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Electrochemical Biosensors for Rapid Detection of Pesticide Residues in Fresh Produce: A Review of Nanomaterial-Enhanced Platforms

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ABSTRACT: Pesticides residues in fresh produce is an important food safety issue as repeated exposure through the diet can cause neurological, reproductive, endocrine, developmental and carcinogenic effects. Traditional chromatographic techniques are reliable for the identification and quantification of pesticides, but they are costly, need specialized staff, labor-intensive sample preparation and centralized laboratory. The present review explores the electrochemical biosensors based on nanomaterials as rapid, sensitive, portable and cost-effective alternatives for pesticide-residue screening. Metal nanoparticles, metal oxides, carbon nanomaterials, conducting polymers, metal–organic frameworks, two-dimensional materials and hybrid nanocomposites enhance the conductivity of the electrodes, surface area, immobilization of bioreceptors, catalytic activity, and signal amplification. Critically discussed are enzyme-based biosensors, immunosensors, aptamer-based sensors, molecularly imprinted polymer sensors and non-enzymatic platforms developed for organophosphates, carbamates, organochlorines, pyrethroids and neonicotinoids. Sample preparation, matrix effects, electrode fouling, sensitivity, selectivity, detection limits, recovery, reproducibility and comparison with chromatographic reference methods are also assessed in the review. Decentralized monitoring might be possible with emerging screen-printed electrodes, paper-based devices, microfluidic systems, smartphone interfaces, connectivity to the Internet of Things, and artificial intelligence-assisted signal analysis. Yet, there are significant challenges towards stability and safety of sensors, reproducible manufacture of nanomaterials, multiplexing, regulatory validation, and commercialization. To realize these platforms into reliable food-safety tools, standardized fabrication, use of sustainable materials, real-sample validation, and interlaboratory evaluation are key.

1. INTRODUCTION

The use of pesticides in agriculture is very common and has been used for many years to control insects, weeds, fungi, and other destructive organisms. Incorrect use, over-application, high levels of environmental persistence, and not using the correct pre-harvest interval can lead to residues being detected in fresh fruit and vegetables. Occurrence will depend on the class of pesticide, the type of crop, geographical location, farming practice, season and storage conditions, and a number of pesticides are routinely studied in produce-surveillance programmes, such as organophosphates, carbamates, pyrethroids, neonicotinoids and organochlorines. Contaminated fruits and vegetables are a significant route of non-occupational exposure to pesticides, since they are often consumed raw or as minimally processed foods. The highest burden of pesticide-induced disease is in agricultural workers, pesticide applicators, rural populations and low- and middle-income countries; consumers can potentially be exposed to pesticides over their lifetime in low doses via food and water. (2) Monitoring results from around the world show that pesticide residues are consistently found in fresh produce, and that a smaller, but clinically relevant, percentage of samples contain residues above legally established maximum residue limits and/or multiple pesticides. (3) Medically, acute pesticide poisoning can manifest as nausea, vomiting, abdominal cramps, excessive salivation, sweating, difficulty breathing, muscle weakness, altered level of consciousness, seizures or instability of the cardiovascular system, especially after significant exposure to organophosphates or carbamates. (4) Repeated or chronic exposure has been epidemiologically linked to neurological impairment, endocrine disruption, reproductive and developmental abnormalities, respiratory disorders, cardiovascular disease, and some cancers at varying levels of risk depending on the compound, the dose and the population. Developmental physiology, lower body weight, altered detoxification capacity, and pre-existing health conditions may make children, pregnant women, older adults, individuals with chronic diseases, and individuals with genetic or metabolic susceptibility particularly vulnerable. The Joint FAO/WHO Meeting on Pesticide Residues reviews the toxicological, dietary-exposure and supervised-field-trial data to help develop the Acceptable Daily Intakes, Acute Reference Doses and Recommended Maximum Residue Levels for protection of public health and for international food regulation. (7) Conventional residue confirmation is mainly based on gas or liquid chromatography and mass spectrometry, which has excellent sensitivity, selectivity and multiresidue capability. (8) Although QuEChERS extraction has made lab sample preparation easy, the chromatographic analysis still needs costly instruments, skilled staff, central laboratories, solvents, and a large amount of processing time, which hinders rapid decision-making at the field level. Electrochemical biosensors are another screening method that converts the pesticide–bioreceptor interaction to an electrical signal with potential benefits in speed, portability, low sample consumption, and cost. (10) Analytical sensitivity can be improved by increasing the surface area of the electrodes, the immobilization of bioreceptor, conductivity, electron transfer and signal amplification with nanomaterials like gold nanoparticles, graphene derivatives, carbon nanotubes, metal oxides, and hybrid nanocomposites. The platforms based on enzymes, immunology, aptamers, and molecular imprinting have been able to detect pesticides in real fruit and vegetable samples, and increasingly, platforms that are screen-printed, connected to a smartphone, and wearable enable monitoring on-site. Based on this, this review critically summarizes the principles of rapid electrochemical biosensing platforms, nanomaterials, analytical performance, real produce application, limitations, and future clinical and food safety relevance of pesticide exposure and their epidemiological and medical importance.

