potential range of -0.4 V to 0.8 V. Ethanolic hydrochloric acid was utilised to generate the recognition cavities to perform this study. The relative standard deviation (RSD) was calculated

using the following formula [32]:

$$\text{RSD} = \frac{\sigma}{\mu} \times 100 \quad (4)$$

where σ is the standard deviation and μ is the mean of the measurements.

Results and Discussion

This study involved the electro-synthesis of molecularly imprinted polymer (e-MIP) and non-imprinted polymer (e-NIP) on a SPCE using an electrochemical method. The characterisation of both polymers was conducted using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The binding capacity of e-MIP and e-NIP for the adsorption of the template (DMP) were examined. The study on adsorption was conducted using the following optimisation parameters: electropolymerisation cycles, incubation time, and pH values.

Synthesis of dimethyl phthalate-imprinted polymer and non-imprinted polymer

Cyclic voltammetry was used for synthesis of DMP-imprinted polymer and non-imprinted polymer on screen printed carbon electrode. The parameters used were scan rate at 50 mV/s in the range of -0.3 V to 0.9 V. **Table 1** showed the result obtained from the synthesis. The signal from incubated e-MIP was lower than leached e-MIP as DMP had been successfully filled in imprinting sites after DMP incubation. There was small difference between leached e-NIP and incubated e-NIP as lower porosity and permeability of redox marker [24].

Electropolymerisation of pyrrole on the surface of carbon electrode

This experiment was conducted with template molecules (DMP) at pH 7. The optimised scan cycle, which was 5 scans and 50 mV/s, was used and required to obtain the electropolymerisation cycle of polymer film on screen-printed carbon electrode. **Figure 2** shows cyclic voltammograms for the electropolymerisation of pyrrole (100 mM) on the carbon electrode with or without the presence of DMP. As seen from Figure 2, in the potential range from -0.3 V to 0.9 V, significant differences can be observed in the first scan of e-MIP and the last scan of e-MIP.

Table 1. The peak height of the signal recorded for e-MIP and e-NIP

Type	e-MIP (μA)	e-NIP (μA)
Bare signal	75.2	75.2
After template removal	149.35	110.86
After DMP incubation	119.39	106.73

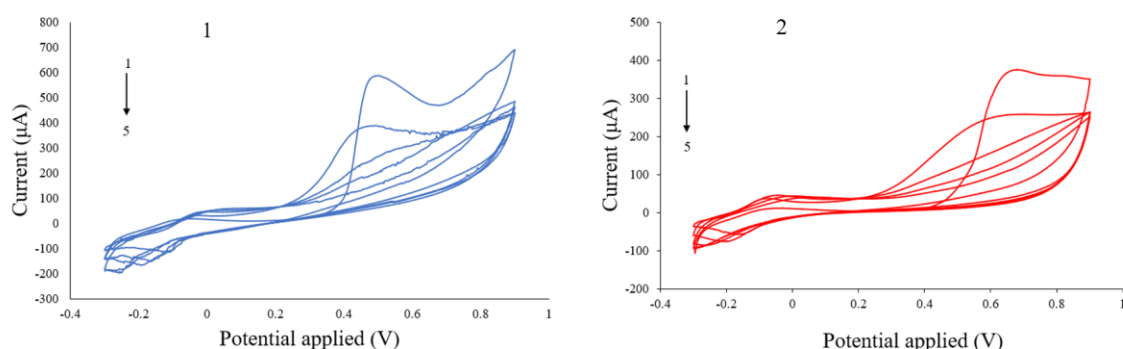


Figure 2. The electropolymerisation of pyrrole (100 mM) on the SPCE; 1) with the presence of DMP and; 2) without the presence of DMP (5 cycles)

As seen from **Figure 2**, there was an anodic oxidation peak observed at a potential of 0.5 V in the first scan in the presence of DMP. There was a significant decrease in the anodic oxidation peak when the cycles occurred during the complete polymerisation process, indicating that the electrode had been coated in a dense polymeric film. Following electropolymerisation, a significant loss of current response appeared, indicating the hindrance of redox access to the electrode surface. Here, redox access refers to the ability of electroactive species to diffuse and reach the electrode surface to undergo electron transfer; however, this process was restricted due to the dense polymer film and the absence of accessible cavities prior to template removal [33]. The electropolymerisation of pyrrole (100 mM) on the carbon electrode without the presence of DMP was also shown. An anodic oxidation peak appeared at a potential 0.65 V in the first scan. Subsequently, the anodic oxidation peak decreased when the scan cycles increased as complete polymerisation process [34].

