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Research Article

Modified Carbon Paste Electrode for Sensitive Detection of Organophosphate Pesticide Dichlorvos in Environmental Water Samples

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Abstract

The pervasive utilization of organophosphorus pesticides, exemplified by dichlorvos, engenders substantial environmental and public health concerns due to their capacity to persist in water and agricultural systems. This study presents the development of a modified carbon paste electrode that incorporates zinc oxide as an electroactive material. This modified electrode is designed for the rapid, sensitive, and selective detection of dichlorvos in aqueous media. The composition of the electrodes was optimized through the adjustment of the proportions of graphite powder, plasticizer, and active material. This adjustment yielded a Nernstian response with a slope of 56.68 mV/decade across a concentration range of 1×10^{-3} to 1×10^{-6} mol/L. The sensor exhibited a detection limit of 2.458×10^{-6} mol/L, stable performance within a pH range of 6–8, and a response time of 39–47 seconds. Selectivity studies confirmed minimal interference from common ions except phosphate, while validation against high-performance liquid chromatography (HPLC) demonstrated strong agreement, with recovery rates approaching 99%. The electrode demonstrated stability over a period of more than two months, thereby substantiating its practical durability. A comparison of the proposed method with conventional analytical techniques reveals its cost-effectiveness, portability, and field-deployability as an alternative for pesticide monitoring. Its application in environmental engineering is particularly relevant for water quality assessment, pollution control, and sustainable agricultural management.

Keywords: *Dichlorvos Detection; Modified Carbon Paste Electrode; Organophosphorus Pesticides; Electrochemical Sensor; Environmental Water Monitoring.*

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Introduction

The issue of environmental pollution has emerged as a primary focus of research studies, as it poses a significant threat to the planet's safety. Organophosphorus pesticides have garnered attention due to their substantial adverse impact on the health of living organisms, attributable to their extensive utilization. These pesticides have been employed for over half a century to safeguard crops and livestock (Derbalah et al., 2019). It is estimated that approximately 40% of all pesticides utilized are classified as organophosphorus compounds (Kaushal et al., 2021). This is largely attributed to the substantial reliance in agriculture on chlorine-based pesticides. However, organophosphorus compounds possess a comparatively brief half-life prompting the employment of these compounds due to their relatively brief half-life and notable effectiveness. Less than 1% of the utilized organophosphorus compounds reach their intended targets, with the majority persisting within the environment (Wang et al., 2022). Organophosphorus pesticides are distinguished by their chemical composition, which involves the presence of the element phosphorus connected by a double bond to a terminal oxygen atom. The phosphorus atom is further linked to two lipophilic groups and a leaving group, which is frequently a halide (**Figure 1**) (Sidhu et al., 2019).

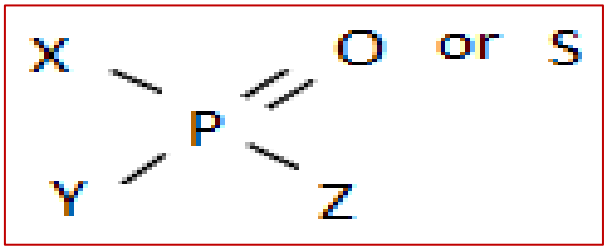

Figure 1. General Formula for Organophosphorus Pesticides

In light of the pressing necessity for environmental safety that is sustainable, scientific research has been directed towards ascertaining the quantity of organophosphorus pesticides present in diverse environmental samples. Dichlorvos (O, O-dimethyl-2,2-dichlorovinyl phosphate) (a chlorinated organophosphorus insecticide) is one of the most prevalent pesticides utilized for the treatment of intestinal parasites. It is employed in feed mixtures as a larvicide to eradicate the threat posed by plant fly larvae. Dichlorvos is instrumental in the management of insects in enclosed environments, such as warehouses and greenhouses. Its popularity is attributable to its efficacy and cost-effectiveness (Liu et al., 2009). A variety of analytical techniques have been employed to identify dichlorvos, a pesticide. Dichlorvos was determined in pure and natural water samples using gold microelectrodes and square wave voltammetry, and the detection limit was reached (7.8.26) µg/L (De Souza & Machado, 2005). Dichlorvos was determined through the reaction between luminol and H_2O_2 in the presence of a surfactant. The detection limit for this method was determined to be 0.008 µg/ml (Wang, 2001).

A study was conducted to ascertain the levels of dichlorvos, a pesticide, in three lettuce vegetables (kale and cabbage). The levels of the pesticide residues were determined using HPLC-UV technology. The results of the study indicated that the levels of the pesticide residues were above the permissible limit (Sinyangwe et al., 2016). The presence of organophosphorus pesticides, including dichlorvos, methyl parathion, malathion, and parathion, has been detected in groundwater samples using a SPE-GC-MS (solid phase extraction-gas chromatography-mass spectrometry) analytical method. According to Ma et al. (2009), the detection limits for water samples were found to be within the range of 4–10 ng/L. A surface-enhanced Raman scattering (SERS) sensor was developed for the detection of dichlorvos in pears, with platinum-coated gold nanoparticles (Au@PtNPs) serving as signal amplifiers. The method demonstrated a linear range for dichlorvos from 20 to 2000 µg/L, with a detection limit of 20 µg/L. In the case of pears, the recovery of dichlorvos ranged from 80.25% to 94.86%. This sensor effectively quantified the pesticide with strong SERS signals and minimal interference (Yu et al., 2022). Additionally, an enzyme-regulated probe, a fluorometer, and a photothermal probe were developed for the quantitative detection of organophosphorus pesticide residues, including dichlorvos. The probes that were developed demonstrated sensitive responses within a wide linear range (a crucial reference in the introduction) (0.1-8000) ng/ml (Jiang et al., 2023). In this study, the pesticide dichlorvos (**Figure 2**) will be determined by an electroanalytical method using a modified carbon paste electrode. This method has been selected for its chemical stability, good conductivity, good voltage range, relatively large surface area, and economic practicality compared to other electrodes.