2. REVIEW METHODOLOGY

A structured literature search was conducted using PubMed, Scopus, Web of Science, ScienceDirect, and Google Scholar for studies published up to July 2026. Search terms included “electrochemical biosensor,” “pesticide residue,” “fresh produce,” “nanomaterial,” “fruit,” and “vegetable,” combined using appropriate Boolean operators. Original peer-reviewed studies reporting biosensor design, analytical performance, or real-sample validation were included. Reviews, conference abstracts, duplicate records, non-English publications, and studies lacking pesticide-specific findings were excluded. Titles and abstracts were screened before full-text evaluation. Relevant information concerning nanomaterials, bioreceptors, pesticide targets, detection limits, linear ranges, recovery rates, and fresh-produce matrices was systematically extracted.

3. FUNDAMENTALS OF ELECTROCHEMICAL PESTICIDE BIOSENSORS

Electrochemical pesticide biosensors are devices that combine a biorecognition element and an electrode-based transducer to transduce the interaction of pesticides into an electrical signal. They are made up of a working electrode, reference electrode, counter electrode, recognition layer, interface modified with nanomaterials, and a signal-processing system. The sensing reaction is facilitated by the working electrode, and the nanomaterials enhance the surface area, electrical conductivity, catalytic activity, electron transfer, and immobilization of the bioreceptor. The immobilization of acetylcholinesterase has been improved by the use of gold nanoparticles and by the use of composites based on graphene, and the sensitivity of the measurements of the inhibition of the enzyme by pesticides has been improved. (11) If a pesticide is bound to or inhibits an immobilized bioreceptor, the current, potential, conductivity, capacitance, and/or interfacial resistance is changed. It is noted that the complete recognition, transduction, amplification and signal output is shown in Figure 1. Amperometric sensors are used to monitor oxidation or reduction current at a fixed potential, while voltammetric methods (such as cyclic voltammetry, differential-pulse voltammetry and square-wave voltammetry) measure current over a range of applied potentials. Organophosphate and carbamate pesticides have been detected sensitively using nanocomposite-modified amperometric electrodes. (12) The changes in potential are detected by potentiometric sensors, and the changes in charge-transfer resistance and electrode capacitance are detectable by electrochemical impedance spectroscopy. The reduction of reagent use, sample volume and testing time for the portable analysis using screen-printed electrode systems.The sensor selectivity is given by (13) Biorecognition elements. Organophosphates and carbamates are detected by enzyme inhibition by acetylcholinesterase and butyrylcholinesterase, and degradation of organophosphate-by-organophosphate hydrolase. Devices which detect pesticide residues using hydrolase have been used successfully to detect pesticide residues in fruit and vegetables. All three materials (14) have different forms of antigen-specific recognition, namely antibody, conformational changes upon binding to the antigen, and selective synthetic cavities of molecularly imprinted polymers. Simultaneous pesticide determination has also been made possible by aptamer-based nanostructured platforms. (15) Analytical performance evaluated by sensitivity, selectivity, linear range, detection and quantification limit, response time, accuracy, precision, recovery, repeatability, reproducibility, stability, and reusability. The matrix-matched calibration and recovery test is necessary because the sugars, pigments, acids, and other components of the produce may affect the activity of the bioreceptors or affect the responses of the electrodes. As a result, an ideal biosensor should be able to detect pesticides with a high degree of sensitivity and specificity in a short period of time, without extensive sample preparation and in a repeatable manner, down to the maximum residue limit (MRL) established for them.

