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Pesticide biosensors: trends and progresses

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Abstract

Pesticides, chemical substances extensively employed in agriculture to optimize crop yields, pose potential risks to human and environmental health. Consequently, regulatory frameworks are in place to restrict pesticide residue concentrations in water intended for human consumption. These regulations are implemented to safeguard consumer safety and mitigate any adverse effects on the environment and public health. Although Gas Chromatography- and Liquid Chromatography- Mass Spectrometry (GC-MS and LC-MS) are highly efficient techniques for pesticides quantification, their use is not suitable for real-time monitoring due to the need for sophisticated laboratory pretreatment of samples prior to analysis. Since they would enable analyte detection with selectivity and sensitivity without sample pretreatment, biosensors appear as a promising alternative. These consist of a bioreceptor allowing for specific recognition of the target and of a detection platform, which translates the biological interaction into a measurable signal. As early detection systems remain urgently needed to

promptly alert and act in case of pollution, we review here the biosensors described in the literature for pesticide detection to advance their development for use on field.

Introduction

Pesticides are essential for agriculture to increase crop yields and to provide suitable food production levels. Since their launch, they enabled substantial economic benefits and are thus widely utilized [1]. However, their widespread use concomitantly affects our health [2–5] and our environment [6, 7]. The International Agency for Research on Cancer (IARC) plays a crucial role in assessing the impact of pesticides on human health. As a renowned authority in identifying carcinogenic agents, it provides valuable information to decision-making bodies responsible for alerting and safeguarding the public from cancer-causing agents found in food, the environment, and workplaces. Notably, the IARC has classified s-metolachlor, a pesticide of particular concern in France, as probably carcinogenic. In response, the French Agency for Food, Environmental and Occupational Health & Safety (ANSES) has taken steps to phase out its primary use in phytopharmaceuticals [8]. Additionally, the IARC has classified other pesticides, such as captafol (a fungicide used in seed treatments), chlordane, dichlorvos, and heptachlorophenol, as probably carcinogenic [9]. These assessments highlight the importance of rigorous monitoring and control measures to mitigate the potential health risks associated with these substances.

The use of pesticides also leads to the contamination of surface waters [6, 7, 10]. Over the last 20-25 years [11], public concerns about the presence of pesticide residues in food and drinking water raised, leading to the implementation of strict regulations by legislative authorities in order to control the quality of consumer products and especially of drinking water. According to the 98/83/EC EU Directive, specific regulations have been implemented regarding the quality limits of pesticides active substances and their relevant metabolites in water. The general quality limit is set at $0.1 \mu\text{g L}^{-1}$ per individual substance for most pesticides. However, certain highly

toxic substances such as aldrin, dieldrin, heptachlor, and heptachlor epoxide are currently banned, and their quality limit is set at a stricter level of $0.03 \mu\text{g L}^{-1}$. Additionally, to address the potential simultaneous presence of multiple pesticides and relevant metabolites, a cumulative approach is adopted. The sum of concentrations of all pesticides and relevant metabolites in water should not exceed $0.5 \mu\text{g L}^{-1}$, considering the combined effect of these substances. In parallel, the EU Directive No 396/2005 ensures the quality of food products by setting Maximum Residue Limits (MRLs) for pesticides that may be present. These MRLs are continuously updated to accommodate the introduction of new pesticides on the market, reflecting the dynamic nature of agricultural practices.

These regulations are designed to ensure the safety and quality of water resources, considering both individual substances and their potential cumulative impact on water quality.

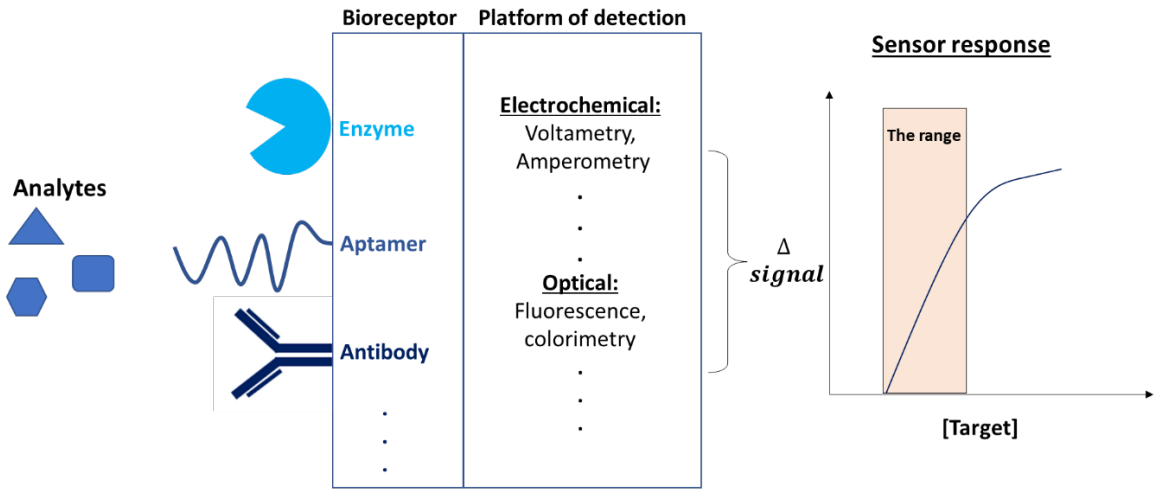
To detect pesticides at the concentration limits set by the competent authorities, sophisticated techniques are required. Gas chromatography and liquid chromatography coupled with mass spectrometry (GC-MS and LC-MS) are classical techniques used for the sensitive, selective and reproducible analysis of pesticide residues in water [12–15]. Although these techniques are well suited for the quantification of pesticides, the samples studied must be pre-treated and then analyzed in sophisticated laboratories, which renders these techniques unsuitable for survey analyses of running water that require monitoring at a suitable frequency to detect an eventual pollution peak in real time and to promptly take an action. In order to meet these requirements, increasing efforts are devoted to explore alternative measures to detect pesticides with selectivity and sensitivity. Biosensors appear as elegant tools to replace conventional methods as they could enable the detection of analytes in real time, minimizing tedious sample pretreatments. **Table 1** shows a detailed comparison of critical properties between classical techniques and biosensors employed for the detection of pesticides.

Table 1 Comparison of characteristic parameters between traditional analytical techniques and biosensors employed for the detection of pesticides.

Parameters	Traditional Analytical Techniques	Biosensors
Analysis time	Collection of samples, storage, and transport	Limited sample preparation, rapid monitoring
Cost	Sophisticated laboratory detection, high-tech equipment, trained laboratory personnel	Cost-effective, portable and simple in-situ detection
Eco-friendly and reusability	More organic solvent consumption, Not reusable	No organic solvent used, reusable
Sensitivity and selectivity	Highly sensitive and selective	Sensitive and specific
Commercialization	/	Limited commercial applications

A biosensor is the combination of a bioreceptor and of a detection platform (**Figure 1**). The bioreceptor is a biological molecule that allows the specific recognition of the target, whereas detection platform translates the biologic interaction into a measurable, optical, magnetic or electrochemical signal [16–18].

Fig. 1



Schematic illustration of the different types of bioreceptors and transducers used in a biosensor. Due to their high sensitivity, electrochemical platforms are extensively used in pesticide biosensors [19–21]. In parallel, and due to their ease of use, simple detection techniques, and satisfactory sensitivity, optical biosensors are also largely used in biosensors developed for the detection of pesticides [20, 22].

Different types of biomolecules have been employed in biosensors, mainly antibodies, enzymes and aptamers [23]. These biomolecules, due to their nature, undergo specific recognition with their target by different types of interaction, notably electrostatic interactions, hydrogen bonding, aromatic ring stacking and van der Waals interactions. The bioreceptor ensures the specificity of the analysis, whereas the sensitivity is ensured by the detection platform. Biosensors, as point-of-care devices, offer advantages such as rapid detection, user-friendliness, accuracy, portability, cost-effectiveness and easy on-site detection [24, 25]. This review covers the bioreceptors the most used and investigated for biosensors development for on-site monitoring of pesticides, namely antibodies, enzymes and aptamers. Aptamers, which can be considered as chemical antibodies, are synthetic biological molecules that have been widely investigated in the last decade to develop biosensors for detecting pesticides. In this context, an in-depth description of the use of aptasensors as tools for pesticide detection is also reported here.

