PLANT SCIENCE TODAY
ISSN 2348-1900 (online)
Vol 11(sp4): 01–16
https://doi.org/10.14719/pst.5725

HORIZON
e-Publishing Group
HePG

REVIEW ARTICLE

Application of sensing methods in agricultural sector for the detection of pesticide residues: An overview

Aishwarya Dixit[1], Nishant Kumar[1], Ashutosh Upadhyay[1*], Vivek K Bajpai[2], Youngjin Cho[3], Yu-jeong Yang[4], Yun Suk Huh[4] & Shruti Shukla[5*]

[1]Department of Food Science and Technology, National Institute of Food Technology Entrepreneurship and Management, Kundli, Sonepat 131028, Haryana, India

[2]Department of Energy and Materials Engineering, Dongguk University-Seoul, 30 Pildong-ro 1-gil, Seoul 04620, Republic of Korea

[3]Food Safety and Distribution Research Group, Korea Food Research Institute, Wanju 55365, Republic of Korea

[4]NanoBio High-Tech Materials Research Center, Department of Biological Sciences and Bioengineering, Inha University, Incheon 22212, Republic of Korea

[5]Department of Nanotechnology, North-Eastern Hill University (NEHU), East Khasi Hills, Shillong 793022, Meghalaya, India

*Email: ashutosh@niftem.ac.in; shrutishukla1983@gmail.com

OPEN ACCESS

ARTICLE HISTORY
Received: 11 October 2024
Accepted: 27 October 2024
Available online
Version 1.0 : 18 December 2024

Check for updates

Additional information
Peer review: Publisher thanks Sectional Editor and the other anonymous reviewers for their contribution to the peer review of this work.

Reprints & permissions information is available at https://horizonepublishing.com/journals/index.php/PST/open_access_policy

Publisher's Note: Horizon e-Publishing Group remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Indexing: Plant Science Today, published by Horizon e-Publishing Group, is covered by Scopus, Web of Science, BIOSIS Previews, Clarivate Analytics, NAAS, UGC Care, etc
See https://horizonepublishing.com/journals/index.php/PST/indexing_abstracting

CITE THIS ARTICLE
Dixit A, Kumar N, Upadhyay A, Bajpai VK, Cho Y, Yu-jeong Y, Huh YS, Shukla S. Application of sensing methods in agricultural sector for the detection of pesticide residues: An overview. Plant Science Today.2024;11(sp4):01-16. https://doi.org/10.14719/pst.5725

Abstract

Pesticides negatively affect the environment and human health, primarily through bioaccumulation in the food system. The detection of pesticides in the agriculture system is needed to reduce their negative impacts. Furthermore, there are several conventional methods such as chromatography, etc. available to detect and quantify the different types of pesticides, but these methods have limitations including higher cost, requirement of complex methodology, expertise and specialized gear and are inappropriate for real-time field screening. To overcome the challenges posed by conventional methods, nanotechnological approaches are gaining huge popularity in agriculture sector as nano-sensing strategies played an important role for remediation, detection and pollution control in the environment. Nano-sensors have potential advantages such as low cost, selectivity, sensitivity, robustness and real-time monitoring of the pesticides present in the food system and helps in improving the crop productivity management. Therefore, the present study was conducted to explore the importance and role of nanotechnology approaches in the agriculture sector for real time detection of pesticides. This review also describes the different types of biosensors such as optical, enzymatic, colorimetric, electro-chemical, potentiometric and immune sensors while highlighting their mechanism and nanoparticle interactions in the agriculture sector for pesticide detection. The recent study on the development of low-cost nanoparticle based nano sensors for pesticide detection is focused on gathering detailed information using databases such as Google Scholar, ResearchGate, Scopus, PubMed and Web of Science, etc.

Keywords

biosensors; nanocomposite; nanomaterials; nanosensors; pesticides; portable sensors

Introduction

The agricultural sector plays an important role in the socio-economic development in developing and developed countries around the world. About 60-70 % of the population relies primarily on agriculture sector in India for employment and this sector contributes around 28 % of the total Gross Domestic Product (GDP) of the country (1). Nowadays, food security has become a serious concern for humankind; therefore, the agriculture sector is forced to fulfill the rising needs of food for increasing population. Pesticides are being used to control a variety of crop-related diseases to improve the productivity of the agricultural sector to ensure fulfilling the needs for increasing population (2). Agri-technology, food technology, nano-biotechnology and nanotechnology can enhance agricultural productivity and improve product quality (3). The use of pesticides in the agriculture sector includes a variety of chemical substances such as nematicides, insecticides, fungicides, rodenticides, molluscicides, etc. (4). According to the Food and Agriculture Organization (FAO), pesticides are defined as the combinations of compounds that include chemicals or biological components intended to repel, eliminate or control any forms of pests (5). Pesticides are crucial in food production because they protect or improve produce and allow crops to be grown on the same land many times in a year. Although pesticides can efficiently reduce weeds and pest infestations, their usage poses a serious hazard to both human health and the environment, due to eutrophication and bioaccumulation in food chain system (6). The other consequences of this practice include air pollution from pesticide spraying, which farmers inhale and this negatively impacts human health and being a leading cause of numerous diseases (7). Therefore, the developed countries have prohibited the use of chemical pesticides due to their negative impacts on agriculture, environment and human health (8, 9). Therefore, proper detection of these pesticides is an important aspect and remains a challenge to agro-food processing sector. The detection of pesticides is generally performed in two different phases, including preparation of the sample through QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) techniques and their analytical detection (10). Several conventional analytical techniques, including immunological methods, capillary electrophoresis, FTIR (Fourier-transform infrared) spectroscopy, HPLC (High-performance liquid chromatography), GC (Gas Chromatography) and NMR (Nuclear magnetic resonance) spectroscopy have been used for pesticide detection in agro produce. Besides, the advantages of conventional methods such as sensitivity, reliability and efficiency for pesticide detection, they are extremely sophisticated, expensive and time-consuming techniques and need highly skilled employees for their operation (11). To overcome the challenges of conventional methods, sensing methods have been introduced for onsite detection of pesticides in produces within a shorter period. Therefore, nano-technological approaches such as sensors and electronic-tongue (E-tongue) technology are one of the most effective technologies to detect pesticides in agriculture sector

Sensor consists of two primary types of components such as transducer and receiver. The transducer permits the energy and analytical signal to be completely analysable and electronically presentable (12, 13). According to the recent classification proposed by Pure and Applied Chemistry International Union (IUPAC), biosensor is one of the effective and potential sensors for application in different sectors for real time monitoring and detection of substances (14, 15). A nanosensor is any biological, chemical or operational sensing point, which transmits information regarding nanoparticles to the macroscopic environment (16). A characteristic defining feature of the nanomaterials is their number 100 or less is at least one structural dimension. Apart from this, their compact size, greater surface area-to-volume ratios (larger signals, enhanced catalysis and rapid motion) and good optical characteristics (fluorescence, quenching and SRS) offer substantial benefits over macroscale materials (17).

The farmers rely on pesticides to protect the crops from pests and increase productivity (18). Various countries have established maximum residue limits (MRL) to regulate and control negative impacts of pesticides (19). Still, they are used in excessive quantities, but only a small amount of pesticide is required for plants, while the rest remains as residue in food and environment as a contaminant and persists for several decades. Therefore, it is a major concern for food regulatory organizations and food businesses to detect pesticides as they decrease food safety and security of the country. Highly sensitive, selective and accurate conventional analytical procedures are required for the detection of pesticides residue. However, to overcome the challenges of conventional detection techniques, advanced sensing methods can be used as an alternative due to their easy to handle, portable, rapid, sensitivity and accuracy features for the real time monitoring and on-site detection of pesticides. Therefore, the aim of the present article is to focus on exploring the use of different types of pesticides in the agriculture sector and their impacts on the environment and health. In addition, the application of different types of biosensing methods (electrochemical, potentiometric, amperometric, calorimetric, optical biosensor and immunosensor) instead of conventional methods for pesticide detection in agriculture sector has been also discussed briefly. Moreover, the mechanism and interactions of nanoparticles, quantum dots, carbon nanomaterials and enzyme inhibition-based sensor with pesticide components is also described in this review. The information provided in this article about the sensing technologies could be potentially used in agriculture sector for real time monitoring and detection of pesticides at lower economic cost with their limit of detection (LOD) and applicability. The databases such as Google Scholar, ResearchGate, Science Direct, Web of Science, Scopus, etc. were used to congregate the information by applying keywords like Nano-biosensors, Pesticides, Nanomaterials, Portable sensors, etc. between the years of 2003-2024. Most of the cited articles were from the last 5 years (2020-2024).