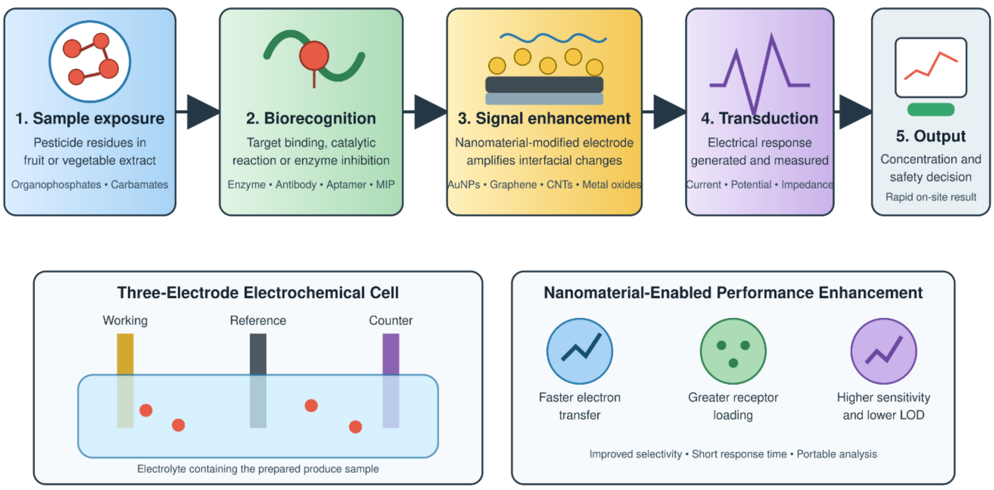

Figure 1. Working Mechanism of a Nanomaterial-Enhanced Electrochemical Biosensor

4. NANOMATERIALS FOR ELECTROCHEMICAL SIGNAL ENHANCEMENT

The use of nanomaterials enhances electrochemical pesticide biosensors in several ways: its use increases the surface area of the electrode, it facilitates the transfer of electrons, it increases the catalytic activity, it helps to stabilize the immobilization of the bioreceptor, and it amplifies the electrical response depending on the presence of the target. They are summarised in Table 1, in terms of their main properties, advantages, limitations and biosensing functions. Among the materials that have a high surface functionalization are the metal nanoparticles especially gold, silver, platinum and palladium, which have excellent conductivity and catalytic activity. Strong interaction between gold nanoparticles and thiol and amino groups is widely used for immobilization of enzymes, antibodies and aptamers, but the problems of aggregation, high cost, and batch-to-batch variability may limit large-scale production. (15) Catalytic activity, chemical stability and desirable adsorption properties are exhibited by metal-oxide nanoparticles such as ZnO, TiO_2, Fe_3O_4, CuO and MnO_2. They have drawbacks, such as particle aggregation, variable conductivity and possible interference from environmental conditions. Carbon based nanomaterials like graphene, reduced graphene oxide, carbon nanotubes, carbon dots, and mesoporous carbon have high conductivity, mechanical strength, chemical stability, and large specific surface area.These properties enable fast charge transport and high bioreceptor loading, but their hydrophobicity, poor dispersion and inconsistency, and the potential for cytotoxicity must be controlled. Graphene–gold nanocomposites have been shown to synergistically enhance the detection of pesticides via acetylcholinesterase. Tunable conductivity, flexible fabrication, low-cost synthesis, and compatible environment for biomolecule immobilization are the special properties of conducting polymers such as polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene). However, long term stability can be affected by polymer degradation or loss of conductivity, and by pH and temperature sensitivity. These polymers when mixed with metallic or carbonaceous nanomaterials give nanocomposites with high conductivity, mechanical strength, and signal amplification. (18) Metal–organic frameworks show extremely porous structures, tunable pore size, large amount of functional groups, and high loading capacity of enzymes, aptamers, or catalytic nanoparticles. The practical constraints are that they are moisture sensitive, have relatively low intrinsic conductivity, and are difficult to synthesize, often due to the need to combine them with graphene or conductive polymers and/or metal nanoparticles. Two dimensional materials like MXenes, molybdenum disulfide, tungsten disulfide and layered double hydroxides offer active sites for exposure, fast electron transfer at the interface and high adsorption. Two-dimensional materials and metals, carbon nanostructures, polymers or frameworks can be combined for more sensitive, selective, stable and multiplexed pesticide detection. However, reproducible synthesis, surface fouling, nanomaterial toxicity, scalable fabrication, and standardized characterization are important hurdles that need to be overcome before commercial translation. Therefore, the selection of nanomaterials needs to take into account not only detection limits but also their biocompatibility, stability, cost, environmental safety, and performance in complex matrices of fresh produce.