I. Enzyme-based biosensors

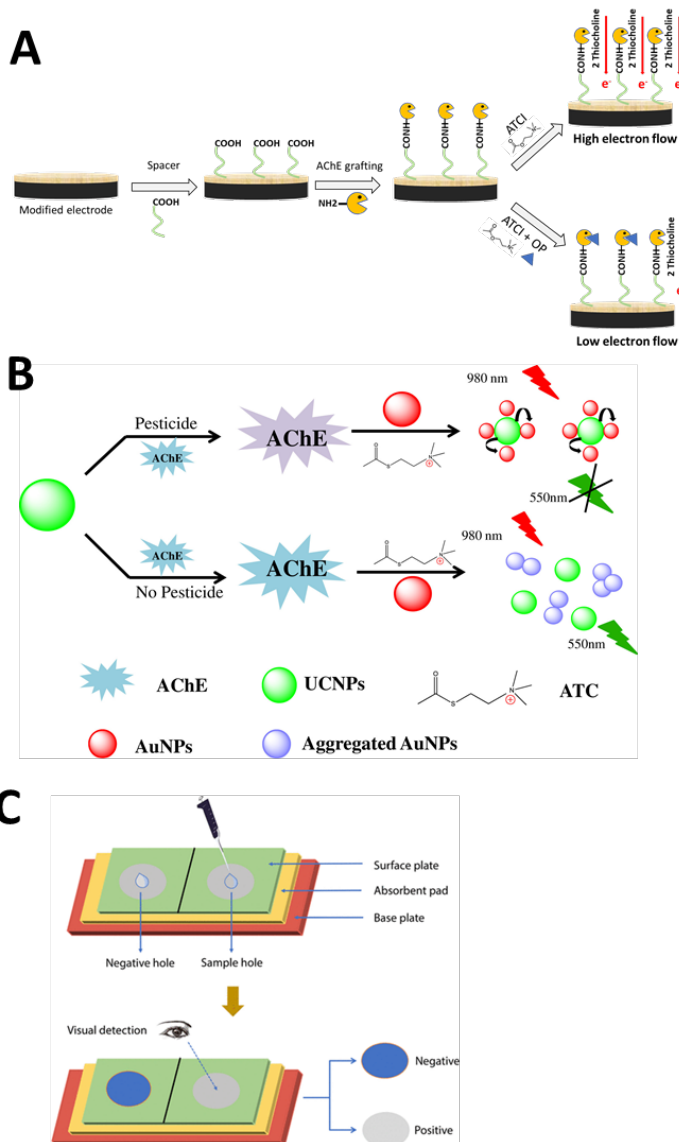
Owing to their high selectivity for their substrates to which they bind and drive catalytic reactions, enzymes are of high potential for biosensors development. They are commonly used for the detection of organophosphate (OP) and carbamate pesticides that inhibit the activity of acetylcholinesterase (AChE), an essential enzyme for the functioning of the central nervous system [26]. The inhibition of AChE by OP and carbamate pesticides takes place via a phosphorylation mechanism, which blocks serine in the active site through a nucleophilic attack and production of a serine phosphoester [27]. On the basis of this reaction scheme, the electrochemical and optical recording of the enzymatic activity reduction enables the detection of this particular type of pesticide in the matrices to be analyzed. Butyrylcholinesterase (BChE) [28], tyrosinase [29, 30], alkaline phosphatase [31, 32], peroxidase [33], acid phosphatase [34] urease [35] and exonuclease I [36] were also used in inhibition-based pesticide biosensors. As

described below, several enzyme-based biosensors were reported for pesticides detection, based on electrochemical and optical transduction [37–39].

I.1. Enzymatic inhibition-based electrochemical biosensors

Electrochemical detection methods, including cyclic voltammetry, alternating current voltammetry (ACV), electrochemical impedance spectroscopy (EIS), square wave voltammetry (SWV), differential pulse voltammetry, photoelectrochemical, and electrochemiluminescence, enable the rapid and sensitive detection of redox-active target analytes without requiring complex sample pre-treatment [40]. These electrochemical techniques generate target-induced signals specifically triggered by the presence of the analyte, allowing for its accurate detection and quantification. In particular, enzyme inhibition-based electrochemical biosensors have emerged as a promising approach for pesticide detection (**Figure 2(A)**), enabling real-time and on-site monitoring of pesticide residues. These biosensors utilize the inhibition of enzymatic activity to achieve precise and frequency-appropriate detection of pesticides, making them valuable tools in pesticide analysis and environmental monitoring.

Fig. 2

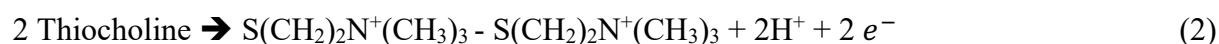


Comparative schematic diagram of AChE inhibition-based: (A) electrochemical, (B) fluorometric, and (C) colorimetric biosensors for detection of organophosphorus compounds. (B) Reprinted from [41], with permission from Elsevier. (C) Reprinted from [42], with permission from American Chemical Society.

I.1.1. Differential pulse voltammetry

Chauhan et al. [37] have selectively detected several organophosphorus pesticides (malathion, chlorpyrifos, monocrotophos and endosulfan) with a high sensitivity by covalently immobilizing AChE onto iron oxide nanoparticles (Fe₃O₄NPs) and carboxylated multiwalled

carbon nanotubes (c-MWCNTs) modified Au electrodes. The acetylcholine (ATCI) is enzymatically hydrolyzed by AChE into thiocholine that undergoes electrocatalytic oxidative dimerization at +0.4 V vs. an Ag/AgCl reference electrode and produces a disulphide compound. The oxidation of thiocholine at the working electrode surface (equations 1 and 2) is correlated to the activity of AChE.



In the presence of pesticides, AChE activity is reduced involving a decrease of thiocholine production, resulting in a decreased electrical signal which is proportional to pesticides concentration. Under optimal conditions, the degree of inhibition caused by those pesticides was found to be directly proportional to their concentrations, within the following ranges: 0.1-40 nM for malathion, 0.1-50 nM for chlorpyrifos, 1-50 nM for monocrotophos, and 10-100 nM for endosulfan. The detection limits were determined to be 0.1 nM for malathion and chlorpyrifos, 1 nM for monocrotophos, and 10 nM for endosulfan.

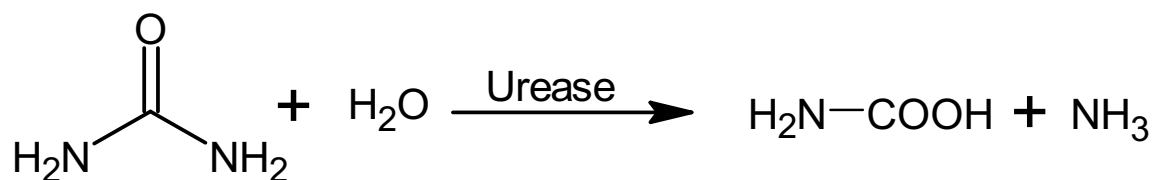
Ma et al. [43] have described the fabrication of PtPd@NCS core-shell structured nanocomposites consisting of a bimetal core (Pt and Pd) encased in an N-doped carbon shell (NCS). The nanocomposites were prepared using a simple one-pot approach, involving reduction of metal salt precursors, self-polymerization of dopamine, and co-assembly of Pluronic F127. The nanocomposites were then used to prepare an AChE-inhibition based biosensor for detecting the following organophosphate pesticides: malathion, chlorpyrifos and parathion methyl. The inhibition rate is defined following equation 3 where I_0 represents the original signal recorded by DPV measurements with the as-prepared AChE/PtPd@NCS/graphene carbon electrode (GCE) biosensor in phosphate buffer saline (PBS, pH 7.5) containing ATCI (2.0 mM). I_1 represents the residual signal.

$$\text{Inhibition (\%)} = \frac{I_0 - I_1}{I_0} \times 100\% \quad (3)$$

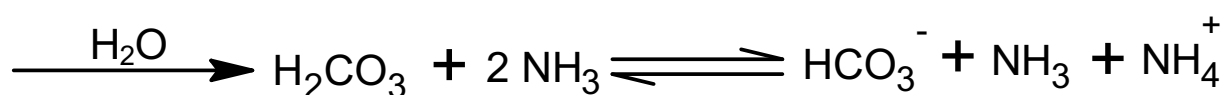
The biosensor functions in a linear detection range for each pesticide, at extremely low limits of detection in the range of femtomoles to attomoles (7.9×10^{-15} M, 7.1×10^{-14} M, and 8.6×10^{-15} M for malathion, chlorpyrifos, and parathion-methyl, respectively). These results underscore the exceptional sensitivity of the AChE biosensor prepared using PtPd@NCS nanocomposites. Recently, nanozyme-based biosensors also show tremendous potential for pesticide detection [44]. In their study, Wu et al. [45] presented an innovative electrochemical biosensor for detecting organophosphate pesticides using a two-dimensional MnO₂ nanozyme by DPV measurements. The researchers used manganese dioxide nanosheets (MnNS), more specifically two-dimensional (2D) MnO₂ sheets, in conjunction with acetylcholinesterase (AChE) to create a homogeneous electrochemical biosensor. This novel biosensor demonstrated excellent performance, exhibiting a linear response for paraoxon in the 0.1 to 20 $\mu\text{g L}^{-1}$ range, with a LOD of 0.025 $\mu\text{g L}^{-1}$. Importantly, these results align with the maximum residue limit (MRL) requirements established by the European Union (EU).

1.1.2. Potentiometry

Vaghela et al. [35] have described a potentiometric electrochemical biosensor based on bio-nanoconjugate of urease with gold nanoparticles (AuNPs) entrapped in agarose-guar gum to detect glyphosate. The action of urease catalyzes the formation of ammonium ions (equation 4) that are measured by their selective electrode. In the presence of glyphosate, the urease activity is inhibited, leading in a decrease of ammonium ions formation. According to this inhibition mechanism, the decrease in potentiometric signal indicates the presence of glyphosate and can be used for its detection.



(4)



181 According to this mechanism of detection, a linear response with respect to glyphosate
182 concentration is obtained in the range of 0.5 to 50 $\mu\text{g L}^{-1}$, which is within the maximum residual
183 limit established by the World Health Organization (WHO).

