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Current Applications and Advantages of Electrochemical Methods for Sensitive Determination of Diphenyl Ether Herbicides

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ABSTRACT

Pesticides, while effective in controlling pests and boosting agricultural yields, pose significant negative effects on the environment and human health. Their widespread use can lead to soil and water contamination, harm non-target organisms, contribute to the development of pesticide-resistant pests, and raise concerns about the potential long-term impact on ecosystems. Electrochemical sensors are one of the leading technologies due to their ability to quickly determine and monitor pesticide levels in several matrices. With the advantages of electrochemical analysis and advanced structural/chemical properties of nanomaterials/biomaterials, advanced electrochemical sensors offer outstanding performance for specific pesticide detection. This is because nanomaterials contribute to the development of advanced (multi)functional electrochemical sensing platforms thanks to their tunable pore diameters, biocompatibility, high surface area and pre-concentration capabilities. This review comprehensively explores the contemporary applications and advantages of electrochemical methods for the sensitive determination of diphenyl ether herbicides, elucidating their pivotal role in modern analytical chemistry. Current uses and developments of electrochemical sensors are presented for practical applications in diphenyl ether herbicides detection and monitoring to end with some concluding remarks, perspectives, and trends.

KEYWORDS
Analysis;
Determination;
Electrochemical;
Herbicides;
Pesticides

1. Introduction

Nowadays, the use of pesticides in agriculture offers several advantages, primarily in the context of crop protection and increased agricultural productivity. Pesticides help control and manage pest populations, preventing damage to crops caused by insects, weeds, and diseases. This contributes to higher yields and improved food quality. Pesticides also play a role in safeguarding public health by controlling vectors of diseases such as mosquitoes and ticks. Moreover, these chemical agents can be instrumental in preventing post-harvest losses during storage and transportation. However, the use of pesticides comes with notable disadvantages. One major concern is the potential environmental impact, including the contamination of soil, water, and air (1–3). Pesticides may harm non-target organisms, including beneficial insects,

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birds, and aquatic life, disrupting ecosystems and posing risks to biodiversity (Figure 1). Additionally, the overuse or misuse of pesticides can lead to the development of pesticide-resistant pests, rendering certain chemicals less effective over time. Furthermore, there are growing concerns about the potential health risks associated with pesticide residues in food, as well as the occupational hazards faced by farmers and workers involved in pesticide application. Nevertheless, striking a balance between the benefits of pest control and the need for environmental and human safety remains a crucial challenge in sustainable agriculture (4–7).

