

Research Article

A Highly Sensitive Electrochemical Sensor Based on Electrocatalytic Reduction Effect of Cu^{2+} on Trace Determination of Malathion in Soil and Other Complex Matrices

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The current strategy reports a highly sensitive and selective square wave-cathodic stripping voltammetric protocol for malathion determination. The established method was based on the controlled adsorptive accumulation of malathion in the presence of Cu^{2+} ions in an aqueous solution of pH 2 onto the hanging mercury dropping electrode (HMDE) and measuring the resulting cathodic peak current of the adsorbed species at -0.42 V versus Ag/AgCl electrode. The low limits of detection (LOD) and quantification (LOQ) of malathion of the assay were estimated to be 3.1×10^{-10} and 1.03×10^{-9} M with a linear dynamic range of 1.03×10^{-9} – 2.0×10^{-7} M, respectively. The method was satisfactorily applied and validated for malathion determination in environmental samples. The experimental Student t_{exp} and F_{exp} values did not exceed the tabulated t_{tab} (2.78) and F_{tab} (6.39) at 95% ($P = 0.05$) confidence ($n = 5$), confirming the precision and independence on the matrix. The developed sensing platform for the detection of malathion shows superior performance to conventional electrochemical methods. The proposed sensor offered simple, economical, reproducible, and applicable approach for the determination of malathion in environmental samples.

1. Introduction

Nowadays, pesticides are inevitably used in agriculture to improve the quality of products and resist various pests. However, their heavy use in the production activities and slow degradation in the environment may lead to residues in the food and the environment [1, 2]. Organophosphorus pesticides (OPPs) are extensively used in agriculture and could cause many neurotoxic effects on humans, such as disruption of cholinesterase [3]. The growing human populace and significant agriculture also stress water supplies and contribute to water pollution [4]. Thus, the development of simple, sensitive, rapid, and reliable electrochemical methods for trace determination of pesticides has become a challenge in many fields, such as food industry and environmental protection [7].

OPPs have conveyed justifiable nutrition security to many areas such as agriculture, horticulture, and forestry on a worldwide scale [7–9]. Malathion IUPAC, named diethyl(dimethoxythiophosphorylthio)succinate (Supplementary Information, SI. 1), is typical OPPs and most extensively used in agriculture due to its insecticidal properties, and its residues display low toxicity to human health when absorbed by the human body [10, 11]. High consumption of malathion and its durability compared with other pesticides (e.g., organochlorines) have been linked to its lower potency [12–14]. Malathion and its commercial formulations could adversely affect the immune and central nervous systems, liver, blood, and adrenal glands [15, 16]. Thus, the development of the low-cost and selective protocol for trace determination of malathion in environmental samples is of great importance [8, 10].

Numerous techniques, such as Fourier transform (FT) infrared [17, 18], FT-Raman spectrometry [19], GC-MS [20–23], cloud point extraction (CPE) [24], fluorescence [7, 10], spectrophotometry [25, 26], dispersive liquid-liquid microextraction combined UV spectrophotometry [27], indirect atomic absorption spectrometry [28], opposite changing dual-emission luminescence of gold nanoparticles by sulfhydryl [6], carbon dots [7], and screen-printed enzyme electrodes [29], have been reported for trace determination of malathion in complex matrices. Despite the reliability of the protocols mentioned above, some complexities and drawbacks (e.g., use of toxic constituents and solvents, high cost, and expensive instrumentation linked with operational complications) have been associated with most of these techniques [17–23]. Thus, the request for a simple, selective, cost-effective, and reliable strategy for trace determination of malathion residues in its formulations, soil, food products, and water is crucial and highly needful [30, 31].

Recently, a series of electrochemical techniques have been reported for trace determination of reducible pesticides on various modified electrodes, including mercury [3, 20, 30–33]. Pulse polarography [32, 33] and cathodic/anodic stripping voltammetric techniques at HMDE and other modified electrodes [34–42] for trace determination of malathion and other analogs have been reported. However, most of the published sensors-based modified electrodes still have many drawbacks, such as complications in the synthesis, fabrication, characterization, and interference by other thiols [18–20]. Hg, DME, and HMDE are hazardous chemicals and have serious harmful effects on human life and trouble on Hg disposal and storage. Mercury is volatile and water-soluble, and Hg^{2+} is the main form of mercury pollution found in the water systems [21]. In addition, Hg^{2+} can be converted into methyl mercury by microorganisms which causes great harm to human health [43, 44]. On the contrary, HMDE is extensively used in stripping voltammetry for trace determination of various metal ions and pesticides [31–33, 45, 46] and metal ions [47–49] because it has good reproducibility and selectivity towards sulfur compounds [45, 46]. Moreover, if the disposal and storage of Hg are employed in a controlled and protected manner, the HMDE becomes safe for use. HMDE also exhibits a strong affinity towards the $P = S$ group of malathion and provides stable and quantitatively reproducible analytical results [45, 46].

The extraordinary prerequisite for trace determination of malathion has encouraged the development of low detection, cost-effective, simple implementation, and high sensing approach, such as square wave voltammetry (SWV). Frequently SWV provides better sensitivity and allows one to perform fast and sensitive measurements. Hence, the current strategy is aimed at (i) studying the redox characteristics of malathion at the HMDE; (ii) assigning the most probable electrochemical catalytic reduction mechanism of malathion by Cu^{2+} at HMDE; (iii) developing a simple and low-cost electrochemical probe for malathion determination based on its electrocatalytic reduction by Cu^{2+} ions in combination with square wave-cathodic stripping voltammetry (SW-CSV); and finally, (iv) applying the established assay for malathion determination in

environmental samples (water, soil, plants, and pesticide commercial formulations). To the best of our knowledge, the proposed methodology represents the first application of the electrocatalytic reduction effect of Cu^{2+} ions on the malathion determination in environmental samples.

2. Experimental

2.1. Instrumentation. The electrochemical experiments were performed on a Metrohm 746 VA trace analyzer and 747 VA stand equipped with a three-compartment (Metrohm) electrochemical cell (10.0 mL) incorporating HMDE (0.38 mm^2), Ag/AgCl double-junction in KCl (3.0 M), and platinum wire (BAS model MW-1032) as working, reference, and counter electrodes, respectively. A Shimadzu (MultiSpec-1501) double beam spectrophotometer (190–800 nm) with 1.0 cm (path length) quartz cell was used for recording the UV-Visible spectra of malathion and its copper (II) complex. Validation of the developed method for malathion determination was also performed by a Shimadzu GC-17A, GC-MS QP-5000 mass spectrometer under the optimized operational parameters [21]. Digital micropipettes 10–100 μL (Volac) and a digital pH-meter (model MP 220, Mettler Toledo) were employed to prepare the standard and working solutions and pH measurements, respectively. A Millipore Direct Milli-Q Plus system (Millipore Corporation, Bedford, MA, USA) was used for providing ultrapure water throughout the work.

2.2. Reagents, Materials, Glassware, and Reagent Control. Analytical-reagent (AR) grade chemicals and spectroscopic grade solvents were used as received. Glasswares were soaked in hot detergent for 30 min, precleaned with 50% HCl and HNO_3 (10% v/v), washed with acetone and deionized water to avoid contamination of any organic and inorganic species, and finally dried at 125°C . The voltammetric cell was precleaned by soaking in hot detergent for 30 min; washed with HNO_3 (50% v/v), deionized water, and ether; and finally dried in an oven. A stock solution ($10.0 \mu\text{g mL}^{-1}$) of malathion in ethanol was purchased from the Riedel-de Haen with a purity of 99.9%. Diluted standard solutions (1.0×10^{-3} and $1.0 \times 10^{-5} \text{ M}$) of malathion were prepared daily by dilution of a suitable volume of its ethanolic solution with Milli-Q water. A series of Britton–Robinson (B-R) buffer (pH 2–11) was prepared and used as supporting electrolytes [50]. Merck $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Darmstadt, Germany) was used for preparation of standard stock solution of Cu^{2+} (1000 mg L^{-1}) in water. Ultrapure water (Millipore, USA) was used for preparation of more diluted solutions.