Characterisation of dimethyl phthalate-imprinted electrochemical sensor

Fourier transform infrared spectroscopy

In order to effectively manage the incorporation of DMP molecules into the overoxidized polypyrrole network, both e-NIP and e-MIP films were evaluated using ATR-FTIR spectroscopy. Chemical structure determination of bare SPCE, leached e-MIP, incubated e-MIP, leached e-NIP, and DMP were presented in the FTIR spectra as shown in Figure 3. As illustrated in **Figure 3e**, the functional groups in

activated SPCE by 0.1M sulphuric acid are graphitic C-C, aliphatic C-H, C-O, and C=O [35]. The peak at around 2964 cm^{-1} and 1465 cm^{-1} in the SPCE's infrared spectra indicated aliphatic C-H stretching vibrations and CH_2 bending vibrations in activated SPCE. Peaks around 3057 cm^{-1} and 720 cm^{-1} indicated sp^2 C-H stretch and sp^2 C-H out-of-plane bend, respectively, while the peak around 1240 cm^{-1} was attributed to the presence of a C-O bond in activated SPCE. The C=O vibrations appeared in a peak around 1709 cm^{-1} [35].

As shown in **Figure 3a and c**, FTIR spectra from leached e-MIP and e-NIP had the same properties as the polypyrrole film that was produced on the electrode surface. Sharp peak at about 3429 cm^{-1} indicated N-H stretching in the IR spectra of leached e-MIP and e-NIP. Since bare SPCE in **Figure 3e**, which lacks of polypyrrole coating, it was not visible in its infrared spectrum. The polypyrrole film becomes overoxidized. The tertiary nitrogen atoms and carbonyl group are produced. Thus, the intensity of N-H decreased. The overoxidized e-MIP and e-NIP film showed an absorption band at 1713 cm^{-1} , which was linked to the C=O vibrations. Peak from C=O group in spectra from leached e-MIP and e-NIP was more intense than C=O on the spectrum of bare SPCE as the nucleophilic attack by the chloride ions during cyclic voltammetry. This finding confirmed the existence of carbonyl groups in the matrix of the overoxidized polypyrrole [36].

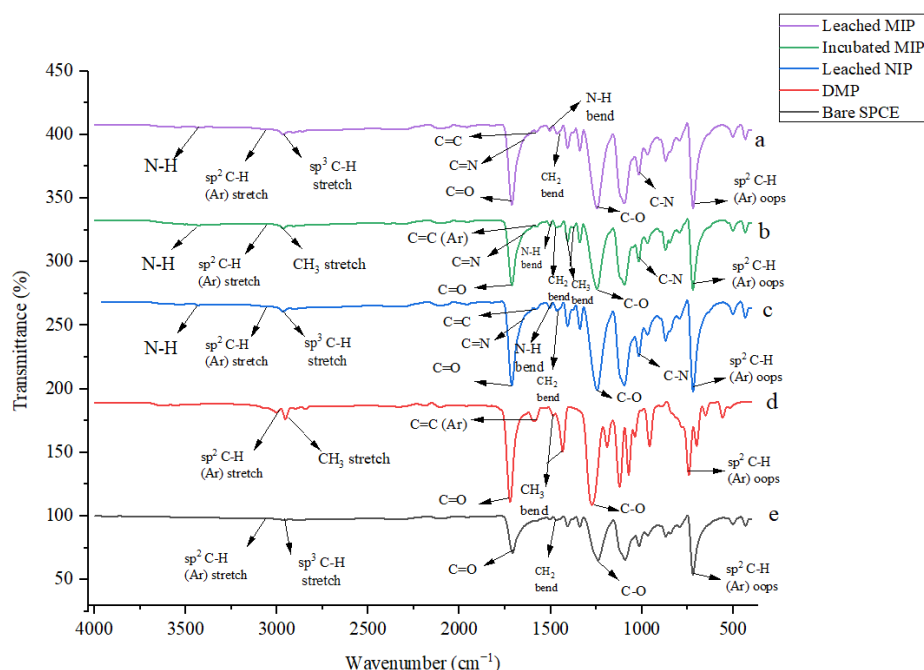


Figure 3. FTIR spectra of a) leached e-MIP; b) incubated e-MIP; c) leached e-NIP; d) DMP and; e) bare SPCE

As illustrated in **Figure 3a and c**, the leached e-MIP and e-NIP spectra exhibited characteristic absorption peaks for polypyrrole film at 1017, 1096, 1340, 1505, 1578, 1640, 1713, 3429 cm^{-1} corresponding to C-N, C-H in-plane stretching, C-H vibration of 2,5-substituted pyrrole, N-H bend, C=C, C=N, C=O, N-H stretching band, respectively [34].