Types and impacts of pesticides

Any substance or combination of compounds used to prevent, eradicate or control pests such as fungi, rodents, insects or undesired plant species (weeds) that cause harm to crop during production and storage is known as a pesticide. There are several types of pesticides such as herbicides (kill weeds), insecticides (kill insects) and fungicides (anti-fungus) (4). Some other pesticides are rodenticides (kill rodents), fumigants (a pesticide in gas or vapor form is discharged into the air or injected into the soil to kill pests), nematicides (to kill plant-parasitic nematodes), acaricides (to kill mites or ticks), algicides (poisonous to algae), bird repellents and mammal repellents (20). Pesticides are further categorized as chemical pesticides or biopesticides based on their sources of origin (21). Fig. 1 summarizes the different types of pesticides used in the agriculture sector to improve crop productivity. Bio-pesticides are more environmentally friendly than chemical pesticides since they are less

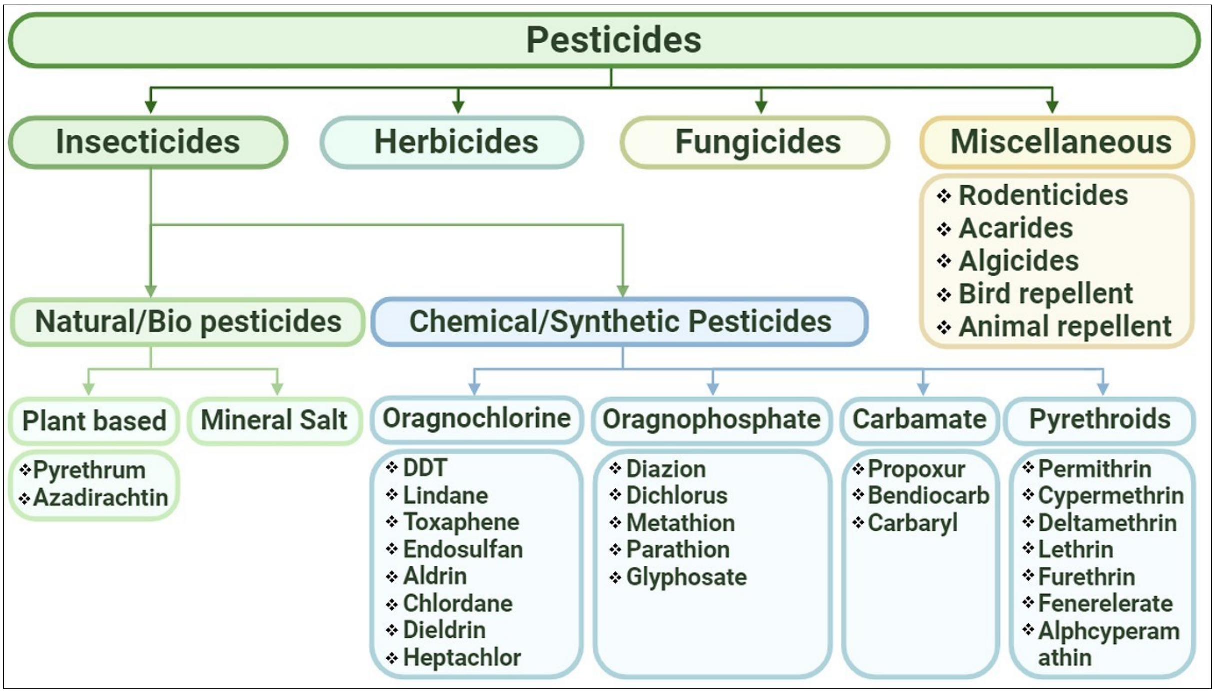

Fig. 1. Pesticides used in agriculture sector (20, 22).

harmful, break down more rapidly and are only needed in minimal amounts (22). However, these chemical pesticides such as organophosphate (OPP), carbamate, pyrethroids, etc. have potential to degrade the ecosystem due to their toxicity and lack of biodegradability (22). Therefore, development of detection system against harmful chemicals or synthetic pesticide residues is the most important step to prevent the degradation of environment and human health. Bio-sensing methods can be used to detect these chemical pesticides on-site for mitigating their effects on ecosystem. In past decades, many researchers have reported simple, highly sensitive, reliable and cost-effective advanced bio-sensing methods using different nanomaterials. These nanomaterials proved to be a very effective and promising tool to enhance the efficiency of sensing techniques. In the current review article, recently developed biosensing methods that can be used for on-spot detection of toxic pesticides are discussed.

Hazardous chemical pesticides and their sensing methods

Organochlorine

Organochlorines are the agrochemicals used in agricultural sector to kill pests. They are defined as an organic compound having at least one covalently bonded chlorine atom that influences the chemical behaviour of the molecule. Examples of such compounds include dieldrin, endosulfan, endrin, heptachlor, hexachlorobenzene, lindane (γ-hexachlorocyclohexane), dicofol, mirex, kepone and pentachlorophenol (20). Organochlorine pesticides are regarded as the most harmful class of pesticides because of their certain active chemicals that may remain in the environment for more than 30 years (21). Therefore, their detection and remediation are important and it comprises the implementation of several detection techniques to limit the adverse effects of organochlorine pesticide contamination on the environment and food supply chain. For example, gold nanoparticle (AuNP)-based colorimetric sensor was developed to detect organochlorine, endosulfan pesticide (ESP). The natural red-wine color of AuNPs changes to blue when varied amounts of ESP solutions are added. Recently, a glassy carbon electrode modified with titanium oxide-aluminium oxide nanocomposite-based sensor was developed for the detection of trichlorophenol (organochlorine compound) pesticide (23). This sensor was developed using electrochemical method, which exhibited excellent sensitivity with LOD of 1.85×10^{-9} M.

Organophosphate

Organophosphorus pesticides (OPPs) are phosphoric acid-derived pesticides, which can prevent the growth of weeds and pests and can control plant diseases (22). They cause epilepsy and cholinergic crisis due to inhibition of acetylcholinesterase (AChE, neurotransmitter) which results in paralysis and even death (24). Parathion, malathion, dichlorvos, diazinon and glyphosate are some of the most often used OPPs in the agriculture sector. There are so many detection systems available for organophosphate compound detection, for example, an AChE inhibition-based optical sensor was developed using Cadmiun-Tellurium semiconductor quantum dots (QDs) (CdTe-QDs) combined with AChE enzyme to detect OPPs. The limits of detection (LODs) of the developed biosensors were 3.72×10^{-8} ppm and 1.58×10^{-7} ppm for paraoxon and parathion, respectively (25).

Carbamate

Carbamate pesticides are carbamic acid-derived pesticides, which control the pests to improve productivity and some of the commonly used carbamate pesticides are carbofuran, aminocarb and carbaryl. An AChE enzyme inhibition-based nanocomposite was developed using gold nanoclusters manganese dioxide (AuNCs-MnO_2), which was used for the detection of carbamate insecticide with limit of detection (LOD) of 1.2×10^{-2} ppm.

