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Progress of rapid detection of pesticides in fruits and vegetables

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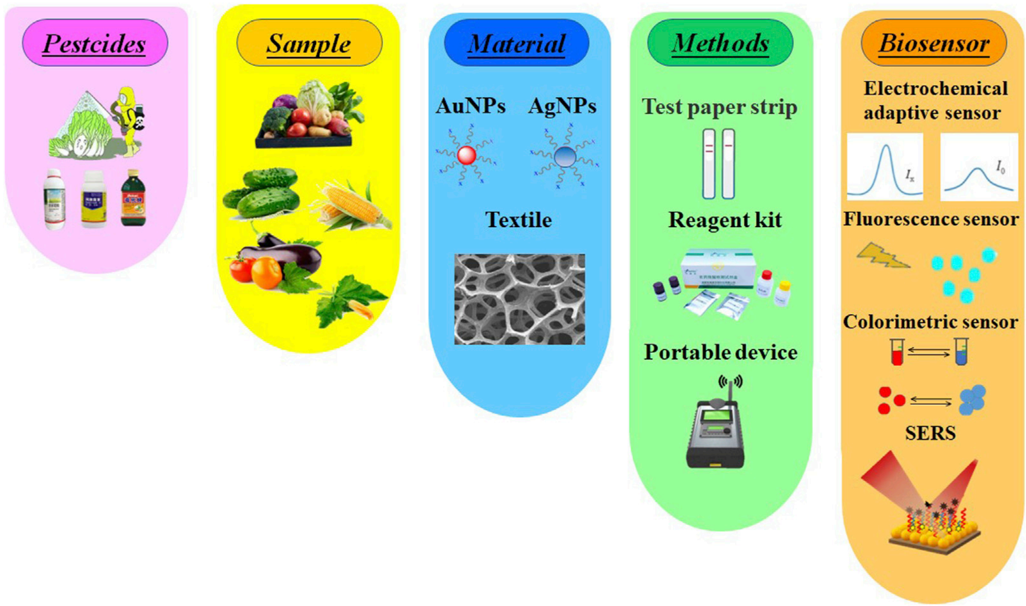
Pesticide residues in fruits and vegetables present a significant concern for human health and safety. By 2022, an average of 3 million people worldwide is poisoned by pesticides every year, and the mortality rate can reach about 20%. This comprehensive review summarizes recent research on the detection of pesticide residues, focusing on the main detection methods and their implications. The study highlights the growing importance of biosensors as a prominent technique, offering enhanced efficiency and accuracy in pesticide residue analysis. The review addresses the challenges associated with pretreatment methods and discusses the advantages and limitations of biosensors. Furthermore, it emphasizes the need for further research to optimize the adaptive capabilities of biosensors, particularly their anti-interference abilities. The findings underscore the significance of developing intelligent adaptive sensors for on-site pesticide residue detection, eliminating the need for complex sample pretreatment. This comprehensive review serves as a valuable reference, facilitating future advancements in pesticide residue analysis, ensuring food safety, and safeguarding consumer health in modern agriculture.

KEYWORDS

pesticide residues, fruits and vegetables, detection, biosensor, high-efficiency

1 Introduction

Pesticide contamination in fruits and vegetables has become a serious concern due to its detrimental effects on human health and the environment. Currently, the widespread utilization of pesticides such as Glyphosate, Chlorpyrifos, Neonicotinoids, Mancozeb, and Pyrethroids during fruit and vegetable cultivation has been associated with adverse health effects in humans. These effects encompass symptoms such as headaches, dizziness, skin irritations, nausea, vomiting, and more severe implications involving the nervous system, endocrine system, and immune system. Additionally, extended or repetitive exposure to specific pesticides may be linked to chronic illnesses, including cancer, fertility issues, and neurodegenerative diseases. Furthermore, from an environmental standpoint, pesticides have the potential to inflict harm upon ecosystems by disrupting the balance and unintentionally targeting non-beneficial organisms, including beneficial insects and wildlife. Residues of these pesticides can infiltrate soil and water sources, resulting in detrimental consequences for both soil ecosystems and aquatic life, ultimately undermining ecological equilibrium. The indiscriminate use of pesticides in agricultural practices has led to the accumulation of harmful residues in food products, posing significant risks to consumers. Consequently, the development of reliable and sensitive detection methods for pesticide residues has gained substantial attention.



GRAPHICAL ABSTRACT

The conventional detection methods for pesticides, as well as the national standard methods, primarily involve High Performance Liquid Chromatography (HPLC), Mass Spectrometry (MS), and Gas Chromatography (GC). These methods have been widely recognized for their reliability (Cunha et al., 2011). However, these traditional approaches suffer from inefficiency, requiring complex sample pretreatment, expensive instrumentation, and trained personnel. With global crop production reaching unprecedented levels, the demand for pesticide detection exceeds the capabilities of traditional methods.

To address these limitations, recent research has focused on the development of innovative sensing platforms for pesticide detection. One promising avenue is the utilization of sensors based on various transduction principles, such as fluorescence, colorimetry, and electrochemistry. These sensor-based approaches offer several advantages over traditional methods, including simplicity, rapidity, cost-effectiveness, and the potential for on-site analysis.

In this review, we aim to provide a comprehensive overview of sensor-based detection methods for pesticide residues in fruits and vegetables. We will discuss the principles, characteristics, and applications of fluorescence sensors, colorimetric sensors, and electrochemical sensors. By examining the latest advancements in sensor technology, we will highlight the potential of these approaches in addressing the challenges associated with pesticide detection.

2 Application of various biosensors in pesticide residues

2.1 Selection of aptamers for biosensors

In the construction of biosensors, proper selection of aptamers is a crucial step. Aptamers have garnered significant attention in recent years as recognition elements for various targets, making aptamer-based detection systems an emerging trend in analytical technology development (Phopin and Tantimongcolwat, 2020). Oligonucleotide sequences, including both deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), possess the ability to fold into specific conformations and bind rapidly to homologous ligands with high affinity and specificity. This characteristic makes them ideal recognition elements for diverse analytical systems (Zamora-Sequeira et al., 2019). For instance, a research team utilized MX ENE/Carbon Nanohorn/β-Cyclodextrin-Metal-Organic Frameworks (MOFs) as an aptamer for adsorbing the carbendazim pesticide, thereby establishing an electrochemical sensor. The aptamer exhibited excellent catalytic activity for carbendazim oxidation due to its high electronic conductivity and abundant electrocatalytic active sites of β-CD- MOFs. Consequently, the sensor demonstrated a wide linear range from 0.003 to 10.0 microns, along with a low detection limit (LOD) of 1.0 nm (Tu et al., 2020). Therefore, during the biosensor construction stage, the selection of aptamers directly influences the detection efficacy of pesticide residues post-construction.

