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Full Paper

Voltammetric Determination of Trace Methyl Parathion using Electrochemically Reduced Graphene Oxide Modified Carbon Screen-Printed Electrodes

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Abstract- Timely, efficient on-site detection of pesticides such as methyl parathion (MP) is crucial to ensure public health. This study introduces the first disposable electrochemically reduced graphene oxide (ErGO) modified electrode for rapid MP detection. A square wave anodic stripping voltammetry method for the detection of MP was developed using these ErGO-modified carbon screen-printed electrodes. Based on this study, graphene's high electric conductivity and unique structure enhanced the sensitivity of the electrode for MP detection. Following optimization of the pH, equilibrium period, deposition potential, and period, the methodology demonstrated high sensitivity and reproducibility. Using the enhanced experiment conditions, calibration experiments were performed with a concentration range of 0 to 150 µg L^{-1} of MP. A consistent oxidation peak was observed at -0.180 V. The calibration data showed the increase in the peak height was linearly correlated to the increase in MP concentration, with a correlation coefficient of 0.9854. The sensitivity of the developed methodology was 0.0887 µA (µg $L^{-1})^{-1}$, and the limit of detection was 9.06 µg L^{-1}. The methodology was successfully applied to multiple water samples, specifically river water, groundwater, and General Test Water, with recovery rates of 106.01% (standard deviation = 1.46%), 109.51% (standard deviation=0.44%), and 97.69% (standard deviation=1.49%), respectively.

Keywords- Methyl parathion; Screen-printed electrode; Reduced graphene oxide; Square wave anodic stripping voltammetry

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1. INTRODUCTION

The use of insecticides has benefited agriculture industries by significantly improving crops yields and assisted public health by controlling vector-borne diseases such as malaria [1]. Despite these benefits, the increasing usage of insecticides has affected the environment and public health in harmful ways, especially in developing countries [2]. Organophosphates have been the most widely used class of insecticide during the 21st century[3]. Currently, 36 organophosphates are approved by the United States government for use, and all can cause acute and subacute toxicity [3]. In the past decade, the usage of some organophosphates have been restricted by the United States Environmental Protection Agency (U.S EPA) [3]. Methyl parathion (MP) is one of these restricted insecticides [3]. MP, known as a cotton poison, has been manufactured and used in the United States since 1952 for a number of different crops [4]. In 1978, MP was classified as a “Restricted Use Pesticide” by the EPA due to its harmful effect on humans [5] and animals [6]. The main toxic effects of MP impact the hematopoietic system, cardiovascular system, reproductive system, and nervous system [7-9]. MP poisoning can lead to cholinergic overstimulation with symptoms including sweating, dizziness, vomiting, diarrhea, convulsions, cardiac or respiratory arrest, and death[9]. As a result, MP is strictly limited for use on certain open field crops, including cotton, corn, wheat, and barley. Due to widespread use, residual of MP can be found ubiquitously in soil, air, and surface water. In addition, it can be detected from groundwater, which may directly pose a threat to drinking water safety [9].

The conventional detection methods for MP in water are high-performance liquid chromatography and gas chromatography [10]. Since MP is usually present in low concentrations in water samples, these detection methods require additional steps to ensure the necessary accuracy [10]. One of the typical methods to extract MP for analytical determinations is solid-phase extraction [11], which requires reagents to wash, separate, and concentrate water samples. The U.S EPA recommends gas chromatography using capillary columns equipped with a flame photometric detector or a nitrogen-phosphorus detector for detection of MP [12]. Furthermore, using gas chromatography requires derivatization before the analysis of MP, which demands expensive and toxic reagents. Additionally, using high-performance liquid chromatography requires a large quantity of ultrapure solvents, such as triethylamine[13] and acetonitrile[14], which are toxic and expensive. Thus, detection of MP using gas chromatography or high-performance liquid chromatography requires a centralized laboratory and professional technicians [15]. These limitations have created a demand for inexpensive techniques for quantitative analysis of MP.

Electrochemical detection can achieve sensitive and accurate determination of a wide range of analytes [16-18], including MP, offering a promising alternative to conventional detection methods. Different electrodes and electrochemical methods have been used to detect MP. For instance, Parham and Rahbar [19] studied voltammetric detection of MP by using ZrO_2

modified carbon paste electrode and square wave voltammetry. Kumaravel and Chandrasekaran [20] developed a method using nanosilver/Nafion composite electrodes and differential pulse voltammetry (DPV) to quantitatively analyze MP. Kang, Wang, Lu, Zhang and Liu [21] used gold nanoparticles/Nafion modified glassy carbon electrodes to conduct SWV to detect MP in water. However, electrode preparation in these studies was relatively complex, time-consuming, and sometimes required corrosive substances.

Carbon paste or glassy carbon electrodes are often used in electrochemical studies to detect MP. Based on reported electrochemical studies, non-modified electrodes have limited sensitivity to MP, but it's possible to improve the sensitivity of electrodes by modifying their surfaces with nano-materials [19-22]. Graphene has great potential for electrode modification due to its excellent electrical conductivity [23], high surface area [24], strong mechanical strength [25], and ease of surface functionalization[26]. For Instance, Wang and his colleagues [27] used a graphene modified glassy carbon electrode (RGO/GCE) to detect ascorbic acid, dopamine, and uric acid. Du and his coauthors [28] studied graphene modified glassy carbon electrodes for sensitive detection of rutin. Kang and his fellow researchers [29] investigated the electrochemical behavior of paracetamol using cyclic voltammetry and square-wave voltammetry with graphene-modified glassy carbon electrodes. Furthermore, GO and reduced GO have oxygen functional groups, such as alkoxy, carboxy, and carbonyl, attached to the edge of their sheets, which will result in hydrophilic properties. This makes them an ideal candidate for fabrication of novel electrodes for electrochemical sensing of pesticides such as MP[30-32]. For instance, Jeyapragasam and her colleagues [33] reported detection of MP using ErGO modified glassy carbon with promising results, but this methodology would be difficult to apply for onsite detection of MP, due to fouling of the glassy carbon electrode after multiple tests. Modified CSPE are disposable, cheaper, and do not require mechanical polishing, making them significantly more practical for rapid onsite testing, compared to modified glassy carbon electrodes.