2.3. Recommended SW-CSV Procedure. An accurate volume (10.0 mL) of B-R buffer solution of pH 2.0 (supporting electrolyte) containing copper (II) solution ($3.4 \times 10^{-7} \text{ M}$) was transferred into the cell. The test solution was purged with a stream of dry N_2 gas while the solution was stirred for 10 min. After 10 s of quiescence time, the background SW-CS voltammogram of the solution was recorded in the potential range of $-0.2.0$ to -1.0 V under the optimized

analytical parameters of accumulation potential (-0.2 V), deposition time (360 s), starting potential (-0.2 V), pulse amplitude (50 mV), scan rate (60 mVs^{-1}), and 50 Hz frequency. The corresponding cathodic peak current at -0.42 V versus Ag/AgCl reference electrode was measured. Under identical experimental parameters and after recording the background SW-CSV of the blank solution, a known volume ($100 \mu\text{L}$) of malathion (1.3×10^{-9} – 2.8×10^{-7} M) was introduced into the test solution in the cell. Under the optimized deposition potential and accumulation time, the test solution was purged with N_2 gas, stirred for 3–5 min, and left for 10.0 s quiescence time, and the corresponding SW-CSV was recorded under the optimized parameters of accumulation by applying a negative potential scan from -0.2 to -1.0 V. The corresponding cathodic peak currents at -0.42 V versus Ag/AgCl were finally measured after correction of the background current of the blank. These results were further used for the construction of the calibration plot. Malathion concentration was finally calculated with the aid of the standard calibration curve.

2.4. Analytical Applications

2.4.1. Determination of Malathion in Commercial Pesticide Formulations

(1) *Determination of Malathion in Liquid Pesticide Formulations.* To an accurate volume (5.0 mL) of the liquid pesticide formulations (0.57% w/v), 5 mL of methanol was added. The sample solution was shaken for 5 min, filtered through a $0.22 \mu\text{m}$ filter membrane. The filtrate and the washing solutions were transferred to the measuring flask (50 mL) and completed to the mark with deionized water. An accurate volume (5.0 mL) of the prefiltered sample was transferred to the cell in the presence of B-R buffer solution (5.0 mL, pH 2) as a supporting electrolyte and Cu^{2+} solution (3.4×10^{-6} M). Under the optimized parameters, the SW-CSVs were recorded in the absence and presence of known fractions (20.0–100 μL) of the standard malathion (5.0×10^{-6} M) under the optimized parameters. The corresponding cathodic peak current ($i_{p,a}$) of each individual solution at -0.42 V was subsequently measured versus Ag/AgCl electrode. The concentration of malathion was then computed via extrapolated abscissa of the plot of the standard addition. Malathion concentration was then evaluated from the linear plot of standard addition using the following equation:

$$[\text{DCS}] = b \frac{C_{\text{stand}}}{m} \cdot V_x, \quad (1)$$

where b is intercept, m is the slope of the linear standard plot, C_{stand} is the standard malathion concentration, and V_x is the volume of the water sample, respectively.

Alternatively, the cathodic peak current was determined without and with known fractions (20.0–100 μL) of the standard malathion under the optimal parameters. Malathion concentration was calculated via extrapolated abscissa of the linear plot of the standard addition employing the following equation [51]:

$$[\text{DCS}] = [\text{Cs}] \times \frac{i_{p,a}(\text{sample})}{(i_{p,a})_{\text{stand}}}, \quad (2)$$

where $[C_{\text{stand}}]$ is the known malathion concentration and $(i_{p,a})_{\text{sample}}$ and $(i_{p,a})_{\text{stand}}$ are the cathodic peak currents displayed by the sample and after the addition of the standard malathion in μA , respectively. The calculated recovery percentages via the standard addition plot at room temperature ($\sim 25^\circ\text{C}$) were further used for assigning the precision, accuracy, and validation of the proposed method.

(2) *Determination of Malathion in Solid Pesticide Formulations.* An accurate mass of (0.67 ± 0.001 g) of the solid DB Malatox (0.5 w/v) was shaken vigorously with methanol (10.0 mL) for 5 min and filtered with the Whatman filter paper. The filtrate and washing solutions were precisely placed into a measuring flask (25.0 mL) and completed to the mark with methanol. The test solution was analyzed using the standard addition following the recommended SW-CSV procedures described above.

2.4.2. *Determination of Malathion in Environmental Water Samples.* Tap-water samples were collected from our Chemistry laboratory at King Abdulaziz University (Jeddah, Saudi Arabia). To remove the impurities, the samples were filtered through a $0.22 \mu\text{m}$ filter membrane before the experiments. Malathion residues in the test solution were then determined under the optimized experimental procedures of its determination at pH 2–3 via the calibration plot of the SW-CSV procedures at -0.42 V.

The standard addition method was also performed under the optimized condition of the established SW-CSV at various known concentrations (0.0 – $20.0 \mu\text{gL}^{-1}$) of malathion to minimize the matrix interference. The peak current at -0.42 V displayed before and after spiking the test solutions with standard malathion was measured versus Ag/AgCl electrode.

2.4.3. *Determination of Malathion in Soil Samples.* Soil samples were collected from the local soil samples, Jeddah, Saudi Arabia. Almost 4 ± 0.001 g of the soil samples were precisely weighed and ground to a uniform powder (30–40 meshes) and transferred into a clean beaker (250.0 mL). The soil samples were mixed with methanol (25–30.0 mL), stirred for 1 h with a magnetic stirrer at 2000 rpm, centrifuged for 10 min, and separated. The supernatants were filtered through a $0.22 \mu\text{m}$ filter membrane, and the filtrate and the washing solutions were concentrated with a rotary evaporator and finally transferred to a measuring flask (50.0 mL). The test solution was completed to the mark with water, and the concentration of malathion in the sample solution was then determined following the recommended SW-CSV procedures as described before. After the correction of the background cathodic peak current displayed at -0.42 V, malathion concentration was determined with the aid of standard curve.

The standard addition method was also employed using known volumes (10–40 μL) of malathion ($5.0 \times 10^{-6} \text{ M}$) using the recommended SW-CSV procedures. Malathion concentration was then determined with the aid of the linear plot of the standard addition after correction of the background cathodic peak current displayed by the unknown solution.

2.4.4. Determination of Malathion in Plant Samples. Cabbage or spinach plant samples were randomly purchased from the local market in Jeddah City, Saudi Arabia. Accurate sample weights ($4.0\text{--}5.0 \pm 0.001 \text{ g}$) were cut into 1.0 cm pieces, dried, and blended, followed by transferring a representative portion of the sample into a measuring flask (25.0 mL). Several organic solvents (e.g., acetonitrile, ethyl acetate, and methanol (20 mL)) were tested for malathion extraction from the sample after shaking for 30 min at 2000 rpm. The solutions were equilibrated for 30.0 min and filtered through a $0.45 \mu\text{m}$ cellulose membrane filter at room temperature. The filtrate and washing solutions (20 mL) were evaporated by a rotary evaporator at 40°C . The residues were washed with deionized water, quantitatively transferred into a measuring flask (25.0 mL), and completed to the mark with water. The test solutions were then analyzed using the recommended SW-CSV procedures at -0.42 V . Malathion concentration in the sample was then estimated as described in Section 2.4.3. Good recovery of malathion was achieved using methanol as an efficient extractor. Thus, in the subsequent study involving the standard addition method, methanol was chosen as a proper extraction solvent with known concentrations of malathion also employed.