There are many choices of materials for biosensors. As a kind of hydrophobic colloid with negative charge, gold nanoparticles (AuNPs) have a large surface area and are simple to prepare. The particle size can be uniformly controlled, and the surface can be effectively modified by thiols or other biological ligands (Gong et al., 2023). AuNPs provide a large number of effective and promising general platforms for biomolecules such as antibodies, enzymes, aptamers and DNA because of their unique and efficient characteristics and low toxicity (Geng et al., 2014).

In addition, silver nanoparticles have the highest electrical conductivity, thermal conductivity and reflectivity, and are almost harmless to human body. Therefore, silver nano particles often appear as an aptamer for biosensors (Song et al., 2010).

In recent years, the appearance of magnetic nano-materials (MNPs) with unique physical and chemical properties has greatly simplified the complicated traditional experimental steps and shortened the experimental time (Zhu et al., 2018). MNPs is a kind of nano-sized particle, which is usually composed of iron (Fe), cobalt (Co), nickel (Ni) and other metal oxides (Koul et al., 2021). MNPs is usually used as an electrode modifier in the integration of pesticide residue determination and detection technology. When used as an electrode modifier, MNPs can significantly enhance the electron transfer between analyte and electrode due to its very high charge transfer ability (Mollarasouli et al., 2021). Especially Fe_3O_4, which has high biocompatibility and simple preparation, has a wide range of applications. For example, acetylcholinesterase (AChE) can be covalently immobilized on the surface of iron oxide nanoparticles (Fe_3O_4-NP), and then immobilized on the gold electrode modified by carboxylated multi-walled carbon nanotubes (c-MWCNT) as the working electrode (WE), Ag/AgCl as the standard electrode and platinum as the auxiliary electrode. The LOD of this biosensor for malathion (MLT) and chlorpyrifos (CLPF) is 0.1 nM, monocrotophos is 1 nM and endosulfan is 10 nM. The biosensor has a good sensitivity of 0.475 mA μM^{-1}, can be reused for more than 50 times, and the detection effect is stable within 2 months (Chauhan and Pundir, 2011).

At present, the appearance of MOF provides a highly selective platform for biosensor detection. MOF is a crystalline material with inorganic metal centers connected by organic ligands, which has unparalleled adjustability, large surface area, high porosity, excellent catalytic activity and rich active sites (Kajal et al., 2022). At present, a large number of MOF materials have been applied to the construction of biosensors, such as Cu-MOF (Dang et al., 2020), zirconium-based (Zr-MOF), nickel-based (Ni-MOF) (Gao et al., 2020), Fe-MOF and Co-MOF. In order to further endow MOF with more functions and improve its performance, it is an effective strategy to modify MOF by introducing heteroatoms, functional groups and metal ions.

For the visual detection of organophosphorus pesticides (Ops), a biosensor based on aptamer-mediated bimetallic organic skeleton nano-polymer was developed. Based on pyrolysis reaction, Fe-Co MNPs and Fe-N-C nano-enzyme were prepared and labeled with broad-spectrum aptamers and complementary chains of Ops respectively. In the presence of target pesticides, they compete with the complementary chains of nucleic acid aptamers on Fe-Co MNPs, resulting in a large number of Fe-N-C nano-enzyme signal markers being released into the supernatant. In order to complete the visual detection of Ops. It has good stability and specificity for phorate, profenofos, isocarbophos and omethoate. The LOD of the four pesticides are 0.16, 0.16, 0.03 and 1.6 ng/mL respectively, and the recovery rate of Ops in vegetable samples is satisfactory, reaching as high as 89.19%–108.35%, with a relative standard deviation (RSD) of less than 11.31%. (Shen et al., 2022).

2.2 Different types of biosensors

2.2.1 Electrochemical adaptive sensor

In recent years, electrochemical sensors based on aptamers have exhibited promising development prospects in the field of biosensors. These sensors offer several advantages, including multiplex analysis, rapid response, high sensitivity, specificity, and cost-effectiveness. The construction of an electrochemical aptamer-based sensor primarily involves three key processes: signal amplification, selection of analytical methods, and strategy determination (Dauphin-Ducharme et al., 2019).

The strategy employed in electrochemical sensors relies on measuring the electrical signals generated at the interface between the sensing electrode and the target analyte, such as potential, current, and charge. Typically, an electrochemical cell consists of three essential components: the counter electrode (CE), the WE, and the reference electrode (RE) (García-Miranda Ferrari et al., 2020). Voltammetry, for instance, employs a reference electrode, such as the Ag/AgCl electrode, whose voltage changes over time. By simultaneously measuring the current response at the WE and CE, the voltammetry technique enables the detection and quantification of target analytes (Usmani et al., 2021). This detection principle is based on the movement of electrons produced during oxidation-reduction reactions (Teymourian et al., 2020). The three-electrode system can be conveniently integrated onto a single substrate, allowing for the construction of simple biosensors and facilitating micro-detection (Kaushik et al., 2020).

For the immobilization methods of electrochemical aptamer sensors, the most commonly used immobilization methods are covalent bond formation, attractive force reaction and self-assembly strategy (Ferentinos et al., 2013). For example, a portable paper-based electrochemical biosensor using office paper in daily life has been developed. Compared with traditional plastic tape, this kind of sensor allows people to print conductive tape for electrochemical connection, load bio-hybrid nano-probes (Prussian blue, carbon black and butyrylcholinesterase), evaluate pesticides and reduce waste disposal. The portable system has been characterized by a low LOD of 1.3 ng/mL, and according to the total discovered pesticide contents in EU agricultural soils, up to ca. 3 μg/mL, a good recovery rate of 90%–110% was obtained in different substrates. It can offer a valuable tool for fast monitoring (Cioffi et al., 2021).

Furthermore, a successful construction of a voltammetric biosensor for the detection of acetylcholine (ATCh) and paraoxon was achieved. A platinum (Pt) electrode surface was coated with polypyrrole (PPy), and subsequently, chitosan (Chi) was applied as a protective layer on the PPy-coated Pt electrode (Pt/PPy/Chi). AChE was immobilized onto the surface of the Pt/PPy/Chi electrode, resulting in the fabrication of a voltammetric biosensor (Pt/PPy/Chi/AChE) (Akdag et al., 2021).

The operational stability of the biosensor was assessed, and after conducting a set of 20 consecutive measurements, it exhibited a stability rate of 94%. Notably, the biosensor displayed a linear range of 30–50 μM for ATCh, as well as a linear range of 0.46–1.84 nM for oxygen and phosphorus. The LOD for ATCh was determined to be 0.45 μM, while the LOD for oxygen and phosphorus was found to be 0.17 nM.