Following a comprehensive literature review and extensive preliminary experiments, the objective of this study was to develop a safe and inexpensive methodology for the sensitive detection of MP using modified carbon screen-printed electrodes. In addition, for the first time, square wave anodic stripping voltammetry (SWASV) was used to detect MP to reduce the common interference of oxygen. To achieve these goals, the authors used electrochemically reduced graphene oxide (ErGO) modified carbon screen-printed electrodes and Britton-Robinson (B-R) buffer. The buffer pH and the SWASV parameters (deposition potential, deposition time, and equilibrium period) were optimized to detect the lowest concentration of MP possible. Following the optimization, experiments were performed in deionized water, General Test Water, and real-world water samples to evaluate the performance of the methodology.

2. EXPERIMENTAL SECTION

2.1. Chemicals and reagents

All chemicals used were of analytical reagent grade. No additional purification was performed. Methyl parathion was purchased from Sigma-Aldrich®. Unless otherwise stated, all solutions were prepared using deionized water with a resistivity of 18.20 MΩ-cm. The MP stock solution (1,000 mg L^{-1}) was prepared by dissolving the MP powder in 70% ethanol. The B-R buffer was prepared by dissolving 2.40 g L^{-1} acetic acid, 3.92 g L^{-1} phosphoric acid, 2.47 g L^{-1} boric acid, and 73.489 g L^{-1} potassium chloride in deionized water. This produced a buffer solution with a pH of 1.8 and an ionic strength of 1 M, and further pH adjustment was done by adding 1.00 M sodium hydroxide with mild stirring. During all the electrochemical tests, 2.00 mL of B-R buffer solution was added to each 10 mL sample, which produced an ionic strength of 0.20 M in the samples.

2.2. Instrumentation

For all voltammetric experiments, a WaveNow potentiostat (Pine Research Instrumentation, Inc) was used with Aftermath software. Carbon screen-printed electrodes (CSPE) purchased from Pine Research Instrumentation, Inc were used for all experiments, and all CSPE were used once. An AR15 AccumetTM pH meter with a Gel-filled polymer body pH combination probe was used for all pH measurements.

2.3. Electrode preparation

The improved Hummers method was used to synthesize the graphene oxide (GO) [34,35]. First, the oxidants, 10 g of flake graphite, 6 g of potassium permanganate and 4 g of potassium ferrate , and a stabilizer, 0.01 g of boric acid, were dispersed in 100 mL of concentrated sulfuric acid. The suspension was then stirred for 1.5 hours at a temperature below 5 °C. To complete the deep oxidation, another 5 g of potassium permanganate was added, and the mixture was heated to 35 °C using a water bath and stirred for 3 more hours. Then, 250 mL of deionized water was added to the solution, and the temperature was increased to 95 °C. After approximately 15 minutes, the color of the suspension changed to brown, indicating hydrolysis and the formation of graphene oxide. Afterward, 12 mL of 30% H_2O_2 was added to the suspension. The suspension was then centrifuged at 10,000 rpm for 20 min, and the supernatant was pipetted off to remove residual graphene. Finally, the residual was washed multiple times with 1 M hydrochloric acid and deionized water to purify the GO. The fully oxidized GO was subsequently sonicated for 12 hours to exfoliate and disperse in deionized water, to produce a 1 mg mL^{-1} dispersion of GO. The CSPE was then drop-casted using 15 µL of this GO dispersion and air-dried.

2.4. Sampling and Sample Preparation Procedures

The methodology for detection of MP was tested in deionized water, groundwater, river water, and General Test Water. Groundwater was sampled from a drinking water well in North Chelmsford, Massachusetts, and was the only sample used in the methodology validation that was drinkable without additional pre-treatment. River water was sampled from the Merrimack River in Lowell, Massachusetts. General Test Water was prepared based on specifications from the World Health Organization, provided in Harmonized Testing Protocol: Technology Non-Specific Version 2.1[36]. General Test Water is designed to provide a standard media that replicates conditions typically found in natural bodies of water, for evaluation of water purifying and testing technologies. The specific characteristics of the General Test Water were a chlorine concentration below 0.05 mg L^{-1}, a pH of 7.0 ± 0.5, total organic carbon of 1.05 ± 0.95 mg L^{-1}, turbidity of less than 1 NTU, a temperature of 20 ± 3°C, total dissolved solids of 275 ± 225 mg L^{-1}, and alkalinity of 100 ± 20 mg L^{-1} as $CaCO_3$. To obtain the specified values, hydrochloric acid (CAS# 7647-01-0) and sodium hydroxide (CAS# 1310-73-2) were used to adjust the pH, tannic acid (CAS# 1401-55-4) was used to add total organic carbon, sea salt (CAS# 7732-18-5) was used increase the total dissolved solids, and sodium bicarbonate (CAS# 144-55-8) was used to adjust the alkalinity. All samples were refrigerated at 4 °C and analyzed within two days of collection. Prior to the analysis of each water sample, 1 M B-R buffer was added as supporting electrolyte accordingly to reach 0.2 M concentration in each solution.