2.5. Statistical Treatment and Validation of the Proposed Methodology. The data were expressed as average \pm standard deviation (SD) of five measurements and treated by SPSS V.13 (SPSS Inc., Chicago, USA). A one-way ANOVA was used for analyzing the differences between the samples, followed by the least significant difference (LSD) at $P < 0.05$. ANOVA was also used for the data obtained within-bottle mean square (MS_{within}) and between-bottle mean square (MS_{among}) using the following equations [52]:

$$S_{bb} = \sqrt{\frac{MS_{\text{among}} - MS_{\text{within}}}{n}}, \quad (3)$$

$$u_{bb} = \sqrt{\frac{MS_{\text{within}}}{n}} \cdot \sqrt[4]{\frac{2}{v_{MS_{\text{within}}}}},$$

where $v_{MS_{\text{within}}}$ is the freedom of MS_{within} and S_{bb} and u_{bb} are the between-bottle variance and the between-bottle variance incorporating the effect of analytical variation, respectively.

3. Results and Discussion

In stripping voltammetry, the choice of the working electrode is vital as its performance in developing a highly sensitive method for analyzing the target compound mainly depends on its strong interaction with the analyte. The

availability of HMDE with its strong interaction with OPPs containing oxon ($-\text{P}=\text{O}$) and thion ($-\text{P}=\text{S}$) (e.g., malathion, parathion, chlorpyrifos) compared to nonmodified electrodes (e.g., glassy carbon electrode GCE, carbon paste, and Au) is important for its use for determination of trace levels of pesticides in environmental samples [45–47]. At the surface of modified and nonmodified solid electrodes (GCE, CPE, Au), the redox behavior of OPPs also has limitations of intense adsorption of pesticide onto the electrode surface, which damages the response and reproducibility [45, 53]. On the contrary, HMDE is safe as long as storage and disposal of Hg is undertaken in a safe, controlled, and protected manner. Moreover, HMDE has a strong affinity towards sulfur and also provides stable and quantitatively reproducible analytical results.

3.1. Electronic Spectra of Interaction of Malathion with Cu^{2+} Ions. The interaction of malathion with Cu^{2+} ions in aqueous media was found pH-dependent, as noticed from the color intensity of the developed species. At pH 2–3, a stable blue-colored complex was noticed. The visible spectrum of the Cu^{2+} -malathion complex showed one broad peak at $\lambda_{\text{max}} = 798 \text{ nm}$ (Electronic Supplementary Information (SI. 2 A)). In contrast, the electronic spectrum of malathion showed one well-defined peak in the UV region at 273 nm safely assigned to n [54] and no peaks in the visible region. After 60 min shaking time in ethanol at $\lambda_{\text{max}} = 798 \text{ nm}$, the broad peak of Cu^{2+} -malathion at $\lambda_{\text{max}} = 798 \text{ nm}$ is most likely attributed to complex formation between Cu^{2+} ions and malathion [54]. The stoichiometry of the copper (II)-malathion in a buffer solution of pH 2 as determined from the continuous variation method [54] at λ_{max} revealed the formation of a 1 : 3 molar ratio of Cu^{2+} : malathion. Thus, it can be concluded that Cu^{2+} -malathion complex has the stoichiometry of 1 : 3 molar ratios (SI. 2 B) of Cu^{2+} to malathion and the chemical structure of the formed complex can be proposed as $\text{Cu}(\text{L})_3$, where L = malathion.

3.2. Redox Behavior. The SW-CSV, peak potential, and peak current height are strongly influenced by the solution pH. Thus, the SW-CSVs of malathion ($4.8 \times 10^{-7} \text{ M}$) in the absence and presence of Cu^{2+} ions ($3.5 \times 10^{-6} \text{ M}$) at the HMDE in the potential range -0.2 to -1.0 V versus Ag/AgCl electrode were recorded over a wide range of pH (pH 2–11) using Britton–Robinson (B-R) buffer. Representative SW-CSVs at selected pH are illustrated in Figure 1. On increasing the solution pH, the cathodic peak current decreased, suggesting protonation–deprotonation processes of the $\text{P}=\text{S}$ and the involvement of proton/electron transfer in the cathodic process [45, 53]. At the HMDE and low pH, the protonation of malathion was found fast, promoting the best condition for its determination in agreement with the data reported [38, 45]. At high pH, the observed decrease in the observed cathodic peak current is most likely attributed to the formation of polyhydroxy complex species of Cu^{2+} [53, 54]. Thus, in the subsequent study, SW-CSV was used

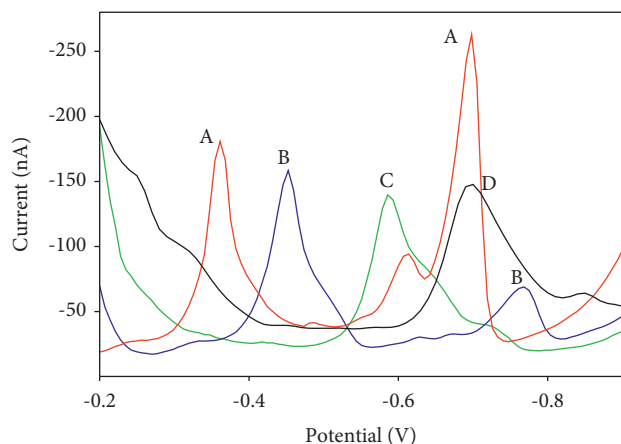


FIGURE 1: SW-CSV of malathion in the presence of Cu^{2+} at pH 2 (a), pH 3 (b), pH 7 (c), and pH 9 (d) at HMDE versus Ag/AgCl electrode. Conditions: $[\text{Malathion}] = 6 \times 10^{-8} \text{ M}$, $[\text{Cu}^{2+}] = 3.4 \times 10^{-7} \text{ M}$, $E_{\text{acc}} = -0.2 \text{ V}$; $t_{\text{acc}} = 120 \text{ s}$; scan rate = 0.1 V/s , 50 mV pulse amplitude, and 60 Hz frequency.

for developing a method for trace determination of malathion in the presence of Cu^{2+} ions at pH 2.

The SW-CSVs displayed in Figure 2 exhibited two well-defined and sharp reduction peaks in the potential range of -0.39 – -0.42 V (peak 1, E_{pc1}) and -0.70 to -0.82 V (peak 2, E_{pc2}). The first cathodic peak at potential range -0.39 – -0.42 V (peak 1, E_{pc1}) originates from the cathodic/stripping response of malathion immobilized on the surface of the HMDE because of the formation of an insoluble compound with Hg [30]. The cathodic peak at more negative potential (-0.70 to -0.82 V) (peak 2) is most likely attributed to adsorptive stripping response of Cu^{2+} -malathion complex formed with Cu^{2+} ions or due to copper (0) dissolution rather than adsorptive stripping response of the electrochemical reduction of Cu^{2+} -malathion complex [55]. It also seems that malathion splits the reduction of Cu^{2+} from one to two, which is actually common sense, and the available anion can stabilize the intermediates [3, 45]. On the contrary, the cathodic peak potentials were shifted to more negative values on increasing the solution pH, confirming the involvement of the H^+/e^- in the reduction of $-\text{C}=\text{O}$ to the corresponding hydroxyl species $\text{HC}-\text{OH}$ [55, 56].