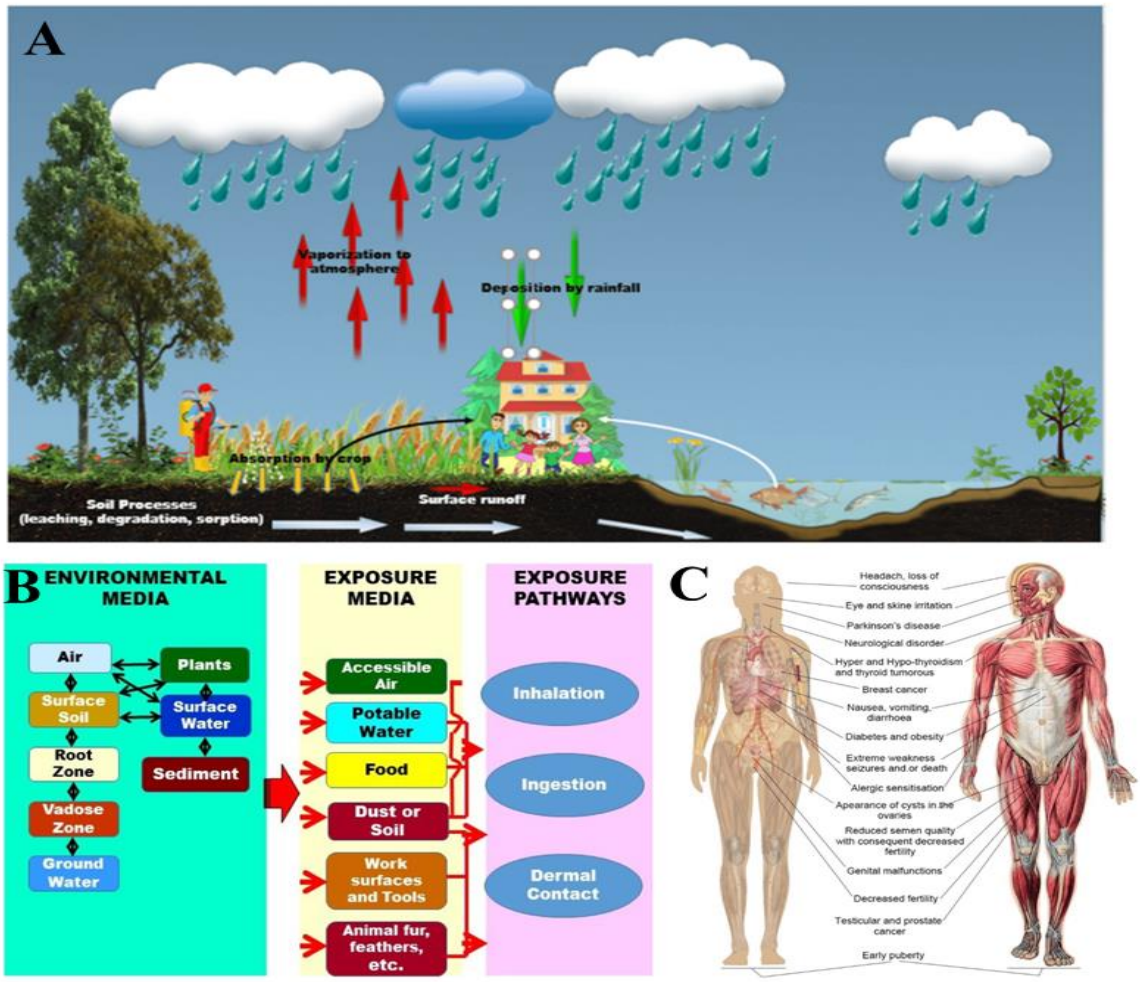

Figure 1. Pesticide behavior in the natural environment in a crop field (A), Routes of exposure to pesticides (B), and Health problems due to pesticide exposure (C). Reprinted with permission from (7).

Pesticides are classified into different categories based on their target pests, chemical structure, and mode of action. The main classifications include insecticides, herbicides, fungicides, and bactericides. Insecticide pesticides target

and control insect populations. They can be further categorized based on their mode of action, such as neurotoxins, growth regulators, and stomach poisons. Designed to control and eliminate weeds, herbicides are crucial for weed management in agriculture. They can be selective, targeting specific types of plants, or non-selective, affecting a broad range of plant species. Fungicides are used to prevent or control fungal diseases in crops, protecting plants from infections that can lead to reduced yield and quality. Moreover, bactericide pesticides specifically target bacteria, helping prevent the spread of bacterial diseases in plants (8,9).

Diphenyl ether pesticides, which belongs to herbicides class of pesticides, are the ones that interfere with the photosynthetic process in plants. A well-known example is acifluorfen which belongs to the isoxazolidinone family, and has been used for the control of annual grasses and broadleaf weeds in peanut, pea, celery, spinach, cotton, etc. Diphenyl ether herbicides inhibit the enzyme protoporphyrinogen oxidase (PPO), disrupting chlorophyll synthesis and causing damage to the plant's ability to photosynthesize. These herbicides are effective against a broad spectrum of weeds, and their mode of action makes them particularly useful for post-emergence applications. While diphenyl ether herbicides, such as acifluorfen, have proven effective in weed control, their use is not without potential negative effects on the environment and human health. Diphenyl ether herbicides can cause unintended damage to non-target plants. Their broad-spectrum activity may lead to the elimination of beneficial or native plant species in treated areas. Some diphenyl ether herbicides can persist in the environment, accumulating in soil and water. This persistence can contribute to long-term ecological impact and the potential for off-target effects on aquatic ecosystems. Residues of diphenyl ether herbicides may be present in crops, and their consumption can lead to human exposure. Therefore, authorized organizations closely monitor and set acceptable levels for pesticide residues in food to ensure they are within safe limits. Moreover, agricultural workers who handle and apply diphenyl ether herbicides are at risk of occupational exposure. This exposure can occur through skin contact, inhalation, or ingestion during the mixing and application processes, potentially leading to adverse health effects. Therefore, to reduce these negative effects, regular monitoring and analysis of diphenyl ether herbicides and taking necessary precautions have become a necessity (10–14).