2.5. Electrochemical experiments procedures

The GO electrode was reduced electrochemically in B-R buffer (pH 7) before starting each experiment, producing the electrochemically reduced graphene oxide on carbon screen-printed electrode (ErGO/CSPE). The reduction was performed using 10 cyclic voltammetry (CV) scans with a scan range of 0.00 to -1.50 V and a sweep rate of 50 mV s^{-1} (Figure 1).

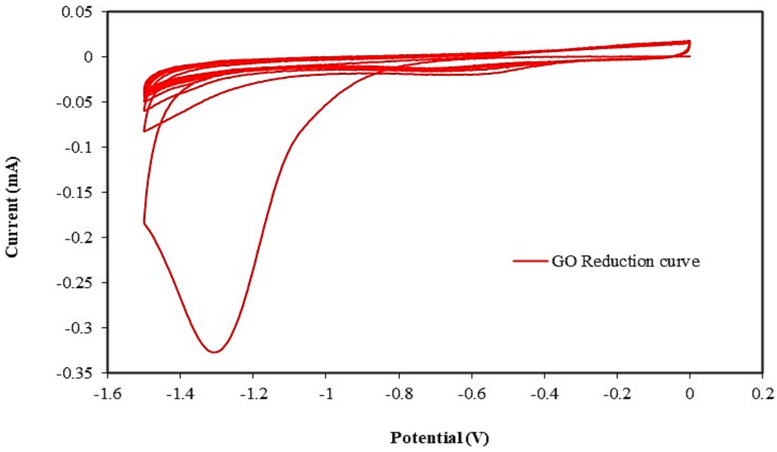

Figure 1. Cyclic voltammogram for reduction graphene oxide in water (Electrolyte: 2 mL, 0.2 M, pH 7 B-R buffer)

CV was used to measure the change in electroactive surface area of the CSPE from the modification with ErGO. The redox probe was 10 mM ferrocyanide/ferricyanide, $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, with a supporting electrolyte of 100 mM potassium chloride. The test parameters were a scan rate of 20 mV s^{-1}, a lower potential of -0.3 V, and an upper potential of 0.7 V. The Randles-Sevcik equation was used to determine the electroactive surface area:

$$I_p = 268600n^{3/2}AD^{1/2}Cv^{1/2} \qquad (I)$$

where I_p is the peak current (amps), n is the number of electrons transferred in the redox event, A is the electroactive surface area (cm^2), D is the diffusion coefficient (cm^2 s^{-1}), C is the concentration of the redox probe (mol cm^{-3}), and v is the scan rate (V s^{-1}) [38].

The effects of the electrode modification were further characterized using electrochemical impendence spectroscopy (EIS). These experiments were performed using a WaveDriver 200 EIS Bipotentiostat purchased from Pine Research Instrumentation. The test parameters were a frequency range of 0.001 to 10 kH and an amplitude of 10 mV. This resulted in 48 data points per EIS experiment. The midpoint of redox reaction from the CV analysis was used as the initial voltage for the EIS experiments, to compensate for shifts in measured potential from the reference electrode. The AfterMath Data Organizer Software from Pine Research Instrumentation was used to determine the charge transfer resistance (R_{CT}) and double layer capacitance (C_{DL}), from the resulting EIS data. The Randles circuit was used as the equivalent circuit for interpretation of the impedance spectra [39].

The electrochemical behavior of the MP was studied using CV with the scan range 0.50 V to -1 V and a sweep rate of 50 mV s^{-1}. Unless stated otherwise, SWASV was performed using a deposition potential of -0.6 V, deposition time of 120 seconds, and equilibrium period of 10 minutes at a potential of 0 V. The SWASV range was from -0.30 to 0.30 V with the following specification: period of 20 ms, amplitude of 70 mV, an increment of 8 mV and sampling width of 5 ms. The peak height was measured using the peak height measurement tool in AfterMath with secant lines used to approximate the baseline, and the standard curves were created using peak heights from the analysis of prepared MP concentrations in deionized water. The limit of detection (LoD) was calculated using the following equation:

$$LoD = \frac{3\sigma}{m} \qquad (II)$$

Where σ is the standard deviation of replicate blank samples and m is the slope of the calibration curve.

Recovery Rate percentage (R) was calculated as:

$$\mathrm{R} = \left(\frac{MP_i}{MP_{Spike}}\right) * 100\% \qquad (III)$$

MP_i is concentration of MP recovered by the proposed method in a spiked solution. MP_i was calculated using the regression equation derived from the calibration data in Section 3.3. MP_{spike} is the known concentration of MP added to the solution.

3. RESULTS AND DISCUSSION

3.1. ErGO Electrode Characterization

CV and EIS were performed to characterize the ErGO/CSPE and bare CSPE electrodes. GO electrodes were prepared and reduced to ErGO/CSPE based on the method explained in the previous section. The voltammograms from the CV experiments showed clear reversible peaks for both the unmodified CSPE and ErGO/CSPE (see Figure 2A). From this data, the electroactive surface areas for the CSPE and ErGO/CSPE were determined to be 20.71 mm^2 and 40.11 mm^2, respectively. The separation between the oxidation and reduction peaks decreased from 326.6 mV for CSPE to 127.4 mV for the ErGO/CSPE. This decrease indicated the modification of the electrode with ErGO improved the efficiency of the electron transfer process. This finding is further supported by the EIS data shown in the Nyquist plots (Figure 2B). The decrease in the semicircular component of the Nyquist plot indicates a lower impedance at the ErGO/CSPE. Based on the circuit fitting analysis, the bare CSPE was determined to have an R_{CT} of 1598.2 Ω and a C_{DL} of 0.762 µF, while the ErGO/CSPE had an R_{CT} 147.2 Ω and a C_{DL} of 40.4 µF. The analysis showed the resistance associated with the electrolyte was effectively unchanged with a value of 115.35 Ω for the CSPE and 118.37 Ω for the ErGO/CSPE.