In addition, for Ops, diazinon (DZN), MLT, and CLPF, an improved method of combining pyrolytic graphite electrode (PGE) with batch injection analysis system (BIA-MPA) with multi-pulse amperometric detection was established. Two potential pulses were used to detect the MPA of DZN, MLT, and CLPF. Under the optimized conditions, the linear range of the sensor is 0.1–20 $\mu mol\ L^{-1}$ for DZN, 1.0–30 $\mu mol\ L^{-1}$ for MLT and

0.25–50 μmol L^{-1} for CLPF. The LOD and limits of quantification (LOQ) of DZN were 0.35 and 1.18 μmol L^{-1}, MLT was 0.89 and 2.98 μmol L^{-1}, CLPF was 0.53 and 1.78 μmol L^{-1}, respectively. The detection sensitivities of DZN, MLT, and CLPF were 0.068, 0.030, and 0.043 mA L μ mol^{-1}, respectively, and the recovery values were between 77% and 124% (Porto et al., 2022).

A team constructed a highly sensitive electrochemical biosensor for CLPF detection, which was composed of human serum albumin and Pd-doped CdTe quantum dots (Pd:CdTe). The formation of CLPF-HAS complex in its nano-matrix led to the increase of the resistance of the electrode surface. SIF and faradaic electrochemical impedance spectroscopy (FEIS) technologies were used to analyze the resistance data. The results show that the TGA-capped Pd:CdTe improves the electron transfer rate and provides a good environment for the immobilization of HAS. The LODis as low as 0.16 p.m., and the recovery rate is as high as 96.6%–105.9% (Ehzari et al., 2022).

A polyaniline/coal-like double hydroxide composite material (PANI/CoAl-LDH) prepared by using PANI- and CoAl-LDH- structural units which are uniformly mixed by ultrasound is used as a modified glassy carbon electrode (GCE), which can realize rapid electron transfer and mass transfer between the substrate electrode and the analyte. And the angular sensor gives rise to a wide linear range of 0.1–150 μm for both carberry and isoprocarb at 0.19 and 0.39 V (vs. SCE) respectively. Their LOD are respectively 6.8 and 8.1 nM. This sensor is successfully used for the determination of carbaryl and isoproc arb pesticides in real vegetable samples with a RSD below 4% (Jiao et al., 2022).

In response to the challenge of on-field detection of pesticide residues in complex fruit and vegetable matrices, a dual-channel sensing platform based on immunoassays has been developed. This electrochemical sensor is coated with Glyphosate antibodies on one side and Chlorpyrifos antibodies on the other. The sensor response was assessed using non-faradaic EIS, revealing a linear response to Glyp/Chlp concentrations ranging from 0.3 ng/mL to 243 ng/mL in both low-fat and high-fat matrices, with detection limits of 1 ng/mL. It demonstrates high selectivity in detecting target antigens, even within complex matrices containing inherent nutritional components (Poudyal et al., 2023).

The main advantage of electrochemical technology is that it is difficult to make mistakes in the color, overlap, interference and similar colors of interference components in the detection of actual samples (Kwon et al., 2021). At the same time, electrochemical technology is not easily influenced by colored and turbid substrates, and has high binding affinity with targets, so it only needs less sample volume (usually μL) (Shin et al., 2021). Based on this, many portable electrochemical sensors have been developed to detect pesticide residues in fruits and vegetables. For example, a new electrochemical sensor constructed by integrating laser-induced graphene (LIG) electrode on polyimide (PI) foil and MnO_2 is used to detect Ops, as shown in Figure 1. This sensor triggers the decomposition of MnO_2 through the hydrolysis product catalyzed by AChE, and releases auxiliary DNA to start the recovery and amplification of nicking enzyme. When Ops exists, the activity of AChE is inhibited. The detection linear range of the biosensor is 3–4,000 ng/mL, and the LODis as low as 1.2 ng/mL (Liu et al., 2022). It is not difficult to see that the portable electrochemical sensor has the advantages of economy, portability, simplicity, labor saving, portability, easy operation, high throughput and on-site detection ability. At the same time, it can realize the connection with digital port and Bluetooth, and observe the detection data more intuitively and conveniently (Umapathi et al., 2022a).

Electrochemical biosensors exhibit certain limitations when employed for the detection of pesticide residues in fruits and vegetables. Primarily, their sensitivity is often constrained, potentially rendering them incapable of detecting low-concentration pesticide residues, consequently heightening food safety risks. Furthermore, the selectivity of biosensors relies on the biological components employed, occasionally resulting in cross-reactivity with various pesticides, thereby leading to erroneous positive or negative outcomes. Moreover, intricate compounds and impurities inherent in fruit and vegetable samples may compromise the sensor's performance, necessitating complex sample pretreatment procedures to enhance precision. Additionally, electrochemical biosensors are typically customarily tailored for specific pesticide categories, constraining their versatility in comprehensive pesticide residue analysis. The maintenance of biosensor activity demands periodic replacement or reconfiguration, thereby escalating operational expenses, while stability may be susceptible to environmental factors and storage conditions. Lastly, the development and maintenance of these sensors require substantial time and resources, potentially inflating detection costs. Despite these limitations, electrochemical biosensors remain a promising technology, affording rapid, user-friendly, and real-time detection methodologies that contribute to upholding food safety.

2.2.2 Fluorescence sensor

Fluorescence sensor is one of the most commonly used sensing technologies for biomolecular interaction, which is suitable for a large number of detection directions. Fluorescence sensor has always had the advantages of high sensitivity, high detection efficiency, simple method and fast analysis (Dong et al., 2020). In recent years, the vigorous rise of aptamers has driven the development of fluorescence sensors, and various kinds of fluorescence sensors have appeared. The sensing mechanism of fluorescence sensor mainly includes fluorescence resonance energy transfer, electron energy transfer, photoinduced electron transfer, intramolecular charge transfer, twisted intramolecular charge transfer and metal ligand charge transfer (Hildebrandt et al., 2017). However, this is also the difficulty in the construction of fluorescence sensor. An ideal interaction system based on the principle of resonance energy transfer requires a pair of suitable fluorescent substances, that is, the emission spectrum of the donor obviously overlaps with the absorption spectrum of the acceptor. Moreover, when the excitation wavelength of the donor has no effect on the acceptor, the emission spectra of the donor and acceptor should be completely separated, otherwise, it is easy to cause spectral interference and make the reaction system unstable (Fang et al., 2020), the commonly used donor-acceptor molecular pairs, mainly include green fluorescent proteins (GFPs) and dyes. The detection types of fluorescence technology can also be divided into single-wavelength detection and dual-wavelength detection; Dual-wavelength detection, that is, ratiometric fluorescence method, combines the reference signal with the response signal, which can eliminate the false signal caused by matrix effect and further improve the sensitivity of the sensor (Han et al., 2020), as shown in Table 1.