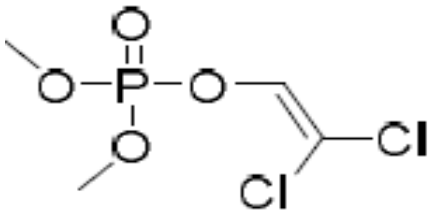

Figure 2. Chemical Formula of Dichlorvos

The objective of this study to address the challenge of accurately detecting organophosphorus pesticides through simple, practical, and field-deployable methods, as conventional analytical techniques are often costly, labor-intensive, and require sophisticated instrumentation. The research endeavors to develop an

innovative electroanalytical approach for the monitoring and quantification of dichlorvos, a widely utilized organophosphorus pesticide that poses considerable environmental risk to water and agricultural soils. The work involves establishing optimal operating conditions—including pH, temperature, and critical technical parameters such as the ratio of electrode components, reaction time, and retention time—to ensure accurate and efficient detection. Subsequent to the collection of the initial set of standard solutions, statistical analyses will be conducted to evaluate the method's validity, precision, and detection limits. Thereafter, the application of the aforementioned method will be conducted on real samples. The ensuing results will be juxtaposed with those obtained from established reference techniques to assess the proposed method's accuracy, reliability, and practical applicability.

Materials and Methods

Materials, Equipment, and Electrode Design

The experimental work in this study was conducted using a range of precision instruments and high-purity reagents to ensure accurate and reproducible results. The primary instruments employed for this study included a Vici digital millivoltmeter (type VC97) for precise potential measurements, a silver/silver chloride (Ag/AgCl) reference electrode for stable and reproducible reference potentials, and a WTW pH/mV meter equipped with a glass probe to accurately monitor the pH and potential changes during measurements. Mass determinations were performed using a Sartorius analytical balance with a resolution of 0.0001 g, ensuring high accuracy in weighing electrode components and reagents. The preparation and handling of solutions were facilitated by an assortment of calibrated glassware, including beakers and volumetric flasks of varying capacities, enabling precise volumetric measurements essential for standard solution preparation.

The chemical reagents employed in the study comprised graphite powder (99% purity) as the conductive matrix material, paraffin oil, dioctyl phthalate (DOPH), and dibuthyl phthalate (DBPH) as plasticizers to enhance the paste's mechanical properties and ion exchange capabilities, and zinc oxide (ZnO) as the electrochemically active ingredient providing selectivity toward dichlorvos. Analytical-grade dichlorvos was utilized in both standard solution form and as a 50% commercial formulation (manufactured in China) to assess the sensor's efficacy with real-world samples. The following reagents were utilized: acetic acid, sodium hydroxide, potassium phosphate, sodium sulfate, sodium chloride, potassium nitrate, and distilled water. These reagents were employed in solution preparation, pH adjustments, and selectivity assessments. The judicious selection and utilization of these chemicals and instruments proved to be instrumental in achieving the research objectives and ensuring the reliability of the experimental results.

The electrode utilized in this study is a carbon paste electrode, which is fabricated by blending graphite powder with a suitable plasticizer to yield a conductive, cohesive paste. A salient benefit of this electrode type is its readily renewable surface, which facilitates uncomplicated reconditioning through simple polishing. This ensures consistent ion-exchange performance over an extended period of use. The fabrication process is characterized by its simplicity, cost-effectiveness, and the absence of requirements for sophisticated equipment, which renders the electrode highly practical for routine analytical applications. When the carbon paste is further modified by incorporating specific active materials or ionophores—such as ZnO in this study—the resulting device functions as a chemically modified carbon paste electrode, capable of providing enhanced selectivity and sensitivity for target analytes (Tantawy et al., 2022; Zayed et al., 2020). These electrodes offer a unique combination of benefits, including low-cost fabrication, flexibility in composition, and adaptability to various sensing applications. This makes them well-suited for the development of portable, field-deployable analytical systems.

Fabrication of the Modified Carbon Paste Electrode and Preparation of Standard Solutions

The modified carbon paste electrode (CPE) was fabricated following a multi-step procedure to ensure optimal sensitivity and reproducibility (**Figure 3**). Initially, graphite powder was thoroughly mixed with the electrochemically active ingredient in predetermined proportions within a clean Petri dish. Subsequently, a suitable plasticizer was incorporated, and the mixture was homogenized until a consistent paste was formed. The prepared paste was stored for 24 hours at refrigerator temperature to enhance its stability prior to use (Khadem et al., 2017).

For the assembly of electrodes, the paste was packaged into a plastic cylindrical tube containing a movable piston, around which a copper wire was wound to function as an electrical conductor. The electrode tip was then pressed onto a glass surface that had been rendered smooth, and the surface was subsequently polished with filter paper until a uniform, glossy surface was obtained. This process ensured consistent electrochemical performance (Nasser et al., 2019).