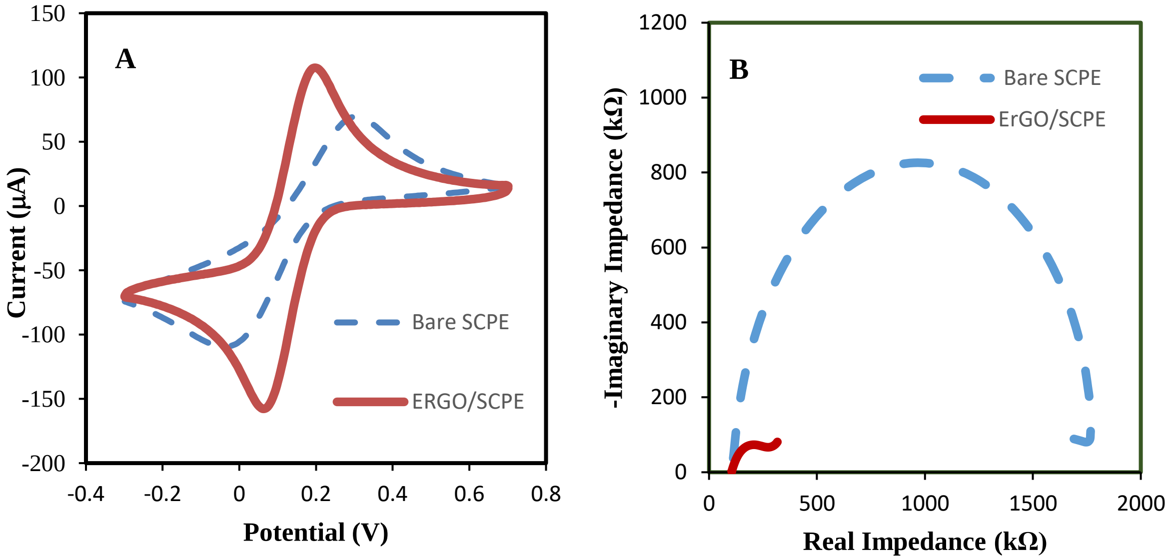

Figure 2. Representative (A) voltammograms from the CV and (B) Nyquist plots from the EIS for the bare CSPE and ErGO/CSPE.

3.2. Study of Electrochemical Behavior

CV was performed to examine the electrochemical behavior of MP at the ErGO/CSPE (Figure 3). Figure 3 shows the cyclic voltammogram with 2 segments obtained in the potential range of -1 V to 0.5 V in 0.2 M B-R buffer (pH 7) containing 0 and 2200 µg L^{-1} MP with a scan rate of 50 mV s^{-1}. As can be seen in Figure 3, CV detected three separate peaks, two reversible peaks and one irreversible peak, resulting from the oxidation or reduction of MP. In the first cycle, during the reverse scan, a large reduction peak is observed at -0.7 V. In the forward scan, a small cathodic peak occurs at -0.2 V with a corresponding anodic peak at -0.3 V. These peaks are consistent with perversely reported results in other studies [21,22]. The irreversible peak at -0.7 V is attributed to the 4e- reduction of the nitro group to 2-phenylhydroxylamine (Figure 4, Reaction I). The reversible peaks in the range of -0.1 to -0.3V is attributed to the 2e- nitrosobenzene-phenylhydroxylamine redox process to reactions II and III (Figure 4). Following the CV observations, SWASV was used next for sensitive detection of MP. In this process, a potential of -0.6 V was applied so that the first reaction occurs, reducing the NO_2 group to the NHOH group[33]. This reduction process enhanced the peak heights of the reversible reactions. The preliminary SWASV results for samples containing 0 and 150 µg L^{-1} MP is presented in Figure 5. As it is observed in Figure 5 the cathodic peak potential for MP is -0.18 V, which corresponds to findings from the CV examination.

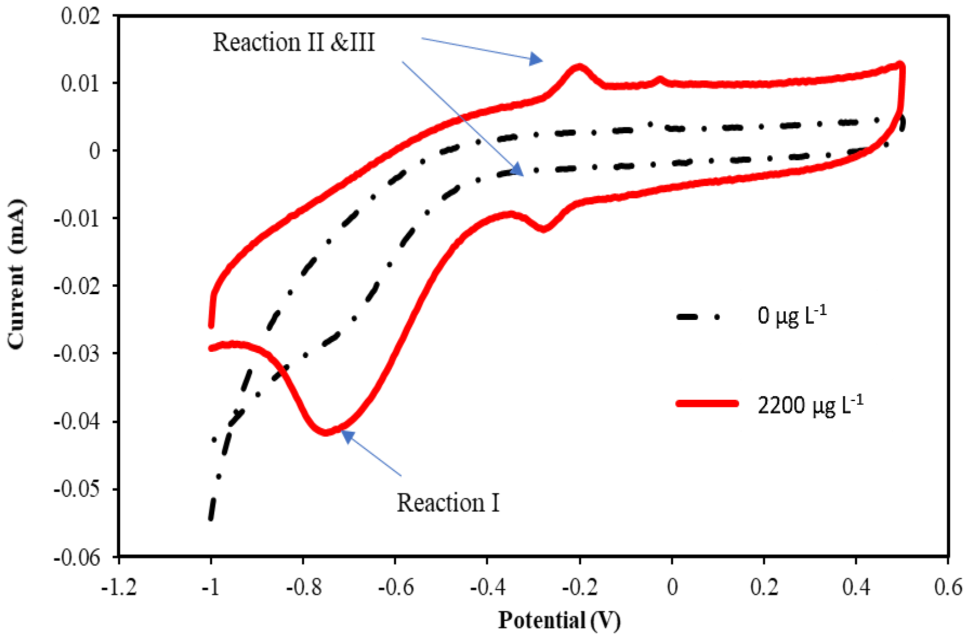

Figure 3. Two-segment cyclic voltammograms of 0 and 2200 µg L^{-1} MP in 0.2 M B-R buffer (pH 7), with a scan rate of 50 mV s^{-1} and scan range of 0.5 V to -1 V