The analysis of diphenyl ether herbicides is of paramount importance to ensure their effective and responsible use in agriculture while mitigating potential environmental and human health risks. Accurate quantification and identification of these herbicides are essential for regulatory compliance, as there are established maximum residue limits (MRLs) for pesticide residues in food products. Analytical methods, such as chromatography techniques (e.g., gas chromatography and liquid chromatography) coupled with mass spectrometry, play a key role in the sensitive and selective quantification of diphenyl ether herbicides in various matrices, including crops, soil, and water. However, these techniques often require sophisticated equipment and trained personnel, making them resource intensive. Additionally, the complexity of sample preparation in chromatography may pose challenges, leading to potential loss of analytes and increased analysis time. Moreover, the need for costly instrumentation and consumables can contribute to higher overall analysis costs, limiting accessibility for smaller laboratories or agricultural facilities (15–18).

Electrochemical methods offer distinct advantages over chromatographic methods in the quantification and identification of diphenyl ether herbicides. Electrochemical sensors are often more cost-effective, portable, and require simpler instrumentation, making them accessible for on-site and point-of-care applications. Additionally, these methods generally involve simpler sample preparation procedures, reducing the risk of analyte loss and enabling faster analysis times, while still providing high sensitivity and selectivity for diphenyl ether herbicide detection (19–21). The purpose of this comprehensive review is to critically examine and summarize the current state of electrochemical methods for the quantification and identification of diphenyl ether herbicides. This review systematically evaluates the advantages, limitations, and recent advances in electrochemical detection methods, contributing to a comprehensive understanding of their applicability and effectiveness in the analysis of diphenyl ether herbicides.

2. Superiority of Electrochemical Sensors for Diphenyl Ether Herbicides Determination

In analytical chemistry, electrochemical methods play a pivotal role in the

quantification and identification of compounds, offering advantages such as high sensitivity, rapid response, and cost-effectiveness. These methods find extensive use in environmental monitoring, pharmaceutical research, and medical diagnostics, allowing for the detection of pollutants, drug compounds, and biomarkers (22–25). Moreover, in materials science, electrochemical methods contribute to the development and characterization of novel materials, while in energy research, they are essential for investigating and optimizing electrochemical processes, such as those in batteries and fuel cells. The adaptability of electrochemical methods, coupled with their ability to provide real-time data, positions them as invaluable tools in advancing scientific knowledge, facilitating technological innovation, and addressing critical challenges in diverse fields (26–29).

Voltammetric methods are a subset of electrochemical methods that play a crucial role in diverse applications, offering unique advantages in analytical and research contexts. These methods, including cyclic voltammetry, differential pulse voltammetry, and square wave voltammetry, provide detailed insights into the electrochemical behavior of compounds by measuring the current response as a function of applied potential. Voltammetric approaches are particularly valuable in the quantification and identification of various analytes, ranging from organic and inorganic species to biomolecules. Their ability to offer information about redox processes, reaction kinetics, and thermodynamic parameters makes them indispensable in fields such as environmental monitoring, pharmaceutical analysis, and electrocatalysis (30–33).

Voltammetric methods in electrochemistry have been instrumental in the development of highly sensitive and selective sensors through the integration of nanomaterials. The use of voltammetry allows for the precise control of electrode potential and the measurement of current responses, making it ideal for characterizing the electrochemical behavior of nanomaterials. Nanomaterial-modified electrodes, fabricated using voltammetric methods, exhibit enhanced electrocatalytic activity, improved surface area, and excellent electron transfer kinetics. These features are particularly advantageous in sensor applications, where nanomaterials such as carbon-based structures, metal nanoparticles, and metal oxides significantly enhance the sensor's performance. The nanomaterial-modified electrodes not only enhance the sensor's sensitivity but also enable the selective

detection of target species. Therefore, the combination of voltammetric methods and nanomaterials represents a powerful synergy, fostering the development of cutting-edge electrochemical sensors that exhibit improved analytical performance, increased stability, and expanded applicability in various fields. Furthermore, voltammetric biosensors leverage the specificity and selectivity of biological recognition elements, such as enzymes, antibodies, or DNA, in conjunction with the precise control of electrode potential provided by voltammetry. This synergy results in biosensors that are highly sensitive and capable of detecting specific molecules with exceptional accuracy. In this review, applications of different diphenyl ether herbicides using voltammetric methods are presented in the next section. In this context, all bare, nanosensor, and biosensor-based applications are mentioned (34–38).