The electrochemical measuring cell was configured using the following arrangement: The system under consideration consists of an Ag/AgCl reference electrode, a measuring solution, and a

modified carbon paste working electrode. The configuration was connected as illustrated in **Figure 4**, enabling precise potential measurements for dichlorvos detection.

Standard solutions were prepared for the purpose of calibrating and validating the proposed electrode. A parent dichlorvos solution of 10^{-1} M was meticulously prepared from a 500 g/L commercial pesticide formulation. To this end, 4.4195 mL of the aforementioned formulation was meticulously measured and subsequently diluted to 100 mL with double-distilled water. From this stock, a series of standard solutions at concentrations of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7} M were obtained using serial dilution according to Moore's law. Furthermore, standard solutions of CH3COOH and NaOH were prepared at concentrations of 0.1 M for the purpose of pH adjustment. A series of standard solutions of potassium phosphate, sodium sulfate, potassium chloride, and potassium nitrate were also prepared within the concentration range of 10^{-1}–10^{-8} M to assess electrode selectivity.

(a) (b) (c)

Figure 3. Stepwise Fabrication and Use of the Modified Carbon Paste Electrode: (a) Homogenization of Graphite with the Electroactive Component, (b) Packing the Prepared Paste into the Electrode Body, and (c) Electrochemical Measurement Setup.

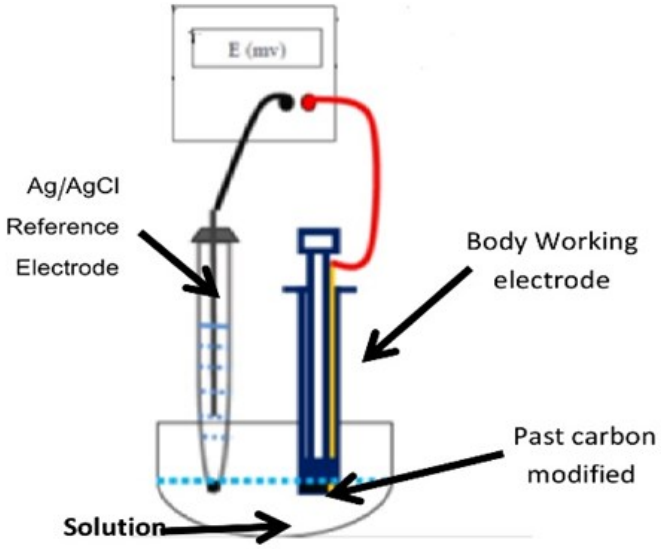

Figure 4. A Schematic Representation of the Electrochemical Measurement Cell

Results and Discussions

Effect of Carbon Paste Components and Ionophore Determination

The sensitivity and selectivity of a selective electrode are contingent upon its composition. It has been established that the content and nature of the chemically active substance, as well as the type and proportion of the plasticizer, exert a major influence on the electrode's potentiometric response (Nasser & Alabid, 2022).

The concentration of dichlorvos pesticide was determined according to the Nernst equation:

$$E_{cell} = E^{o}{}_{cell} - \frac{0.059}{n} log\, C_{dichlorvos} \qquad \textbf{(1)}$$

According to the aforementioned equation, a Nernstian slope constitutes a fundamental requirement for quantization.

$$Slope = \frac{59}{n}\ ; n = 1 \qquad \textbf{(2)}$$

Consequently, the effect of the electrode composition on its potentiometric response was investigated (**Table 1**). The voltage responses were plotted as a function of the logarithm of dichlorvos molar concentration within the range of 1×10^{-2} - 1×10^{-7} mol/L. The experiment involved the amalgamation of varying quantities of graphite powder (2–12% w/w) with the active substance, in conjunction with the plasticizer. The ratio of graphite powder to plasticizer was investigated at two levels: 1:1 and 2:1 (w/w).

The experimental results indicated that electrodes with a 1:1 ratio of graphite powder to plasticizer demonstrated no quantifiable response. Conversely, when the ratio was adjusted to 1:2 and the active material content was 11%, the electrode displayed a clear Nernstian response with a slope of 56.682 mV/decade across a linear concentration range of 1×10^{-3} - 1×10^{-6} mol/L, as shown in **Figure 5**.

These findings are consistent with earlier reports highlighting the critical role of electrode composition in determining potentiometric performance. For instance, Abdel-Haleem et al. (2021) demonstrated that modifying carbon paste electrodes with graphite, graphene oxide, and plasticizers permitted precise calibration of slope values and linear response ranges, thereby directly enhancing sensitivity and selectivity for pharmaceutical analytes.

The voltage response of the proposed electrode was studied using several active materials (TiO_2, ZnO, CuO). Three electrodes were prepared with a graphite to plasticizer ratio of 2:1 and an active material ratio of 11 % . It was observed that when using ZnO inside the paste, the modified electrode exhibited a linear response and a significant Nernstian response with a slope of 56.682 mV/decade in the concentration range from (1×10^{-3} - 1×10^{-6}) M.