In the absence and presence of Cu^{2+} ($3.4 \times 10^{-7} \text{ M}$), the redox behavior of malathion ($6.0 \times 10^{-8} \text{ M}$) at pH 2 was studied by cyclic voltammetry (CV). The CV of the supporting electrolyte in the absence of malathion or Cu^{2+} showed no signals in anodic and cathodic directions in the potential range of -0.2 to -1.0 V versus Ag/AgCl electrode. Typical CV of malathion and Cu^{2+} at pH 2.0 at 100 and 800 mVs^{-1} are shown in Figures 3(a) and 3(b). In the presence of Cu^{2+} ($5.0 \times 10^{-5} \text{ M}$) at pH 2, the CV showed cathodic peak in the same potential window. This peak is most likely coming from redissolution of Cu (0) at the HMDE. In the presence of malathion ($1.0 \times 10^{-4} \text{ M}$) and Cu^{2+} ($5.0 \times 10^{-5} \text{ M}$), two well defined irreversible cathodic peaks at the HMDE in the range of -0.42 to -0.45 (peak 1) and -0.72 – -0.75 V (peak 2) were observed. Peak 1 was most

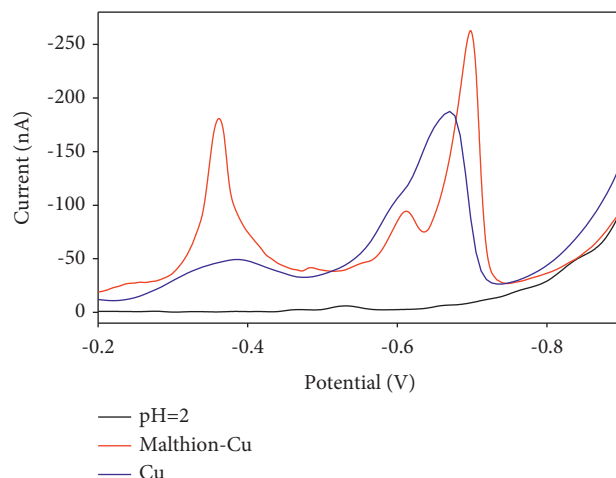


FIGURE 2: SW-CSVs of the supporting electrolyte at pH 2 (black line), in the presence of Cu^{2+} ions (green line), and in the presence of malathion and Cu^{2+} ions (red line). Conditions: $[\text{Malathion}] = 6 \times 10^{-8} \text{ M}$, $[\text{copper (II)}] = 3.4 \times 10^{-7} \text{ M}$, $E_{\text{acc}} = -0.2 \text{ V}$; $t_{\text{acc}} = 120 \text{ s}$; sweep rate = 0.1 V/s , pulse amplitude of 50 mV , and frequency 60 Hz .

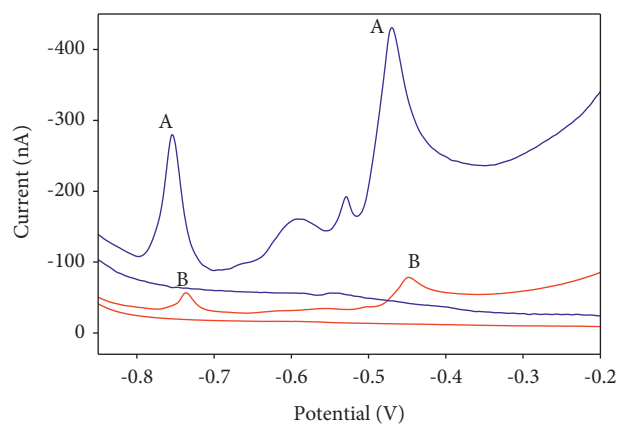
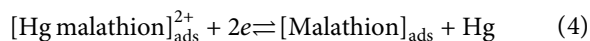


FIGURE 3: Linear sweep voltammetry of malathion in the presence of malathion in the presence of Cu^{2+} ions at pH 2 at 800 (a) and 100 (b) mV s^{-1} scan rate at pH 2 at the HMDE versus Ag/AgCl electrode. $[\text{Malathion}] = 6.0 \times 10^{-8} \text{ M}$ and $[\text{Cu}^{2+}] = 3.4 \times 10^{-7} \text{ M}$.

likely attributed to forming an insoluble Hg salt of HMDE with malathion. In contrast, peak 2 at more negative potential was simply due to Cu^{2+} redissolution rather than electrochemical reduction of Cu^{2+} -malathion complex at the HMDE surface. No anodic peaks were observed in the reverse scan, confirming the irreversible nature of the electrode processes [56, 57]. Based on the mechanism of the adsorptive voltammetric behavior of chlorpyrifos and other sulfur containing compounds at the mercury electrode [45, 46], the electrochemical reduction process of malathion could be presented by this reaction:



The dependency of the peak current, peak potential, and the peak areas on the scan rates are well known, helping in

properly describing and assigning the type of the electrode mechanism and reversibility. Thus, the cyclic voltammograms (CV) of Cu^{2+} -malathion at pH 2.0 at various scan rates (20–2000 mV/s) were studied as presented in Figure 3. In the cathodic scan, two well-defined cathodic peaks were observed at all scan rates (20–2000 mV/s), whereas no anodic peaks were noticed in the reverse scan. The plots of the cathodic peak currents, $i_{p,c}$ of peak 1 and peak 2 versus the square root of the scan rates ($\nu^{1/2}$), were not linear (SI. 3 A&B). Thus, the electrode processes are adsorption-controlled features [58, 59]. The values of $i_{p,c}$ of both electrochemical processes were proportional with raising the scan rate supporting the occurrence of an adsorption-controlled reaction, which is further expressed by the Laviron model [60].

The influence of the scan rate on the current function ($i_{p,c}/\nu^{1/2}$) for both cathodic peaks 1 and 2 of malathion (5.1×10^{-5} M) was studied. The current function ($i_{p,c}/\nu^{1/2}$) increased on raising the scan rate for malathion as shown in SI. 4. Thus, the electrochemical reduction process of malathion fitted well EE type mechanism and the electron transfer process is coupled with an irreversible electrochemical step in a rapid follow-up charge transfer [58, 59]. The results are also correlated with irreversible electrochemical processes for peaks 1 and 2 of the complex. At high scan rate, an ill-defined reduction peak (peak 1) was also noticed in the CV.

The values of αn_α involved in the observed cathodic processes at pH 2 were determined from the slope ($\Delta E/\Delta \log \nu$) of the linear plots of $E_{p,c}$ of peaks 1 and 2 versus $\log \nu$ at HMDE. Assuming $n\alpha = 1$ or 2 electron transfers, the values of α computed from the slopes of the straight lines employing the equation $\Delta E/\Delta \log \nu = -29.58/\alpha n_\alpha$ were found > 0.5 , supporting the irreversible nature for the observed reduction steps and the product of this reduction step may also undergo a rapid follow-up chemical reaction [58, 59].