3. Comprehensive Overview of Current Applications

In 2013, Inam and Cakmak developed the square wave voltammetry (SWV) method for the determination of aclonifen. In this study for the first time, a cyclic voltammogram of aclonifen was observedutilizing a bare glassy carbon electrode (GCE) at pH 4.0. rDistinct anodic and cathodic peaks at +1175 mV and +350 mV respectively were revealed. The sensitive voltammetric anodic peak at +1220 mV exhibited linearity with aclonifen concentrations ranging from 0.245 to 3.70 µg/mL. Notably, the developed method demonstrated a low limit of detection (LOD) of 0.073 µg/mL and a limit of quantification (LOQ) of 0.245 µg/mL. In soil and water samples spiked with aclonifen, percent recoveries were 98.80% and 102.40%, respectively, with relative standard deviations (RSD) of 1.82% and 3.61%. These findings underscored the accuracy and precision of the proposed electrochemical method, as evidenced by high recoveries and low standard deviations (39).

In another study conducted by Demir and Inam, to elucidate the electrochemical behavior of the fomesafen herbicide, cyclic voltammetry (CV) and SWV measurements were conducted using multiwall carbon nanotube paste electrodes (MWCNTPE). In this study, pH variations were explored, revealing that protons played a role in the electro-reduction process, as indicated by the E_p versus pH plot. The electrochemical studies attributed the reduction process to the $–NO_2$ group. Constructing a linear relationship within the concentration range of 0.30-40 mg/L, the method yielded LOD (0.089 mg/L) and

LOQ (0.297 mg/L). Fomesafen determination in the presence of other pesticides showed recoveries of 103.7±0.9%, 94.3±0.4%, and 97.9±0.5% for anilazine, pymetrozine, and triflumizole, respectively. The accuracy of the method was corroborated by analyzing fomesafen in spiked real samples (apricot juice, cherry juice, and lake water), resulting in relative errors of -4.2%, -2.8%, and -1.8%, respectively. These findings affirmed the recommended method's accuracy, selectivity, and precision (40).

In today's technology, the incorporation of nanomaterials in electrochemical sensors represents a transformative approach, harnessing the unique properties of nanoscale materials to enhance sensitivity, selectivity, and overall performance, thereby unlocking new dimensions in the realm of analytical chemistry. Therefore, nanomaterial-based sensors are frequently preferred in the determination of herbicides, as in many areas (41–43). In the study of Chen et al., a nanocomposite featuring silver nanoparticles decorated iron pyrite flowers (FeS_2@Ag NL) was successfully synthesized using a sonochemical method (**Figure 2)**, as confirmed by various analytical techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HR-TEM). This nanocomposite was integrated into a screen-printed carbon electrode (SPCE) to fabricate an efficient sensor platform for the electrochemical detection of the herbicide acifluorfen. Under optimal conditions, illustrating the remarkable electrocatalytic efficacy, the FeS_2@Ag NL-modified SPCE showcased superior performance in facilitating the electrochemical reduction of acifluorfen. Utilizing differential pulse voltammetry (DPV) under optimized conditions, the FeS_2@Ag NL/SPCE sensor exhibited a linear relationship between current and concentration in the range of 0.05-1126.45 µM for acifluorfen, with a low LOD of 0.0025 µM. The modified sensor demonstrated exceptional electrochemical performance characterized by a broad linear range, nanomolar detection limit, high sensitivity, and excellent stability. Importantly, the practical utility of the sensor was demonstrated by successfully quantifying acifluorfen concentrations in biological samples (44).