In recent years, the detection of Ops based on enzyme activity inhibition has attracted great attention. A research team successfully detected Ops by alkaline phosphatase. In this fluorescence strategy, Scopoletin (SC) and Amplex Red (AR) are used as probe pairs, and by utilizing the catalytic activity of MnO_2 nanosheets (MnO_2 NS) similar to peroxide, the team can quench the fluorescence of SC through oxidation, while enhancing the fluorescence of non-fluorescent substance AR. In the absence of organic phosphorus, AChE hydrolyzes ATCh into choline (TCh) and acetate. TCh resulted in MnO_2 NS decomposing into manganese ions (Mn^{2+}), which enhanced the signal of SC and decreased the signal of AR. On the contrary, when Ops exists, the presence of Ops inhibits the activity of AChE and hinders the decomposition of manganese dioxide, so the fluorescence intensity of SC is weak and that of AR is obviously enhanced. Therefore, by recording the ratio of fluorescence intensity response on AR/SC, a novel ratio fluorescence biosensor can be constructed (Yao et al., 2019). The method has wider linear range of 5.0 pg/mL ~500 ng/mL with a LOD of 1.6 pg/mL, which is superior to previously reported methods.

A team prepared a biosensor with dual recognition strategy for accurately and sensitively identifying a target organophosphorus in complex vegetable samples. In this biosensor, besides phosphorus, molecularly imprinted polymers with high selectivity for some parts were used as selective sample pretreatment agents to selectively enrich phosphorus from the samples. Then the acephate (AP) captured by molecularly imprinted polymer (MIP) was quantified by acetylcholine. Selective pretreatment ensures that the biosensor can identify AP from analogues, carbamate pesticides and other interferents in the sample. When analyzing vegetables with high matrix effect, the accuracy of the sensor is much higher than that of the traditional AChE inhibition chemiluminescence assay, and the LOD for Ops is 1 μg/Kg (Qi et al., 2021).

In addition, in recent years, upconversion nanoparticles (UCNPs), a new probe for Ops, has been introduced. The traditional probe is prone to photobleaching, which directly leads to the failure of imaging. UCNPs has unique physical and chemical characteristics, which can ignore the changes of chemical characteristics caused by photobleaching and long-term storage. Moreover, UCNPs is not easy to receive the interference of autofluorescence under infrared spectrum. A research team synthesized a new type of dopamine-functionalized UCNPs (UCNP-DA). This method can inhibit the fluorescence characteristics of UCNP-DA through the inhibition of the activity of organic phosphorus pesticides on the complex amino acid enzyme, so as to successfully construct an efficient fluorescence sensor (Liu et al., 2019). Under the optimal conditions, CLPF can be analyzed in a wide range of 1.0–1,000 ng mL^{-1}, with a LOD of 0.38 ng mL^{-1} (3σ). Some other groups pesticides, including organonitrogen pesticide, organochlorine pesticide and chloronicotinyl insecticide all showed negligible interference. The proposed sensor was successfully used to analyze CLPF spiked in Balloon flower and Angelica with acceptable recovery values of 95.4%–120.0%.

A research team proposed a novel optical microfluidic biosensor for detecting Ops and carbamate pesticides. They modified AChE and acetylcholine chloride (AChCl) on a 1 × 17.6 mm paper base with a small hole between them, which was carried by the sample solution to the reaction zone containing bromocresol violet (BCP) through lateral flow and fixed by sol-gel, and then contacted in the reaction zone. This biosensor works at room temperature, and the inhibited rate is used as the analysis signal to analyze the pesticide content. Calibration curves were obtained for CLPF and carbaryl, with a useful concentration range from 0.24 to 20 μg/L for carbaryl and from 2.00 to 45 μg/L for CLPF. The LOD were 0.24 and 2.00 μg/L, respectively, and with reproducibility around 4.2%–5.5%. The method was applied to the determination of pesticides in different water samples, with no sample preparation (Fernandez-Ramos et al., 2020).

For high-throughput and rapid analysis of organophosphorus, a high-throughput nucleic acid aptamer microarray fluorescence detection method based on thiosulfate T (ThT) was established for sensitive detection of phoxim, parathion, fenthion and isocarbophos. In this strategy, the aptamers in the binding buffer tend to have anti-parallel G-quadruplex structure, which can bind ThT and release its potential fluorescence signal. However, when Ops exist, some aptamers tend to bind to them, forcing ThT to be displaced from G-quadruplex, resulting in a significant decrease in fluorescence signal. Under the optimal experimental conditions, the LOD of phoxim, parathion, fenthion and isocarbophos are 25.4 ng/mL, 12.0 ng/mL, 7.7 ng/mL and 9.9 ng/mL, respectively. The developed aptamer microarray technology not only has low sensitivity and broad spectrum, but also allows high-throughput and rapid analysis of various organophosphorus, which overcomes some shortcomings of other organophosphorus detection methods (Wang et al., 2022).

It exhibits some advantages like low cost, high sensitivity and free of auto fluorescent interference and photobleaching. It has practical application potential in applied samples.

In recent years, in addition to the above-mentioned organic small molecule fluorescent probes with simple structure and simple synthesis, the rapid development of nanomaterials, MOFs, quantum dots and metal nanoparticles has also provided a new way for the development of fluorescent probes (Liu et al., 2020). Among them, MOFs shows higher surface area due to its unique compactness and porous structure. In addition, it can protect the coated active molecules from being dissolved in cells or complex environment, and at the same time, it also plays a good role in enhancing the performance of the probe (Kumar et al., 2019). Quantum dot is a new semiconductor nanomaterial (Chung et al., 2021), It has good optical and chemical properties, high quantum yield and good biocompatibility. Some quantum dots do not even need infrared excitation light to achieve high sensitivity and rapid analysis (Iravani and Varma, 2020).

Fluorescence sensing strategy has become the cornerstone of the possibility of pesticide field detection in the future, but there are still many challenges in making field devices that meet international standards. At present, the fluorescence sensors mainly used for on-site detection are mainly based on paper-based, liquid-based and gel-based optical technologies (Umapathi et al., 2022b).

In addition, fluorescence sensors are subject to sensitivity limitations and encounter difficulties in detecting trace amounts of pesticides. Furthermore, the selectivity of fluorescence sensors depends on the antibodies or fluorescent labels used, which may lead to false positives. Moreover, fluorescence signals can be influenced by environmental factors and storage conditions, resulting in signal instability, necessitating additional calibration and standardization steps.