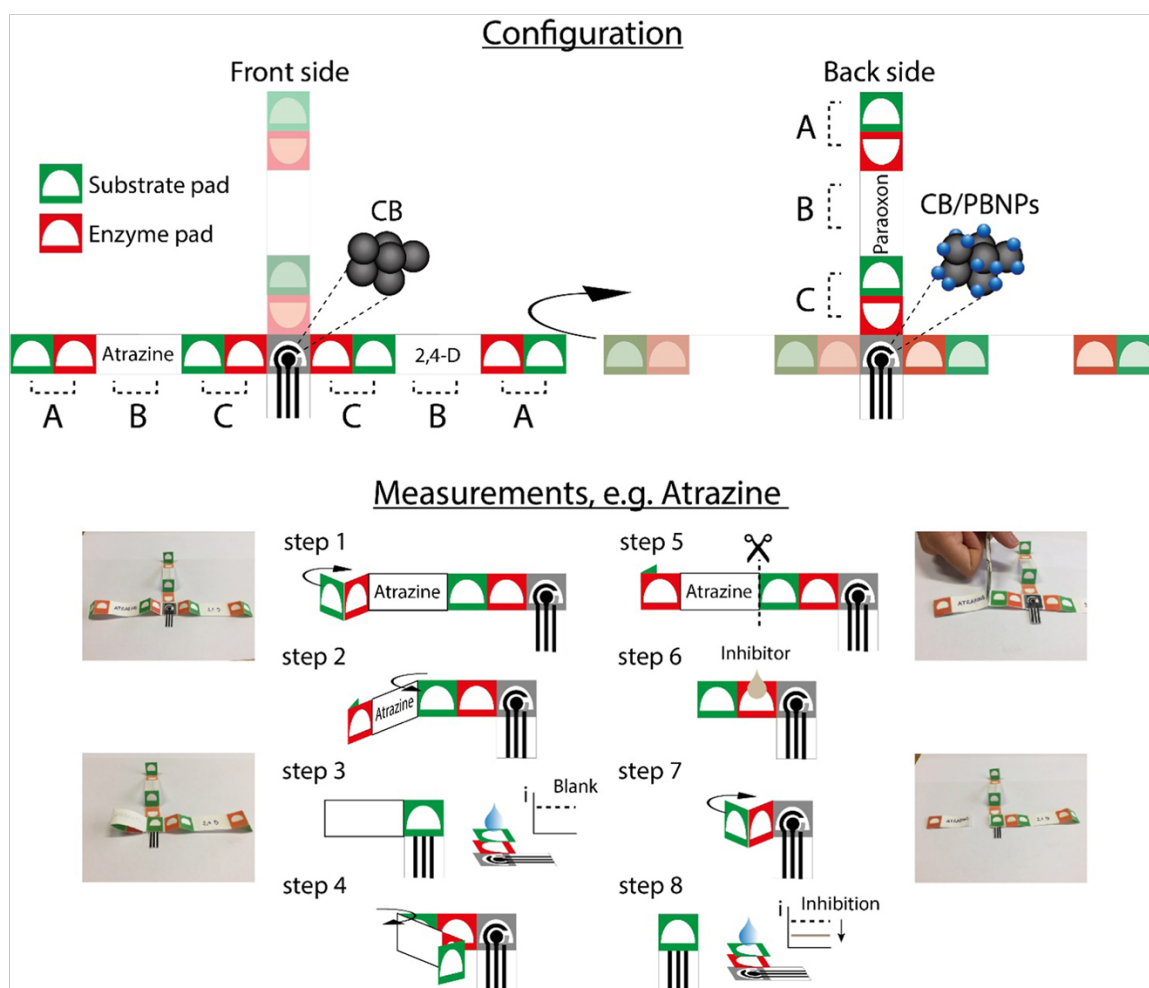
184 1.1.3. Cyclic voltammetry

185 Five pesticides were detected by glutathione-S-transferase (GST) based electrochemical
186 biosensing: carbendazim, chlorpyrifos, dichlorodiphenyltrichloroethane (DDT), dinocap and
187 ethion [46]. Cyclic voltammetry was used to detect all five pesticides. GST was immobilized
188 onto platinum electrodes using a graphene oxide-gelatin matrix. The immobilization of GST
189 was confirmed through cyclic voltammetry, electrochemical impedance spectroscopy, scanning
190 electron microscopy and chronoamperometry. The developed GST biosensor has several
191 advantages over other biosensors: it is cost effective as it is reusable for 8-10 consecutive
192 measurements, and real-time monitoring was demonstrated when using the
193 chronoamperometric mode.

194 1.1.4. Chronoamperometry

195 BChE, alkaline phosphatase and tyrosinase were used to develop a novel three-dimensional
196 origami paper-based device that utilizes enzyme-inhibition to detect several pesticides:
197 paraxon, 2,4-dichlorophenoxyacetic acid and atrazine [28]. This device combines two office
198 paper-based screen-printed electrodes with multiple filter paper-based pads for loading
199 enzymes and their substrates. By folding and unfolding the filter paper-based structure, the
200 device can analyze pesticides without any need for reagents or sample treatment (**Figure 3**).

Fig. 3



Schematic illustration of configuration and measurement procedure of the paper-based platform. Reprinted from [28], with permission from Elsevier.

The paper-based platform is advantageous due to its low cost, portability, and ability to analyze multiple pesticides. However, it is based on enzyme inhibition and may not be suitable for detecting certain types of pesticides. Zhao et al. [47] reported on an electrochemical sensor based on AChE inhibition to detect paraoxon. The mentioned biosensor is composed of a screen-printed carbon electrode (SPCE) modified with electrodeposited gold nanoparticles (AuNPs) on which MoS₂ nanosheets were immobilized. AChE was immobilized in the last step onto MoS₂ via a glutaraldehyde crosslinker. Using amperometry under optimized conditions, paraoxon could be detected at a very low limit of detection (LOD = 0.013 $\mu\text{g L}^{-1}$).

1.2. Optical biosensors

Although enzyme-based biosensors relying on electrochemical detection are highly sensitive and could be used for real time detection of pesticides, the immobilization of enzymes on the electrode surface is generally tedious and time consuming. In order to overcome these difficulties, optical biosensors have been used as an alternative since they are reliable, easy to use, fast and reveal high sensitivity.

1.2.1. Fluorescence spectroscopy

A fluorometric AChE-based biosensor allowed the rapid, simple and sensitive detection of parathion-methyl (**Figure 2(B)**) [41]. Gold nanoparticles immobilized on the surface of NaYF₄:Yb,Er up-conversion nanoparticles (UCNPs) enable fluorescence resonance energy transfer (FRET). Thiocholine present in the solution, after hydrolysis of acetylthiocholine by AChE, interacts with the AuNPs via electrostatic interactions preventing the formation of AuNPs-UCNP complexes, which leads to an increased fluorescence signal. In the presence of parathion-methyl, AChE activity is inhibited, thus preventing the production of thiocholine, which favors the FRET phenomenon, and thus the decrease of fluorescence. The biosensor developed in this study exhibited high sensitivity and stability, indicating its potential for detecting organophosphate pesticides in real samples. Moreover, the biosensor preparation process is less time-consuming compared to grafted enzyme biosensors as the enzyme is not immobilized onto the nanoparticle surfaces but only adsorbed. This advantageous feature makes the biosensor a promising tool for practical applications in detecting pesticides.

1.2.2. Colorimetric assay

The rapid and onsite detection of several pesticides remains challenging, like glyphosate, which is of high polarity, has metal-chelating properties and interfere with organic substances in the environment. Besides, its similarity with its by-products renders its detection difficult. Enzyme-based methods along with colorimetric detection reveal several advantages matching with glyphosate analysis, i. e. simple preparation, rapid detection and ease of results acquisition [48,

49]. Luo et al. [42] have reported a novel colorimetric nanozyme sheet for the rapid detection of glyphosate (**Figure 2(C)**). Physically adsorbed peroxidase enzymes catalyze the oxidation of chromogenic substrates to produce a color change, the intensity of which is measured by UV-Visible spectrophotometry. In the presence of glyphosate, peroxidase is inhibited which results in a decrease of the color intensity.

Targeting the same glyphosate analyte, Li Haiyin et al. [50] have reported a peroxidase-mimetic nanozyme to develop a portable Paper-based Analytical Device (PAD) allowing for its detection. In this article, the preparation of 2D nanosheet-like V_2O_5 (2D-VONz) with exclusive peroxidase-mimetic activity under optimal reaction conditions is described. Interestingly, the activity of 2D-VONz is inhibited by glyphosate, which was then exploited to develop a PAD, on which, glyphosate reduces the activity of 2D-VONz to prevent the catalytic oxidation of 3,3',5,5'-tetramethylbenzidine, thus contributing to rapid, naked-eye and portable analysis of glyphosate using a smartphone. Another highly efficient biosensor, based on an enzyme-mediated dephosphorylation nanozyme, has been developed for the rapid, specific, and sensitive detection of paraoxon [51]. This biosensor utilizes a novel $CeO_2@N$ -doped carbon ($CeO_2@NC$) nanozyme [98]. The mechanism underlying the degradation of phosphotriesters, catalyzed by $CeO_2@NC$, involves $Ce(IV)/Ce(III)$ species acting as active sites for the polarization and hydrolysis of phosphoester bonds. Additionally, the N-doped carbon (NC) material acts as synergistic sites, facilitating the adsorption of the paraoxon substrate and promoting the hydrolysis process. The characteristic properties of this biosensor are presented in **Table 2** that shows different types of enzyme-based biosensors developed against pesticides. Different types of enzyme-based biosensors developed against pesticides are described in **Table 2**.