As illustrated in **Figure 3b and d**, the presence of the C=O bond was shown by the peaks seen within the region 1713 cm^{-1} – 1722 cm^{-1} whereas the C-O group was detected within the region 1240 cm^{-1} - 1274 cm^{-1} . The presence of the C=C aromatic group was indicated by the peaks at 1559 cm^{-1} - 1594 cm^{-1} , whereas the aliphatic C-H group was indicated by the peaks at 2965 cm^{-1} in incubated e-MIP and 2953 cm^{-1} in DMP. The existence of an aromatic ester in the incubated e-MIP spectra was therefore indicated by the obtained spectral data [37]. Due to the fact that DMP was incubated in polypyrrole film, the incubated e-MIP spectrum differed somewhat from the others. The characteristic absorption of DMP was observed in the incubated MIP spectra at 720, 1246, 1378, 1445, 1559, and 3059 cm^{-1} , which corresponded to the C-H out-of-plane bend, C-O from the ester group, CH₃ bend, aromatic C=C and aromatic C-H stretch, respectively, in comparison to the leached e-MIP spectra [38]. These findings provided more proof that DMP was successfully incorporated into the polymer network [36]. The broad peak observed at 3429 cm^{-1} was due to the hydrogen bonding between N-H bond in polypyrrole and C=O in DMP molecules. As overoxidized polypyrrole formed, the intensity of N-

H vibration decreased. Incubated e-MIP has all characteristics which are similar to leached e-MIP, leached e-NIP, DMP and bare SPCE.

Scanning electron microscopy

The change in the surface of the resulting alterations was examined microscopically using scanning electron microscopy (SEM). The morphology of the bare SPCE electrode, DMP-imprinted and non-imprinted polymers differed from one another, according to SEM pictures. The SEM images of the bare SPCE were displayed in **Figure 4**. The bare SPCE showed corrugations, which were more noticeable at higher magnification and were characteristic of the carbonaceous covering found in commercial working electrodes [33].

Numerous tiny particles were scattered throughout the bare carbon electrode, which showed a sheet-like shape. Based on the composition of carbon paste, it appeared that the black sheets can be classified as graphite powders and the tiny particles as binding agents [39].

The synthesised e-MIP and e-NIP were microspherical particles with varying sizes of 6.2–7.5 mm, according to the SEM images displayed in **Figure 5**. The difference between the leached e-MIP and the incubated e-MIP was the presence of imprinted cavities. In **Figure 5b**, a regular porous structure appeared on the surface of leached e-MIP after template removal. The incubated e-NIP and leached e-NIP in **Figure 5c and d** revealed that similar

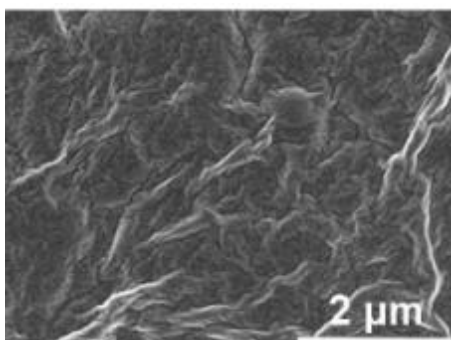


Figure 4. SEM image of bare SPCE [48]