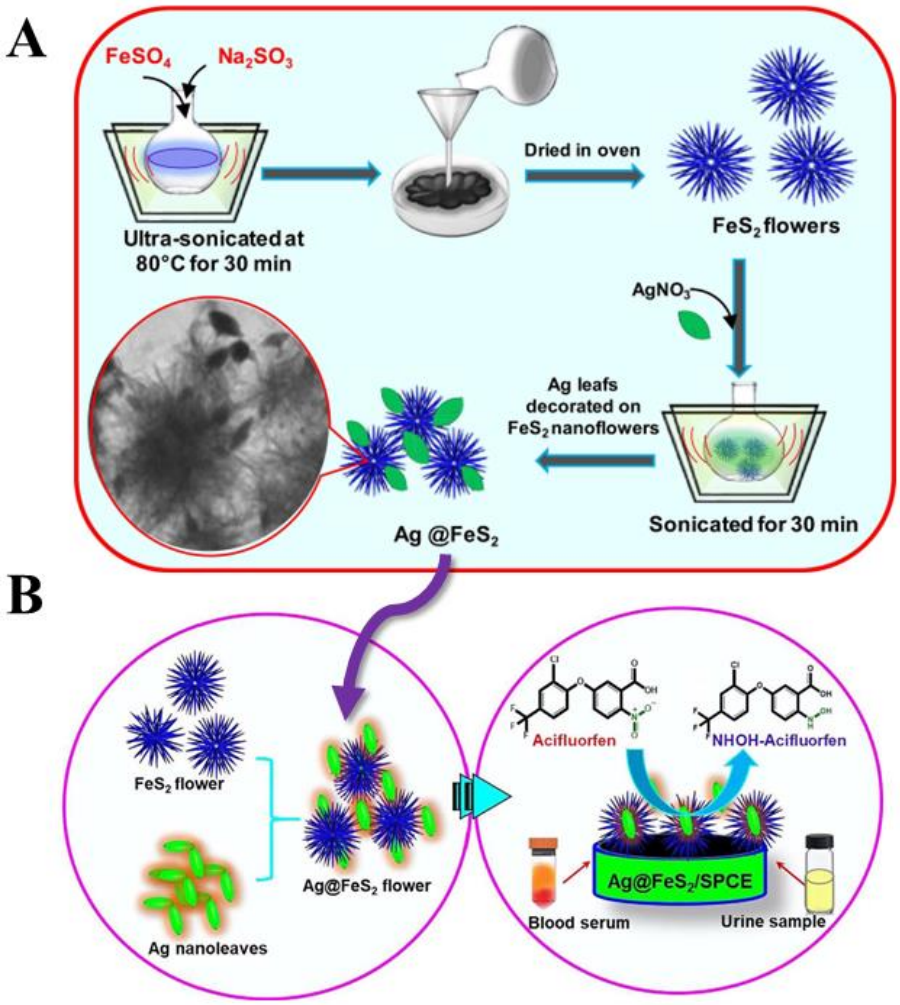

Figure 2. The synthetic route for FeS_2@Ag NL nanocomposite (A), a sensitive electrochemical determination of acifluorfen based on FeS_2@Ag NL nanocomposite modified SPCE (B). Reprinted with permission from (44).

The study conducted by Gopi et al., investigated the voltammetric analysis of the herbicide aclonifen in real soil and river water samples using an electrochemical method. A novel sensing device for aclonifen determination was developed, employing a GCE modified with gadolinium niobate ($GdNbO_4$) nanoparticles. The $GdNbO_4$ sensing material was synthesized through a straightforward co-precipitation method, and its structural features were thoroughly characterized using TEM, XRD, XPS, Energy dispersive spectrometry (EDS), and Brunauer-Emmett-Teller (BET) techniques (**Figure 3A**). Comparative analyses indicated improved electrochemical behavior of the $GdNbO_4$-modified GCE towards aclonifen in comparison to the bare GCE. CV responses highlighted the lower negative potential and a significant increase in the peak current of aclonifen on the prepared sensor compared to the bare GCE. In DPV, the aclonifen LOD (1.15

nM) and sensitivity (23 μA μM^{-1} cm^{-2}) on the $GdNbO_4$-modified GCE surpassed those of previously proposed aclonifen-based sensors (**Figure 3B and 3C**). The sensor demonstrated excellent selectivity, repeatability, reproducibility, and long-term stability, exhibiting satisfactory recovery results in the detection of aclonifen in river water (**Figure 3D**) and soil (**Figure 3E**) samples (45).