Table 1. Properties, Advantages, Limitations, and Biosensing Functions of Major Nanomaterials

Nanomaterial	Key properties	Advantages	Limitations	Biosensing function
Metal nanoparticles	High conductivity and catalytic activity	Rapid electron transfer and strong signal amplification	Expensive and aggregation-prone	Bioreceptor immobilization and electrocatalysis
Metal oxides	Stable, catalytic and adsorptive	Low cost and good enzyme loading	Limited conductivity and possible aggregation	Pesticide oxidation and enzyme support
Carbon nanomaterials	Large surface area and high conductivity	High sensitivity and rapid charge transport	Difficult dispersion and variable toxicity	Electrode modification and signal amplification
Conducting polymers	Flexible and tunable conductivity	Simple fabrication and biomolecule compatibility	Limited long-term stability	Receptor entrapment and electron mediation

Metal–organic frameworks	Highly porous and chemically tunable	Target enrichment and high receptor loading	Poor conductivity and moisture sensitivity	Pesticide adsorption and catalytic sensing
Two-dimensional materials	Exposed active sites and layered structure	Rapid electron transport and high sensitivity	Oxidation and restacking	Target enrichment and electrochemical transduction
Hybrid nanomaterials	Combined catalytic and electrical properties	Improved sensitivity, selectivity and stability	Complex fabrication and higher cost	Signal amplification and multiplexed detection

5. ELECTROCHEMICAL BIOSENSING PLATFORMS

The electrochemical pesticide biosensing platforms are divided based on the recognition element and signal generation mechanism. Acetylcholinesterase or butyrylcholinesterase are generally used as the enzyme in enzyme-based biosensors for the detection of organophosphate and carbamate pesticides by enzyme inhibition. Organophosphate hydrolase has an alternative catalytic mechanism but it directly hydrolyzes organophosphate compounds. They have high sensitivity and fast response, but enzyme instability, irreversible inhibition and interference of complex food matrix may have an impact on the repeatability of the results. (21) Immunosensors contain antibodies that bind a pesticide molecule or a conjugates of a protein and a pesticide with a high specificity. Amperometric, voltammetric or impedimetric methods are used for measuring electrochemical changes occurring as a result of the binding of the antigen to the antibody. They have the following drawbacks: high cost of antibody, short storage life, and the potential for cross-reactivity with structurally related compounds. (22) Aptamer-based sensors are sensors that use synthetic sequences of nucleic acids that undergo conformational changes depending on the target. Aptamers are highly affinity, chemically stable, reproducible and can be surface modified which makes them suitable for portable and multiplexed pesticide detection. (23) Molecularly imprinted polymer sensors are sensors that have artificial binding cavities that are imprinted with a pesticide. These are synthetic receptors which are cheap, chemically stable, thermally stable and can be used repeatedly, but may have a drawback of incomplete removal of the template and non-specifically binding to other substances. Non-enzymatic biosensors detect pesticides by direct oxidation, reduction, adsorption, and/or catalytic interaction with modified electrodes. They are free of enzyme-denaturation difficulties and have more operational stability, but careful engineering of the surface of the nanomaterials is needed to achieve sufficient selectivity. In general, the selection of platform depends on the pesticide structure, detection limit required, sample complexity, operational stability and intended field usage.

6. DETECTION OF MAJOR PESTICIDE CLASSES IN FRESH PRODUCE

Electrochemical biosensors have been designed and developed for detection of the major classes of pesticides in fruits and vegetables. The measurement of organophosphates is often conducted by measuring the inhibition of acetylcholinesterase, the activity of organophosphate-hydrolase, aptamer recognition and/or direct electrochemical oxidation. Nanomaterial-modified electrodes enhance their capabilities of detection by elevating the amount of enzymes that can be loaded into the electrode and the amplification of the signal that is generated from inhibition. Cholinesterase inhibitors: (26) Carbamate pesticides, e.g., carbaryl and carbofuran, can also inhibit cholinesterase activity and can be measured on amperometric or voltammetric platforms. But it can be difficult to tell the difference between carbamates and organophosphates as they both exhibit similar inhibition responses. Organochlorines are typically identified with immunosensors, molecularly imprinted polymers or catalytic nanostructured electrodes due to the lack of strong enzyme-inhibition response. They are hydrophobic and persistent, and as such must be efficiently extracted and recognized on the surface. Electrochemical detection of pyrethroids, although difficult, is possible due to their low water solubility and poor electroactivity, while electro-sensors based on aptamer, molecularly imprinted or direct voltammetric sensors enable the detection of neonicotinoids like imidacloprid, acetamiprid, thiamethoxam, and clothianidin. Multiplexed aptasensors were developed based on a graphene platform, allowing the simultaneous determination of several neonicotinoids. (29) Multipesticide detection involves a combination of electrode arrays, multiple recognition elements, differential signal labels and chemometric or machine learning analysis to detect multiple residues in a single test. The advantage of these systems is that they can save time and help to use less sample for analysis but they have issues with cross-reactivity, overlapping signals, differences in the electrode to electrode and matrix effects. A comparison of the performance of representative nanomaterial-based biosensors in fresh produce samples is summarized in Table 2. (30) In the future, multiplexed detection, portable instrumentation, matrix matched calibration and reliable validation against chromatographic reference methods should be integrated into platforms.