Pyrethroids

Pyrethroid is an organic substance extracted from natural pyrethrum flower, derived from pyrethric acids. Pyrethroids attack sodium channels in the nervous system, which cause paralysis. Permethrin, cypermethrin, deltamethrin, lethrin, furethrin, fenevelerate and alphcyperamethrin are the most extensively used synthetic pyrethroids (22). The detection of cyfluthrin was achieved by using a unique molecularly imprinted silica layer (MIP-FeSe-QDs); that was synthesized and used as a recognition element in the development of a selective and sensitive fluorescent nanosensor. Based on the fluorescence quenching of FeSe-QDs, MIP-FeSe-QDs exhibited good selectivity and sensitivity to cyfluthrin molecules. Cyfluthrin's LOD in sediment and fish samples was observed as 1.3×10^{-2} ppm and 1×10^{-2} ppm, respectively (27).

Types of biosensors used in agriculture sector

The potential benefit for food business is the implications of nanotechnology in food quality assurance. Sensing techniques have potential to detect microbial contamination, pesticides, toxins, volatiles, allergens, pathogens and other pollutants in extremely small quantities with great sensitivity, specificity and repeatability, ensuring the quality of food ingested (Fig. 2a) (28). The nano-sensing technology use chemical, enzymatic and biological processes, as well as mechanical and electrical signals at nano-measurement units. Biosensors including electrochemical, colorimetric, fluorescence, immunosensor, etc. were previously developed for the application in agricultural sector to identify or quantify targeted pesticides and other pollutants in agriculture products. Table 1 summarizes prior research on several types of nanosensors and their applications in detection of pesticides residues.

Types of biosensors

Electrochemical biosensors

Electrochemical biosensor is a type of sensing device, which reacts with target analyte and gives an electrical signal using electrodes. They are widely used for the detection of pesticides because of their high sensitivity and accuracy (35). The electrode in electrochemical biosensor is the key component and helps in the electron movement and immobilization of biomolecules (36). These electrochemical biosensor units comprise of three different electrodes working electrode, reference and counter electrode. All electrodes connect and measure the electrochemical changes that occurred due to electron transfer at the transducer-solution interface. This electron transfer (electron acception and donation) is directly proportional to the concentration of pesticide and helps in identifying the category of pesticides. The electrochemical techniques include amperometric, voltammetric, potentiometric, impedance spectrometric and conductometric (37). In past few decades, these techniques have proved to be an effective alternative for pesticide detection, for determining the identities and quantities of pesticides by measuring the electrical characteristics such as current, potential, etc. The mechanism and functions of electrochemical biosensor are shown in Fig. 2b.

Previously, several researchers have developed different types of electrochemical sensors for the detection of pesticides in the agriculture sector. For example, Zahirifar *et al.* (38) developed a highly sensitive and responsive electrochemical biosensor for the detection of DZN (Diazinon (oo-diethyl-o-(2-isopropyl-6methyipyrimidin-4-yl)momothiophosphate) pesticide using carbon nanotubes (CNTs) electrodes, due to its large surface area. Cyclic voltammetry and differential pulse voltammetry were used to investigate the electrochemical responses of CNTs and carbon paste electrodes (CPE). DZN detection can be controlled by chemical parameters, i.e., pH, modifier quantity, scan rate, etc. which affect the response. This sensor showed a linear concentration range between 3.55×10^{-5} and 2.13×10^{-2} ppm and reactive DZN response. Mariyappan *et al.* (39) successfully developed an electrochemical sensor using graphene oxide incorporating with gadolinium phosphate

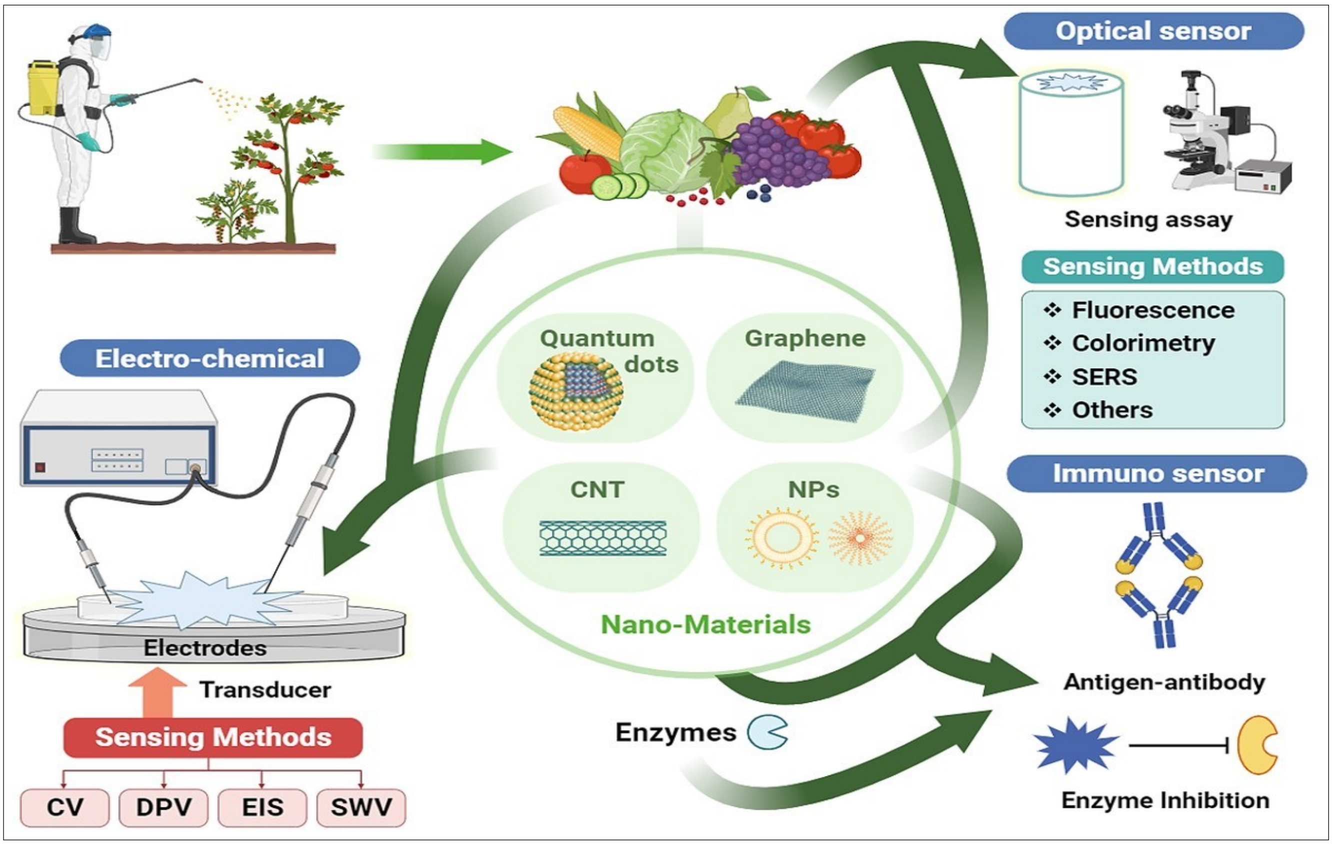

Fig. 2a. Biosensing methods for pesticide detection in agriculture sector.