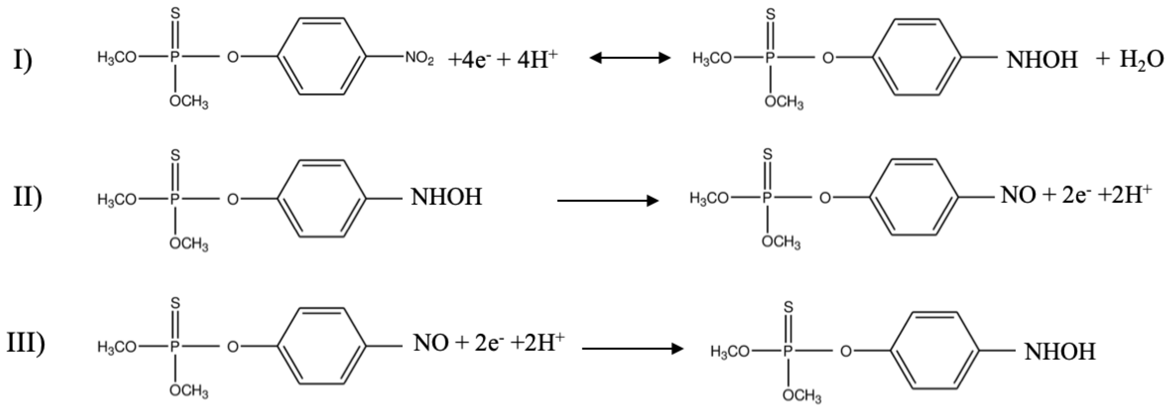

Figure 4. Reduction steps of MP. Reaction I, II, and III

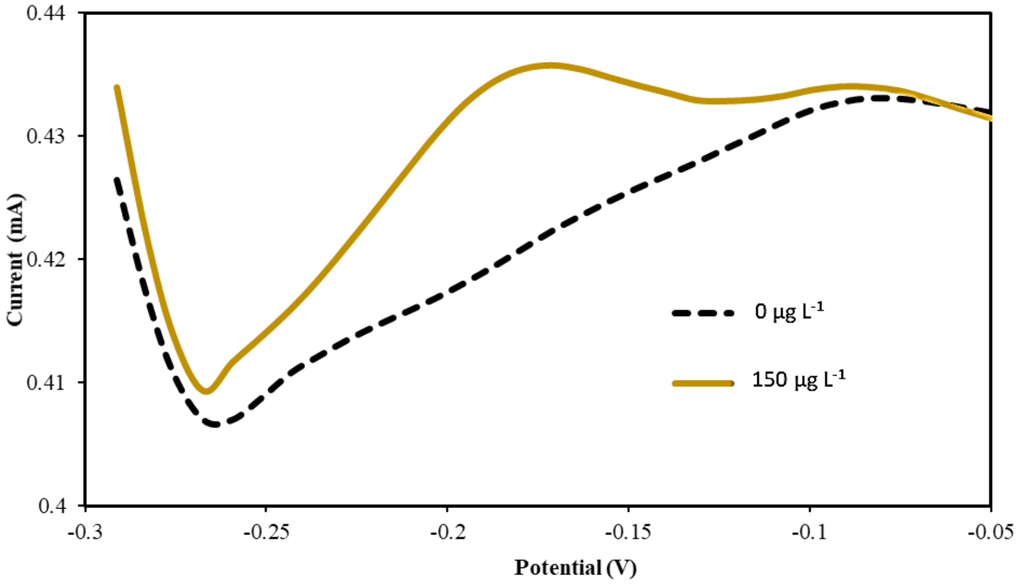

Figure 5. SWASV detection of 0 and 150 µg L^{-1} MP in 0.2 M B-R buffer with pH 7

3.3. Parameter Optimization for MP Detection in Deionized Water

SWASV experiments were conducted on samples containing 100 µg L^{-1} MP with the buffer pH ranging from 5 to 9. The effect of pH on both peak height and potential is plotted in Figure 6A. When pH increased from 5 to 7, the average peak height increased from 5.4 to 10.5 µA, an increase of nearly 100%. These observations are consistent with the results reported by Kang, et al[21]. With pH values higher than 7, the peak height decreased sharply, and the peak almost disappeared. This might be caused by proton-transfer and electron-transfer reaching equilibrium at pH 7. The peak potential remained unchanged at -1.80 V, indicating the potential redox reaction was not affected by the decreased proton concentration. This indicates that

ErGO/CSPE have the maximum adsorption to MP at neutral pH. Based on these results, pH 7 was used for all subsequent experiments.