Based on the irreversible nature of the electrode process of Cu^{2+} -malathion and the linear plots of $E_{p,c}$ versus $\log \nu$, the charge transfer coefficient (α) was computed using the following equation [58]:

$$\frac{\Delta E}{\Delta \log \nu} = -\frac{30}{\alpha n_\alpha} \quad (5)$$

where $n\alpha$ is the number of electron transfers. Assuming $n\alpha = 2$, the calculated value of α was found equal to 0.59, supporting the irreversible nature of the electrochemical steps. The value of α was also calculated employing the following equations [59]:

$$E_{p,c} - \frac{E_{p,c}}{2} = -1.857 \left(\frac{RT}{\alpha n_\alpha F} \right), \quad (6)$$

$$(E_{p,c})_2 - (E_{p,c})_1 = \frac{RT}{\alpha n_\alpha F} \cdot \ln \left(\frac{\nu_1}{\nu_2} \right)^{1/2},$$

where $E_{p,c}$ = peak potential in volt; $E_{p,c}/2$ are the cathodic peak potential at half height of the cathodic peak; R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$); T is the absolute temperature in

Kelvin; F is Faraday constant ($9.6487 \times 10^4 \text{ coul/mol}$); and ν_1 and ν_2 are the scan rates at two different values. The value of α was in the range of 0.48–0.5. The value of α was also calculated using the Laviron equation [60]:

$$E_p = E'^0 + \frac{2.303RT}{\alpha nF} \log \frac{RT^0}{\alpha nF} + \frac{2.303RT}{\alpha nF} \log \nu, \quad (7)$$

where K^0 is the apparent heterogeneous standard rate constant of the electron transfer of the electrode reaction; E'^0 is the standard electrode potential; and other signs have their usual meanings. The plots of $E_{p,c}$ for peak 1 and peak 2 versus $\log \nu$ ($R^2 = 0.9721$) were linear as (SI. 5). The value of α was close to the calculated value from equations (4), (5), and (6), adding further support to the irreversible nature and surface adsorption-controlled electrode process.

The surface coverage (Γ) was calculated from the CVs of the electroactive species of Cu^{2+} -malathion complex at various scan rates (20–2000 mVs $^{-1}$) and pH 2–3 using the following equation [58, 59]:

$$I_{p,c} = \frac{n^2 F^2 \Gamma \nu}{4RT}, \quad (8)$$

where n is the number of transferring electrons, A is the electrode surface area (cm^2), T is the absolute temperature, and R is the gas constant. Assuming $n = 2$, a Γ value of $5.56 \times 10^{-4} \text{ mol/cm}^2$ was obtained. This value provides the possibility of accumulation and indirect determination of trace levels of malathion by the SW-CSV method.

3.3. Optimization of the Analytical Parameters.

Optimization of the experimental parameters in the stripping voltammetry is essential to ensure the optimal sensitivity and selectivity of the target analyte. In the stripping voltammetry, the shape of the voltammogram, peak current, and peak potential is pH-dependent. Thus, the impact of the solution pH (pH 2–10) on the SW-CSV on the cathodic peak current of peaks 1 and 2 was studied over a wide range of pH after 60 s accumulation time. Representative SW-CSVs are illustrated in Figure 1. Maximum cathodic peak currents were achieved at pH 2, where reproducible and sharp cathodic peaks at -0.42 and -0.74 V were observed. In contrast, at $\text{pH} > 2$, the cathodic peak current decreased due to less Cu dissolution rather than the formation of Cu^{2+} -malathion complex [54, 55]. Thus, the pH of the solution was adopted at pH 2.0 in the subsequent study.

It is worth mentioning that $i_{p,c}$ of peak 1 directly increased on growing malathion concentration at pH 2 whereas $i_{p,c}$ of peak 2 at -0.70 V is independent of its concentration. At this pH, peak 1 was also well defined and symmetric. The peak current intensity at -0.42 V increased in the presence of copper. Thus, Cu^{2+} has a synergistic effect on the current signal of peak 1. This behavior is most likely attributed to the ability of Cu^{2+} to enhance the electrocatalytic reduction of malathion by adsorbing on the HMDE surface. Hence, cathodic peak 1 was selected as an indicator for malathion in the following study.

The influence of accumulation time is critical in stripping voltammetry. Thus, the impact of the deposition time (0.0–450 s) was studied. The results are demonstrated in Figure 4(a). A sharp cathodic peak with maximum peak current was noticed at 360 s. At a longer time, the peak current saturates or levels off, suggesting saturation/desorption of some of the accumulated malathion species on the surface of the HMDE. Thus, a deposition time of 360 s was selected in the following experiments.

The influence of deposition potential (0.1 to –0.4 V) on the current intensity of the adsorptive cathodic stripping peak 1 at –0.39 V versus Ag/AgCl electrode was studied in unstirred solution. Maximum cathodic peak current was achieved at an accumulation potential of –0.2 V and decreased rapidly at lower potentials because the reduction of Cu^{2+} -malathion had taken place at –0.2 V (Figure 4B). Thus, an accumulation potential of –0.2 V was adjusted in the following study.

The impact of scan rate ($0.050\text{--}1\text{ V s}^{-1}$) on $i_{p,c}$ was also studied for the developed SW-CSV procedures. The results are demonstrated in SI. 6, where the $i_{p,c}$ increased steadily with increasing the scan rate. The background width and best sensitivity of the cathodic peak was noticed at 100 mV s^{-1} (SI. 6). Hence, a 100 mV s^{-1} scan rate was adopted in the subsequent study.

The effect of varying starting potential (0.1 to –0.8 V) on the SW-CSV was also tested at the optimized parameters. The maximum peak current and well-defined cathodic peak were achieved at a starting potential of –0.2 V, confirming the impact of deposition potential. At a starting potential more positive than –0.2 V, $i_{p,c}$ gradually decreased due to the prior reduction of the complex. Thus, a –0.2 V starting potential was adopted in the subsequent experiments.

The impact of pulse amplitude (20–100 mV) on the $i_{p,c}$ of Cu^{2+} -malathion chelate was studied at optimized parameters. Representative results are shown in SI. 7. The intensity of the peak current increases with pulse height up to 50.0 mV, whereas at a pulse height > 50 mV, the peak current intensity decreases with the broadening of the voltammogram. Hence, 40 mV pulse height was selected in the following study.

The impact of frequency in SW-CSV is vital due to its influence on the generation of capacitive current at higher values, which subsequently causes distortion on the voltammograms. The impact of frequency (20–200 Hz) on the cathodic peak current of peak 1 for Cu^{2+} -malathion complex was studied (SI. 8). Frequencies in the range of 50–80 Hz exhibited high peak current, so a frequency of 60 Hz was selected in the following study.

The effect of varying Cu^{2+} concentration (6.0×10^{-8} – $3.7 \times 10^{-6}\text{ M}$) on the peak current of malathion ($1.0 \times 10^{-7}\text{ mol L}^{-1}$) at pH 2.0 was also studied (SI. 9). The peak current increased on rising Cu^{2+} concentration up to $3.4 \times 10^{-7}\text{ M}$. $i_{p,c}$ at –0.42 V decreased gradually at high Cu^{2+} concentration due to the competitive adsorption of some

other complex species of Cu^{2+} [54, 55]. Thus, Cu^{2+} was adjusted at $3.4 \times 10^{-7}\text{ M}$ in the subsequent study.