Table 1. Recent developed nanosensors for pesticide detection in agriculture produces

Type of nanosensor	Material/Receptor	Targeted pesticide	Agro products	Detection limits (LODs)	Reference
AChE	CdTe semiconductor Quantum	Organophosphate	Fruits and	Paraxon - 3.72×10^{-6} ppm	(25)
Fluorescence	Monoclonal antibodies	Carbamate (Carbaryl carbofuran)	Corn	Carbaryl - 8×10^{-3} ppm Carbofuran- 0.2176 ppm	(29)
Surface enhancement Raman spectroscopy (SERS)	Silver nanoparticles	Phosmet pesticide residues	Oolong tea	0.1 ppm	(30)
Acetylcholinesterase (AChE)	1-D Pd@Au nanorods	Organophosphate	Water	3600 ppm	(31)
AChE (colorimetric)	AuNPs-CTAB	Organophosphate	Apple, water	0.035 ppm	(32)
AChE-Dual mode (Colorimetric-fluorometric)	Rhodamine B modified silver nanoparticles (RB-AgNPs)	Carbamate (carbaryl)	Tomato, apple and water	2.3×10^{-8} ppm	(33)
Fluorescence immunoassay	CdSe@ZnS QDs-	Triazophos	Apple, pear, cucumber and rice	5.08×10^{-7} ppm	(34)

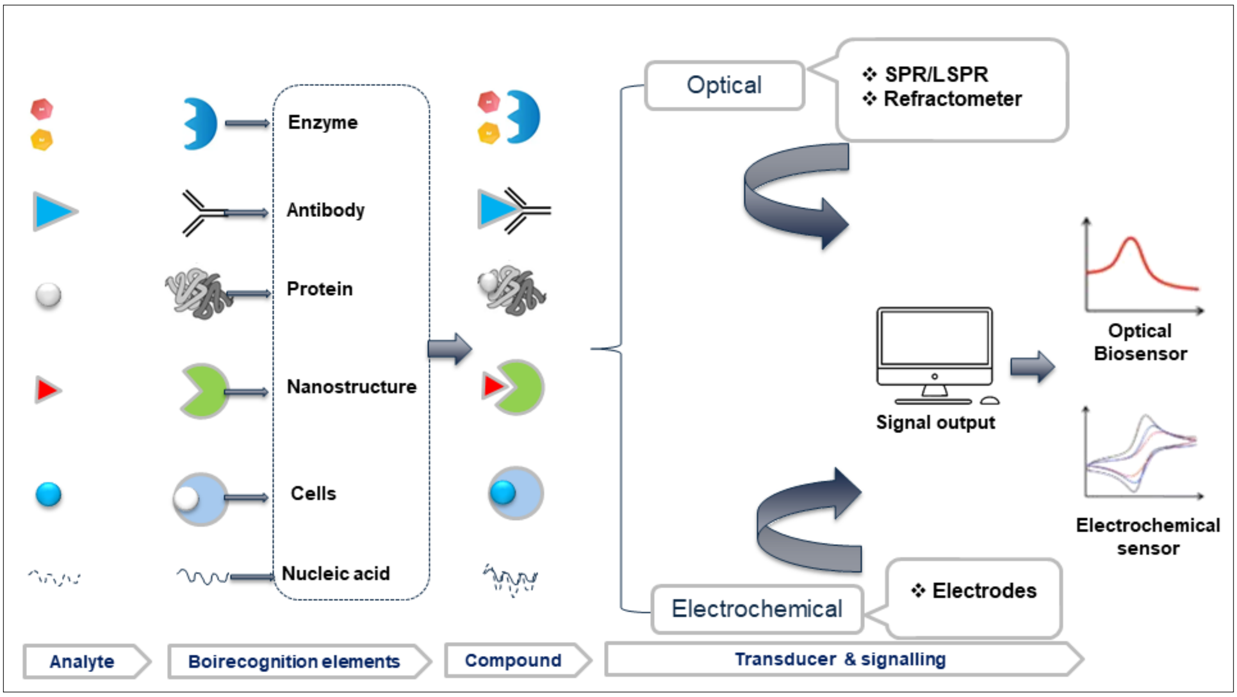

Fig. 2b. Mechanism of optical and electrochemical biosensor.

($GdPO_4$) for the detection of an organophosphorus (OPP) pesticide (fenitrothion) through hydrothermal technique. This sensor showed excellent sensitivity, i.e., 0.8802 µA µM^{-1} cm^{-2} with limit of detection (LOD) of 0.007 µM and linear detection concentration range of 0.01-342 µM. Real-time applicability test for this sensor was done on water samples with recovery rate between 98.3 % and 98.8 %.

Potentiometric biosensors function by evaluating potential of the systems at working electrode through net zero current flow. These sensors offer benefits in terms of compact size, quick response, relatively inexpensive cost, ease of usage, color-resistant intrusion and turbidity. Potentiometry focuses on ion-selective electrodes (ISEs) of a polymer membrane and yields data using ion activity (free ion concentration) and not total concentration (40). ISEs electrodes exhibit good ion selectivity performance along with rapid response and good sensitivity and other advantages like low cost and easy fabrication process, making them a good candidate to be used in portable biosensor (40). Previous research studies have used this technique for pesticide and other toxic pollutants detection in the agriculture sector. For example, glutaraldehyde cross-linked acetate gold electrode based potentiometric sensor was developed for DZN pesticide with LOD of 10^{-6} ppm and linear concentration range of 10^{-6}–1 ppm in response time of 5 min (41). Kamel and Abd-Rabboh (42) developed a potentiometric sensor using a glassy carbon electrode modified with reduced graphene oxide (RGO), which was coated with target pesticide's molecularly imprinted polymer (MIP). The developed sensor was highly sensitive and used for the detection of imidacloprid (IMD) pesticide with LOD of 0.2 µM and linear concentration range of 0.5 µM-1 mM.

Amperometric biosensor is a novel nanotechnological approach, which functions using three different types of groups such as unmediated, mediated and direct electron transfer for the detection purpose. This technique is highly sensitive in nature with cost effectiveness and it easily integrates into a continuous system of analysis. The fundamental operation of this technique is defined by the application of a constant voltage applied between working and reference electrodes, which results in redox reactions that cause a net current to flow (43). These oxidation and reduction reactions and the amount of current flow quantify the concentration of pesticides (36). In amperometric procedures, the approach for pesticide detection is the measurement of the ratio of initial activity of enzymes to its residual activity remaining after exposure of sensor with pesticides (44). Previously several researchers have developed amperometric biosensors for the detection of pesticide (45).

Calorimetric biosensors

Calorimetric biosensors depend on calorimetric transduction to measure heat produced or absorbed during biological reactions (36). It is a reliable and easy method for pesticide detection and does not require regular recalibration. Previous research studies include development of a calorimetric biosensor using a flow injection and chicken liver esterase (bio-recognition compound) for dichlorvos pesticide residues detection. They compare and measure the temperature difference among enzymatic processes produced by inhibition activities (46).

Optical biosensors

Optical biosensors are sensing devices that use optical properties such as refractive index, luminescence, light absorbance, phosphorescence, surface plasmon resonance and fluorescence to convert biological reactions into suitable output signals for the detection of target analyte (47). The optical properties are used to measure the changes in transducer's light characteristics including light polarization, light rotation, total internal reflectance, phase and intensity of light, which are regulated by the biological reactions on the surface of these sensors (47). The mechanism and functions of optical biosensor is shown in Fig. 2b.

Surface plasmon resonance (SPR) biosensors utilize a highly sensitive label free optical sensing technique, widely used for real time monitoring of pesticide residues through multichannel array imaging assay. It depends on the interaction between the electrodes and light in semi-transparent metallic layer (48). Based on their compositions, the SPR biosensors classified into four categories such as fiber optics SPR (FOSPR), SPR imaging (SPRI) transmission SPR (TSPR) and localized SPR (LSPR) (49). Surface plasmons are created via the SPR effect, which reduces the intensity of reflected light at a certain angle known as the resonance angle. These biosensors analyze the binding interaction between two molecules to measure the concentration of pesticides (50). SPR chip as a SPR biosensor was developed using an alkane thiol monolayer with AChE enzyme immobilized on the surface of the sensor for chlorpyrifos pesticide detection with LOD of 5.2×10^{-4}–5.8×10^{-4} ppm (51). Similarly, SPR sensor used nano-film (molecularly imprinted) to detect various toxic pesticides which include simazine, atrazine and cyanazine with LOD of 31, 91 and 95 ppm, respectively. Fluorescence-localized surface plasmon resonance (F-LSPR) technology was developed for the detection of acetamiprid (ACE) and organophosphorus (OPs) pesticides using DNA functionalized AuNP-nanoprobe and reported LOD for ACE and OPs of 16.67×10^{-3} ppm and 1.7×10^{-3} ppm, respectively (52).