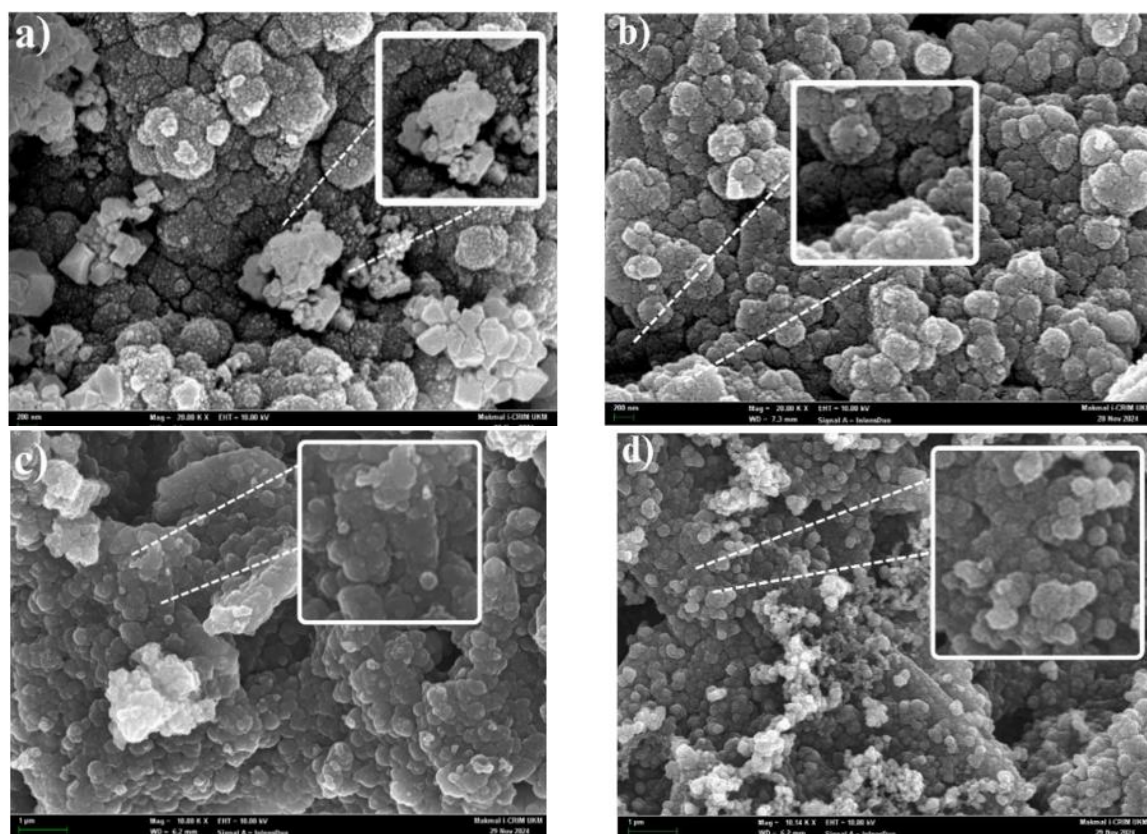


Figure 5. Morphology of a) incubated e-MIP; b) leached e-MIP ; c) incubated e-NIP and; d) leached e-NIP

cauliflower-like structure, which showed the presence of polypyrrole film. Since there were no imprinted spots accessible, the template removal procedure had no discernible impact on the e-NIP surface [29].

In contrast, **Figures 4a and b** confirmed the establishment of e-MIP. Cauliflower-like imprinted layers and pores were visible after electropolymerisation with DMP. After incubation, this structure exhibited a small alteration, and some filled voids relating to the incubation of DMP to the e-MIP matrix were seen on the surface [29]. Since DMP was present during polymerisation, which promoted

the agglomeration of the forming spheres through hydrogen bonding, the NIP was less aggregated than the e-MIP [40].

Compared with the bare SPCE in **Figure 4**, there was a consistent globular-type spheroidal morphology throughout the surface of e-MIP and e-NIP. The polypyrrole films are extremely uniform and small. They had a structure like cauliflower on their surface [41]. As can be observed, it was made up of globule clusters and microspherical grains. Additionally, it had been demonstrated that as thickness grows, a uniform and regular polymer surface becomes increasingly

granular. The smaller size of the Li^+ cation complexed in the polymer matrix was responsible for this fine-grained morphology. These findings suggested that LiClO_4 can be employed as an anionic dopant in addition to a supporting electrolyte, increasing the polymer's conductivity [3].

Electrochemical characterisation of modified electrode

For electrochemical characterisation of e-MIP and e-NIP electrodes, cyclic voltammetry (CV) was used. This study was carried out using 50 μL of a 5 mM solution of ferrocyanide, which is a redox probe prepared in KCl solution (0.1 M). As seen in **Figure 6**, cyclic voltammograms of the e-MIP electrode and e-NIP electrode under different conditions: bare electrode, e-MIP and e-NIP before or after incubation, were shown.