2.2.3 Colorimetric sensor

Colorimetry is widely used to detect pesticide pollutants because of its application in food and environment. Its advantages include easy preparation, low cost and clear observation of results with naked eyes. AuNPs and silver nanoparticles are the most common probes for colorimetric sensing analysis in the detection of pesticide residues by colorimetry (Lan et al., 2017). Therefore, in order to improve the sensitivity of colorimetric sensor based on gold and silver nanoparticles, it is a common method to modify AuNPs. For example, silk fibroin was used to modify AuNPs, and a kind of AuNPs -silk fibroin (SF-AuNPs) was developed, and a colorimetric biosensor with high sensitivity to CLPF was successfully constructed. After degumming, dissolving and enzymolysis, silk protein solution was extracted and dialyzed, this FB Roin solution was used for synthesis of AuNPs *in-situ* without using any external reducing and capping agent. Moreover, this sensor can detect CLPF with a concentration of 10ppb (Mane et al., 2020). In addition to modifying AuNPs particles, a colorimetric sensor sequence was designed based on potassium permanganate assisted by sulfuric acid. H_2SO_4 can help $KMnO_4$ fade in the presence of pesticides, and it can be observed with naked eyes. At the same time, the red, green and blue values of different pesticide $KMnO_4$-H_2SO_4 systems will change. Based on this, a variety of pesticides, such as CLPF, α-666, 2-methyl-4-chlorophenoxyacetic acid sodium salt monohydrate, etc., can be distinguished and identified only by using different concentrations of potassium permanganate and sulfuric acid. This method can be applied to the detection of a large number of pesticide residues, and has a good development prospect (Qiao et al., 2018).

In addition, a colorimetric sensing strategy using terminal transferase to assemble magnetic beads has also been developed to detect kanamycin (Zhao et al., 2022) In this sensing strategy, the free target kanamycin showed more prominent binding advantages to aptamers due to steric effects than that of kanamycin modified on magnetic beads, and the delayed reaction of amplification of template-free DNA strand mediated by terminal deoxynucleotidyl transferase (TdT) was used to realize signal amplification is a new colorimetric sensing strategy (Guo et al., 2018). The sensitivity of this sensor is three orders of magnitude higher than that of commercial kanamycin ELISA kit, and its LOD is only 3.1 nM. The recoveries were from 93.8% to 107.8% with the RSD of 1.22%–4.39% (<5%).

AuNPs is widely used in the application of colorimetric sensors because of its unique optical properties. The surface plasmon resonance (SPR) property of AuNPs leads to the shift of its maximum characteristic absorption peak wavelength in the UV-visible region with the change of inter-particle distance, which is accompanied by the change of solution color. This means that after combining with the target substance, it will lead to the aggregation of AuNPs, resulting in color change.

According to its optical characteristics, there are two kinds of colorimetric sensors made by AuNPs: cross-linking method and deprotection method. The cross-linking method is to modify the scattering of AuNPs by using specific aptamers (Liu et al., 2011). The aptamers should have sulfhydryl groups at one end to adsorb on the surface of AuNPs, and the other end should have functional groups that can bind to target cells. In the presence of target compounds, the aptamers bind to them, leading to the aggregation of AuNPs, resulting in color change. The deprotection method is to make the specific aptamer bind to the surface of AuNPs through weak interaction (Chen et al., 2015). AuNPs will remain dispersed at high salt concentration. When the target compound appears, the aptamer will strongly bind to it, and the aptamer will leave the surface of AuNPs, resulting in the aggregation of AuNPs and the blue color of the solution.

A research team used the principle of high salt concentration to induce the aggregation of AuNPs to detect cyproterone in cucumber. The linear range was 3.0–6.0 μM. It showed a good linear relationship in the range of 1–500 ng mL^{-1}. According to the measurement method, the LOD allows the detection of pesticide residues as low as 1–5 ng/mL. Meanwhile, the analysis also shows a good average recovery rate of 83.7%–104.8%, as shown in Figure 2 (Liu et al., 2015).

As shown in Figure 3, a multi-channel colorimetric sensor for pesticide identification was developed using platinum nanoparticles (Pt-NPs) as molecular probes and 3,3',5,5'-tetramethylbenzidine (TMB) as a chromogenic substrate. The sensor exhibited three significantly enhanced adsorption peaks in a single reaction, providing three sensor elements for response pattern recognition. Five pesticides, namely, DB, DM, 3-KC, GLY, and MA, were successfully identified using this approach. Furthermore, a colorimetric method specifically for DM detection was developed, offering a linear range of 0.5–9 μg/mL.

The current sensing strategy offers several distinct advantages. Firstly, the sensing system is characterized by its simplicity and user-friendly operation. Secondly, Pt-NPs, serving as a single sensing receptor, can be easily synthesized in large quantities. Lastly, all three sensing elements can be simultaneously read out with a single measurement. This work demonstrates significant application potential in the realms of food safety and environmental protection (Li et al., 2022).

Nevertheless, colorimetric sensors often necessitate extensive sample preparation procedures prior to conducting colorimetry. Additionally, their detection range is typically constrained, rendering them less appropriate for samples exhibiting a wide concentration spectrum. Furthermore, colorimetric sensors may require a specific duration for color development, occasionally resulting in delayed detection outcomes.

2.2.4 Surface enhanced Raman reaction sensor

In recent years, rapid detection methods for pesticide residues in fruits and vegetables have witnessed significant advancements, primarily in the areas of immunoassay, electrochemical detection, and capillary electrophoresis. While these methods have made substantial progress compared to traditional chromatography, challenges such as unstable solutions, short storage times, and surface-enhanced Raman spectroscopy (SERS) persist (Visaveliya et al., 2022). SERS, an advanced Raman technique introduced in the 1970s, exhibits exceptional sensitivity for many single-molecule pesticides. Commonly used substrates in SERS include AuNPs and silver nanoparticles, with some semiconductors also

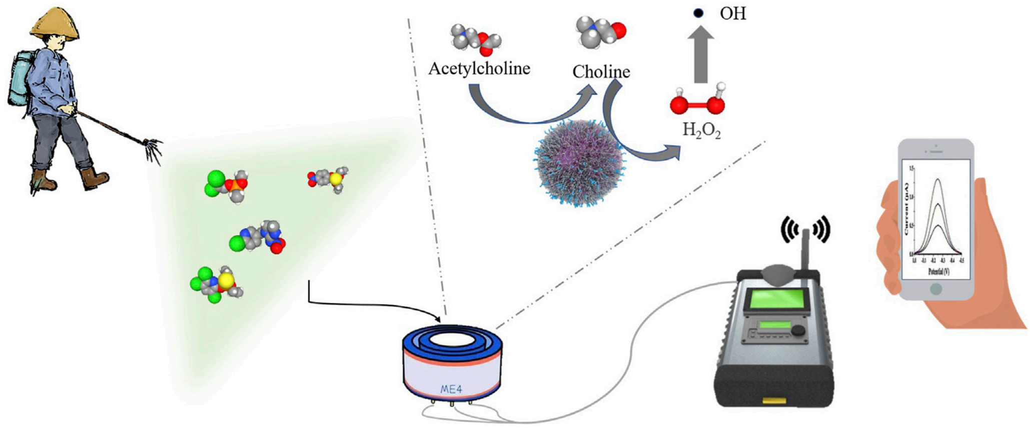


FIGURE 1
Digital terminal connection of portable electrochemical sensor for field detection.