Fluorescence biosensors offer numerous advantages including quick response, simple and easy handling, less complicated instruments with high selectivity and sensitivity. They work on interactions that occur between bio-recognition molecules and the target pesticide (53). Fluorescence is a process consisting of three phases (i) excitation, (ii) lifetime in fluorescence and (iii) fluorescence emission that takes place in particular molecules termed as fluorophores (53). These molecules are used to detect optical signals caused by chemical interactions in the form of a shift in absorption or emission band, which can be used to quantify the target pesticide (54). Various fluorescence sensors were successfully developed to detect the harmful pesticides. A glutathione functionalized gold nanoclusters (GSH-AuNCs) and recombinant carboxylesterase PvCarE1 inhibition activity-based fluorescent sensor was developed for the detection of organophosphates (OPs) pesticide (55). In this sensor, the fluorescence of GSH-AuNCs is quenched by the production of p -nitrophenol (p-NP). When this sensor encounters the target pesticide, the enzyme activity is inhibited and the production of p-nitrophenol (p-NP) decreases which results in a retained fluorescence signal. This sensing assay was shown to be portable, reliable and highly sensitive and exhibited LOD of 5 $\mu g\ L^{-1}$, 5 $\mu g\ L^{-1}$ and 0.2 $\mu g\ L^{-1}$ for trichlorfon, profenfos and dichlorvos, respectively. The apple sample was used to test its real-time applicability. Ma *et al.* (56) has developed QD-based fluorescent assay using hydrothermal method for the detection of glyphosate with LOD of 0.015 mgL^{-1} and detection range of 0.2-1.8 $mg\ L^{-1}$. This sensor used enzyme inhibition detection strategy and was applied on cabbage and potato for real time monitoring with recovery rate of 96.50-107 %. Similarly, Bis-tetraphenylimidazole pyridinium salts and cyclohexanedimide-based fluorescent sensor was developed using "turn on–turn off" strategy to detect the presence of halosulfuron-methyl pesticide. This sensor exhibited blue-green fluorescence in presence of target pesticide with LOD of 1.8×10^{-7} M and it was tested on paper, agro-products and water sample to check its applicability (57).

Immuno-sensor

Immunosensors are analytical instruments that utilize antibodies (Abs) to detect specific target compounds like pesticides. They function by immobilizing Abs on a sensor surface, which selectively attaches to pesticides, thereby generating a quantifiable signal. These sensors exhibit great specificity, sensitivity and allow rapid and real-time detection. These sensors are ideal for pesticide detection due to their accuracy and portability in agricultural samples, ensuring environmental safety and regulatory compliance (58).

Antibody-antigen-based immunosensors are used for the recognition of elements and transduce signal upon binding of antibody and antigens. They exhibit various advantages such as quick and easy to use, making them ideal for point-of-care analysis. These sensors use antigen-antibody interaction as a sensing component for pesticide detection in agricultural products and environment (58). Moreover, immunoassays like enzyme-linked immunosorbent assay (ELISA) method use enzyme, antibody and fluorescent marker to assess the immunological response (36). Immunosensors have been transformed into compact and cost-effective devices for monitoring various environmental samples on the spot (59). Several researchers have developed and used immunosensors to identify and quantify pesticide residues. For example, triazophos pesticide was detected using CdSe-ZnS QD-based fluorescence immunoassay (FLISA) sensing technique. These synthetic QDs were used as a probe in monoclonal antibody (mAb) based immunoassay where the target pesticide and OVA-haptens competed for binding the mAb to the probe's surface.

The fluorescence detection value may be used to calculate the concentration of triazophos. The developed assay showed linear concentration range of 1 × 10^{-4} ppm -0.025 ppm, with LOD (IC_{10}) of 5.08 × 10^{-7} ppm for the target pesticide (34). Furthermore, a lateral flow immunoassay (LFIA)-based immunosensor was developed to detect tebufenozide pesticide. Two haptens of target pesticide were synthesized to develop 8 types of monoclonal antibodies (mAbs). The most sensitive and specific mAb against target pesticide was used to develop AuNPs-LFIA with LOD of 1.25 ng mL^{-1}. The developed immunosensor was tested on kiwi, brown rice, cabbages and spinach to verify its applicability and accuracy (60).

Enzyme-based immunosensors on cholinesterase enzyme inhibition are the simplest and most innovative technique for pesticide detection. AChE and butyrylcholinesterase (BChE) are enzyme-based immunosensors, but the AChE enzyme-based immunosensor is often used to detect OPs pesticides. These enzymes combined with nanostructures (nanozymes) show great enzymatic activity and these nanozymes are gaining a huge appreciation due to their distinct physiochemical properties (61). AChE inhibition-based biosensor developed using AChE modified amperometric transducer quantifies H_2O_2 produced during acetylcholine hydrolysis in presence of choline oxidase enzyme (34). A QD aerogel and microfluidic chip-based sensor was developed to detect mixed OPP compounds. This analysis was based on fluorescent intensity variations in QD aerogel, which was partially quenched due to hydrolytic acetylthiocholine (ATCh) processing catalyzed by AChE. The QD fluorescence was unquenched in the presence of OPP due to decreased enzyme activity. A portable biosensor based on AChE enzyme was developed to detect the presence of organophosphorus pesticides and this sensor measured AChE inhibitors with a LOD of 2.5 ppm (62). On the other hand, Song *et al.* (63) developed a nanozyme-based sensor on single atom Ce-N-C (SACe-N-C nanozyme) with highly active peroxidase enzyme which was further used to develop a 3D printed integrated portable bioactive paper-based sensor for carbofuran, carbosulan, methamidophos and omethoate pesticides detection with LOD of 0.081, 0.074 0.071 and 0.055 ppm, respectively.

Nanostructures for pesticide detection

In recent times, the use of nanomaterials such as nanoparticles, nanotubes and nanocomposites gained more attention in the development of different types of biosensors for pesticide detection in agriculture sector. The nanomaterials are more efficient and improved the performance of biosensors by increasing their affordability and allowing real time detection of pesticide. The nanomaterials have potential to generate high contact surface-to-volume ratio, electric conductivity, biocompatibility and catalytic activities due to their unique nanosize, electrical, florescence and optical properties (14, 21, 64). These biosensors can be widely used for the detection of pesticides in different agriculture sources and products such as fruits and vegetables, etc (64). These NPs are widely used for many purposes in the fields of pharmaceuticals, cosmetics, renewable energy, bioremediation and other biological applications due to their unique properties (65). Different types of nanoparticles such as AuNPs, AgNPs, bimetallic NPs, quantum dots (QDs) and carbon nanomaterials are used for detection in agriculture sector (64).

Silver nanoparticles (AgNPs)

AgNPs have been used extensively in many industries such as food, agriculture, pharmaceuticals, textiles, etc. because of their unique physiochemical properties including high surface-to-mass ratio, high sensitivity and nanometer-scale dimensions (10^{-9} m) (66). Their physical, chemical and electrical properties like melting temperature, magnetic behavior, redox potential and color are size-dependent; they show variations by changing shape and size (1-100 nm). The performance of an AgNP-based sensing device was evaluated by determining numerous attributes including size, shape, size distribution, surface area, solubility, aggregation, structure, toxicity and biocompatibility. The AgNPs were used by chemiluminescent (CL) sensor array to distinguish OPP and carbamate pesticides. Luminol-functionalized silver nanoparticles (Lum-AgNPs) and hydrogen peroxide (H_2O_2) based CL system were used to develop biosensors (Fig. 3). These properties are altered specifically by the interaction with pesticides and produce specific CL response patterns as fingerprints. This chemiluminescent array has been used to distinguish five different categories of organophosphates and carbamates pesticides at 24 ppm with 95 % accuracy (67).