The peak current for the bare electrode was lower compared to the leached e-MIP electrode and the incubated e-MIP electrode to the absence of a conducting polymer film on the electrode and a lack of redox response [3]. When polypyrrole was used to modify the electrode surface, the peak became clearly defined and showed an increase in current. The enhanced electrical conductivity and higher electron transfer rate of the polymer coating were responsible for this, and they may have enhanced the modified electrode's active surface area [3]. Since DMP was removed by ethanolic HCl, leaving empty spaces in the polymer that allow the redox probe to enter the electrode surface, the leached e-MIP had the largest anodic oxidation peak [33]. Since the imprinting sites were reoccupied and the permeability of the redox marker to the electrode decreased, the anodic peak in incubated e-MIP lowered in comparison to leached e-MIP [24, 34].

Binding capacity of molecularly imprinted and non-imprinted polymers

Effect of the electropolymerisation cycle

The thickness of the imprinted membrane and the permeability of the polymeric film, which is the presence of imprinted sites, might affect the imprinted sensor's response [34, 42]. The number of electropolymerisation cycles allows for the adjustment of the polymer thickness. One factor that may affect the MIP sensor's stability and sensitivity is the film's thickness [43].

As seen in **Figure 7**, this study investigated a range of CV numbers, including 1, 3, 5, 7, and 10 scans. A significant decline in the e-MIP sensor's analytical performance was seen below and above 5 cycles for variations of 1, 3, 5, 7, and 10 scan cycles. As can be

observed, the peak current produced by the sensor rise for up to five cycles. An increased number of imprinted sites that make it easier for the ferrocyanide to reach the electrode surface can account for this observation [43]. The coated film may become more stable as the thickness of the polymer layer increases [29].

The peak current decreased when the cycles beyond 5. The mass transfer resistance explains the observation. Increased cycles lead to a thicker sensing film with poor site accessibility, even while they favour the formation of more imprinted sites. Mass transfer resistance may make it more difficult to reach the imprinted areas as membrane thickness increases [34]. Additionally, when excessive cycles were applied, the thick e-MIP exhibited electrochemical responses similar to an e-NIP, as the buried recognition sites became inaccessible [44]. Accordingly, the rebinding ability and repeatability of the e-MIP sensor in thicker polymer films can be adversely impacted in proportion to the diffusion of DMP molecules [34]. Furthermore, after polymerisation, it becomes more difficult to efficiently extract the template from a thicker film [45]. Therefore, 5 cycles were used to produce an optimum film thickness in the proposed e-MIP sensor.

Effect of incubation time

After removal of template molecules from the e-MIP sensor, the sensor was incubated in DMP (10 mM) for different periods (5, 10, 15, 20 and 25 min). **Figure 8** shows the effect of incubation time. The change in current means the difference in peak current between the incubated e-MIP electrode and the leached e-MIP sensor. When most of the imprinted sites were filled with DMP molecules, the peak current was lower in the incubated e-MIP. The optimum incubation time was chosen based on the larger difference of the incubated e-MIP and the leached e-MIP.

The main factor influencing the sensitivity of molecularly imprinted sensors is the incubation period. The effects of template incubation duration on rebinding were systematically examined in order to assess e-MIP efficiency in identifying the DMP molecule. As illustrated in **Figure 8**, the e-MIP sensor's net current increased from 5 to 15 minutes before sharply declining after that. It showed that the equilibrium of adsorption has been achieved [31,46]. The ideal incubation time for the optimisation is 15 minutes. On the other hand, until 15 minutes after incubation, no noticeable change in the e-NIP sensor's electrochemical response was seen. As expected, this finding was consistent with the lack of specific binding sites on the e-NIP sensor surface [34].