Table 1. Effect of Carbon Paste Components on the Voltage Response of the Proposed Electrode

Electrode Number	Components			Nernstian Slope mv/decade	Linear range mol/L
	Electrochemically Active Material (%)	Graphite Powder (%)	Paraffin Oil (%)		
1	2	49	49	-	-
2	3	48.5	48.5	-	-
3	4	48	48	-	-
4	5	47.5	47.5	-	-
5	6	47	47	-	-
6	7	46.5	46.5	-	-
7	8	46	46	-	-
8	2	65.34	32.66	-	-
9	3	64.67	32.33	-	-
10	4	64	32	-	-
11	5	63.33	31.67	-	-
12	6	62.67	31.33	-	-
13	7	62	31	38.75	1×10^{-3}-1×10^{-5}
14	8	61.33	30.67	46.05	1×10^{-3}-1×10^{-5}
15	9	60.67	30.33	50.005	1×10^{-3}-1×10^{-5}
16	10	60	30	53.1	1×10^{-3}-1×10^{-6}
17	11	59.33	29.67	56.682	1×10^{-3}-1×10^{-6}
18	12	58.67	29.33	54.027	1×10^{-3}-1×10^{-6}

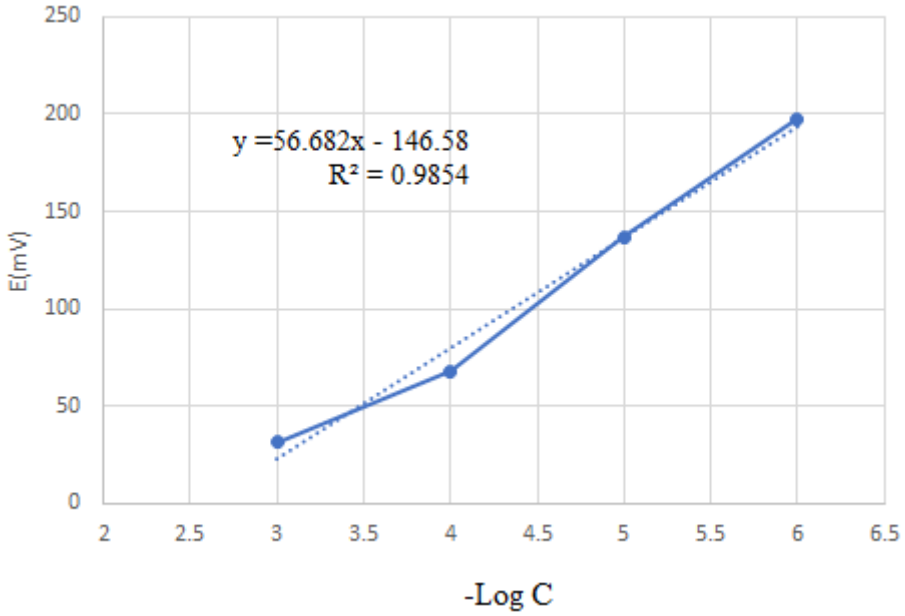

Figure 5. Graph of the Relationship of -log [Dichlorvos] with the Potential Value of selective Carbon Paste Electrode with Composition (11% Active Ingredient, 59.33% Graphite Powder and 29.67% Plasticizer)

Effect of the Type of Plasticizer on Electrode Response

The nature of the plasticizer is of paramount importance for the optimization of ion-selective electrode performance. This method ensures homogeneous integration of components, imparts flexibility to the carbon paste matrix, and enhances ion exchange at the electrode interface. The properties that are considered essential include water insolubility, chemical inertness, and the ability to sufficiently soften the carbon paste to facilitate ion diffusion (Audic & Chaufer, 2005; Carey, 2015).

Building on this, studies have confirmed that the type of plasticizer exerts a significant influence not just on physical attributes but also on analytical performance, including detection limits, selectivity, and Nernstian behavior. For instance, one review asserts that the plasticizer can significantly modify electrode selectivity, sensitivity, and slope (i. e., Nernstian response) (Abass et al., 2022). Another work focusing on calcium-selective electrodes underscores how plasticizers affect detection limits and sensitivity (Bedlechowicz et al., 2002).

In the present study, three plasticizers were compared: paraffin oil, di-n-butyl phthalate (DBP), and di-octyl phthalate (DOP). The electrode containing Dibutyl Phthalate and 11% active material exhibited the closest approximation to an ideal Nernstian slope, while electrodes employing paraffin oil demonstrated suboptimal response and those incorporating DOP failed to manifest a Nernstian trend (**Figure 6**).

This observation is consistent with broader findings in the field. For instance, Hwang et al. (2022) optimized a carbon paste electrode for ascorbic acid by using DBP as the plasticizer. The optimized electrode demonstrated a Nernstian slope of approximately 57 mV/decade and retained this response over an extended duration.

Effect of pH on Electrode Response

The proposed electrode was immersed in solutions containing dichlorvos at concentrations of 1×10^{-4}, 1×10^{-5}, and 1×10^{-6} mol/L, with the pH adjusted using 0.1 M NaOH and 0.1 M CH_3COOH. At each concentration, the potential (latency) response was measured across a range of pH values and plotted (**Figure 7**). The findings indicate that the potential remains stable within the pH range of 6 to 8, suggesting optimal ion-exchange efficiency and minimal interference within this pH range. This observation is attributed to chemical alterations in the pesticide at higher pHs and the fact that dichlorvos, an organophosphorus compound, is more effectively absorbed or distributed in neutral to slightly acidic/alkaline media.

The adjustment of the pH of samples to a near-neutral state (approximately pH 7) constitutes a standard procedure in dichlorvos analysis, with the objective being the reduction of hydrolysis prior to detection, particularly in chromatographic methods (Richter & Corcoran, 1997). This finding underscores the importance of maintaining a neutral pH environment to ensure the stability of pesticides during measurement.