Moreover, the AgNPs modified with L-cysteine (L-cys-AgNPs) were used for the identification of pesticides including cypermethrin and monosultap. The solution of L-cysteine was used as a colorimetric indicator and *Diospyros blancoi* leaf infusion was used to reduce and stabilize silver nitrate (Ag^+ to Ag^0) solution. L-cys-AgNPs solution was dark brownish yellow in color with SPR absorbance at 422 nm. Depending on the pesticide concentration increased by 20, 50 and 100 ppm, addition of sodium chloride (NaCl) caused the colour to shift from brownish yellow to white or transparent. When cypermerthrin pesticide interacted with L-cys-AgNPs sensing assay, the color became transparent and the absorption peak dropped from 1.15 to 0.17 while the effect of monosultap on these nanoparticles was insignificant. Addition of cypermethrin also led to aggregation of AgNPs, resulting in the clearance of the solution. This special colorimetric sensor had a clear quantitative check for cypermethrin detection (68). Additionally, the Rhodamine B-silver nanoparticles (RB-AgNPs) were used to detect carbamate pesticides. Carbamate pesticides inhibit the action of AChE and thus, the production of thiocholine is ceased. Thiocholine can alter the RB-AgNPs solution from yellowish to greyish color and

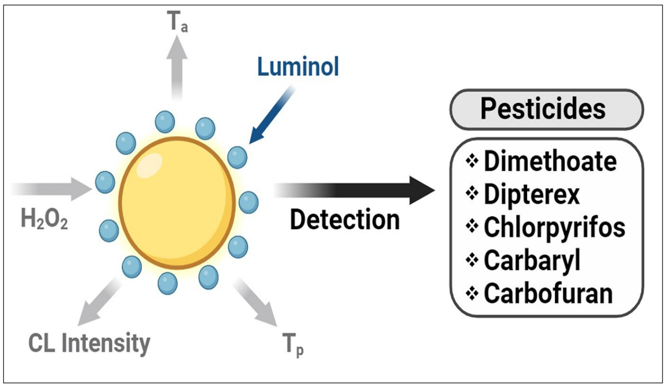

Fig. 3. A schematic representation of pesticide detection using CL sensor array based on the triple-channel properties of the Lum-AgNP-H_2O_2 CL system (67).

unquench the Rhodamine B (RB) fluorescence. The RB-AgNP solution maintains its yellow color and the fluorescence of RB molecules remains quenched when AChE is inhibited by carbamates. Fig. 4 indicates detection of carbaryl pesticide by RB -AgNPs. As shown in figure, the color of the RB-AgNPs in well-dispersed form was yellow; however, in the presence of AChE and ATCh, RB-AgNPs aggregate and the color changes to grey. After addition of carbaryl, RB-AgNPs remained dispersed and thus retained the yellow color. The concentration spectrum of carbaryl ranged from 1×10^{-7} to 8×10^{-5}ppm with 2.3×10^{-8}ppm as LOD (33). Using a colorimetric assay, AgNPs with a citrate cap (Cit -AgNPs), along with an on-off type mechanism, were used to detect triazophos quantitatively. Cit-AgNPs were aggregated in the presence of triazophos, which contributed to the simple shift in color from yellow to prune by hydrogen bonding, π-π interactions and substitution. The LOD was 5000 ppm for this special colorimetric sensing (69). Bare AgNPs were utilized as a chemical sensor for the detection of diazinon pesticides in fruits and vegetables. The detection of diazinon was based on the color transition of AgNPs from yellow to rose-rouge accompanied by the LSPR and UV-Visible zone red shift in the AgNPs solution (Fig. 5). Only diazinon molecule due to a combination pyrimidine nitrogen mold and unique orientation for the diazinon molecule was found to facilitate the change of color and transfer of the LSPR AgNP band and supported non-associations with AgNPs with a LOD of 0.007 ppm (70).

Furthermore, AgNPs can rapidly detect pesticides, utilizing the surface-enhanced Raman scattering (SERS) technique. SERS substrate synthesis was accomplished through a method of reduction by synthesizing AgNPs. AgNPs were extremely monodispersed and spherical, producing extraordinary electromagnetic fields to measure phosmet (pesticide) in the methanol solution during SERS activities. AgNPs coupled with SERS served as a reliable technique for the rapid pesticide detection of phosmet residues in Oolong tea with LOD 0.1 ppm (30).

Highly sensitive secnidazole capped AgNPs (SEC-AgNPs) were synthesized using a chemical reduction for the colorimetric detection of carbendazin fungicide with LOD of 0.021 µM in the linear range of 0.5-22 µM (71). The real sample applicability of this sensor was tested using tap water and human blood sample. Similarly, Ali *et al.* (72) reported detection of cymoxanil fungicides using triazole-N-acetamide thiazole (TAT) functionalized AgNPs-based nano-sensor with an LOD of 0.013 µmol/L. The applicability of this fabricated sensor was tested using river water, tap water and human blood samples.

Gold nanoparticles

Gold nanoparticles (AuNPs) have been extensively used for detection purpose because they are cost-effective, rapid, highly sensitive, reliable, selective and have some unique properties specifically, surface plasmon resonance and capacity to quench the fluorophores by acting as electron acceptors during photo-induce electron transfer (PET) process (73). The charging and releasing process of AuNPs was used as a sensing strategy in the fabrication of nanosensors using the PET process. In this process, the electron is transferred to ground state molecules from photo-excited molecules. It plays an important role in fluorescence sensors, photoluminescence sensors, etc. where it provides intramolecular electron transfer mechanism, helping in the signalling process along with the switching fluorescence ability.

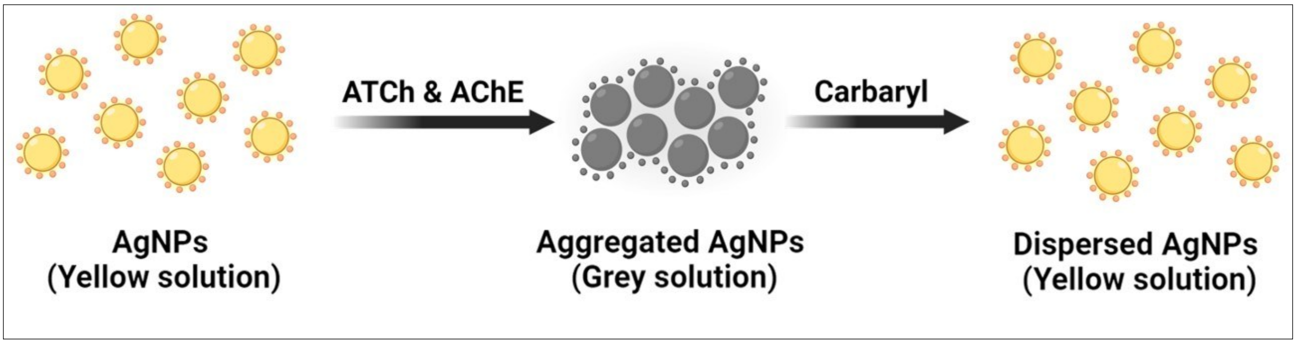

Fig. 4. Schematic representation of detection process of carbaryl pesticide by RB-AgNPs (33).

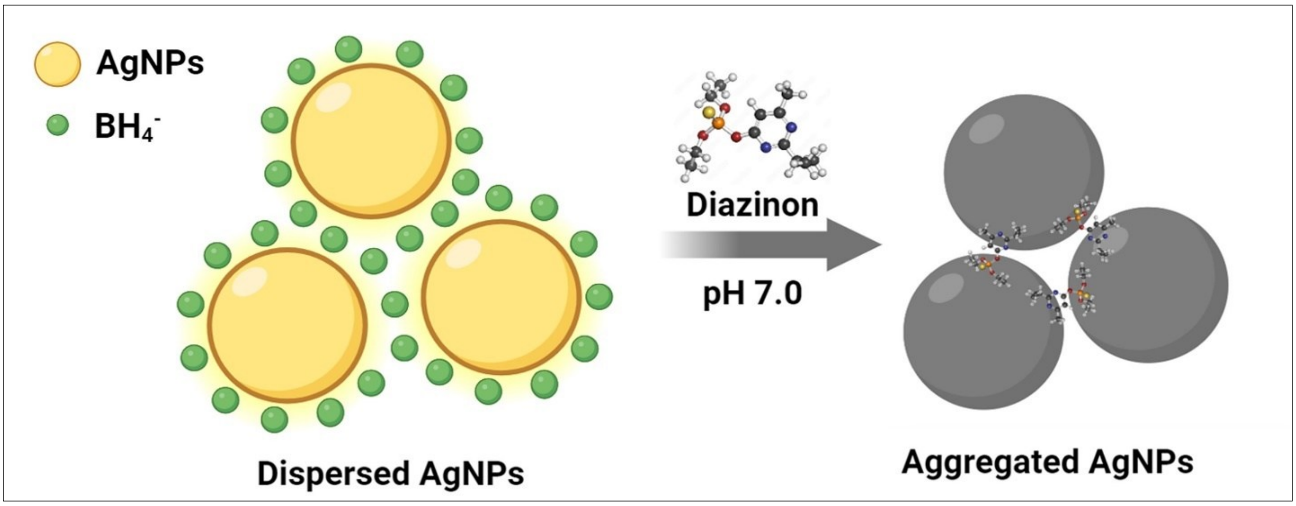

Fig. 5. Bare AgNPs dispersed in aqueous solution (yellow color) and after adding diazinon pesticide solution AgNPs aggregated and showing red shift of LSPR band (70).