3.4. Analytical Performance and Figures of Merits. The dependence of the cathodic peak current at –0.42 V versus Ag/AgCl electrode on the malathion concentration was noticed for successive additions of known malathion into the cell at the optimized conditions. The SW-CSVs are demonstrated in Figure 5(a). The respective calibration plot of the cathodic peak current ($i_{p,c}$) versus malathion concentration at –0.42 V was found linear over a wide range of concentrations (1.03×10^{-9} – $2.0 \times 10^{-7}\text{ M}$) (Figure 5B). On growing malathion concentration up to $2.0 \times 10^{-7}\text{ M}$, the cathodic peak current increased, followed by a constant peak current at a higher analyte concentration. The increase in the sensitivity is most likely attributed to rising in both adsorption and electrolytic accumulation of Cu^{2+} -malathion complex at HMDE surface. The cathodic peak current tended to be leveled off at malathion concentration $> 2 \times 10^{-7}\text{ M}$ because of adsorption saturation and low Cu^{2+} concentration [56, 60]. Based on the least square analysis, the regression of the SW-CSVs of malathion concentration can be expressed by the following equation:

$$i_{p,c}(\text{nA}) = 4.8 \times 109 C(\text{mol L}^{-1}) + 29.8 \quad (R^2 = 0.995). \quad (9)$$

$i_{p,c}$ is the stripping voltammetric peak current in amperes, C is the analyzed malathion concentration, and R^2 is the correlation coefficient. The computed values of LOD and LOQ based on $\text{LOD} = 3\sigma_{xy}/b$ and $\text{LOQ} = 10\sigma/b$ [52] were found equal to 3.1×10^{-10} and $1.03 \times 10^{-9}\text{ M}$, respectively, where σ is the standard deviation of y -residual of the current signal of the blank sample to the corresponding peak current of analyte reduction at –0.42 V under the optimized parameters of the established method and b is the sensitivity factor (i.e., the slope of the linear calibration plot) of the established method [52]. A favorable comparison between the figures of merits of the present study and some of the other published analytical techniques is summarized in Table 1 [5, 17, 19, 23, 30, 46, 61, 62]. The performance of the planned assay is better and simpler (drop-casting formation), low cost (without metal nanoparticles), and easier than most of the reported methods (Table 1). The proposed probe also exhibits promising results (e.g., fast, short analytical time, selective and sensitive for malathion determination). The HPLC methods are incapable of detecting malathion at concentrations lower than $1.8\text{ }\mu\text{M}$ while the established assay detects $1.03 \times 10^{-3}\text{ }\mu\text{M}$ with appropriate RSDs. The established assay had some advantages, such as low-cost instrumentation, better reproducibility, and reduced sample size to determine OPPs in complex matrices [45, 46, 63]. The repeatability and recovery in terms of relative standard deviation (RSD) of known concentrations of malathion at

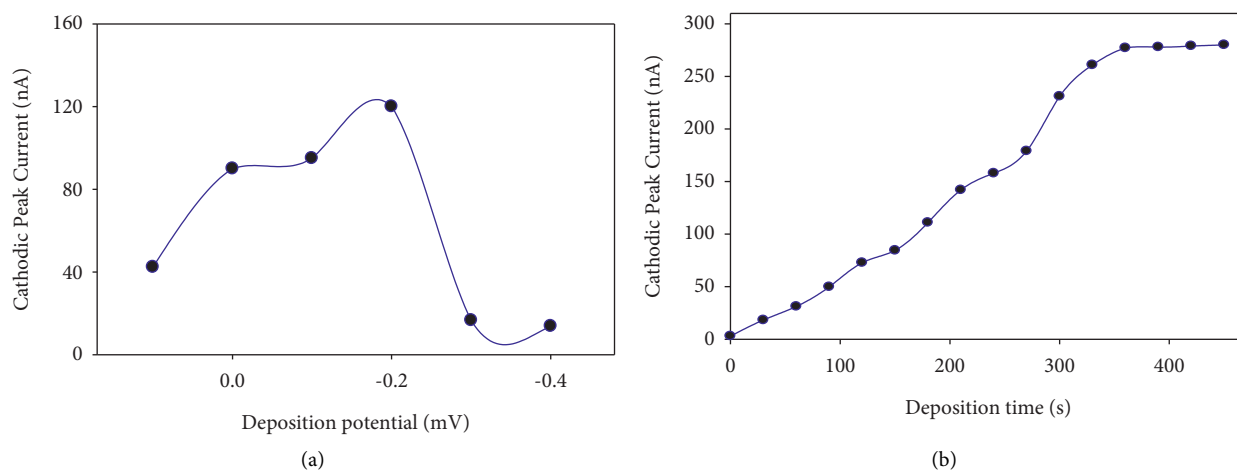


FIGURE 4: Plot of the cathodic peak current of the SW-CSV versus accumulation potential (a) and deposition time (b) of malathion and Cu^{2+} ions in B-R buffer of pH 2 at HMDE versus Ag/AgCl reference electrode. Scan rate = 100 mV/s; pulse amplitude = -50 mV.

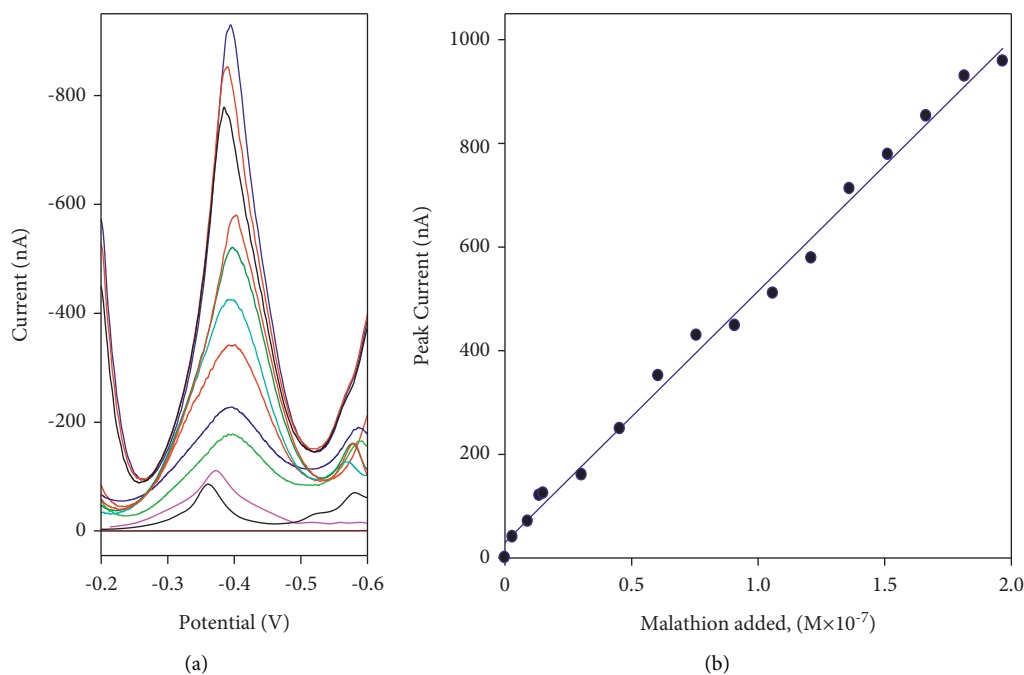


FIGURE 5: SW-CS voltammograms (a) and the respective linear calibration plot of the cathodic peak current ($i_{p,c}$) versus malathion concentration at -0.42 V (b) of malathion and Cu^{2+} at pH 2 of peak 1 at HMDE versus Ag/AgCl electrode. Deposition and starting potential -0.2 V, deposition time 360 s, scan rate = 100 mV/s, pulse amplitude = 50 mV, and 60 Hz frequency.

TABLE 1: Figures of merits ($\mu\text{g L}^{-1}$) of the developed SW-CSV and some of the published methods for malathion determination*.