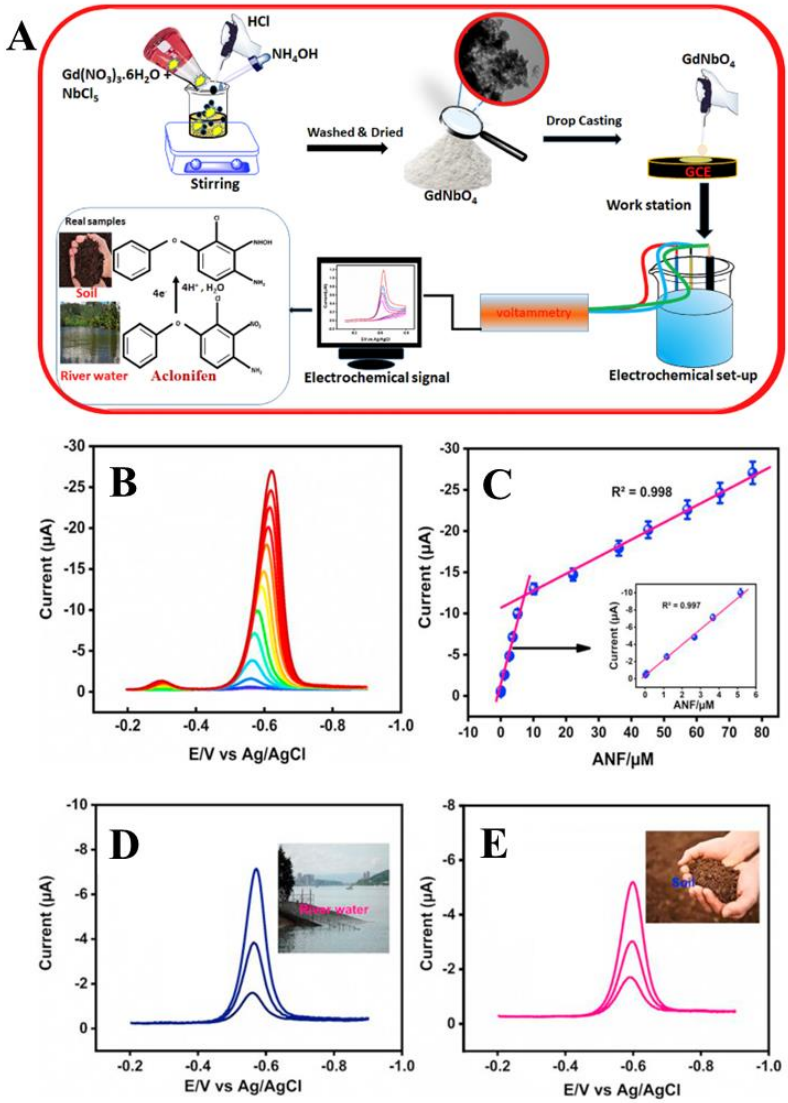

Figure 3. Pictorial representation of the formation of $GdNbO_4$ nanoparticles and its application of the electrochemical reduction of aclonifen (A), DPV response of $GdNbO_4$ modified GCE in 0.1 M acetate buffer with various concentrations of aclonifen (0.02-78 μM) at 50 mV/s (B), the linear plot between the current response vs. concentration of aclonifen (C), DPV response of the $GdNbO_4$ modified GCE for the real sample analysis in 0.1 M acetate buffer with aclonifen (2-4 μM) spiked river water (D) and soil samples at 50 mV/s (E). Reprinted with permission from (45).

The integration of biological materials into electrochemical systems presents a useful system, harnessing the unique biological recognition elements to enhance

specificity, sensitivity, and functionality, thereby advancing the capabilities of electrochemical sensors for precise and selective analyte detection. Compared to other biomolecules, enzymes stand out in biosensors due to their unparalleled catalytic efficiency, substrate specificity, and ability to operate under mild conditions. Their exceptional selectivity and catalytic activity make enzymes superior to other biological molecules in facilitating highly specific and efficient recognition of target analytes, rendering them invaluable components in biosensor applications as in the determination of diphenyl ether herbicides (46–48).

In the study of Chen et al leveraging the customizable structure of hollow hierarchical porous ($Cu_3(BTC)_2(H_2O)_3$, BTC = 1, 3, 5-benzenetricarboxylate) (Cu-BTC) with cuprous oxide (Cu_2O) as the template immobilized the *Candida rugosa* lipase (CRL) enzyme, boosting loading capacity by approximately 1.89 times compared to microporous Cu-BTC. The resulting CRL@HH-Cu-BTC, where CRL is immobilized cross-linked enzyme crystals, exhibited enhanced pH resistance, thermal stability, and recyclability due to the favorable microenvironment provided by the hollow hierarchical porous structure. The designed biosensor (**Figure 4**) displayed a linear detection range (0-78 μM), a low LOD of 1.15 μM, and remarkable recovery, offering advantages in cost-effectiveness, rapid response, and straightforward device assembly for the diphenyl ether pesticide nitrofen detection (49).