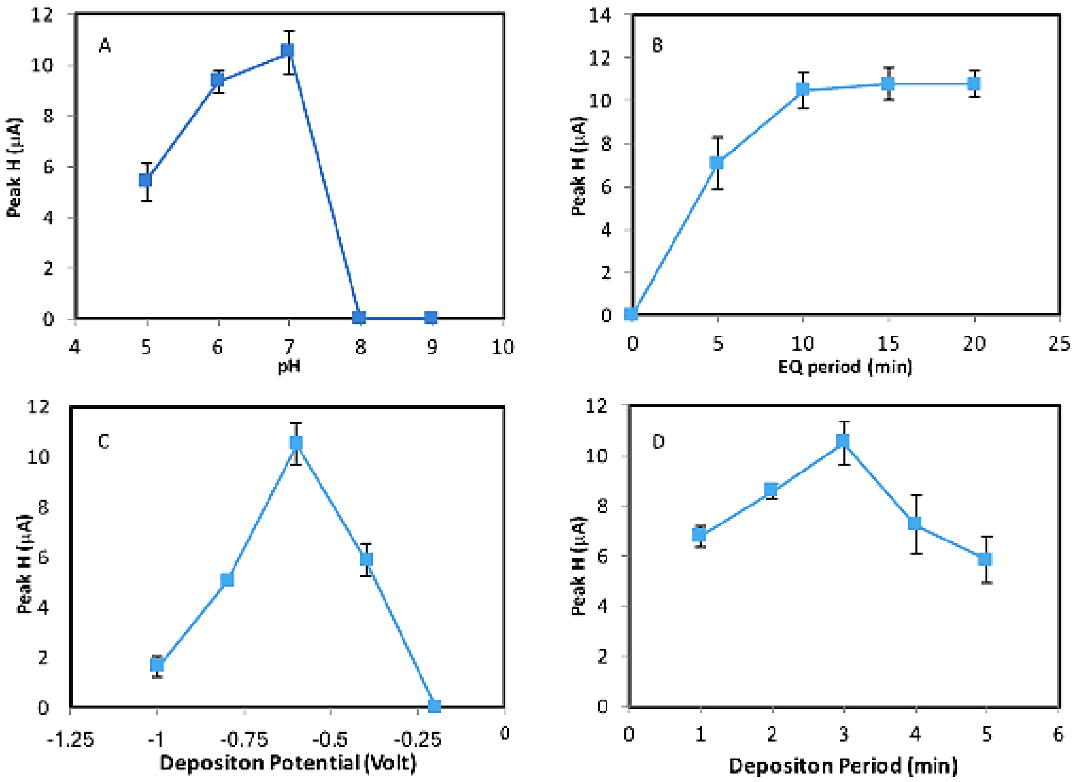

Figure 6. (A) Peak heights versus pH in 0.2 M B-R buffer, (B) Peak height versus equilibrium period, (C) Peak height versus deposition potential, and (D) Peak height versus deposition time, for SWASV experiments performed on samples containing 100 µg L^{-1} MP

The effect of the equilibrium period on the peak height was investigated and the results are presented in Figure 6B. Samples with 100 µg L^{-1} of MP were tested with an equilibrium period ranging from 0 to 20 min with 5 min steps. No reduction peak was detected at 0 minutes. The peak then appeared with a 5 min equilibrium period with an average height of 7.09 µA and increased approximately 70% to 10.5 µA with a 10 min equilibrium period. Peak height did not increase significantly with further increases in equilibrium period, suggesting the MP adsorption on ErGO had reached its equilibrium and saturated rebinding of MP on the electrode surface has achieved.

Similar to graphene, ErGO has a layered and macroporosity structure [40], so MP may have required time to reach the deeper layers of ErGO and saturate the electrode surface. Based on these results, an equilibrium period of 10 minutes with 0 V potential was used in subsequent experiments.

As discussed in Section 3.1, a conditioning deposition potential must be applied to working electrode before recording the voltammograms in order for reaction I to occur, producing the reactant needed for reaction II. Deposition potentials, ranging from -0.2 to -1 V, were tested to detect 100 µg L^{-1} of MP. As seen in Figure 6C, with the applied potential of -0.2 V no peak was detected. The peak height steadily increased from -0.2 V until -0.6 V (10.5 µA) These results are consistent with the results in Section 3.1, as Reaction I began to occur at a potential of -0.6 V during the CV scans (Figure 3). The peak height decreased approximately 55% and 85 % for -0.8 V and -1 V, respectively. Based on these results, the applied potential of -0.6 V was used in all future tests for MP detection.

The deposition periods from 0.5 minutes to 4 minutes were examined to detect 100 µg L^{-1} of MP using SWASV. The average peak height for 0.5 minutes was approximately 6.77 µA and it increased with greater deposition periods until 2 minutes, as more MP was reduced at electrode surface. As seen Figure 6D the peak height started to decrease significantly with deposition periods greater than 2 minutes. Based on these results, 2 minutes was chosen as the optimal deposition period to detect MP using SWAVS.

3.4. Methodology Calibration

Based on the optimization experiments performed in Sections 3.3, a deposition period of 2 minutes, a deposition voltage of -0.6 V, an equilibrium period of 10 minutes at 0 V, and B-R buffer with a pH of 7 were chosen as the optimal parameters to detect MP. The electrode response was tested for MP in solutions with concentrations ranging from 0 to 150 µg L^{-1}, using the optimal parameters mentioned above. The average voltammetric response of 3 iterations for each concentration is presented in Figure 7A.