1.2.3. Chemiluminescence Assay

Chang et al. [52] introduced a highly sensitive nanozyme chemiluminescence-based (CL) biosensor for the specific detection of glyphosate. The biosensor utilizes a porous hydroxy

zirconium oxide nanozyme (ZrOX-OH) obtained through a straightforward alkali solution treatment of $\text{UIO}_{66}\text{ZrO}_x\text{-OH}$ which demonstrates remarkable phosphatase-like activity, enabling the dephosphorylation of 3-(2'-spiroadamantyl)-4-methoxy-4-(3'-phosphoryloxyphenyl)-1,2-dioxetane (AMPPD), which results in the generation of an intense CL signals. Notably, the phosphatase-like $\text{ZrO}_x\text{-OH}$ exhibited a distinctive response to glyphosate due to the unique interaction between the carboxyl group of glyphosates and the surface hydroxyl group, leading to the development of a CL biosensor for the direct and selective detection of glyphosate without the need for bio-enzymes.

Table 2 Enzyme-based biosensors developed for pesticides detection.

Pesticide	Detection technique	Enzyme used	LOD	Validation with real samples	Reference
Malathion, chlorpyrifos, monocrotophos and endosulfan	DPV	AChE	33 ng L ⁻¹ , 35 ng L ⁻¹ , 223.2 ng L ⁻¹ , and 4 µg L ⁻¹	Milk	Chauhan and Pundir (2011) [37]
Glyphosate	Potentiometric assay	Urease	0.5 mg L ⁻¹	Tap water	Vaghela et al (2018) [35]
Carbendazim, chlorpyrifos, dichlorodiphenyltri chloroethane (DDT), dinocap, and ethion	CA and CV	Glutathione-S-transferase	2 µg L ⁻¹ , 60 µg L ⁻¹ , 40 µg L ⁻¹ , 50 µg L ⁻¹ , and 100 µg L ⁻¹	Potatos	Borah et al (2018) [46]
Chlorpyrifos	High open circuit voltage (photoelectrochemical enzymatic fuel cell)	AChE	0.012 µg L ⁻¹	Not mentioned (PB)	Gai et al (2018) [39]
Omethoate	DPV	AChE	0.36 ng L ⁻¹	Cabbage and cucumber	Ma et al (2018) [38]
Paraoxon	DPV	2D MnO ₂ sheets/AChE nanozyme	25 ng L ⁻¹	Pakchoi	Wu et al. [45]
Paraoxon	CA	AChE	13 ng L ⁻¹	Apple and pakchoi	Zhao et al (2017) [47]

Paraoxon, 2,4-dichlorophenoxyacetic acid, and atrazine	CA	BChE, alkaline phosphatase, and tyrosinase	2 $\mu\text{g L}^{-1}$, 50 $\mu\text{g L}^{-1}$, and 10 $\mu\text{g L}^{-1}$	River water	Arduini et al (2019) [28]
Malathion	CV and EIS	AChE	0.39 $\mu\text{g L}^{-1}$	Cabbage and carrots	Li et al (2020) [53]
Nitrofen	DPV	Candida Rugosa Lipase	7.38 $\mu\text{g L}^{-1}$	Apricot	Cheng et al (2021) [54]
Ethyl paraoxon	CV	AChE-ChOx	0.46 ng L^{-1}	Pakchoi, cabbage and lettuce	Yang et al (2021) [55]
Paraoxon	DPV	AChE	1.7 $\mu\text{g L}^{-1}$	Apple and Eggplant	Li et al (2020) [56]
Chlorpyrifos	DPV	AChE	20 ng L^{-1}	Cabbage and spinach	Wang et al (2016)[57]
Chlorpyrifos	CV	AChE	50 ng L^{-1}	Cabbage, rape and lettuce	Chen et al (2017) [58]
Malathion and methyl parathion	CV	AChE	0.31 pg L^{-1} and 0.188 pg L^{-1}	Tap water and Chinese cabbage	Jian et al (2019) [59]
Fenthion	CV and EIS	AChE	100 $\mu\text{g L}^{-1}$	Cabbage juice	Cui et al (2019) [60]
Phosmet	CV and EIS	Tribolium castaneum acetylcholinesterase	1.14 $\mu\text{g L}^{-1}$	Wheat flour	Bial et al (2021) [61]
11 organophosphorus and methomyl	DPV and EIS	AChE	Organophosphorus: 19 – 77 ng L^{-1} Methomyl: 81 ng L^{-1}	Trichlorfon and dichlorvos: Apple and cabbage	Zhao et al (2021) [62]
Paraxon	CV	AChE	1.4 $\mu\text{g L}^{-1}$	Vegetable leaves	Jia et al (2020) [63]
Paraxon	CV	AChE	4 $\mu\text{g L}^{-1}$	Chinese chives and cabbage	Chen et al (2020) [64]
Paraoxon, dichlorvos, malathion and triazophos	Fluorescence	AChE and ChOx	0.44 pg L^{-1} , 16.6 pg L^{-1} , 76 $\mu\text{g L}^{-1}$ and 3 ng L^{-1}	ND	Korram et al (2020) [65]
Pirimicarb, dichlorvos and carbaryl	Fluorescence	AChE	50 $\mu\text{g L}^{-1}$, 10 $\mu\text{g L}^{-1}$ and 10 $\mu\text{g L}^{-1}$	Pirimicarb: Lettuce, choy and rice	Apilux et al (2017)[66]

Ethylparathion	Fluorescence	AChE	0.7 ng L ⁻¹	Tap water, soil water, apple and orange juice	Sharma et al (2021) [67]
Parathionmethyl, monocrotophos and dimethoate	Fluorescence	AChE	0.67 ng L ⁻¹ , 23 ng L ⁻¹ and 67 ng L ⁻¹	Apple, cucumber and capsicum	Long et al (2015) [41]
Carbaryl, ethodan, endosulfan and acephate	Colorimetry and fluorescence	AChE	0.4 to 3 µg L ⁻¹	River water	Luo et al (2018) [68]
Glyphosate	Fluorescence	Exonuclease I	/	Drinking water	Berkal et al (2023) [36]
Glyphosate	Colorimetry	peroxidase-mimetic nanozyme/ 2D-VONz	/	/	Li Haiyin et al. (2023) [50]
Paraxon	Colorimetry	Phosphatases-mimetic nanozyme/CeO ₂ @NC	0.82 mg L ⁻¹	Garlic chives	Gai et al. (2022) [51]
Glyphosate	Chemiluminiscence	Phosphatases-mimetic nanozyme /ZrO _x -OH	55.8 mg L ⁻¹	Cabbage juice	Chang et al. [52] (2023)

Upon reviewing **Table 2**, notable disparities in the Limit of Detection (LOD) become evident among biosensors utilizing the same bioreceptor and targeting the identical pesticide. This variability predominantly stems from the choice of the detection technique employed. Certain detection methods prove more accurate to detect pesticides than others. Furthermore, additional factors, such as the composition of the analyzed matrix, whether it is a simple medium like water or a more complex one like food or vegetables, also contribute significantly to the observed variation in LOD values.

I. Immunosensors

Immunosensors are characterized by the directed and highly selective interaction between a ligand, or antigen (Ag), and its antibody (Ab), immobilized on the transducer surface [69–72]. Once the equilibrium is reached, the ratio of bound-to-free antigen is quantitatively related to the global amount of ligand. Unlike AChE inhibition based biosensors, immunosensors have

the advantage of being specific [73]. Several immunosensors have been developed for pesticides detection, based essentially on optical and electrochemical transduction methods. Given the relatively small size of pesticides, competitive assay schemes are frequently utilized for analyzing pesticides with immunosensors [74]. Based on the detection principle, these immunosensors can be classified into two main categories, namely optical and electrochemical immunosensors. In contrast, electrochemical immunosensors utilize changes in current or potential to detect pesticides, offering several advantages, such as rapid detection, portability, and low cost.

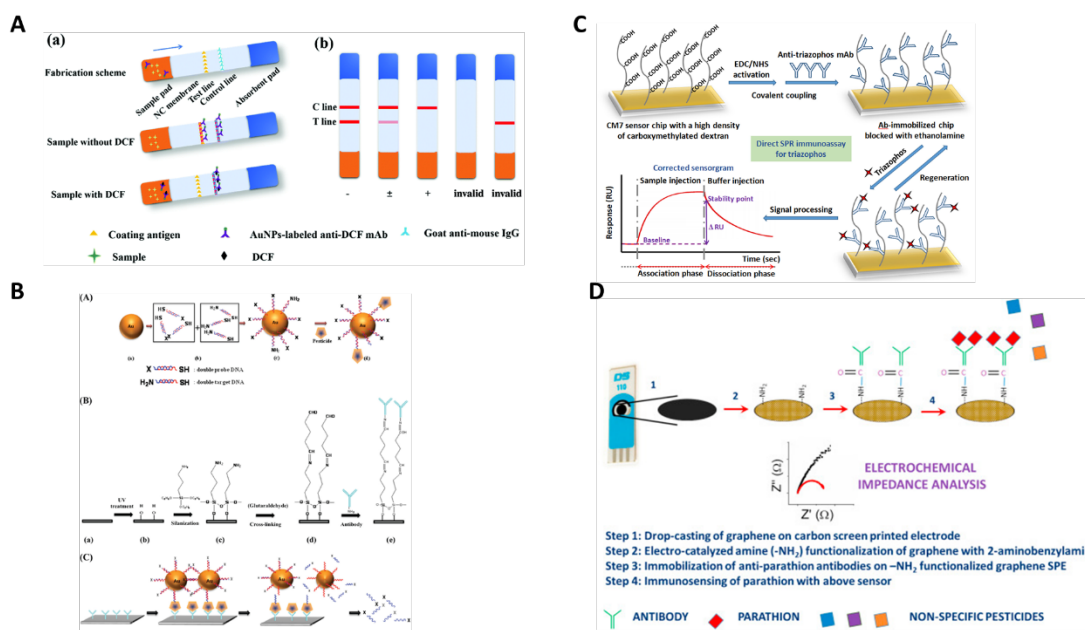
I.1. Optical immunosensors

Optical immunosensors rely on the specific binding interactions between an antibody or antigen and its corresponding analyte, resulting in a detectable signal change that can be measured using optical techniques such as absorbance, fluorescence, or surface plasmon resonance. These immunosensors offer several benefits, including high sensitivity, selectivity, real-time detection, and the ability to be easily miniaturized for use in portable devices.