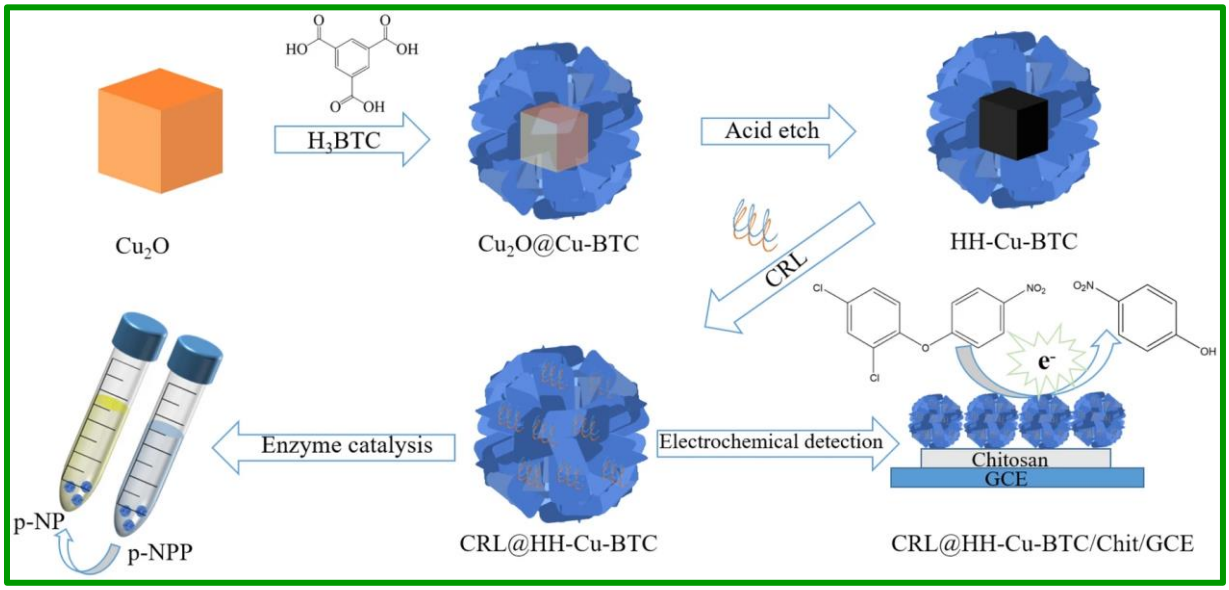

Figure 4. Schematic of the preparation of CRL@HH-Cu-BTC and the formation of electrochemical biosensor. Reprinted with permission from (49).

However, immobilization of enzymes to surfaces often causes conformational changes in lipases, which reduces lipase catalytic activity. Therefore, increasing the stability of lipase enzymes increases the commercial value and industrial applications of lipase. In other enzyme-based sensors for the sensitive determination of the diphenyl ether herbicide nitrofen, the stabilities of CRL and *Burkholderia cepacia* lipase (BCL) using metal-organic framework (MOFs) (50) and zeolitic imidazolate framework (ZIF) (51) were increased and used in electrochemical biosensor designs. In this way, the designed biosensors showed superior performance compared to other methods.

In this context, the applications of bare, nanomaterial, and enzyme-based sensors for the electrochemical determination of diphenyl ether group herbicides are presented in detail in **Table 1**. The selected sensor designs, experimental conditions, and some basic validation parameters are summarized in this table.

Table 1. Selected literature studies on the analysis of diphenyl ether herbicides from different samples using electrochemical methods.

Pesticide	Method	Sensor platform	Linear range	LOD	Application	Ref.
Aclonifen	SWV	GCE	0.245-3.70 µg/mL	0.073 µg/mL	Soil and water samples	(39)
Fomesafen	SWV	MWCNTPE	0.30-40 mg/L	0.089 mg/L	Apricot and cherry juice and lake water samples	(40)
Acifluorfen	DPV	FeS_2@Ag NL/SPCE	0.05-1126.45 µM	0.0025 µM	Human urine and blood serum samples	(44)
Aclonifen	DPV	$GdNbO_4$/GCE	0.02–78 µM	1.15 nM	Soil and river water samples	(45)
Nitrofen	CV	GCE/Chit/CRL@HH-Cu-BTC	0-78 µM	1.15 µM	Apples samples	(49)
Nitrofen	CV	GCE/Chit/CRL@UIO-66	0-100 µM	0.026 µM	Apricot samples	(50)