In general, potentiometric biosensors for organophosphate pesticides, including dichlorvos, frequently depend on pH alterations resulting from enzymatic hydrolysis. Potentiometric transducers, including ion-selective electrodes (ISE) and pH ISFETs, are capable of detecting proton release from such reactions, thereby enabling the precise

measurement of pesticide concentrations (Jaffrezic-Renault, 2001). These sensors generally demonstrate optimal performance at pH values that maintain enzymatic activity and electrode stability.

In dual-mode biosensors that integrate potentiometric and amperometric detection, potentiometric channels are employed to measure local pH changes resulting from organophosphate hydrolysis, while amperometric channels are utilized to monitor byproducts such as p-nitrophenol (Mostafa, 2010). These systems often demonstrate optimal performance under conditions that ensure consistent and uncontaminated enzymatic catalysis and proton release, free from pH-induced degradation.

Despite the paucity of direct literature on dichlorvos-specific potentiometric pH effects, the general design principle is evident. Maintaining a stable, moderate pH (e.g., 6–8) ensures minimized chemical degradation, optimal sensor function, and reproducible responses.

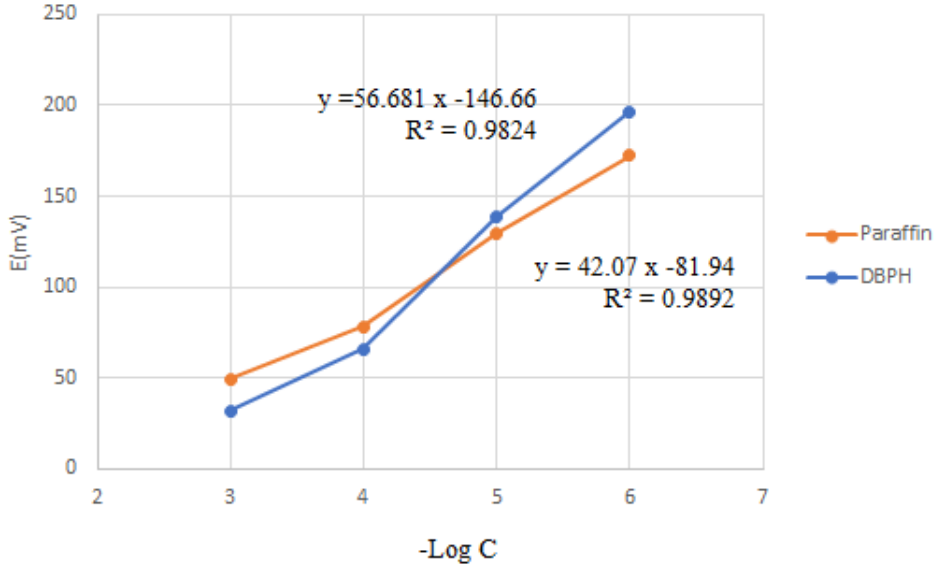

Figure 6. Effect of Plasticiser Type on Electrode Response (11% Electrochemically Active Material, 59.33% Graphite Powder and 29.67% Plasticiser)

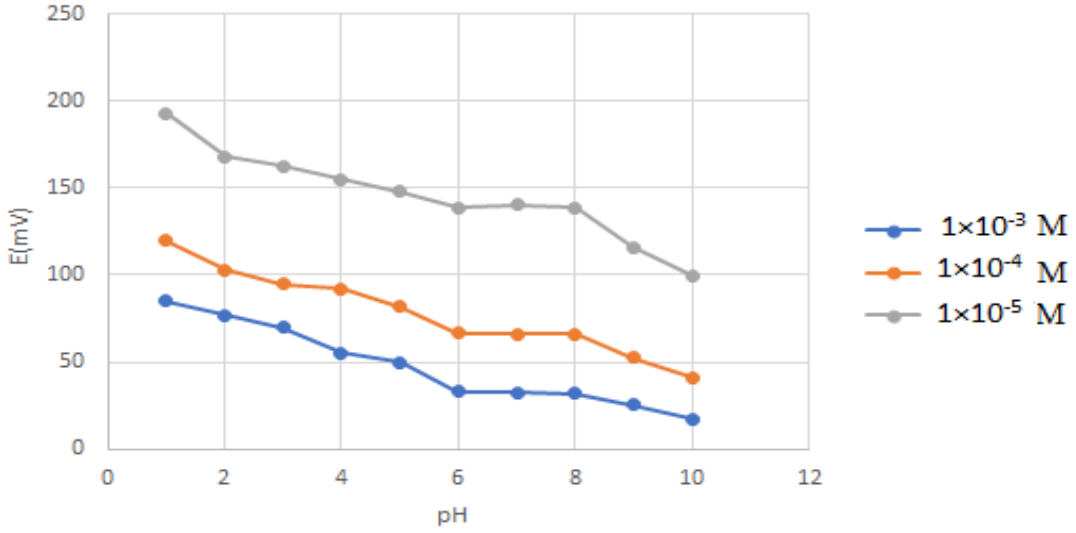

Figure 7. Effect of Medium pH on the Response of the Proposed Electrode

Response Time and Electrode Life

The response time of the proposed electrode was determined by measuring the time required for the latency to reach a constant value in solutions with pesticide concentrations ranging from 1×10^{-3} to 1×10^{-6} mol/L. As demonstrated in Figure 8, the latency exhibited a consistent value over a time span ranging from 39 to 47 seconds. The alterations in the analytical properties of the proposed electrode were also monitored, and it was ascertained that the electrode could be utilized for period exceeding two months without a substantial alteration in its properties. This observation was supported by the constant response time and the maintenance of a constant Nernstian slope (**Figure 8**).