Method	LOD (M)	Linear range (M)	Reference
Spectropoto	9.1×10^{-8}	$3.3 \times 10^{-7} - 3.6 \times 10^{-6}$	[26]
DPV	3.3×10^{-8}	$1.0 \times 10^{-7} - 8 \times 10^{-7}$	[41]
Electrochemical Senso	1.7×10^{-10}	$6.0 \times 10^{-10} - 2.4 \times 10^{-8}$	[35]
LC-MS	3.8×10^{-7}	$7.6 \times 10^{-7} - 6.06 \times 10^{-6}$	[59]
UPLC-MS	6.06×10^{-8}	$3.0 \times 10^{-7} - 3.0 \times 10^{-6}$	[60]
DLLME	1.5×10^{-9}	$6.0 \times 10^{-9} - 7.6 \times 10^{-7}$	[5]
FTIR	3.63×10^{-5}	$1.03 \times 10^{-9} - 2.0 \times 10^{-7}$	[17]
FT-Raman	5.45×10^{-9}		[19]
SW-CSV	3.1×10^{-10}	$-1.03 \times 10^{-9} - 2.0 \times 10^{-7}$	Present work

*UPLC-MS=ultra-performance liquid chromatography-mass spectrometry; FTIR = Fourier transform infrared; CPE = cloud point extraction; LC-API-MS=liquid chromatography atmospheric pressure ionization mass spectrometry; HPLC = high-performance liquid chromatography, FT-Raman = Fourier transform-Raman; DLLME = dispersive liquid-liquid microextraction, CPE-GC-FPD = cloud point extraction-gas chromatography with flame photometric detection.

4.0×10^{-8} and 9.0×10^{-8} M based on the regression were found to be 2.1 and 2.4%, respectively. Thus, the proposed method showed good precision.

3.5. A Comparison between DP-CSV and SW-CSV. A comparison of the sensitivity of SW-CSV and DP-CSV under the optimized parameters of malathion determination in the presence of Cu^{2+} ions was performed. The effective scan rate (SR) in the SW-CSV is given by the product of the frequency (f) and the height of the potential step (ΔE), according to the following equation:

$$SR = f(\text{Hz}) \times \Delta E(\text{mV}). \quad (10)$$

The ratio of the slopes obtained by SW-CSV was ~ 10 times sensitive compared to DP-CSV in the employed concentration range [58, 59].

3.6. Selectivity Study

3.6.1. Effect of Foreign Ions and Organic Pesticides. The suitability of the established method for malathion (8.0×10^{-7} M) determination was performed individually in the presence of a series of metal ions that could theoretically interfere with the proposed method, for example, Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{2+} , Cd^{2+} , Ni^{2+} , Zn^{2+} , and the anions: Cl^- , Br^- , SO_4^{2-} , CO_3^{2-} and PO_4^{3-} at 10–100-fold mass concentration excess over malathion. The tolerance limit (w/w) was defined as the concentration of the added interfering species causing a relative error of $\pm 5\%$ of the cathodic peak current of malathion at -0.39 V. The ions Fe^{3+} , Co^{2+} , VO_3^- , and Cr^{3+} interfered seriously even at 10-fold concentration excess over malathion. In contrast, other diverse species showed negligible (within $\pm 5\%$) interference. The ability of the metal ions Fe^{3+} , Co^{2+} , VO_3^- , and Cr^{3+} to form complex species with malathion at pH 2.0 may account for this behavior [54, 55]. The interference of Fe^{3+} and VO_3^- were tolerated after masking with triethanolamine. The other inorganic species also showed no significant changes in the cathodic peak current. Moreover, the impact of some other analogs of malathion, such as diazinon, and chlorpyrifos at 1:1 ratio was also investigated. The data revealed no significant changes in the cathodic peak current ($\pm 5\%$) at the optimized pH.

3.6.2. Effect of Surfactants. The developed SW-CSV procedure was also applied for the determination of malathion (3.0×10^{-8} M) in the presence of a relatively high excess (5.0 mg mL^{-1}) of Triton X-100, sodium dodecyl sulfate, and tetraheptylammonium chloride as “model” surfactants individually. The surface-active agent interfered seriously at concentrations higher than 10.0 mg L^{-1} by causing distortion of the Cu^{2+} -malathion peak. This effect was masked by shaking the test solution with dichloroethane (5.0 mL) to remove most of the nonpolar organic species prior to analysis by the developed SW-CSV. The reason behind this behavior is most likely attributed to the ability of the surfactant to enhance/decrease the electrochemical reduction of

malathion, causing a synergistic effect of the current signal. Due to the fact that malathion is an amphiphilic molecule with lipophilic nature, thus, it is capable to be adsorbed on the surface of the HMDE by forming self-micelle aggregates and/or mixed aggregates with the surfactant [64].

3.7. Validation of the Established Methodology and Analytical Applications

3.7.1. Determination of Malathion in Liquid and Solid Pesticide Formulations. The proposed SW-CSV procedure was used for the assay of malathion in solid ($3.10 \pm 0.10 \text{ mg g}^{-1}$) and liquid ($1.95 \pm 0.05 \text{ mg mL}^{-1}$) in the pesticidal formulations. For validation of the established SW-CSV, the malathion content in both samples was determined by GC-MS. The results of the developed SW-CSV and GC-MS are given in Table 2. In solid and liquid pesticide formulations, malathion contents were $2.1 \pm 0.03 \text{ mg mL}^{-1}$ and $3.3 \pm 0.05 \text{ mg g}^{-1}$ with a relative standard deviation (RSD) of ± 1.5 – 2.6 and ± 1.4 – 2.1 , respectively. These values were validated by the determination of malathion by the official GC-MS. There was a satisfactory agreement between the malathion content determined by the established SW-CSV and the official GC-MS method at 95% confidence ($P < 0.05$). The results are summarized in Table 2. The calculated values of the Student t_{exp} (1.06–1.11) and F_{exp} (1.02–1.79) values for both solid and liquid pesticide formulations were found lower than the tabulated t_{tab} (2.78) and F (6.39) values [52], respectively, revealing the precision, selectivity, and suitability of the proposed method in complex matrices. Thus, the developed method has the advantages of short analytical time, economical, reproducible, and applicable for routine analysis of environmental samples compared to the conventional methods.

3.7.2. Determination of Malathion in Environmental Samples. Determination of malathion residues in tap water samples was performed by the established SW-CSV procedures using the standard addition as mentioned before. The results are summarized in Table 3. A recovery percentage of $107.5 \pm 0.47\%$ was achieved for malathion added to the tap water. The calculated Student t_{exp} and F_{exp} values were lower than the theoretical t_{tab} (2.78) and F (6.39) values [52], supporting the precision and selectivity of this method.

The developed SW-CSV method was also applied to analyze malathion in soil. The results are summarized in Table 3, and a representative linear plot of the standard addition method is shown in Figure 6(a). The SW-CS voltammograms in the presence of and absence of copper in the soil showed a negligible effect within $\pm 5\%$.

The SW-CSV method was also applied to analyze malathion in plants (e.g., cabbage and spinach samples). The results are also given in Table 3, and a representative linear plot of cabbage by the standard addition is shown in Figure 6(b), respectively. The sensitivity attained by the developed SW-CSV allows the determination of trace

TABLE 2: Average concentrations of malathion determined in solid (mg g^{-1}) and liquid (mg mL^{-1}) pesticide formulations by the developed SW-CSV (a) and the standard GC-MS (b) methods*.