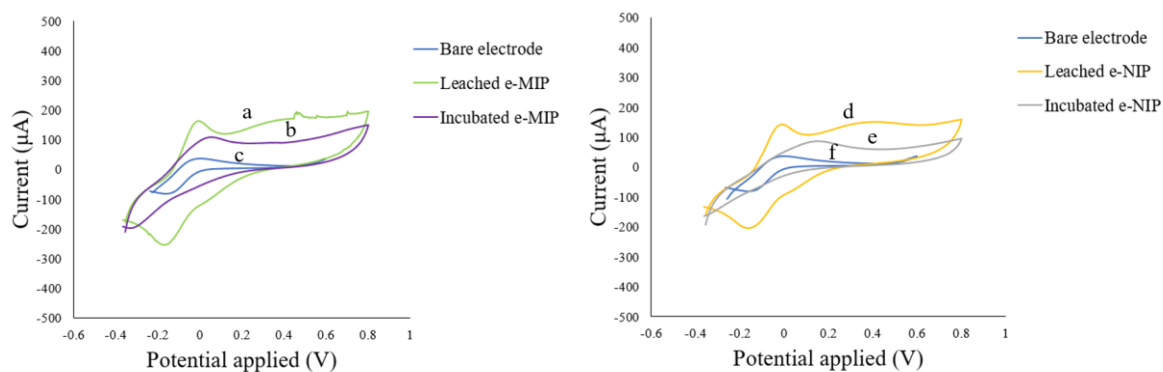


Figure 6. The cyclic voltammogram of the e-MIP and e-NIP electrodes under different conditions; 1a) leached e-MIP; 1b) incubated e-MIP; 1c) bare electrode; 2d) leached e-NIP; 2e) incubated e-NIP and; 2f) bare electrode