Electrode Selectivity

Selectivity is a pivotal factor in ensuring the provision of sufficient information regarding the effects of interferences during the analysis process with ion-selective electrodes. The selectivity of an ion is defined as the electrode's capacity to discern that ion within a solution containing multiple ions. The Matched Potential Method (MPM) was employed to assess the impact of various ions on the performance of the proposed electrode. In this method, the effectiveness of the studied ion was augmented from $a_A=1.0\times10^{-6}$M (standard solution) to $a'_A=1.0\times10^{-4}$M. The change in the measured latency (ΔE) corresponding to the enhancement in the effectiveness of the studied ion was then determined. The standard solution (0×10^{-6}M) is adjusted to $a'_A=1.0\times10^{-4}$M, and the change in measured latency (ΔE) corresponding to the increase in effectiveness of the studied ion is recorded. Subsequently, a solution of the blocking ion with a concentration ranging from 1.0×10^{-1} to 1.0×10^{-8}M is added to a new standard solution of the studied ion with the same previous concentration (1.0×10^{-6}M). This process is repeated until the same change (ΔE) is recorded (Umezawa et al., 2000). The following text is intended to provide a comprehensive overview of the subject matter.

The concentration of the blocking ion is calculated subsequent to the addition, and then the selectivity coefficient is calculated by the following relationship:

$$K_{A,B}^{M\,P\,M} = \frac{(a'_A - a_A)}{a_B} \qquad (3)$$

This approach does not depend on the Nicolsky–Eisenman equation and is regarded as advantageous for providing analytically relevant and practical selectivity coefficients (Umezawa et al., 2000). The selectivity coefficients determined by MPM are described in **Table 2**.

The findings indicate significant interference by phosphate, which exhibits a selectivity coefficient >1, suggesting that the electrode responds more to phosphate than to dichlorvos. Conversely, sulfate and nitrate exhibit negligible interference, while chloride displays a moderate impact.

A selectivity coefficient $K_{A,B}>1$, indicates that the electrode exhibits a higher degree of responsiveness to the interfering ion in comparison to the analyte of interest (Le Goff et al., 2004). In this case, phosphate appears to act synergistically with dichlorvos in its interaction with the sensor membrane, potentially due to similar physicochemical affinities or entry mechanisms into the carbon paste matrix.

Despite the paucity of studies specifically addressing phosphate interference in dichlorvos detection, phosphate ions are recognized as posing significant challenges in ion-selective sensing due to their high hydration energy and complex molecular structure (Kim et al., 2007). This can result in significant interactions that overshadow the target analyte, particularly in membranes not explicitly designed for phosphate discrimination.

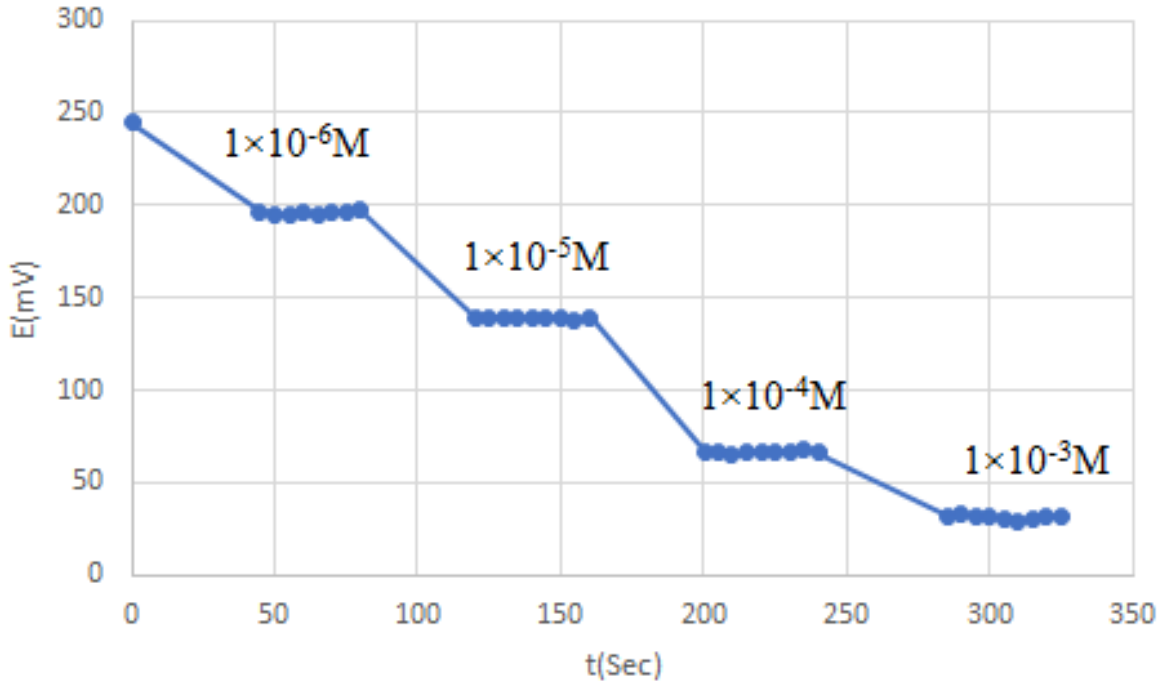

Figure 8. Effect of Time on Electrode Response

Table 2. Values of the Selectivity Coefficients of the Proposed Electrode Measured by (MPM)