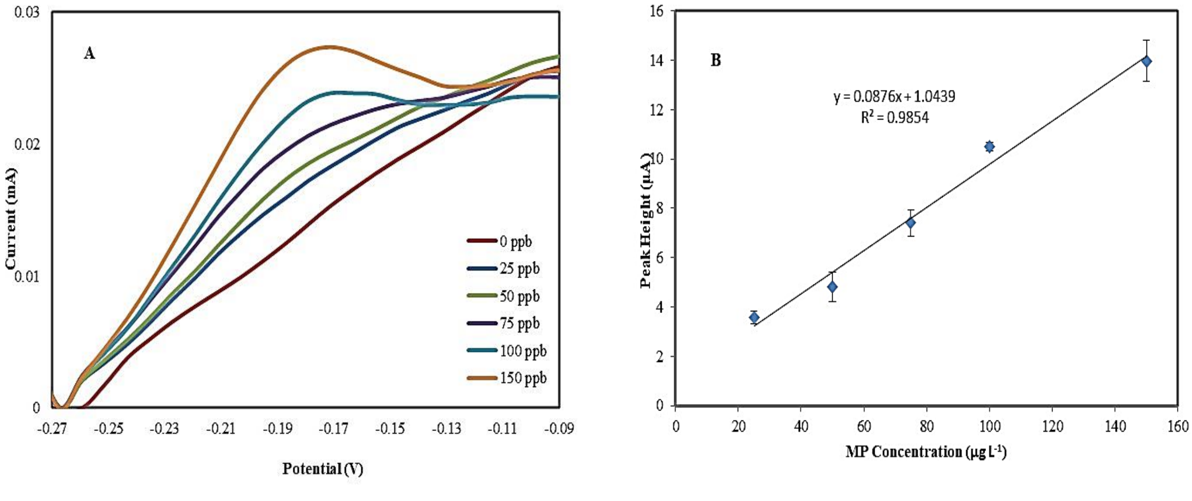

Figure 7. (A) Voltammograms and (B): Calibration curve for MP concentrations of 25, 50, 100, and 150 µg L^{-1} (Electrolyte: 0.2 M, pH 7 B-R buffer)

Voltammogram were shifted downwards to compensate for shifts in background current and to more clearly show the change in current from increasing MP concentration. The peak location for MP is located at -0.18 V as it was precisely shown in Figures 3 and 5. Figure 7B illustrates that SWASV response is linearly correlated to the concentrations of MP with a regression equation of $Y = 0.0876[MP] + 1.0439$, where [MP] is concentration of MP in µg L^{-1}. The methodology had a sensitivity of 0.0876 µA (µg $L^{-1})^{-1}$ and R-squared (R^2) of 0.9854. The LoD of 9.06 µg L^{-1} was calculated using equation (II).

3.5. Method Validation Using Environmental Water Samples

The method developed in the previous section for the detection of MP in deionized water using CSPE/ErGO was applied to 3 different water samples, including groundwater, river water, and General Test Water. All samples were prepared as discussed in Section 2.4, and were immediately tested without any additional conditioning, such as filtration and pH adjustment. Each testing solution was prepared by adding 2 mL of B-R buffer pH 7 to 8 mL of water samples. First, unspiked water samples were analyzed using the proposed method, and no response corresponding to MP was observed. Next, each water sample was spiked with 100 µg L^{-1} of MP and SWASV responses were recorded. Each standard addition was tested with 3 iterations and average peak heights were used to calculate recovery rates using equation (III), defined in Section 2.5. The recovery rates for different water samples are presented in Table 1. As can be seen from Table 1, the recoveries for all samples are within ±10% of the spiked concentration with General Test Water having the best recovery rate of 97.69 %. The results presented in this table showed that it is possible to determine the MP concentration in real sample solutions using this proposed method.

Table 1. Recovery rates of MP in different water samples. The results are the average found MP concentration and average recovery rate for triplicate tests in each sample media

Sample Media	**MP Added (µg L^{-1})**	**MP Found (µg L^{-1})**	**Recovery rates (%)**
River Water	100	106.01±1.46	106.01
Ground Water	100	109.51±0.44	109.51
General Test Water	100	97.69±1.49	97.69

3.6. Comparison With Other Voltammetric Studies

Comparison of detection limits and ranges for MP previously reported in the literature and this study are provided in Table 2. It can be observed in Table 2 that our detection limit is comparable with and even in most cases better than values of LoD achieved by other studies. The LoD obtained in this study is significantly lower than the U.S EPA 1-Day and 10-Day health advisory level of 300 µg L^{-1} (10-kg child) in drinking water [41]. Thus, the proposed analytical protocol is a practical implication of MP detection in different water samples.

Table 2. Comparison of the proposed voltammetric method with other similar studies for MP detection in different matrixes

Electrode	Method	Matrix	LoD (μg L^{-1})	Detection range (μg L^{-1})	Reference
BiF/GCE	SWV	Water and garlic samples	1.2^a	3 to 100^a	[42]
ZrO_2-MCPE	SWV	Tap water and River water	2	5 to 3000	[19]
Silver/nafion GCE	DPV	Water	23^a	79 to 379^a	[43]
Au/Nafion/GCE	SWV	River water and vegetable samples	26.3^a	132 to 31572^a	[21]
HAuNPs/rGO/GCE	SWV	Fruit and vegetable samples	31.5^a	79 to 2631^a	[22]
ErGO/CSPE	SWASV	Deionized water, groundwater, river water, General Test Water	9.06	25-150	This work

^{a} Value with the original unit (i.e., mol L^{-1}) converted to μg L^{-1}

4. CONCLUSION

In this study, a quick and inexpensive SWASV method was developed for detection of MP in water using novel ErGO/CSPE and nontoxic electrolytes. Based on our experiments, the optimal conditions for MP detection were B-R buffer with pH of 7, an equilibrium period of 10 min, a deposition potential of -0.6 V, and a deposition period of 2 min. This analytical method was applied to multiple water samples without any sample pretreatment and acceptable recovery rates were reached for detection of MP. The LoD of 9.06 μg L^{-1} achieved in water samples by our proposed methodology is more than 30 times lower than the limit set by the EPA for human consumption. The novel ErGO/CSPE and methodology introduced in this study pave the way for onsite detection of MP using handheld devices.

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Declarations of interest

The authors declare no conflict of interest in this reported work.

REFERENCES

[1] M.W. Aktar, D. Sengupta, and A. Chowdhury, Interdiscip. Toxicol. 2 (2009) 1.

[2] S.O. Igbedioh, Arch. Environ. Health 46 (1991) 218.

[3] Recognition and Management of Pesticide Poisoning, (2013) U.S. Environmental Protection Agency.