During the sensing process, the quenching effects of ionophore are inhibited by the coordination of cation and ionophore, which further influences the quantum yield. There are several photo-induced electron transfer sensors such as sodium, potassium and calcium sensors commercially available for the applications. In aqueous solution, spherical and monodispersed AuNPs exhibit a variety of colors such as brown, orange, red and purple as the core diameter rises from 1 to 100 nm and show absorption peak between 500 and 550 nm (73). These AuNPs show aggregation due to their distinct distance and size-dependent SPR characteristics and extremely high coefficients of molar extinction at lowest concentration. Many researchers have successfully developed nanosensors using AuNPs, for example, an AChE enzymatic hydrolysis and dissolution of AuNPs in Au^{3+}-cetyltrimethylammonium bromide (Au^{3+}-CTAB) based colorimetric solution was developed to detect OPP pesticide. In the presence of target pesticide, the activity of AChE enzyme is suppressed, thus it cannot make thiocholine to use the Au^{3+} ion. The colorimetric approach may detect OPPs at concentrations as low as 0.0007 ppm under ideal conditions (37). A highly sensitive cellulose paper based AuNP coated dipsticks were synthesized to monitor the presence of OPPs pesticide with LOD of 0.035 ppm (26). On the other hand, an osmium carbonyl functionalized AuNPs (10OsCO-AuNPs)-based SERS probe was developed to detect glyphosate pesticide with LOD of 0.0001 ppm. In the absence of glyphosate pesticide, AChE is triggered and is hydrolyzes acetylthiocholine to thiocholine, which adsorbed into the surface of AuNPs and induced heavy aggregation through electrostatic interactions. The thiocholine-induced aggregation of 10OsCO-AuNPs and fluctuations in the SERS-CO signal intensity caused the solution's color to change from red to purple (74).

In addition, AuNPs functionalized with ytterbium (Yb^{3+}) (AuNPs-Yb) were synthesized for the detection of OPP. The AuNPs-Yb was synthesized using oxygen functional groups and a potent Yb^{3+} complexation process. The synthesized AuNPs exhibited good sensitivity with an LOD of 0.03 ppm and in the European Union pesticide database, it is far below than the actual residue value (0.01 ppm) (75). Furthermore, Abdali *et al.* (76) successfully developed a non-enzymatic colorimetric sensor using AuNPs of varying sizes for the detection and discrimination of harmful pesticides including thiometon, diazinon, carbendazim, paraquat, chlorpyrifos and bifenazate with LOD of 7.4, 9.7, 17.7, 22.4, 22.8 and 23.8 ng/mL, respectively. The linear concentration range varied with variety of pesticides, carbendazim, paraquat and chlorpyrifos showed between 50-800 ng mL^{-1} and bifenazate and thiometon showed the linear concentration range of 25-800 ng mL^{-1}. The real-time applicability test of this sensor was done using water (tap, sewage and well), soil, fruits, leaves and strawberry cultures.

Bimetallic nanoparticles (BNPs)

Bimetallic nanoparticles (BNPs) are developed using a combination of two different metals. BNPs have attracted more interest from both standpoints, scientific and technical, as compared to monometallic nanoparticles as they have very distinct size-dependent optical, thermal, electrical and catalytic properties than the monometallic nanoparticles (77). Several forms of BNPs have been developed using different metals for detecting harmful chemical pesticides.

Silver/gold nano-complex

In past few decades, there has been a lot of concern regarding the physical and chemical characteristics of nanoparticles developed of noble metals, specifically AgNPs and AuNPs, due to their LSPR. Such features enable the Raman surface enhanced spectroscopy implementation performance, drug delivery system, catalysts and active substrates as well as any other biomedical applications. Silver and gold bimetallic nanoparticles modified with Rhodamine B (RB @Ag-Au BNPs) were developed in "Turn-off-on detection mode" (Fig. 6) (78). In presence of OPP pesticide, the fluorescence of developed RB @Ag-Au BNPs remains quenched since Ag-Au BNPs with OPPs have better coordination in comparison to RB-Ag NPs/RB-Au NPs. The developed fluorescence sensor exhibits good sensitivity with LOD of $1.8{\times}10^{-5}$ ppm, so this approach can detect the presence of OPPs in crops (69). Three types of pesticides, profenofos (organophosphate), thiacloprid (carbamate) and oxamyl (neonicotinoid), were detected on peach fruit using an Au/Ag NPs bimetallic core- shell based SERS technique with LOD of 0.01, 0.1 and 0.01 ppm, respectively (79).

Palladium/gold nano-complex

Palladium coupled AuNPs have potential to function as a catalyst in the ligand-free Suzuki coupling process. They exhibit remarkable catalytic, electrochemical properties, structural stability and cost-effectiveness. These nanoparticles continue to act as catalysts even after several cycles (77). Palladium-gold nanocomplex was developed to determine the presence of pesticides on the surface of agriculture produce. For example, 1D Pd-Au core-shell nanorod-based BNPs were synthesized for the detection of OPP pesticides with LOD of 3600 ppm. 1D Pd-Au core-shell nanorod improves the photocatalytic performance of sensors due to their size and unique microstructure (31). They are low in cost, non-toxic in nature and possess higher conductivity and mobility with large surface areas due to lower particle size range. Amberlyst resin supported Pd-Au BNPs (Pd-Au/Amberlyst) -based bimetallic photocatalyst were developed to effectively degrade the herbicide parathion with reusability rate up to 6 times without degradation of catalytic activity. The recovery rate of 0.15 % for Au and 0.15 % for Pd was reported, which indicates good stability of the nanocatalyst (80).

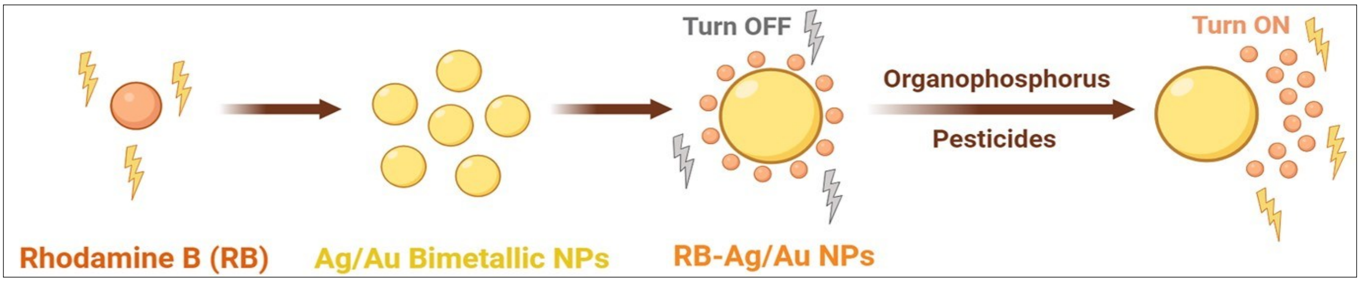

Fig. 6. The detection mechanism for organophosphorus pesticides (OPP) by "Turn-off-on detection mode" with the help of RB-Ag/AuNP (69).