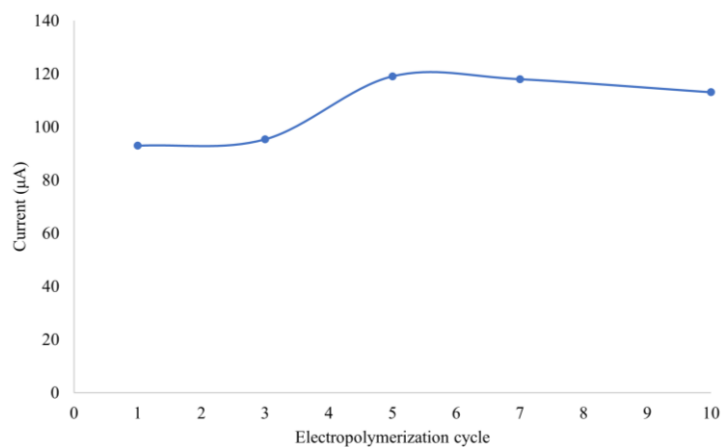


Figure 7. Effect of electropolymerisation cycles on the e-MIP electrode

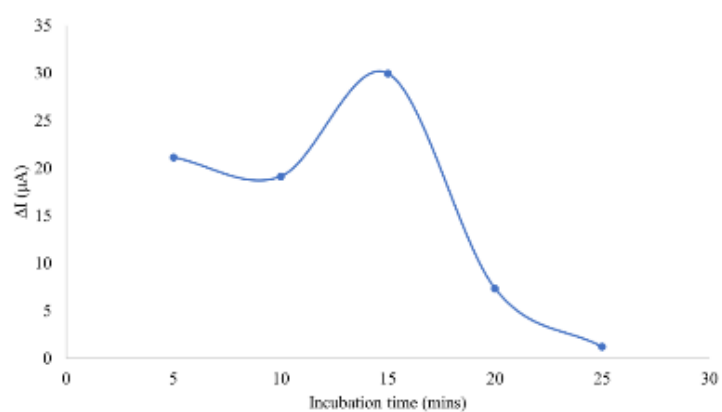


Figure 8. Effect of incubation time on the e-MIP electrode

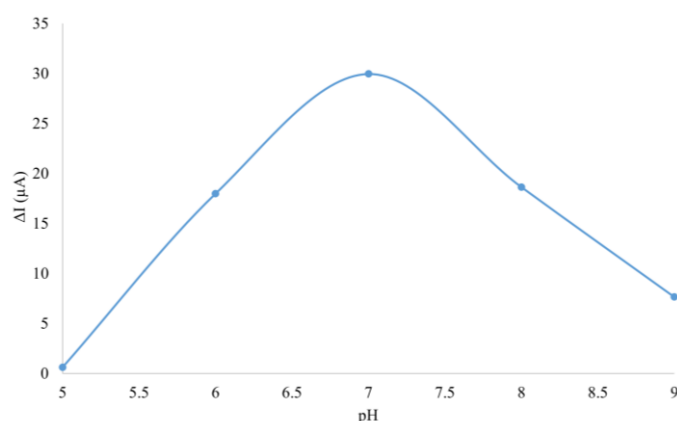


Figure 9. Effect of pH on the e-MIP electrode

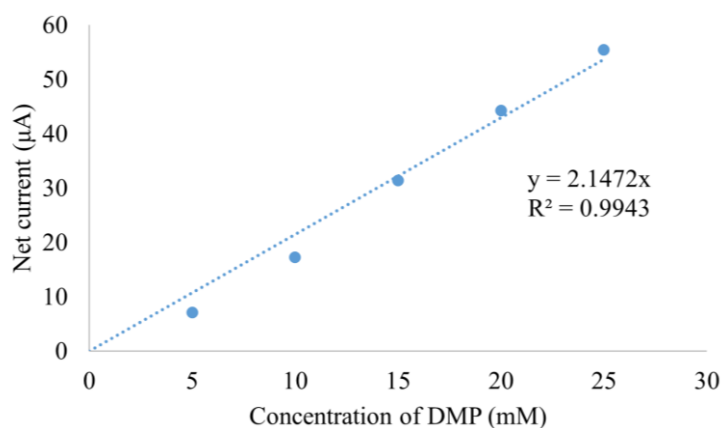


Figure 10. The calibration curve of DMP

Effect of pH

The net current indicates the difference in peak current between the leached e-MIP sensor and the incubated e-MIP electrode. As seen in **Figure 9**, the impact of pH on the proposed sensor's CV response was assessed in a different incubation investigation. It was confirmed that pH significantly affected the e-MIP sensor's sensitivity and selectivity towards DMP molecules following incubation with DMP solutions at various pH values ranging from 5 to 9. It was discovered that the peak current response dramatically increased as pH increased from 5 to 7, and then steadily declined as pH increased from 7 to 9. At neutral pH, the e-MIP reached its greatest sensitivity.

The imprinted film's structure, transfer rate, template shape, and template molecular adsorption may all be impacted by the rebinding solution's pH [31]. Esters do not react much with water at pH 7 because they are far less electrophilic. Thus, DMP can still be detected by the sensor response, which results in a higher net current. The following factors are responsible for these outcomes: higher peak current in incubated e-

MIP is most likely caused by the hydrolysis of phthalate ester and a structural alteration in DMP in an environment that is more acidic ($pH < 7$). Alcohol and carboxylic acid are produced when DMP undergoes acidic hydrolysis [1]. An increase in peak current in incubated e-MIP variation is likely to occur in a medium with a pH higher than 7 because of the high alkalinity. This will result in the formation of DMP in an anionic structure and an issue in the stability of the imprinted film [34, 1]. Alcohol and carboxylate esters will be produced when DMP is hydrolysed by a base.

Performance of the modified sensor

Analytical curve

In this research, a calibration line was plotted as shown in **Figure 10** which shows the calibration curve to analyse DMP using the e-MIP electrode prepared under optimal experimental conditions. e-MIP-modified electrodes were incubated with DMP solutions at different concentrations ranging from 5 mM to 25 mM following the template's removal. Cyclic voltammetry was conducted following a 15-minute incubation period, and a linear relationship

between current response and DMP concentration was generated in the range.

The correlation coefficient, R^2 is 0.9943. The linear regression equation is $I (\mu A) = 2.1472x$. The limit of detection was calculated to be 1.796×10^{-3} M, which is enough to detect DMP levels, as can be seen in **Table 2**.

As Table 3 illustrates, the reported LOD (1.796×10^{-3} M) is relatively high compared to previously reported electrochemical sensors. This observed sensitivity is primarily attributed to the utilization of an unmodified screen-printed carbon electrode (SPCE) without the incorporation of highly conductive, signal-amplifying nanomaterials, such as graphene or metallic nanoparticles, which are frequently employed in advanced MIP architectures to maximize surface area and electron transfer rates. Instead, the proposed sensor design intentionally prioritizes establishing a foundational proof-of-concept that emphasizes simplicity, rapid fabrication, and low cost.