[4] Toxicological Profile for Methyl Parathion. Draft for Public Comment, ATSDR (2001) U.S. Department of Health and Human Services.

[5] Z. Ruckart Perri, K. Kakolewski, J. Bove Frank, and E. Kaye Wendy, Environmental Health Perspectives 112 (2004) 46.

[6] L.W. Brewer, C.J. Driver, R.J. Kendall, C. Zenier, and T.E. Lacher Jr, Environ. Toxicol. Chem. 7 (1988) 375.

[7] A. Wasley, L.A. Lepine, R. Jenkins, and C. Rubin, Environ. Health Perspect. 110 (2002) 1053.

[8] L.F. Edwards and B.P. Tchounwou, Int. J. Environ. Res. Public Health 2 (2005) 430.

[9] S. Garcia, A. Abu-Qare, W. Meeker-O'Connell, A. Borton, and M. Abou-Donia, J. Toxicol. Environ. Health, Part B 6 (2003) 185.

[10] Methyl Parathion in Drinking-Water, Background Document for Development of Who Guidelines for Drinking-Water Quality, (2004) World Health Organization.

[11] Method 3535a (Sw-846): Solid-Phase Extraction (Spe), (2007) U.S. Department of Environmental Protection.

[12] Sw-846 Test Method 8141b: Organophosphorus Compounds by Gas Chromatography, (2007) U.S. Department of Environmental Protection.

[13] C. Fuke, T. Arao, Y. Morinaga, H. Takaesu, K. Ameno, and T. Miyazaki, Leg. Med. (Tokyo) 4 (2002) 156.

[14] T. Zou, P. He, J. Cao, and Z. Li, J Chromatogr. Sci. 53 (2015) 204.

[15] S. El Kasmi, S. Lahrich, A. Farahi, M. Zriouil, M. Ahmamou, M. Bakasse, and M.A. El Mhammedi, J. Taiwan Inst. Chem. Eng. 58 (2016) 165.

[16] E.S. Almeida, E.M. Richter, and R.A.A. Munoz, Anal. Chim. Acta 837 (2014) 38.

[17] M. Li, Y.T. Li, D.W. Li, and Y.T. Long, Anal. Chim. Acta 734 (2012) 31.

[18] S. Legeai, and O. Vittori, Anal. Chim. Acta 560 (2006) 184.

[19] H. Parham, and N. Rahbar, J. Hazard. Mater. 177 (2010) 1077.

[20] A. Kumaravel, and M. Chandrasekaran, J. Electroanal. Chem. 638 (2010) 231.

[21] T.F. Kang, F. Wang, L.P. Lu, Y. Zhang, and T.S. Liu, Sens. Actuators, B 145 (2010) 104.

[22] J. Lu, Y. Sun, G.I.N. Waterhouse, and Z. Xu, Adv. Polym. Technol. 37 (2018) 3629.

[23] N.O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang, and X. Duan, Adv. Mater. 24 (2012) 5782.

[24] M.D. Stoller, S. Park, Y. Zhu, J. An, and R.S. Ruoff, Nano Lett. 8 (2008) 3498.

[25] C. Lee, X. Wei, J.W. Kysar, and J. Hone, Science 321 (2008) 385.

[26] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C.N. Lau, Nano Lett. 8 (2008) 902.

[27] C. Wang, J. Du, H. Wang, C.E. Zou, F. Jiang, P. Yang, and Y. Du, Sens. Actuators B 204 (2014) 302.

[28] H. Du, J. Ye, J. Zhang, X. Huang, and C. Yu, Electroanalysis 22 (2010) 2399.

[29] X. Kang, J. Wang, H. Wu, J. Liu, I.A. Aksay, and Y. Lin, Talanta 81 (2010) 754.

[30] Y. Yang, A.M. Asiri, D. Du, and Y. Lin, Analyst 139 (2014) 3055.

[31] Y. Li, M. Xu, P. Li, J. Dong, and S. Ai, Anal. Methods 6 (2014) 2157.

[32] N. Gao, C. He, M. Ma, Z. Cai, Y. Zhou, G. Chang, X. Wang, and Y. He, Anal. Chim. Acta 1072 (2019) 25.

[33] T. Jeyapragasam, S. Ramiah, S.-M. Chen, and B. Lou, Int. J. Electrochem. Sci. 8 (2013) 12353.

[34] W.S. Hummers and R.E. Offeman, J. Am. Chem. Soc. 80 (1958) 1339.

[35] H. Yu, B. Zhang, C. Bulin, R. Li, and R. Xing, Sci. Rep. 6 (2016) 36143.

[36] Harmonized Testing Protocol: Technology Non-Specific Version 2.1. (2018) World Health Organization.

[37] H.L. Guo, X.F. Wang, Q.Y. Qian, F.B. Wang, and X.H. Xia, ACS Nano 3 (2009) 2653.

[38] P. Zhu, and Y. Zhao, Mater. Chem. Phys. 233 (2019) 60.

[39] R. Pauliukaite, M.E. Ghica, O. Fatibello-Filho, and C.M.A. Bretta, Electrochim. Acta 55 (2010) 6239.

[40] H. Wang, D. Zhang, T. Yan, X. Wen, J. Zhang, L. Shi, and Q. Zhong, J. Mater. Chem. A 1 (2013) 11778.

[41] Toxicological Profile for Methyl Parathion, (2001) U.S. Department of Health and Human Services Agency for Toxic Substances and Disease Registry.

[42] D. Du, X. Ye, J. Zhang, and D. Liu, Electrochim. Acta 53 (2008) 4478.

[43] M. Govindasamy, V. Mani, S.-M. Chen, T.-W. Chen, and A.K. Sundramoorthy, Sci. Rep. 7 (2017) 46471.