I.1.1. Colorimetric immunosensors

Colorimetric immunoassays have several advantages over conventional methods for pesticides analysis, such as rapid detection, ease of use, suitability for high-throughput analysis with limited technical requirements [75]. Liu and coworkers [76] have developed a colorimetric immunochromatographic strip (ICA) using a monoclonal antibody (mAb) for the detection of dicofol (**Figure 4(A)**), an organo-insecticide widely spread on vegetables, fruits, teas, ornamental plants, and field crops [77]. The ICA displayed high sensitivity with a limit of detection of $50 \mu\text{g L}^{-1}$ with both apple and cucumber, and the cross-reactivity test revealed a good specificity for dicofol. These results were consistent with LC-MS and immunocapture ELISA, suggesting that the ICA method is reliable and practical for detecting dicofol in fruits and vegetables.

Fig. 4



(A) Schematic of the ICA strip (a) and interpretation of the test results (b). Reprinted from [76], with permission from Royal Society of Chemistry. (B) Novel immunoassay containing glyphosate-double DNA-gold nanoparticles based on competitive inhibition reaction. Reprinted (adapted) from [78], with permission from American Chemical Society. (C) Preparation of mAb-immobilized sensor chip for direct detection of triazophos and real-time SPR sensorgram for association and dissociation of the immunocomplex. Reprinted (adapted) from [79], with permission from Elsevier. (D) Schematic of the graphene-based screen-printed immunosensor for parathion. Reprinted (adapted) from [80], with permission from Elsevier.

1.1.2. Fluorescence-based immunosensors

Gonzalez-Martinez and coworkers [81] have developed a fluorescent immunosensor based on an immunocomplex capture assay protocol to detect glyphosate. The described immunosensor is fully automated and performs on-line analyte derivatization prior to the assay. It utilizes a highly selective anti-glyphosate serum, a glyphosate peroxidase enzyme tracer, and fluorescent detection system for high sensitivity and accuracy. Its specific and sensitive detection reaches a limit of detection of $0.021 \mu\text{g L}^{-1}$, which is lower than the concentration limit set by the European council directive [82]. Lee et al. [78] have also described a new method for detecting glyphosate using Co-B/SiO₂/dye nanoparticles in a water-in-oil microemulsion (**Figure 4(B)**). The nanoparticles have been surface-modified to enhance their detection limit. The approach utilized fluorescence magnetic nanoparticles (FMP) and a glyphosate antibody. With this

method, a limit of detection of 45.6 ng L^{-1} was reached, with a linear correlation in the range of $0.169 \text{ } \mu\text{g L}^{-1} - 1.69 \text{ mg L}^{-1}$.

1.1.3. Reflectometric interference spectroscopy immunosensors

Reflectometric interference spectroscopy presents several advantages over classical optical techniques such as simple instrumentation, no-need for optical alignment and low cost of the sensing element. Koukouvinos et al. [83] have developed a white light reflectance spectroscopy (WLRS) based immunosensor for the fast, real time and label-free simultaneous detection of chlorpyrifos, imazalil and thiabendazole pesticides in drinking water and wine samples. The biosensor allowed the entire detection of those pesticides within 10 min. The accuracy of the measurements was evaluated through recovery experiments and comparison of the results with validated liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). Recovery values ranged from 86 to 116%, and the results were in good agreement with LC-MS/MS.

1.1.4. Surface Plasmon Resonance-(SPR) based immunosensors

SPR is an optical detection platform widely used for the detection of large molecules, with which the high mass of the analyte and the use of a sandwich immunoassay format provide a high signal and thus the desired sensitivity [84, 85]. In contrast and due to the low change of refractive index induced by the binding of these analytes to the sensor surface, small molecular compounds such as pesticides present at low concentrations are very difficult to be directly detected by traditional SPR immunosensors [86]. Recent improvements in SPR devices, including lower-noise valves and improved microfluidics with more efficient vacuum pumps, have reduced the overall noise of these systems and thus improved sensitivity and reliability [87, 88]. Owing to these improvements, SPR immunosensors could be employed for pesticide monitoring. Guo et al. [79] have described an SPR immunosensor for the detection of an organophosphate pesticide, triazophos (**Figure 4(C)**). They immobilized two anti-triazophos monoclonal antibodies (mAbs) on the sensor chip, and characterized them by SPR-based kinetic

analysis. The mAb, characterized by a relatively slow dissociation rate, could be used for the development of a non-competitive SPR-immunosensor for direct monitoring of triazophos residue in environmental and agricultural samples.

1.2. Electrochemical immunosensors:

Electrochemical immunosensors are interesting alternatives to classical chromatographic methods for pesticide analysis. Owing to their ability to detect specific targets with high sensitivity, they are promising tools for rapid and on-site analysis of pesticides [89–91].

1.2.1. Cyclic voltammetry

Talan et al. [92] have described a highly sensitive fluorine doped tin-oxide (FTO) based electrochemical immunosensor to detect chlorpyrifos using gold nanoparticles (AuNPs) and anti-chlorpyrifos antibodies (Chl-Ab). The developed biosensor allowed, via cyclic voltammetry measurements, the successful detection of chlorpyrifos with very -high sensitivity ranging from 1 fM to 1 μ M with a LOD of 10 fM.

1.2.2. Chronoamperometric assay

Bettazzi et al. [93] developed an electrochemical competitive immunoassay that utilizes antibody-modified magnetic particles. The assay works by employing a Horseradish Peroxidase (HRP)-conjugated glyphosate tracer and anti-glyphosate IgG-modified magnetic beads (MBs) for detection. A screen-printed electrochemical cell has been used to detect glyphosate. The calibration curve demonstrated a linear concentration range of 0 – 10000 ng L⁻¹ with a LOD of 5 ng L⁻¹ and LOQ of 30 ng L⁻¹ which is well below the EU legislative recommendations. Furthermore, the developed biosensor showed a good applicability for the analysis of real samples, namely spiked beer samples.

1.2.3. Impedance spectroscopy

A graphene-based immunosensor was developed and used to detect parathion [80] (**Figure 4(D)**). The process involved modifying screen-printed carbon electrodes with graphene sheets and their functionalization with 2-aminobenzyl amine before bio-interfacing with anti-parathion antibodies. The biosensor demonstrated a broad linear range of detection (0.1–1000

ng L⁻¹) and a very low limit of detection (52 pg L⁻¹) with high selectivity towards parathion. The biosensor was also successfully used to detect parathion in real samples such as tomato and carrot and was cross-calibrated against high performance liquid chromatography (HPLC) to confirm its viability. **Table 3** provides a summary of the various types of immunosensors developed for the detection of pesticides.

Table 3 Immunosensors developed against pesticides

Pesticide	Detection technique	LOD	Validity for real samples	Reference
Parathion, methyl-parathion, and fenitrothion	ELISA	2.5 µg L ⁻¹ for parathion and methyl-parathion 5 µg L ⁻¹ for fenitrothion	Tap water	Jiao et al. (2018) [94]
Glyphosate	Fluorometric assay	0.021 µg L ⁻¹	Water and soil	Gonzalez-Martinez et al. (2005) [81]
Glyphosate	Fluorometric assay	10 µg L ⁻¹	Not mentioned (PBS buffer)	Lee et al. (2010) [78]
Acetochlor and fenpropathrin	Colorimetry	0.6 µg L ⁻¹ and 0.24 µg L ⁻¹	Corn, apple and cabbage	Cheng et al. (2019) [95]
Glyphosate	Chronoamperometric assay	5 ng L ⁻¹	Commercial beer	Betazzi et al. (2018) [93]
Chlorpyrifos	DPV and CV	3.5 pg L ⁻¹	Apple, cabbage and pomegranate	Talan et al. (2018) [92]
Thiazophos	SPR	96 ng L ⁻¹	Environmental water	Guo et al. (2018) [79]
Chlorpyrifos, amazalil, and thiabendazol	WLRS	0.6 µg L ⁻¹ for chlorpyrifos and imazalil 0.8 µg L ⁻¹ for thiabendazol	Drinking water and wine	Koukouvinos et al. (2017) [83]
Chlorpyrifos	EIS	70 pg L ⁻¹	Chinese cabbage and lettuce	Hou et al. (2020) [96]
Malathion	DPV	0.33 pg L ⁻¹	Lettuce	Kaur et al. (2021) [97]
Endosulfan and paraoxon	CV and SWV	0.05 µg L ⁻¹ and 2 µg L ⁻¹	Environmental water	Liu et al. (2014) [98]
Paraquat	Amperometry	1.4 µg L ⁻¹	Potatos	Valera et al. (2014) [99]
Parathion	EIS	52 pg L ⁻¹	Tomato and carrot	Mehta et al. (2016) [80]

II. Aptasensors

The development of the Systematic Evolution of Ligands by Exponential enrichment (SELEX) technique has led to the discovery of aptamers, oligonucleotide sequences composed of nucleotide bases (Adenine, Thymine, Cytosine, Guanine), capable of complexing a target with very high affinity and specificity. Aptamers offer many advantages over antibodies (**Table 4**) and are specific to a wide variety of targets: ions [100–102], proteins [103], small molecules

[104–106], and cells [107, 108]. These characteristics make aptamers excellent candidates to replace antibodies in various fields, more particularly environmental analysis that requires stable and robust sensors.