Despite the relatively high LOD, the sensitivity of the developed sensor remains highly relevant in the context of practical regulatory requirements. For instance, DMP concentrations in cosmetic products have been reported to reach up to 34% [47], which falls well within the detection capabilities of this sensor. Furthermore, the calculated LOD is equivalent to approximately 348 mg/L of DMP, a value proximate to the ambient water quality criterion of 313 mg/L established for the protection of human health [8]. While trace-level environmental detection might necessitate prior sample pre-concentration, the current sensor provides a viable, low-cost screening tool for identifying threshold breaches. With future

optimization, such as integrating conductive nanomaterials into the electrode design, the sensitivity could be further enhanced for direct environmental monitoring applications.

Calculations of imprinting factor

The peak current of e-MIPs incubated with DMP or blank solution, and e-NIPs incubated with DMP or blank solution, was shown in **Table 4**. The imprinting factor (IF) is a measure of the imprinted electrode's specific-to-nonspecific binding ratio. ΔI for e-MIP and e-NIP electrodes were calculated using the difference in current response ($\Delta I = I^\circ - I$) between the voltammetric signals recorded for the electrode while exposed to DMP solution (I) and for the same electrode in blank solution, such as water (I°) [31].

The formula $IF = \frac{\Delta I (MIP)}{\Delta I (NIP)}$ was then used to get the IF.

The e-MIPs electrode's IF value of 7.3 indicates a high affinity for binding DMP, but the e-NIPs electrode had no noticeable effect on peak current [31].

Repeatability of the sensor

Cyclic voltammetry was used to measure the developed e-MIP sensor repeatability study using the same electrode for three consecutive cycles. The investigation of repeatability is another crucial factor in terms of application in real life. As tabulated in **Table 5**, this sensor measured 10 mM DMP three times after optimisation. To get rid of the template molecules, the electrode was rinsed with 0.1 M ethanolic HCl solution following each measurement. With a relative standard deviation (RSD) of 3.3%, this sensor's repeatability is acceptable as there is only a small alteration in the oxidation peak in three consecutive cycles [34, 47].

Table 2. The features of the calibration plot (n=5)

Features	Value
Regression equation	$I (\mu A) = 2.1472x$
Correlation coefficient (R^2)	0.9943
Linearity range (M)	$5 \times 10^{-3} - 2.5 \times 10^{-2}$
LOQ (M)	5.44×10^{-3}
LOD (M)	1.796×10^{-3}

Table 3. Comparison of the performance of the developed sensor with another developed sensor

Detection Method	Modification	Linear Range (M)	Limit of Detection (M)	Ref.
DPV	Metal mediator, Cu^{2+}	$1.4 \times 10^{-5} - 8.6 \times 10^{-5}$	9.0×10^{-6}	[13]
EIS	MIP modified PGE	$1.0 \times 10^{-8} - 1.0 \times 10^{-6}$	4.5×10^{-9}	[4]
CA	MWCNT-based buckypaper	$1.5 \times 10^{-5} - 7.0 \times 10^{-5}$	1.264×10^{-5}	[34]
CV	MIP-polypyrrole	$5 \times 10^{-3} - 2.5 \times 10^{-2}$	1.796×10^{-3}	This study

Table 4. The peak current of incubated e-MIPs with DMP or blank solution and incubated e-NIPs with DMP or blank solution.

Electrode	Peak Current (A)
Incubated e-MIPs with DMP	0.00011939
Incubated e-MIPs with blank solution	0.00014935
Incubated e-NIPs with DMP	0.00010673
Incubated e-NIPs with blank solution	0.00011086

Table 5. The repeatability of the sensor

Times	Peak Current (A)
1	0.00011277
2	0.00010571
3	0.00010786

Conclusion

This study successfully developed an electrochemical sensor based on an electropolymerised molecularly imprinted polymer (e-MIP) on a screen-printed carbon electrode (SPCE) for dimethyl phthalate (DMP) detection. Empirical optimisation revealed that 10 electropolymerisation cycles, a 10-minute incubation time, and a pH of 7.0 maximized the sensor's binding capacity. The e-MIP SPCE demonstrated successful imprinting with an imprinting factor of 2.1, exhibiting acceptable intra-day repeatability (RSD = 5.51%). The sensor achieved a linear response between 5 mM and 25 mM ($R^2 = 0.9943$) with a limit of detection of 1.796 mM, highlighting its potential as a simple, disposable screening tool. To transition this proof-of-concept toward practical application, future studies will focus on validating the sensor against standard techniques like high-performance liquid chromatography (HPLC), as well as comprehensively evaluating its long-term stability, cross-batch reproducibility, and selectivity in real sample matrices.

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