		GCE/Chit/CRL@UIO-66/Pro		0.026 µM		
Nitrofen	CV	GCE/Chit/nano-BCL@ZIF-8	0-114 µM	0.46 µM	Apricot samples	(51)
Oxyfluorfen	DPSV	MoO_2-MWCNT/GCE	2.5-34.5 ng/mL	1.5 ng/mL	River water samples	(52)
Chlornitrofen	SWAdS	Hg(Ag)FE	1.0×10^{-7}-1.5×10^{-6} M	3.0×10^{-8} M	River water samples	(53)
Chlornitrofen	CV	CRL@MAC-ZIF-8/Chit/GCE	1-40 µM	0.03 µM	Water samples	(54)
Aclonifen	SWV	g-C_3N_4/GCE	0.01-1.2 µM	1.28 nM	Wastewater and soil samples.	(55)
Aclonifen	DPV	PNIPAM/PANI-Cu/GCE	0.01-10 µM and 18-76 µM	0.009 µM	Lake water samples	(56)
Bifenox	SWV	MWCNT/GCE	0.2-60.0 µM	0.08 µM	River water samples	(57)
Bifenox	SWV	$MnFe_2O_4$@CTS/GCE	0.3-4.4 µM	0.09 µM	Tap and river water samples	(58)
Bifenox	DPV	m-AgSAE	6.7×10^{-7}-6.9×10^{-7} M	0.9×10^{-9} M	Drinking and river water samples	(59)
Bifenox	DPV	$BiVO_4$/GCE	0.1-20 nM	0.3 nM	Water samples	(60)

Abbreviations: BCL: *Burkholderia cepacia* lipase; $BiVO_4$: Bismuth vanadate; BTC:1, 3, 5-benzenetricarboxylate; Chit: Chitosan; CRL: *Candida rugosa* lipase; CV: Cyclic voltammetry; DPSV: Differential pulse stripping voltammetry; DPV: Differential pulse voltammetry; FeS_2@Ag NL: Silver nanoparticles decorated iron pyrite flowers; GCE: Glassy carbon electrode; g-C_3N_4: Graphitic carbon nitride; $GdNbO_4$: Gadolinium niobate; HH-Cu: hollow hierarchical porous Cu; Hg(Ag)FE: Silver amalgam film electrode; MAC: Ordered macro-microporous; m-AgSAE: Meniscus modified silver solid amalgam electrode; $MnFe_2O_4$@CTS: Chitosan-coated manganese ferrite nanoparticles; MWCNTPE: Multiwall carbon nanotube; MWCNTPE: Multiwall carbon nanotube paste electrode; PANI: poly(aniline); PNIPAM: poly(N-isopropylacrylamide); Pro: Proline; SPCE: Screen-printed carbon electrode; SWAdS: Square-wave adsorptive stripping voltammetry; SWV: Square wave Voltammetry; ZIF: Zeolitic imidazolate skeleton.

4. Conclusions

In conclusion, this comprehensive review discussed contemporary landscape of electrochemical methods for the sensitive determination of diphenyl ether herbicides, emphasizing their paramount significance in modern analytical practices. The versatility and efficiency of electrochemical techniques, such as cyclic voltammetry, differential pulse

voltammetry, and square wave voltammetry, have been showcased, underlining their pivotal role in herbicide analysis. The exploration of the electrochemical behavior of diphenyl ether herbicides provided valuable insights into their redox processes and mechanisms, contributing to a deeper understanding of their detection principles. The review underscored the advantages of electrochemical sensors, including real-time monitoring, cost-effectiveness, and portability, which position them as indispensable tools in herbicide analysis. As we navigate the intricate dynamics of pesticide detection and environmental monitoring, this review serves as a comprehensive resource for researchers, offering a contemporary perspective on the current applications and advantages of electrochemical methods.

5. Ethics approval and consent to participate

This study does not need any Ethics report.

6. Consent for publication

The Authors give consent for publication.

7. Availability of data and materials

All data and materials of the paper are available to the public.

8. Authors' contributions

Cem Erkmen: Conceptualization, Supervision, Writing-review & editing, Funding acquisition, Damla Selcuk: Writing- original draft, Rafia Nimal: Supervision, Writing-review & editing.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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