Table 4 Elevating the Distinctive Attributes of Aptamers over Antibodies: A Comparative Analysis [109].

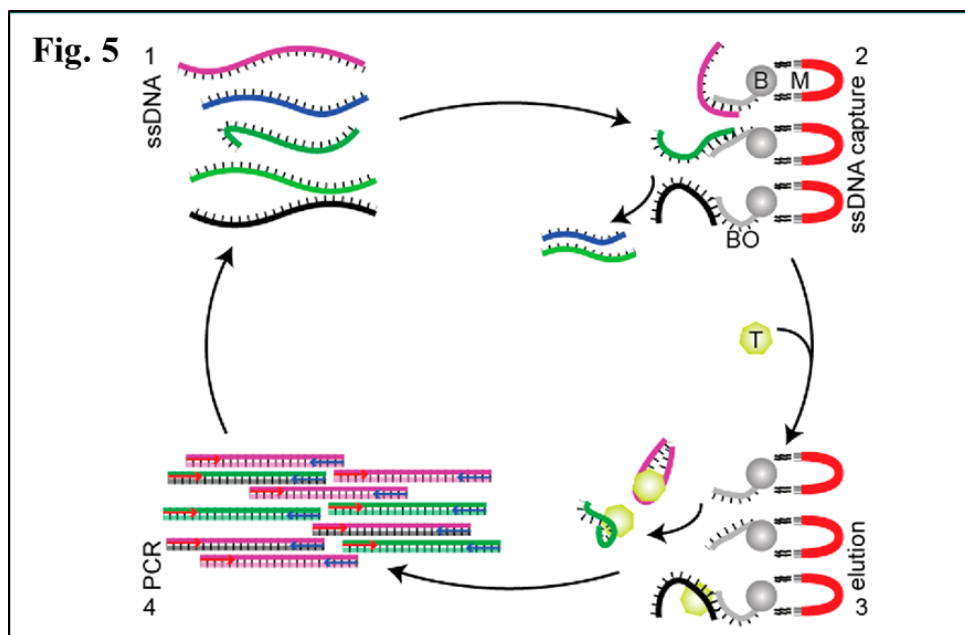
Properties	Aptamers	Antibodies
Stability	Withstand repeated rounds of denaturation/renaturation. Temperature resistant: stable at room temperature. Long shelf life (several years). Can be lyophilized. Degradable by nucleases. Resistant to proteases.	Easily denatured. Temperature sensitive and require refrigeration to avoid denaturation. Limited shelf life. Must be refrigerated for storage and transport. Degradable by proteases. Resistant to nucleases.
Synthesis	In vitro SELEX takes only 2–8 weeks No batch-to-batch variation Cheap to synthesize	Produced in vivo More than 6 months Batch-to-batch variations Laborious and expensive
Target potential	From ions and small molecules to whole cells and live animals	Targets must cause a strong immune response for antibodies to be produced
Size	Small molecules	Relatively large by comparison
Modifiability	Aptamers can readily and easily be modified without affinity loss	Modifications often lead to reduced activity
Affinity	High and increased in multivalent aptamers	Dependent on the number of epitopes on the antigen.
Specificity	Single point mutations identifiable	Different antibodies might bind the same antigen
Tissue uptake/kidney filtration	Fast	Slow

Conventional SELEX methods are however not compatible with small molecules because of the immobilization step that is not only complicated [110], but leaves weak functional groups exposed to the oligonucleotides thus reducing the chance of selecting aptamers. In 2005, Stoltenburg et al. reported a method for selecting fluorophore-labeled aptamers that involves the grafting of oligonucleotides onto magnetic beads (FluMag-SELEX) [111], which subsequently furthered Capture-SELEX, a method suitable for small molecule aptamers selection. Unlike conventional SELEX, the immobilization in Capture-SELEX is done with the oligonucleotides and not with the target molecules, which allows the preservation of all functional groups of these molecules thus increasing the chance of selecting aptamers. The operating principle of the Capture-SELEX can be summarized in the following steps (**Figure 5**):

1. Immobilization: the capture oligonucleotide (DNA complementary to the library) is immobilized on the solid matrix (magnetic beads for example).
2. Hybridization: the oligonucleotide library is hybridized with the immobilized capture oligonucleotides.
3. Incubation: the target is incubated with the oligonucleotide library.

4. Elution: the sequences with an affinity towards the target will detach from the capture oligonucleotide and go into solution.
5. Amplification: the recovered sequences are enriched by Polymerase Chain Reaction (PCR) for the next round.

Similar to conventional SELEX, candidate aptamers are sequenced and cloned at the end of the Capture-SELEX (6 to 20 rounds) to identify the aptamers that have the desired properties.



Schematic illustration of Capture-SELEX using magnetic beads. Reprinted from [112], with permission from American Chemical Society.

II.1. Optical aptasensors

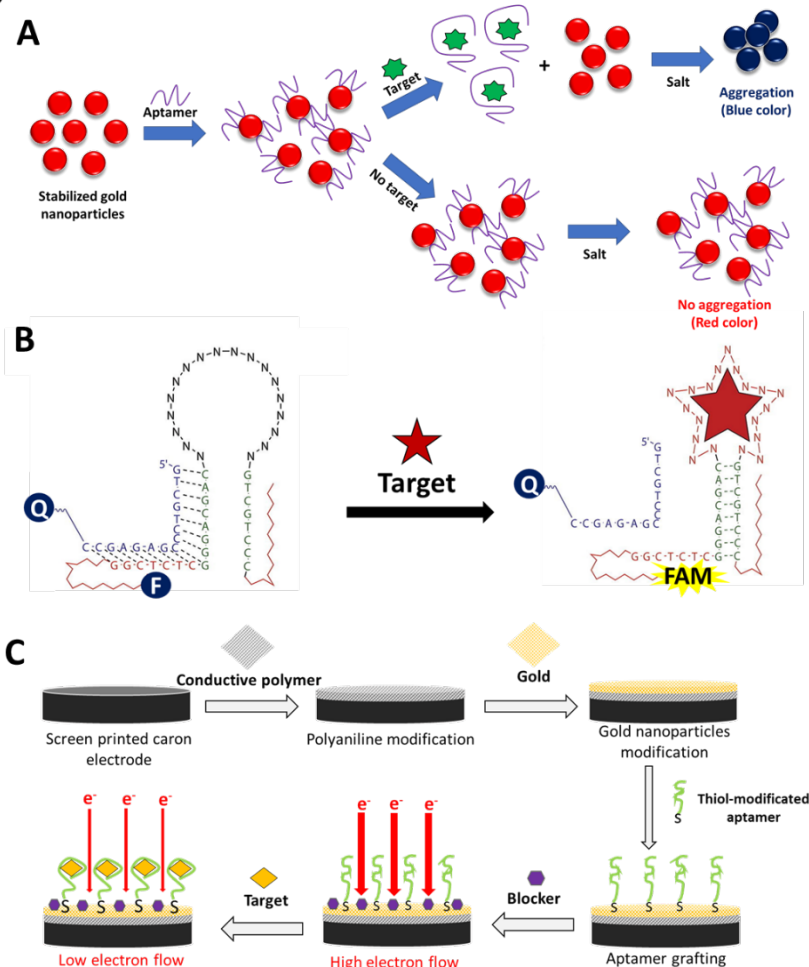
Optical aptasensors have become a well-established technology in the field of bioanalysis, utilizing aptamers as recognition elements to directly target and identify substances. These sensors utilize various light sources, including fluorescence, colorimetry, SERS, etc., and convert signals in the form of UV, visible, and IR radiation into different data formats. Compared to other detection methods, optical aptasensors offer several advantages, such as low cost, repeatable use, high specificity, simple sample preparation, minimal interference, and high

accuracy. These characteristics make optical aptasensors particularly suitable for on-site detection applications [113].

II.1.1. Colorimetric aptasensors

The primary benefit of colorimetric sensing is its straightforwardness and ease of implementation. Colorimetric aptasensors have been extensively employed for detecting pesticides in real samples due to the convenience of visual observation. However, a significant challenge in designing colorimetric aptasensors relies on converting the response change into a noticeable color change. Gold (Au) and silver (Ag) nanoparticles are the most commonly used probes in colorimetric assays, due to their ability to enhance surface plasmon resonance and thus produce robust signals as monitored by colorimetry (**Figure 6(A)**) [114, 115].

Fig. 6



Comparative schematic diagram of (A) colorimetric aptasensor, (B) FRET aptasensor and (C) electrochemical aptasensor. (B) Reprinted from [116], with permission from ScienceDirect.

II.1.2. Fluorescence-based aptasensors

Fluorescence-based aptasensors rely on the correlation between changes in fluorescence intensity and the concentration of the target upon aptamer binding. Fluorescence changes are typically achieved through the introduction of a fluorescence quenching or fluorescence resonance energy transfer agent (FRET, **Figure 6(B)**). FRET occurs between two fluorophores at an appropriate distance and can utilize various materials as fluorescent donors, including dyes, quantum dots, metal nanoparticles, carbon dots, and carbon nanomaterials. Nanomaterials, such as graphene oxide, gold nanoparticles, carbon nanotubes, and nanocomposites, are also used as well-known fluorescence quenchers [117].