Table 2. Comparative Performance of Nanomaterial-Enhanced Electrochemical Biosensors for Pesticide Detection in Fresh Produce

Study	Pesticide	Biosensing platform	Technique	Detection limit	Produce sample	Recovery
Cesarino et al., 2012	Carbaryl; methomyl	AChE/PANI–MWCNT electrode	Chronoamperometry	1.40; 0.95 μM	Apple, cabbage and broccoli	94.6–103.4%
Dong et al., 2019	Malathion; methyl parathion	AChE/AuNPs–3D graphene	Amperometry	2.78×10^{-11}; 2.17×10^{-11} g/L	Vegetable samples	94–106%
Zahirifar et al., 2019	Diazinon	CNT-modified carbon-paste electrode	Square-wave voltammetry	4.5×10^{-10} M	Fruit samples	Satisfactory
Nunes et al., 2022	Carbaryl	AChE/functionalized renewable carbon	Differential-pulse voltammetry	4.5 nM	Apple	102.5–118.6%
Pramadewandaru et al., 2025	Carbofuran	AChE/graphene–Au/carbon foam	Cyclic voltammetry	8.08 μM	Vegetable samples	88.95–111.30%

Abbreviations: AChE, acetylcholinesterase; AuNPs, gold nanoparticles; CNT, carbon nanotube; MWCNT,multiwalled carbon nanotube; PANI, polyaniline.

7. SAMPLE PREPARATION AND ANALYTICAL VALIDATION

The representative sampling and controlled preparation are necessary to obtain reliable electrochemical analysis of pesticide residues in fresh produce. Fruits and vegetables must be picked from various batches or markets in clean containers, kept at a low temperature while in transport and be analyzed as soon as possible to reduce the possibility of pesticides breaking down. Samples are typically not washed unless it is a consumer ready produce.Washing of samples is not recommended when studying a consumer ready produce, unless the study involves the total residues, in which case they are homogenized. The extraction could be carried out by chopping, blending, centrifugation, filtration and/or dilution, extraction in solvents, solid-phase extraction or QuEChERS procedure depending on the polarity, concentration and composition of the produce and the pesticide. QuEChERS is frequently preferred as it allows the extraction and dispersive cleaning of the samples in a short time while using a minimal quantity of solvents. Complex produce matrices include sugars, pigments, organic acids, lipids, salts, fibres and phenolic compounds which can either inhibit or enhance electrochemical signals. These can interfere with receptors and/or alter the conductivity of electrolyte or foul the electrolyte or binding sites of the electrodes causing loss of sensitivity. The possible means of reducing matrix interference in the sample are dilution, filtration, magnetic separation, protective membrane, and standard addition and matrix-matched calibration. Analytical sensitivity is based on the calibration-curve slope and selectivity is assessed by structurally similar pesticides, metabolites, ions and natural food constituents. Blank variability and calibration response should be used to determine the limit of detection and limit of quantification and the results should be compared with applicable maximum residue limits. Evaluation of accuracy is done by comparing concentration values to fortified or reference concentration values. To assess performance over the analytical range, at least three fortification levels, and multiple replicates, should be used for recovery experiments.(30) Repeatability refers to measurements taken under the same conditions, and reproducibility refers to variation between the electrodes, analysts, days, instruments, or laboratories. The stability of the sensor, storage life, response time, and batch variability of the sensor should also be reported. Finally, electrochemical results should be compared to measurements by GC–MS/MS and/or LC–MS/MS. Biosensors offer advantages for preliminary screening in terms of faster analysis, lower cost, need for less solvent and portability, while chromatographic methods are better for compound confirmation and multiresidue coverage. (31)