Pesticide formulations	Function	A	B
Solid	Average RSD	3.3 ± 0.05 1.5	3.1 ± 0.08 2.6
	<i>t</i> value** <i>F</i> value	1.11 (2.78) 1.79 (6.39)	
Liquid	Average% RSD	2.1 ± 0.03 1.4	2.3 ± 0.05 2.1
	<i>t</i> value <i>F</i> value	1.06 (2.78) 1.02 (6.39)	

* Average ($n=5$) \pm standard deviation. * The cited percentages of malathion in the solid and liquid formulations are 3.2 mg g^{-1} and 2.1 mg mL^{-1} , respectively. **The theoretical values of *t* and *F* at $P=0.05$ are given in parentheses.

TABLE 3: Determination of malathion in soil, vegetables (ng g^{-1}), and water (ng mL^{-1}) samples by the developed SW-CSV method*.

Sample matrix	Malathion ($\mu\text{g L}^{-1}$)		Recovery \pm RSD (%)
	Added	Found \pm SD	
Soil**	0	0.60 ± 0.05	-
	5	5.05 ± 0.07	101.0 ± 1.39
	10	10.4 ± 0.08	104.0 ± 0.77
	20	20.8 ± 0.07	104.0 ± 0.34
Cabbage**	0	0.35 ± 0.06	-
	5	5.10 ± 0.05	102.0 ± 0.98
	10	9.72 ± 0.08	97.20 ± 0.82
	20	19.50 ± 0.10	97.50 ± 0.51
Spinach**	0	1.50 ± 0.05	-
	5	4.90 ± 0.04	97.0 ± 0.82
	10	9.70 ± 0.08	98.5 ± 0.82
	20	19.7 ± 0.10	98.0 ± 0.51
Tap water	0	n.d.	-
	5	5.70 ± 0.04	114.0 ± 0.70
	10	10.68 ± 0.08	106.5 ± 0.75
	20	21.50 ± 0.10	107.5 ± 0.47

* Average ($n=5$) \pm standard deviation (SD); n.d. = not detected. **In soil, cabbage, and spinach, the found value was calculated as the difference between the measured value at various spiking concentrations minus the value obtained before adding malathion.

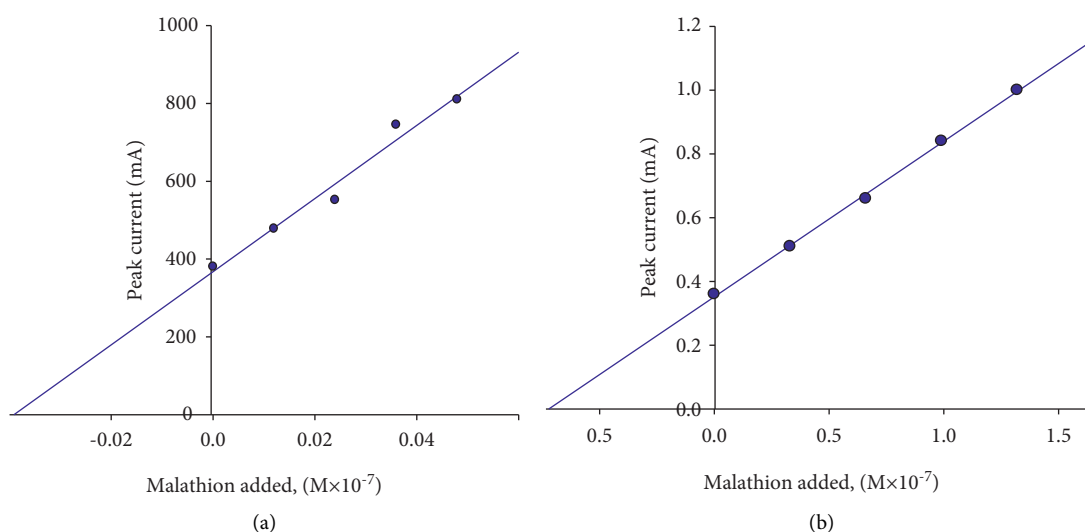


FIGURE 6: Standard addition SW-CSVs for the determination of malathion and Cu^{2+} ions at pH 2 under the optimized parameters in soil (a) and cabbage (b) at HMDE. Deposition and staring potential -0.2 V , accumulation time 360 s scan rate = 100 mV/s , pulse amplitude = 50 mV , and frequency 60 Hz .

concentrations of malathion in plant samples (e.g., spinach and cabbage).

4. Conclusion, Advantages, Drawbacks, and Future Perspectives

The established SW-CSV assay was successfully applied for the determination of malathion in various environmental samples. The method afforded LOD lower than the permissible level of pesticides in drinking water as suggested by US-EPA 2009 and WHO, 2011. The established probe provides a simple and reliable approach with good precision, accuracy, reproducibility, and cost-effectiveness, whereas most of the reported methods suffered from many limitations, such as the use of costly and toxic organic solvents, being time-consuming, multiple steps, and complex apparatus. Thus, the method could be used for routine analysis of malathion. The unique advantages of the potential window and low background noise of HMDE towards malathion could also be improved to ultra-trace (picomolar levels) via microextraction based online preconcentration from large water sample volumes onto dispersed nano-sized-solid phase microextractor ($d-\mu$ SPME) sorbent packed column followed by determination after elution with selective eluent. The use of μ -d-SPME based nano-materials could serve two functions: high sensitivity (masking of matrix effect) and pretreatment. HMDE has several advantages, including selectivity, reproducibility, and extremely wide potential window in the cathodic region for potential targets in biological and complicated environmental matrices. However, the use of mercury has many limitations because this metal is restricted for use in contact with a human in EU and USA. The use of design experiment will also be the issue of follow-up analytical strategies because the one issue at a time has drawbacks and the collaborating effect of numerous parameters variations might enhance the signal intensity.

Data Availability

The data underlying in this study are included in the article, and electronic supplementary information and all are available for readers.

Disclosure

This research was performed as part of the employment of the authors Mohammad El-Shahawi, with the employer King Abdul-Aziz University, Jeddah, KSA.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

SI. 1: chemical structure of malathion pesticide. SI. 2: electronic spectrum (A) and continuous variation plot (B) of copper (II)-malathion complex. SI. 3: plots of the cathodic peak currents versus square root of the scan rate ($v^{1/2}$) of peak 1 (A) and peak 2 (B) of copper (II)-malathion complex at pH 2 at HMDE. SI. 4: plots of the current function ($i_{pa}/v^{1/2}$) of the cathodic peaks 1 and 2 versus scan rate (v) for copper (II)-malathion chelate. SI. 5: plots of $E_{p,c}$ of peaks 1 and 2 versus $\log v$ of the CVs of copper (II)-malathion complex at pH 2 using HMDE versus Ag/AgCl electrode. SI. 6: influence of scan rate (10–100 mV/s) on the copper (II)-malathion in B-R buffer of pH 2 at HMDE versus Ag/AgCl reference electrode. Conditions: pulse amplitude = -20 mV, $E_{acc} = -0.2$ V., and $t_{acc} = 360$ s. SI. 7: influence of pulse amplitude on the copper (II)-malathion complex in B-R buffer of pH 2 at HMDE versus Ag/AgCl reference electrode. Sweep rate = 1 V/s, $E_{acc} = -0.2$ V., and $t_{acc} = 360$ s. SI. 8: influence of frequency on the copper (II)-malathion in B-R buffer of pH 2 at HMDE versus Ag/AgCl reference electrode. Sweep rate = 0.4 V/s, pulse amplitude = -20 mV, $E_{acc} = -0.2$ V., and $t_{acc} = 360$ s. SI. 9: effect of Cu^{2+} concentrations on the cathodic peak current at pH 2 at the optimized deposition time and potential at HMDE versus Ag/AgCl reference electrode. Scan rate = 100 mV/s; pulse amplitude = -50 mV. (*Supplementary Materials*)

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