To create efficient aptasensors with high sensitivity, high throughput, and multiplexing capabilities, various combinations of nanomaterials are employed as fluorescent donors and receptors in sensing assays. Fluorescence detection relies on switching the fluorescence signals on and off to indicate the presence of analytes [118, 119]. In most cases, fluorescence signals are in the "signal-off" state until the target is present and the blocking of signals is lifted, leading to a "signal-on" response. Fluorescence signals can be amplified using a variety of nanomaterials such as gold and silver nanoparticles, known for their superior performance [120, 121]. Su et al. proposed a method for detecting carbendazim (CBZ) in water using a fluorescent aptasensor [122]. The aptasensor used a CBZ-specific aptamer as a sensing probe, gold nanoparticles (AuNPs) and Rhodamine B (RhoB) as an indicator. In the absence of CBZ, the aptamer wrapped around the AuNPs and kept them dispersed in a solution. However, in the presence of CBZ, the aptamer forms a complex with CBZ, leaving the AuNPs which aggregate in a NaCl solution. The concentration of CBZ was determined by measuring the fluorescence intensity. The method had a wide linear range from 2.33 to 800 nM and a LOD of 2.33 nM. The fluorescent aptasensor showed potential for use in detecting CBZ in aquatic environments.

II.1.3. Luminescence-based aptasensors

Common fluorescence techniques that rely on organic dyes are vulnerable to interference from naturally occurring fluorescent substances in the environment [123]. Time-resolved emission spectroscopy (TRES) is a useful method for discriminating between fluorophores with similar emission spectra but varying decay times. TRES records long-lived phosphorescence once the initial short-lived fluorescence background has faded [124–127]. Therefore, luminescent transition metal complexes, such as iridium(III) complexes, have become preferred for TRES due to their excellent optical characteristics and long-lived phosphorescence [128]. Chen et al. [129] have reported on a luminescent G-quadruplex-derived aptasensor for the monitoring of glyphosate using a phosphorescent iridium(III)-based probe. The developed platform displayed excellent sensitivity with good selectivity for glyphosate with a limit of detection of $4.46 \mu\text{g L}^{-1}$ in Tris-buffer, and $13.4 \mu\text{g L}^{-1}$ in Tris-buffer containing soybean extract to simulate a complex environment.

II.1.4. Phosphorescence aptasensors

Persistent luminescence nanorods (PLNRs) have become a subject of extensive research owing to their unique afterglow or phosphorescence characteristics, which unlike fluorophores allow for reduced or even eliminated background luminescence. These nanorods exhibit persistent luminescence, which refers to the emission of light after the cessation of the excitation source. Wang et al. have developed an aptamer-based colorimetric-phosphorescence assay for the detection of isocarbophos [130]. The colorimetric assay used AuNPs that were aggregated by competitive binding of the aptamer between isocarbophos and AuNPs at high salt concentration. The addition of persistent luminescence nanorods (PLNRs) to the system resulted in phosphorescence that was sensitive to the concentration of isocarbophos due to the inner filter effect between PLNRs and AuNPs. The assay showed good linearity within the range of $50\text{--}500 \mu\text{g L}^{-1}$ and $5\text{--}160 \mu\text{g L}^{-1}$, with a limit of detection of $7.1 \mu\text{g L}^{-1}$ and $0.54 \mu\text{g L}^{-1}$ in colorimetry and phosphorescence mode, respectively. The method was successfully

demonstrated for food analysis with the detection of isocarbophos residues in vegetables, showing both sensitivity and selectivity.

II.1.5. SERS-based aptasensors

Surface-Enhanced Raman spectroscopy (SERS) is a powerful spectroscopic technique that leverages plasmonic metal nanostructures for the detection of trace-level chemicals with high sensitivity and selectivity [131]. SERS has been widely adopted in analytical chemistry [132], biochemical analysis [133], and environmental sensing [134, 135], including the detection of harmful agrochemicals, such as pesticides [136–138]. However, the lack of selectivity when the target molecule is mixed with other molecules in a complex matrix and susceptibility to interference from various ambient influences can limit SERS detection techniques. Therefore, sample pretreatment methods, such as purification and extraction, are critical for examining environmental samples. The use of aptamers, specific biomolecules that can enhance the selectivity of target analysis when combined with SERS, can address these limitations. Recently, Kamkrua et al. [139] developed a SERS aptasensor using gold nanoparticles to detect parquat, a commonly used herbicide. The platform used AuNPs-SERS substrates modified with a thiol-modified aptamer as bioreceptor to selectively bind to parquat molecules. The aptamer-modified SERS substrate showed improved sensitivity and selectivity compared to SERS substrates without aptamer modifications, with a limit of detection of $0.10 \pm 0.03 \mu\text{M}$. The platform was evaluated using natural water samples and demonstrated good stability against interferences from other similar herbicides and insecticides present along with parquat in water.

II.2. Electrochemical aptasensors

Electrochemical aptasensors produce an electrochemical signal upon the capture of a particular target substance, achieved through the use of aptamers. The design of electrochemical aptasensors involves three crucial steps, including the utilization of nanomaterials to amplify the signal, binding of the aptamer to the sensor surface, and the detection process itself (**Figure**

521 **6(C))**. Covalent bond formation is the most commonly employed method for aptamer
522 immobilization onto the surface in these types of sensors [140]. Numerous electrochemical
523 aptasensors have been reported for the identification of proteins, which are large molecules
524 producing significant variation in electrochemical signal upon binding to the aptamer, thereby
525 facilitating their detection. However, detecting pesticides which are small molecules requires a
526 notable change in aptamer conformation to enable their detection by electrochemical platforms.
527 To overcome this challenge, multiple approaches have been adopted, one of which is the use of
528 oligonucleotide switching structures generated through the Capture-SELEX method that has
529 proven to be more suitable for detecting pesticides due to the aptamers selection process: a
530 significant conformational change occurs upon binding to the target [141]. This conformational
531 change leads to an improved ability to detect and quantify small molecule pesticides using
532 electrochemical aptasensors. In **Table 5**, various aptasensors that were developed for the
533 detection of pesticides have been listed.

Table 5 Recent advances in aptasensors developed against pesticides.

Target	Detection technique	Aptamer sequence	LOD	Dynamic range	Validity for real samples	Reference
Acetamiprid	EIS	Acetamiprid: 5'-(SH)-(CH ₂) ₆ - TGTAATTTGTCTGCAGCGGTTCTTGATCGCTGA CACCATATTATGAAGA-[FITC]-3'	Acetamiprid: 8.9 ng L ⁻¹	ND	Buffer	Madianos et al (2018) [142]
Atrazine		Atrazine: 5'-(SH)-(CH ₂) ₆ - TACTGTTTGCAGTGGCGGATTTAGCCAGTCAGT G-[FITC]-3'	Atrazine: 1.3 ng L ⁻¹			
Acetamiprid	EIS	Acetamiprid: 5'-(SH)-(CH ₂) ₆ - TGTAATTTGTCTGCAGCGGTTCTTGATCGCTGA CACCATATTATGAAGA-[Flc]-3'	Acetamiprid: 0.2 ng L ⁻¹	Acetamiprid: 2.2 ng L ⁻¹ - 22.2 µg L ⁻¹	Tap water	Madianos et al (2018) [143]
Atrazine		Atrazine: 5'-(SH)-(CH ₂) ₆ - TACTGTTTGCAGTGGCGGATTTAGCCAGTCAGT G-[Flc]-3'	Atrazine: 2.1 ng L ⁻¹	Atrazine: 21.5 ng L ⁻¹ - 215.7 µg L ⁻¹		
Atrazine	Photoelectrochemical assay	5'-SH-(CH ₂) ₆ -TGT-ACC-GTC-TGA-GCG-ATT-CGT-ACG-AAC-GGCTTT-GTA-CTG-TTT-GCA-CTG-GCG-GAT-TTA-GCC-AGT-CAG-TGT-TAA-GGA-GTG-C-3'	0.21 ng L ⁻¹	0.5 ng L ⁻¹ - 0.11 µg L ⁻¹	Lake water, agricultural wastewater and sewage water	Fan et al (2021) [144]
Carbofuran	DPV	5'- CACCTGGGGGAGTATTGCGGAGGAAAGAGAAC ACTGGGGCAGATATGGGCCAGCAGGTC- (CH ₂) ₃ -SH-3'	14.8 µg L ⁻¹	44 ng L ⁻¹ -11 µg L ⁻¹	Vegetables and fruits	Li et al (2018) [145]
Chlorpyrifos	DPV	5'- CCTGCCACGCTCCGCAAGCTTAGGGTTACGCCT GCAGCGATTCTTGATCGCGCTGCTGGTAATCCT TCTTTAAGCTTGGCACCCGCATCGT-3'	70 ng L ⁻¹	0.1 µg L ⁻¹ - 150 µg L ⁻¹	Apple and celery cabbage	Xu et al (2018) [146]