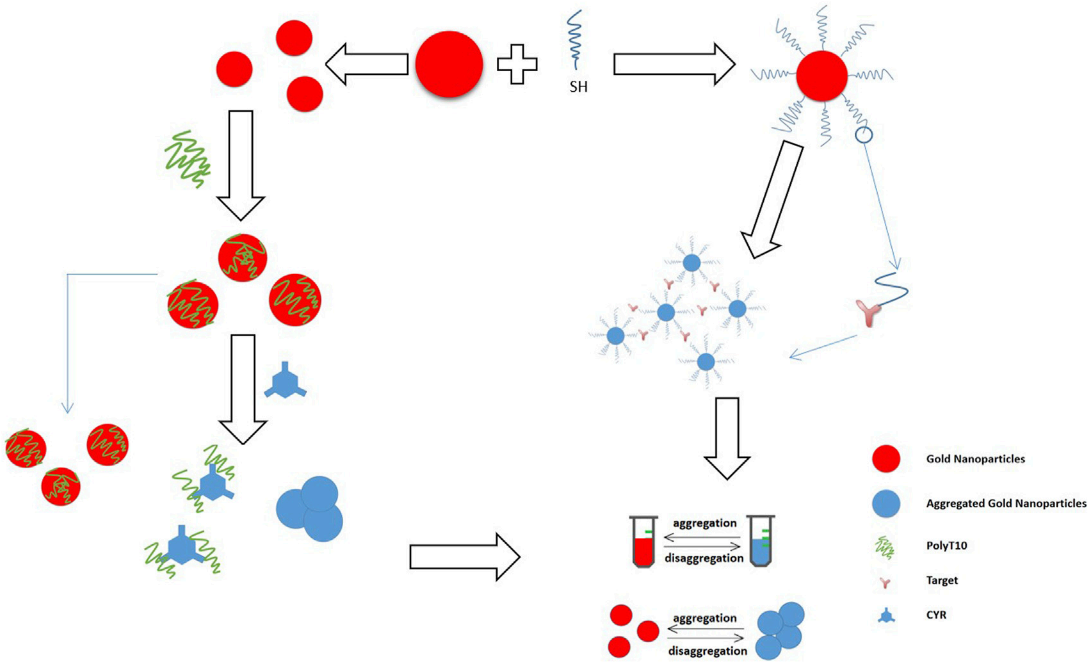


FIGURE 2
Working principle of AuNPs as colorimetric sensor.

demonstrating significant enhancement capabilities. Notably, recent studies have highlighted the remarkable enhancement effects of metal-semiconductor materials. Consequently, a research team successfully demonstrated the synergistic enhancement effects of AuNPs-TiO_2 Nanotube Arrays (TiO2 NTAs @ Hybrid AuNPs) in SERS and Photoelectrocatalysis (PEC). This substrate exhibited excellent sensitivity in detecting organic dyes such as rhodamine B (RhB), the organic herbicide dichlorophenoxyacetic acid (2,4-D), and the organic phosphate pesticide methyl parathion (MP). Moreover, it displayed high reproducibility, stability, and reusability (Yang et al., 2017).

A research team successfully prepared three-dimensional nano-tetrahedrons of Ag@Au nanoparticles based on the self-assembly of DNA molecules. By using the specific recognition of the target and nucleic acid aptamer, the distance between the assembled Ag@Au tetrahedrons was changed, forming SERS hot spots, and then producing a strong Raman enhancement effect. Based on the spatial configuration and multi-structure of tetrahedron, a tetrahedron multi-Raman detection system with three beacon molecules was constructed by introducing three nucleic acid aptamers and three beacon molecules into tetrahedron, so as to realize the simultaneous detection of profenofos, acetamiprid and

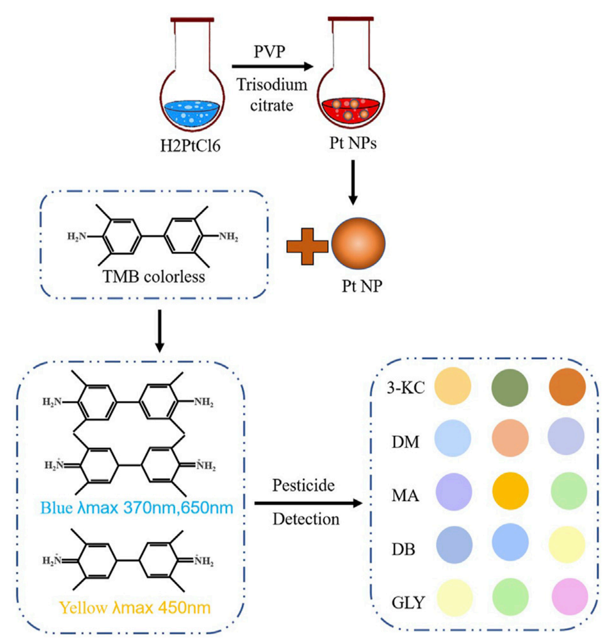


FIGURE 3
Schematically illustration for construction of TMB-Pt NPs multichannel colorimetric sensor array.

carbendazim, and the LOD of these three pesticides were all lower (profenofos:0.0021 ng/mL; acetamiprid:0.0046 ng/mL; carbendazim: 0.0061 ng/mL) (Lu et al., 2021).