8. PORTABLE AND INTELLIGENT BIOSENSING TECHNOLOGIES

Smart and mobile biosensing technologies allow pesticide-residue testing directly in the farm, wholesale markets, retail stores, processing centers and border-control points. Screen-printed electrodes are also very well suited for applications in the field, since the working, reference and counter electrode can be manufactured on a compact and disposable substrate. They are able to process small sample volumes, can be manufactured in large numbers and are amenable to modification with enzymes, aptamers, antibodies, molecularly imprinted polymers and nanomaterials. Humidity, substrate variability, and limited storage life are some of the disadvantages associated with paper based electrochemical sensors, but the sensors are also low cost, light, and powered by capillary driven sample movement with minimal reagent use. (31) Microfluidic and Lab-on-a-Chip systems combine the process of loading, mixing, filtration, separation, recognition and electrochemical measurement into miniaturized channels. With their controlled fluid handling, they minimize reagent use, response time, and enable automated and multi-pesticide detection. Challenges are channel blockage, formation of bubbles, complex product extraction and recovery in complex extracts. Smartphone integration facilitates the wireless or wireless-less transfer of data from portable potentiostats or sensor interfaces via Bluetooth, near-field communication or wired protocols. Mobile Apps can be used to show the level of pesticide, to warn farmers, consumers and regulatory bodies, store geotagged data and compare to the Maximum Residue Limits.The Internet of Things can connect a variety of devices to cloud platforms to monitor residues on the fly, track supply chains and map contamination at a regional level. (33) AI and machine-learning algorithms can correct baseline drift, compensate for matrix effects, classify voltammetric patterns, discriminate overlapping pesticide signals and predict electrode degradation. They remain reliable, however, based on representative training data, external validation, transparency in modelling, and standardized sensor outputs. (34) In an integrated portable platform as shown in the illustrative embodiment of FIG. 3, a fresh-produce sample is subjected to an expedient extraction process prior to using the fresh-produce sample on a disposable nanomaterial enhanced electrode.

Figure 3. Integrated Portable Platform for On-Site Pesticide Monitoring in Fresh Produce

A mini electrochemical reader provides the signal and the signal is sent to a smartphone app which calculates pesticide concentration, gives a safety reading, and uploads results to a secure monitoring network. Simple operation, robust calibration, data security, regulatory compatibility, field validation, and low cost large volume production are important attributes for future systems. (35)

9. CURRENT CHALLENGES AND FUTURE PERSPECTIVES

The use of electrochemical pesticide biosensors is still limited due to sensor instability, inconsistent sensor manufacturing process, interference from the matrix, and limited standardization. The activity of the bioreceptors, the properties of the nanomaterials, the modification of the electrodes, storage conditions, and calibration procedures can cause large differences in sensor batches. The toxicity of nanomaterials, persistence in the environment, use of energy-intensive synthesis methods and issues of disposal need to be tackled with green production, biodegradable substrates and life cycle assessment. Receptor crossreactivity, overlapping electrochemical signals, electrode fouling, and lack of pesticide chemical similarity are all potential problems for multiplexed detection. For commercialization, a reproducible manufacturing process is needed, the recognition elements must be stable, the reader must be portable and affordable, the process must have quality control and sample preparation must be simple. The pre-approval of the regulations will be based on validation of the chromatographic reference methods, interlaboratory testing, certified reference materials, and maximum residue limits. Future research will focus on sustainable nanomaterials, antifouling interfaces, multiplexed electrodes arrays, AI-enhanced signal interpretation, automated calibrations, long-term stability, as well as extensive field testing in various crops, pesticide classes, environmental and food-supply scenarios.

10. CONCLUSION

Electrochemical biosensors with nanomaterials are a potential method for the fast detection of pesticides in fresh products. Metal nanoparticles, metal oxides, carbon nanomaterials, conducting polymers, metal–organic frameworks, and 2D materials enhance the surface area of the electrodes, bioreceptor immobilization, amplification of the signal, and electron transfer. Organophosphates, carbamates, organochlorines, pyrethroids and neonicotinoids have been detected using enzyme-based, immunological, aptamer-based, molecularly imprinted and non-enzymatic platforms. Portable screen printed electrodes, paper based devices, microfluidic systems, smartphones and connected readers are important options for screening at farms, markets, retail outlets, and border-control points. However, the use of complex produce matrices, electrode fouling, poor storage stability, matrix fabrication variability, and inadequate real-sample validation remain as limitations to routine implementation. The advancement of sustainable materials, multiplexing, artificial intelligence, standardized manufacturing, or validation by regulators could enable these biosensors to become reliable tools for decentralized food-safety surveillance, real-time management of contamination, better traceability of the supply chain, and better consumer protection.

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