Atrazine	EIS	5' -TGT ACC GTC TGA GCG ATT CGT ACG AAC GGC TTT GTA CTG TTT GCA CTG GCG GAT TTA GCC AGT CAG TGT TAA GGA GTG C-3'	0.67 ng L ⁻¹	1 ng L ⁻¹ -50 µg L ⁻¹	River and tap water	Zhu et al (2021) [147]
Atrazine	Photoelectrochemical assay	5'-TGT-ACC-GTC-TGA-GCG-ATT-CGT-ACG-AAC-GGC-TTT-GTA-CTG-TTT-GCA-CTG-GCG-GAT-TTA-GCC-AGT-CAG-TGT-TAA-GGA-GTG-C-3'	2.6 pg L ⁻¹	10.7 pg L ⁻¹ –64.7 ng L ⁻¹	Water	Sun et al (2019) [148]
Atrazine	DPV	5'-SH-(CH ₂) ₆ -TGT-ACC-GTC-TGA-GCG-ATT-CGT-ACG-AAC-GGCTTT-GTA-CTG-TTT-GCA-CTG-GCG-GAT-TTA-GCC-AGT-CAG-TGT-TAAGGA-GTG-C-3'	21.5 pg L ⁻¹	53.9 pg L ⁻¹ –53.7 ng L ⁻¹	Lake and river water	Fan et al (2019) [149]
Atrazine	Linear Sweep Voltametry (LSV)	5'-HS-(CH ₂) ₆ -TGT-ACC-GTC-TGA-GCG-ATT-CGT-ACG-AAC-GGCTTT-GTA-CTG-TTT-GCA-CTG-GCG-GAT-TTA-GCC-AGT-CAG-TGT-TAAGGA-GTG-C-3'	1.6 µg L ⁻¹	ND	Environmental water	Wang et al (2020) [150]
Atrazine	Adsorption spectroscopy (ATR-SEIRAS)	5'-HS-(CH ₂) ₆ -TGT-ACC-GTC-TGA-GCG-ATT-CGT-ACG-AAC-GGC-TTT-GTA-CTG-TTT-GCA-CTG-GCG-GAT-TTA-GCC-AGT-CAG-TGT-TAA-GGA-GT ₇ G-C-3'	0.23 µg L ⁻¹	ND	ND	Sun et al (2021) [151]
Atrazine	Ultrafiltration system	5'-/FAM/-TACTGTTTGCCTGGCGGATTTAGCCAGTCAGTG-3'	ND	ND	ND	Romero-Reyes and Heemstra (2021) [152]
Atrazine	Fluorescence	5'-TTT-TTT-TTT-TTA-CTG-TTT-GCA-CTG-GCG-GAT-TTA-GCC-AGT-CAG-TG-3'	2 ng L ⁻¹	ND	River simple	Yao et al (2021) [153]
Atrazine	SERS	5'-(SH)-TACTG TTTGC ACTGG CGGAT TTAGC CAGTC AGTG-3'	0.14 µg L ⁻¹	0.22 µg L ⁻¹ –10.7 µg L ⁻¹	Cherry tomato and grape	Wei et al (2020) [154]
Carbendazim	Fluorescence	5'-CGACACAGCGGAGGCCACCCGCCCCACAGCCCCTGCAGCTCCTGTACCTGTGTGTGTG-3'	0.44 µg L ⁻¹	0.44 µg L ⁻¹ –0.15 mg L ⁻¹	Water	Su et al (2020) [122]
Chloramphenicol	Colorimetry	5'-ACTTCAGTGAGTTGTCCACGGTCGGCGAGTCGGTGGTAG-Biotin-3' and antibody	0.19 µg L ⁻¹ in milk 0.23 µg L ⁻¹ in serum	ND	Milk and mouse serum	Abnous et al (2016) [155]

Chlorpyrifos	Colorimetry	5'- CCTGCCACGCTCCGCAAGCTTAGGGTTACGCCT GCAGCGATTCTGATCGCGCTGCTGGTAATCCTT CTTTAAGCTTGGCACCCGCATCGT-3'	11.3 mg L ⁻¹	10 mg L ⁻¹ - 200 mg L ⁻¹	River water	Weerathunge et al (2019) [156]
Chlorpyrifos and diazinon and	Fluorescence	Chlorpyrifos aptamer 5'- CCTGCCACGCTCCGCAAGCTTAGGGTTACGCCT GCAGCGATTCTTGATCGCGCTGCTGGTAATCCT TCTTTAAGCTTGGCACCCGCATCGT-3'	0.73 ng L ⁻¹ and 6.7 ng L ⁻¹	ND	12 vegetables and fruits	Cheng et al (2018) [157]
Diazinon	Fluorescence	5'-NH ₂ -C ₆ - ATCCGTCACACCTGCTCTAATATAGAGGTATTG CTCTTGGACAAGGTACAGGGATGGTGTGGCT CCCGTAT-3'	23 ng L ⁻¹	0.05 µg L ⁻¹ - 500 µg L ⁻¹	Tea, apple and tap water	Ron et al (2020) [158]
Glyphosate	Fluorescence	5'-CGC ATT CAG GAT TGC ATG ATT GCC AAA AAA AAA A-NH ₂ -3'	10 µg L ⁻¹	10 µg L ⁻¹ - 100 mg L ⁻¹	PBS buffer	Lee et al (2010) [78]
Glyphosate	SERS	5'-TGC TAG ACG ATA TTC GTC CAT CCG AGC CCG TGG CGG GTC TTA GGA CTC TGC GGG CTT CGC GGC GCT GTC AGA CTG AAT ATG TCA-3'	0.34 ng L ⁻¹	0.51 ng L ⁻¹ - 11.8 ng L ⁻¹	Soil	Liu et al (2021) [159]
Glyphosate	Luminiscence	5'- TGCTAGACGATATTCGTCCATCCGAGCCCGTGG CGGGCTTTAGGACTCTGCGGGCTTCGCGGCGCT GTCAGACTGAATATGTCA-3'	4.5 µg L ⁻¹ in buffer 13.4 µg L ⁻¹ in buffer containing soybean extract	8.5 µg L ⁻¹ - 50.7 µg L ⁻¹	Buffer containing soybean extract	Chen et al (2020) [129]
Glyphosate, malathion and trichlorfon	Fluorescence	5'-FAM- AGCTTGCTGCAGCGATTCTTGATCGCCACAGA GCT-3'	88.8 ng L ⁻¹ , 195.37 ng L ⁻¹ and 72.2 ng L ⁻¹ ,	0.1 µg L ⁻¹ -10 mg L ⁻¹	Lettuce and carrot	Jiang et al (2020) [160]
Isocarbophos	Fluorescence	5'- ATTCTTGATCGCCACGGTCTGGAAAAAGAGAA GTGGGTAGGGCGGGTTGG-3'	2.9 µg L ⁻¹	2.9 µg L ⁻¹ - 0.14 mg L ⁻¹	Chinese cabbage and apple	Li et al (2018) [161]

Isocarbophos	Phosphorescence and colorimetric assays	5'-AGCTTGCTGCAGCGATTCTTGATCGCCACAGAGCT-3'	Phosphorescence: 0.54 $\mu\text{g L}^{-1}$ Colorimetry: 7.1 $\mu\text{g L}^{-1}$	Phosphorescence: 5-160 $\mu\text{g L}^{-1}$ Colorimetry: 50-500 $\mu\text{g L}^{-1}$	Chinese cabbage, brassica rape and lettuce	Wang et al (2019) [130]
Isocarbophos and omethoate	Colorimetry	5'-AAG CTT TTT TGA CTG ACT GCA GCG ATT CTT GAT CGC CAC GGT CTG GAA AAA GAG-3'	0.47 $\mu\text{g L}^{-1}$ and 0.35 $\mu\text{g L}^{-1}$	50-1000 $\mu\text{g L}^{-1}$ and 100-500 $\mu\text{g L}^{-1}$	Buffer	Liu et al (2020) [162]
Malathion	Colorimetry	5'-ATCCGTCACACCTGCTCTTATACACAATTGTTT TTCTCTTAACTTCTTGACTGCTGGTGTGGCTCC CGTAT-3'	0.33 ng L^{-1}	1.65 ng L^{-1} –3.3 $\mu\text{g L}^{-1}$	Human serum	Abnous et al (2018) [163]
Malathion	Fluorescence	5'-ATCCGTCACACCTGCTCTTATACACAATTGTTT TTCTCTTAACTTCTTGACTGCTGGTGTGGCTCC CGTAT-3'	0.74 ng L^{-1}	ND	12 vegetables and fruits	Cheng et al (2018) [157]

Conclusion and perspectives

Biosensors have emerged as a promising technology for the detection of pesticides, offering rapid, sensitive, and reliable results. Recent advances in biosensor design, and especially the use of biorecognition elements such as antibodies, enzymes and recently aptamers, have enabled the development of highly sensitive and specific biosensors that can detect a wide range of pesticides with high accuracy.

Despite the numerous advantages of biosensors, several challenges remain to be addressed to unlock their full potential. One key challenge lies in the selectivity of immunosensors and enzyme-based biosensors, which often encounter issues such as cross-interactions among antibodies and a lack of specificity of many enzymes employed in biosensors which are inhibited by organophosphate pesticides, limiting their effectiveness.

Furthermore, biosensors deployed in complex sample matrices face hurdles due to interference from various substances. Mitigating these effects requires the development of effective strategies. Moreover, the limited commercial applications of biosensors call for efforts to scale up production, reduce costs, and comply with regulatory requirements.

To foster wider adoption and successful integration of biosensor technologies, standardized protocols for their development, validation, and manufacturing are essential. Establishing these protocols will ensure consistent performance and facilitate comparability of results across different platforms and laboratories.

Looking to the future, biosensors are expected to play an increasingly important role in the detection and monitoring of pesticides, particularly in the context of environmental and food safety. The integration of biosensors with other technologies, such as smartphone apps and cloud computing, is also expected to further enhance the capabilities of biosensors and expand their applications.

In conclusion, biosensors represent a promising technology for the detection of pesticides, and further research and development in this area is essential to address the challenges and unlock the full potential of this technology for environmental and food safety.

Declarations

No conflicts of interests/Competing interests to declare

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