Hydrazine (N_2H_4), as a chemical with excellent physical and chemical properties, is often used in the processing of combustion-supporting agents because of its combustion-supporting effect. At the same time, N_2H_4, as a strong and effective reducing agent, will also be used in pesticides during the production and processing of some pesticides. Therefore, N_2H_4may exist in pesticide residues. At the same time, $N_2H_4$is extremely toxic to human liver, kidney and nervous system. Therefore, it is very important to test the content of N_2H_4in pesticide residues (Xu et al., 2022). 4-mercaptobenzaldehyde (4-MBA) was modified on alpha-cyclodextrin-silver nanoparticles (α-CD-AgNPs) to generate SERS, and a new type of N_2H_4 biosensor based on surface-enhanced Raman reaction was constructed. This method is simple and brings high sensitivity, and the LOD is lower than that of previous sensors, reaching 38p.m. And The SERS intensity at 1,529 cm^{-1} and the logarithm of the concentration of N_2H_4 presented a good linear relationship from 10^{-9} to 10^{-7} M. At the same time, aiming at the selectivity and stability of this technical method, they applied the proposed analytical method to river water and industrial wastewater. In the actual operation detection, this method showed excellent detection effect, accurately measured and distinguished N_2H_4. Moreover, it is not difficult to see that this detection method has high potential and future market prospects.

In addition, based on spherical silver nanoparticles of SERS, an extremely simple method for trace detection of MLT was established. MLT was hydrolyzed rapidly by β-elimination reaction in alkaline condition, and then Lewis acid (LAs) was used to provide a favorable ion environment for SERS detection, resulting in the maximum additional enhancement of 305 times and the LOD as low as 0.1 ppb. The different alkaline hydrolysis pathways of MLT and other phosphorodithioate organophosphorus molecules were expounded, and the conversion of the molecules on the nano-surface was determined. The method has been successfully applied to a variety of tea samples, and the LOD is as low as 0.05 ppm. Due to the complexity of characteristic peak intensity, multivariate analysis was used for quantitative analysis, and a high determination coefficient (R^2 = 0.9573) and a good dynamic range of 0.1–5 ppm were obtained (Chen et al., 2022).

In recent years, molecular imprinting technology has also attracted great attention. MIP can be prepared by simulating the specificity between enzyme and substrate or antigen and antibody. Based on this, a method for the detection of pentachloronitrobenzene pesticide (PCNB) based on molecular imprinting technique and surface enhanced Raman spectroscopy was developed, as shown in Figure 3. As PCNB is insoluble in water, molecularly imprinted polymer embedded with oil-soluble silver nanoparticles was prepared as SERS substrate, which can specifically identify PCNB. With methyl methacrylate (MMA) as functional monomer, PCNB as template molecule, 1,4-butanediol dimethacrylate as crosslinking agent, lipid peroxide as initiator, and silver nanoparticles with the best SERS enhancement effect as SERS reinforcement material, PCNB targeted molecularly imprinted polymer containing silver nanoparticles was prepared by free radical polymerization. Molecularly imprinted polymer specifically recognizes PCNB in complex matrix. The intensity of the characteristic peak of PCNB is proportional to the concentration, with a linear range of 0.005–0.15 μg/mL and a LOD of 5.0 ng/mL. The recovery of PCNB in rice samples was 94.4%–103.3%, and the RSD was 4.6%–7.4% (Neng et al., 2022, Figure 4). The results are consistent with those of GC-MS, which indicates that SERS-MIPs is reliable for rapid detection of PCNB in food matrix. Since PCNB is insoluble in water, oil-soluble silver nanoparticles were synthesized and extended to detect oil-soluble toxic substances. The proposed method provides a rapid detection method of PCNB in food matrix for the first time, which adopts SERS-MIPs method with high sensitivity and selectivity.

However, SERS still presents several challenges. Firstly, the choice of substrate demands the preparation of highly enhanced, uniformly structured, and pristine surfaces, necessitating surface modifications to enhance biocompatibility and prevent nonspecific adsorption. Secondly, optimizing SERS detection conditions involves the selection of appropriate excitation wavelengths, exposure durations, laser power levels, and other parameters while ensuring a robust signal-to-noise ratio. This is crucial for mitigating potential thermal effects and minimizing the impact of photocatalytic reactions on detection. Additionally, maintaining the normal state of the target analyte during SERS analysis is paramount to obtain authentic information.

As shown in the following Tables 2, 3, at present, various biosensors for detecting pesticide residues are emerging one after another. This section lists electrochemical sensors, fluorescence sensors, colorimetric sensors and SERS reaction sensors respectively. These sensors have their own advantages and disadvantages.

Therefore, addressing the limitations, overcoming challenges, reducing costs, and enhancing efficiency are crucial factors for the advancement of biosensors in pesticide detection. This requires specific problem-solving approaches aimed at improving the performance and effectiveness of these sensors.

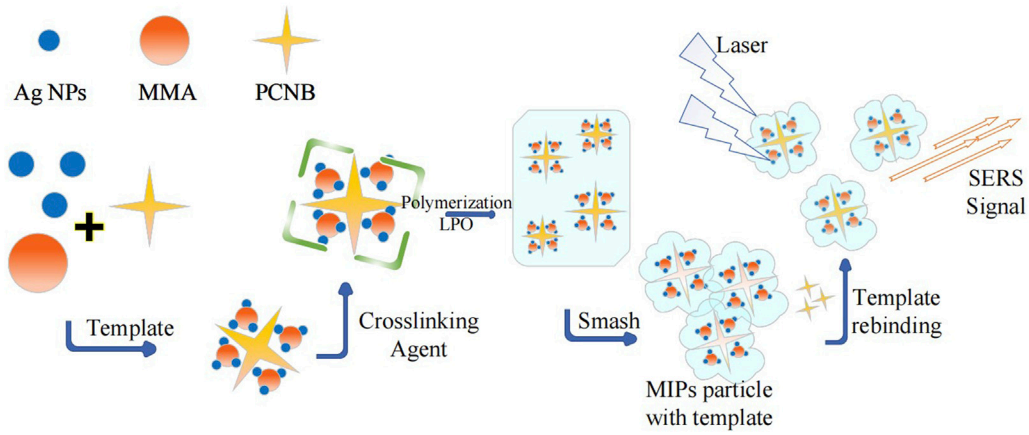


FIGURE 4
Application of molecular imprinting technology in surface enhanced Raman reaction sensor.

TABLE 1 Classification offluorescence sensor.