Blocking Ion	Selectivity Coefficient
PO_4^{3-}	1.98
SO_4^{2-}	2.4×10^{-5}
NO_3^-	4.9×10^{-5}
Cl^-	9.9×10^{-2}

Analytical Validation and Application of the Proposed Electrode for Dichlorvos Determination

The proposed electrode was successfully utilized to ascertain the concentration of dichlorvos pesticide in standard and real samples. This determination was based on the analytically useful linear part of the calibration curve of the electrode. The method was then validated by statistical study of the results.

The analytical performance of the proposed modified carbon paste electrode was initially evaluated using standard aqueous solutions of dichlorvos. As demonstrated in **Table 3**, the method demonstrated high accuracy, as evidenced by the low standard deviation (SD) and relative standard deviation (RSD) values, and strong validity, as indicated by recovery percentages that did not exceed the permissible limit. These results confirm the reliability of the electrode for quantitative analysis under controlled laboratory conditions.

To assess the applicability of the electrode to real-world samples, it was tested using a commercial Dichlorvos pesticide formulation of Chinese origin, marketed under the trade name Dichlorvos 50%. A parent solution with a concentration of 1×10^{-3} M was prepared by meticulously measuring 0.0442 mL of the commercial product into a 100 mL volumetric flask and subsequently diluting to the mark with double-distilled water. From this, a 1×10^{-6} M working solution was prepared by pipetting 100 µL of the parent solution into a separate 100 mL volumetric flask and diluting to volume with double-distilled water.

The concentration of dichlorvos in the prepared real sample was determined using the proposed electrode. The reliability of the method was substantiated by the low standard deviation (SD) and relative standard deviation (RSD) values, while its validity was corroborated by the recovery percentage, as detailed in **Table 4**. These results demonstrate that the electrode maintains precision and accuracy when applied to actual pesticide formulations, making it suitable for practical environmental and industrial monitoring.

To ensure the reliability of the findings, the same authentic sample was examined through the application of a high-performance liquid chromatography (HPLC) reference method, as delineated by Okdeh et al. (2023). In the HPLC procedure, standard solutions of dichlorvos in the range of 0.5–50 ppm were prepared and injected into the chromatographic system. The resulting chromatograms were then utilized to establish calibration curves by plotting peak area against concentration. This enabled the determination of unknown sample concentrations using the derived linear regression equation (**Figure 9**).

A comparative analysis was then performed between the two methods, with a focus on the detection limit (LOD) and limit of quantification (LOQ) for dichlorvos (**Table 5**). The comparison revealed a high level of agreement between the proposed electrode and the reference HPLC method, thereby confirming the electrode's analytical reliability and practical applicability for both laboratory-based and field measurements of dichlorvos (**Table 6**).

Table 3. Determination of the Concentration of Dichlorvos Pesticide in Standard Aqueous Solutions by the Proposed Electrode Cell Method where n=3, p=95%

Taken (mol/L)	Found (mol/L)	Recovery (%)	SD (mol/L)	RSD (%)	LOD (mol/L)	LOQ (mol/L)
1×10^{-6}	1.0513×10^{-6}	105.13	4.644×10^{-8}	4.417		
1.57×10^{-5}	1.543×10^{-5}	98.28	3.786×10^{-7}	2.453	2.458×10^{-6}	8.193×10^{-6}
1×10^{-4}	0.9976×10^{-4}	99.76	4.381×10^{-6}	4.391		

Table 4. Determination of Dichlorvos Pesticide Concentration in the Selected Real Sample by the Proposed Electrode Cell.

Sample Conc. (mol/L)	Measured Conc. (mol/L)	Recovery %	SD (mol/L)	RSD (%)
M 1×10^{-6}	0.988×10^{-6}	98.8	3.798×10^{-8}	3.844

Table 5. The Results of Comparing the Detection Limits of Dichlorvos Pesticide in Calibrated Samples According to the Proposed and Reference Methods.

Method	LOD	LOQ
Proposed	0.543 ppm	1.811 ppm
HPLC	4.4×10^{-4} ppm	17.67×10^{-4} ppm

Table 6. Comparative Analytical Studies on Detection Limits of Dichlorvos

References	Limit of Quantification
(Xu et al., 2010)	94.8 ng/L
(Chen et al., 2008)	0.42 ng/L
(Hou et al., 2016)	3.8×10^{-9}M
(Jain et al., 2023)	0.55 µg/ml and 1.1 µg/g
The current study	1.811 µg/L