		Characteristic	Reference
Sensing probe	Metal-based quantum dot	Strong emission; Tunable emission wavelengths; Photostability; Broad excitation spectra	Sabzehmeidani and Kazemzad (2022)
	Carbon-based quantum dot	Narrow emission spectra; Biocompatibility; Stability; Environmentally friendly	
	Metal nanocluster	Bright fluorescence; Versatile surface chemistry; Tunable emission spectra; Efficient energy transfer	Chen et al. (2023)
Sensing mechanism	Photoinduced electron transfer	Excited-state quenching; Redox properties; Sensing in dynamic environments	Dias et al. (2022)
	Intramolecular charge transfer	Electronic delocalization; Fluorophore design flexibility; Sensitivity to molecular environment	Imato et al. (2019)
	Twisted intramolecular charge transfer	Dual fluorescence emission; Conformational sensitivity; Excited-state relaxation	Sasaki et al. (2016)
	Meral-ligand charge transfer	Ligand-to-metal charge transfer; Redox sensitivity; Tunable emission	Yan et al. (2021)
	Electronic energy transfer	Förster resonance energy transfer; Distance-dependent efficiency; Non-radiative transfer	Kudlacek et al. (2008)
	Fluorescence resonance energy transfer	Non-radiative energy transfer; Distance-dependent efficiency; Spectral overlap requirement	
Sensing type	"Turn On"	Signal enhancement; Quenching reversal; Sensitivity improvement	Das et al. (2022)
	"Turn Off"	Signal quenching; Fluorescence suppression; Decreased emission	Liu et al. (2017)
	"On-off-on"	Reversible switching; Dynamic response; Modulation capability	Liang et al. (2020)
Detected type	Single wavelength fluorescent method	Single emission wavelength; Simplified analysis; Specific target detection	Shin et al. (2021)
	Dual wavelength ratiometric fluorescent method	Ratiometric measurement; Compensation for experimental variations	

2.3 Challenges and prospects

Biosensors continue to confront numerous challenges in the domain of pesticide detection. Firstly, there remains a need for ongoing improvement and optimization of biological components and recognition molecules to enhance both sensitivity and specificity in pesticide residue detection. Secondly, fruit and vegetable samples often contain a plethora of interfering substances, including various chemicals and microorganisms, which can potentially disrupt the accurate detection of pesticide residues. Biosensors must address these matrix effects to bolster detection precision. Thirdly, real-time monitoring of pesticide residues within the fruit and vegetable supply chain is imperative for product safety assurance, thus necessitating biosensors with rapid response times and high-throughput detection capabilities. Moreover, the diversity of pesticides present in fruits and vegetables calls for the development of multifunctional sensors capable

TABLE 2 The comparison of different sensor performance in pesticide detection.

Biosensor type	LOD	Cost	Reproducibility	Characteristic	Reference
Electrochemical sensor	0.88 p.m.-1.2 nM	350	Relatively poor	On-site; detection; Complex; pretreatment	Li et al. (2016), Patella et al. (2021)
Fluorescence sensor	0.13 nM–10 nM	500–5,000	Affected by the lifetime and background of fluorescent substances	High sensitivity detection; Influenced by the lifetime and background of the fluorescent substance	(Li et al., 2018; Arvand and Mirroshandel, 2019)
Colorimetric sensor	5 nM	100–300	Strong	Simple; Practical, Visible to the naked eye; Unable to achieve multiple detection and quantitative detection	Shi et al. (2013)
Surface enhanced Raman sensor	1 nM-0.1 μM	1,000	Relatively poor	Trace detection	(Zhang et al., 2013; Hu et al., 2016)

TABLE 3 Detection level of different pesticides residues in different fruits and vegetables by various types of sensors.

Biosensor type	Fruit and vegetable types	Pesticide type	LOD	Reference
Electrochemical sensor	apple, grape, guava, onion, cabbage, and lettuce	MP	5 p.m.	Gissawong et al. (2022)
Fluorescence sensor	potato, cabbage, tomato, apple, orange, papaya	pendimethalin	0.930 nM	Pratibha et al. (2022)
Colorimetric sensor	Apple, Orange, Spinach, Tomato, Cucumber	CLPF, Profenofos, cypermethrin	Chlorpyrifos 0.235×10^{-6} M, Profenofos 4.891×10^{-6} M, cypermethrin 4.053×10^{-6} M	Zhu et al. (2023)
Surface enhanced Raman sensor	spinach and tomato	Thiram, thiabendazole	Thiram 10^{-7} M, thiabendazole 10^{-8} M	Jiang et al. (2018)

of addressing various pesticide types. Lastly, it is crucial to manage the developmental and deployment costs of biosensors effectively to facilitate their widespread adoption within the agriculture and food production industries.

Simultaneously, biosensors hold promising prospects for advancing pesticide residue detection. Firstly, biosensors are poised to emerge as a pivotal technology in precision agriculture, facilitating more effective pesticide management by aiding farmers in reducing pesticide residues and enhancing the quality and safety of fruits and vegetables. Secondly, biosensors can be seamlessly integrated with automation systems and Internet technology, enabling remote monitoring and data sharing, thereby augmenting oversight and control capabilities across farmland and production lines. Thirdly, by mitigating pesticide residues, biosensors have the potential to drive sustainable agricultural practices, curbing environmental pollution, safeguarding ecosystems, and fostering sustainable agriculture. Furthermore, the advent of more advanced biosensor technologies, such as nanosensors and biochips, may enhance detection performance and expand the range of detectable pesticides in the future.

In summary, biosensors are poised to assume a pivotal role in pesticide residue detection in fruits and vegetables. However, a series of challenges must be addressed, including the enhancement of sensitivity, diversification of pesticide detection capabilities, and mitigation of matrix effects. As technology continues to advance and applications become more widespread, biosensors are anticipated to play an increasingly vital role in ensuring food safety and promoting sustainable agriculture.

3 Conclusion

The presence of pesticide residues in fruits and vegetables has significant implications for public health and safety, making their detection a matter of great concern. This paper presents a comprehensive review of the main detection methods employed in recent research for analyzing pesticide residues in these food samples.

Among various emerging techniques, the application of biosensors in pesticide detection has garnered considerable attention. These methods have played a pivotal role in reducing the pretreatment and detection time for pesticide residue analysis in agricultural produce, thereby enhancing detection accuracy.

Despite the progress achieved by these methods in controlling pesticide pollution, several challenges persist. The pretreatment process still requires substantial human and material resources. Additionally, each biosensor possesses its own set of advantages and limitations, necessitating a comprehensive evaluation and optimization of these sensors to overcome their constraints.

In future studies, it is crucial to leverage the strengths of these adaptive sensors while mitigating their limitations. Enhancing the anti-interference capabilities of these sensors holds significant promise, enabling the development of intelligent adaptive sensors capable of on-site pesticide residue detection without the need for complex sample pretreatment.

This research sets the stage for the design and fabrication of novel intelligent biosensors, ultimately advancing the analysis of pesticide residues in agricultural produce and ensuring food safety and consumer health.

Author contributions

TG: Formal analysis,Writing–Original Draft, JN: Data Curation, ZD: Project administration, WW: Conceptualization, Writing–Review and Editing, Funding acquisition, XL: Visualization. All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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