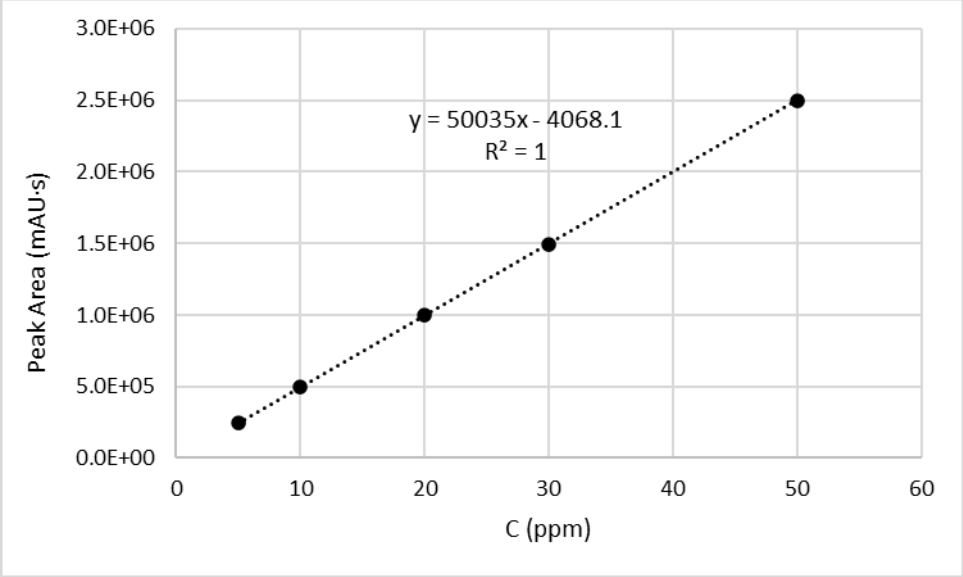

Figure 9. Calibration Curve for Determination of Dichlorvos with the Reference Method

Environmental Engineering Implications

The detection and monitoring of organophosphorus pesticides, such as dichlorvos, is of direct relevance to environmental engineering, given their persistence in agricultural runoff, groundwater, and food systems. The proposed electrode's sensitivity and portability render it a valuable tool for environmental monitoring and risk assessment. Conversely, the carbon paste electrode does not necessitate the same level of sophistication in equipment and laboratory infrastructure as conventional methods, such as HPLC, rendering it a suitable option for field deployment due to its rapid and cost-effective nature.

From an environmental engineering perspective, the integration of this sensor into water quality monitoring frameworks facilitates the detection of pesticide contamination in surface and groundwater, thereby supporting decision-making processes in pollution control and remediation projects. Its application can also extend to agricultural engineering practices, where continuous monitoring of pesticide residues in irrigation water or soils is essential for ensuring compliance with environmental regulations and protecting ecosystems.

Moreover, the provision of early detection capabilities by the electrode could facilitate proactive environmental management, thereby contributing to the mitigation of long-term accumulation of toxic organophosphorus compounds in natural waters and soils. This objective is consistent with broader sustainability goals, as it supports safer agricultural practices and reduces risks to human health and biodiversity.

Conclusion

The present study developed and evaluated a modified carbon paste electrode incorporating zinc oxide as an electrochemically active material for the rapid, sensitive, and selective detection of dichlorvos pesticide in aqueous solutions. The electrode's optimization entailed a systematic adjustment of the ratios of graphite powder, active material, and plasticizer. This adjustment led to a configuration that achieved a Nernstian slope of 56.682 mV/decade, a detection limit of 2.458×10^{-6} M, and a quantitative detection limit of 8.193×10^{-6} M. The electrode exhibited high selectivity within a pH range of 6–8, short response times of 39–47 seconds, and stable performance for more than two months. The validation process, which entailed the comparison of the analytical results against a reference HPLC method, yielded excellent agreement, thereby confirming the suitability of the method for both standard and real sample analysis.

The following conclusions can be drawn:

- The optimized electrode composition (11% active material, 59.33% graphite powder, 29.67% dibuthyl phthalate) demonstrated the optimal analytical performance, attaining linearity within the concentration range of 1×10^{-3} M to 1×10^{-6} M.
- The sensor demonstrated exceptional selectivity for dichlorvos, exhibiting minimal interference from the majority of prevalent ions, with the notable exception of phosphate. This latter ion exhibited a synergistic interaction, indicative of a distinctive response.
- The pH stability range of 6–8 was determined to ensure reliable measurements under typical environmental water conditions.
- The method demonstrated a high degree of accuracy, with recovery rates approaching 100% and low relative standard deviations observed in both standard and commercial pesticide solutions.
- A comparative analysis with HPLC was conducted to ascertain the validity of the proposed electrode as a cost-effective, portable, and reliable alternative for dichlorvos detection.

Future research endeavors should explore the extension of the application of this electrode to detect other organophosphorus pesticides in complex environmental matrices, such as soil, agricultural runoff, and food samples. Furthermore, the incorporation of the sensor into portable, field-deployable electrochemical detection systems has the potential to enhance its utility for on-site monitoring.The investigation of alternative sustainable active materials and plasticizers could further enhance the electrode's environmental compatibility and operational lifespan.

Declarations

Author Contribution

K.K: Methodology, Formal analysis, Investigation, Resources, Writing of the original draft, and review & editing, .

H.N: Conceptualization, Resources, Writing of the original draft, Supervision, Project administration .

T.A: Validation, Data curation, Writing – review & editing, Supervision.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Declaration on the Use of Generative AI and AI-Assisted Technologies

The authors acknowledge that generative AI and AI-assisted technologies were employed in the refinement of this manuscript to enhance the clarity, coherence, and overall quality of the writing.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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The authors declare that there is no acknowledgement to be made.

Ethics

This study did not involve human participants or animals; hence, no ethical approval was required.

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