Iron/nickel nano-complex

Nickel exhibits interesting characteristics when combined with other metals. Nickel (Ni) nanoparticles have been widely exploited due to their catalytic and magnetic properties. Ni-based catalysts are extensively used because of their good stability, cost-effectiveness and rapid recovery rate (81). When combined with iron, these nanoparticles exhibit excellent catalytic activity for dechlorination of chlorinated methanes (77). Bimetallic Fe/Ni nanoparticles were developed and used to catalyze the disintegration of the OPP pesticide, profenofos, with the greatest reduction rate of 94.51 % at pH 5.12 (81). The ionic structure of nanocomplex was influenced under the acidic medium (pH 5.12) and the surface was positively charged due to increased H^+ ions in the medium. In addition, the basic medium (above neutral pH 7.3), the noncomplex surface charge was negative due to OH^- ions.

Copper/silver nano-complex

The synthesis of a spherical covalent organic framework (COF) supports bimetallic Cu/Ag nanoparticles (Cu/Ag-COF). This material exhibited excellent stability, reusability and maintained a high catalytic efficiency even after undergoing 8 cycles of catalyzing the reduction of 4-nitrophenol (4-NP) (82). A smartphone-assisted paper-based biosensor was developed employing core-shell Cu@Ag nanoparticles with citrate capping. The paper-based device is user friendly, easy to use and cost effective, made up of enzymes and substrates separated by empty pieces of the paper and can be connected with the smartphone readout system. The device provides the ability of selective detection of the pesticides based on the higher affinity and interact with the nanoparticles, which leads to change in the color of paper-based device by aggregation of nanoparticles. In addition, the use of paper substrate helps in the production of electrochemical cells, which reduces the degradative effects of the device on the environment. This biosensor could detect and monitor the presence of phenthoate pesticide in water and food samples. This sensor operates based on the aggregation mechanism of AgNPs located on the surface of copper nanoparticles (CuNPs), which leads to a change in color of the paper-based sensor with LOD of 0.015 ppm and linear concentration range of 0.05-1.5 ppm (83).

Silver/ron nano-complex

Many researchers have reported that Ag/Fe nanocomposite has very good catalytic properties for the detection, reduction and real-time monitoring of pesticides and other toxic pollutants in agriculture and industrial sectors. For example, Ag/Fe-based BNPs were synthesized by using extract of *Salvia officinalis* as a reducing agent by green synthesis. The nanoparticles exhibited efficient catalytic activity (94.56 %) in the reduction of 4-NP (4-nitrophenol) to 4-AP (4-aminophenol), exhibiting excellent performance in terms of recycling and reusability for up to five cycles (84). Ag-doped Fe_3O_4 nanoparticles were synthesized by the hydrothermal method to detect methomyl pesticide in a vegetable sample. The electrochemical biosensor was developed by employing chitosan and acetic acid as cross linkers. The electrode's response to methomyl pesticide activity was investigated using cyclic voltammetry (CV) with LOD of 0.738 ppm and linear concentration range of 1.054-12.318 ppm (85).

Quantum dots (QDs)

Quantum dots (QDs) are semiconductor nanostructures that possess exceptional spectrum and photochemical stability. Compared to other bioluminescent dyes, they possess a diverse range of excitation lines, thin emission lines, exceptional luminous performance, flexible luminescent color and reliable light stability, making them an outstanding fluorescent marker. These fluorescent markers are used to enhance sensitivity and resolution by decreasing the LOD value of the sensor (34). QDs also have special electronic and optical properties owing to the impact of quantum containment. They have numerous attractive features, which make them perfect as analytical sensors. Various uses have been identified through disciplines across surface modulation techniques. The new form of carbon QDs can be used in analytical sensing (86). A paper-based sensor for highly responsive visualization was built and used to precisely detect and evaluate three OPP pesticides in "turn-off" detection mode (Turn-off-on). A paper-based nanosensor was developed by linking double quantum dots (QDs) with nano-porphyrin (QDs-nano-porphyrin) of high intensity, double nanometer signal amplification and specific color changes in response to three distinct OPPs. The concept of fluorescence "Turn-off" is based on water-soluble ZnCdSe and CdSe QDs, whereas fluorescent samples are designed for certain pesticides (Fig. 7). Certain pesticides can quench the fluorescence of two QDs to varying degrees.

The fluorescence of the QDs is quenched by pesticides due to weak electrostatic, hydrogen, covalent bonding and substitute reaction. The chemical and physical interaction between QDs and target analytes resulted in the sensing of pesticide, which may also lead to improving quenching. The QDs sensing process involves energy flow between analytes and QD fluorophore and relies on the Förster resonance energy transfer (FRET) mechanism due to absorption of energy by donor, resulting in high quantum yields, broad absorption spectra along with the fluorescence lifetimes. Pesticides can be detected qualitatively and quantitatively in actual samples using chemo metrics techniques with a detection limit of 7.1×10^{-3}ppm and a recognition rate of 100 % (87).

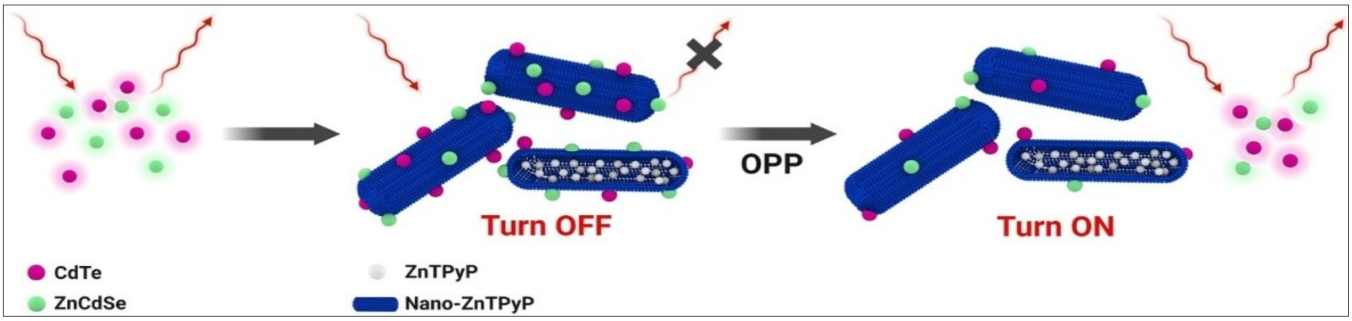

Fig. 7. Schematic representation of the principle of "Turn-off-on" mode for nano-ZnTPyP combined with double QDs (CdTe and ZnCdSe) for the OPP pesticide detection (87).

It has been reported that fluorescence-based core-shell QDs were developed for the detection of carbamate pesticide (methomyl, carbofuran and aldicarb). This approach exhibited great detection sensitivity, with the LOD of 0.003 ppm for carbamate. The fluorescence of QDs is quenched by hydrogen peroxidase, which is produced by hydrolysis and oxidation of acetylcholine (ACh) in the presence of AChE and choline oxidase (ChOx). The interaction between ACh and AChE is inhibited in the presence of carbamate and the effectiveness of this inhibition may be evaluated by observing variations in QD fluorescence. Carneiro *et al.* (88) reported the association of CQDs and AgNPs to establish a fluorescent sensing technique for detecting pesticides in food with LOD of 0.25 ppm. CQDs were synthesized using riboflavin and AgNPs, which effectively quenched the CQDs fluorescence through FRET. Furthermore, an easy and sensitive citrate-functionalized selenium QDs-based fluorescence sensor was developed to detect the presence of endosulfan pesticide with LOD of 2 fM and linear detection range of 2 fM-2 mM (89). The applicability of developed sensor was tested on human blood plasma, milk and water sample and resulted in good recoveries.

Carbon nanomaterials

In recent years, the researcher interest has increased on the use of carbon nanomaterials such as carbon nanotubes (CNTs), graphene and carbon quantum dots (CQDs) because of their distinct structure and characteristics including their electrical, mechanical and physiochemical properties. These nanomaterials are widely used in the fields of medicine, electrical, agriculture, optics and environmental protection (90).

Carbon nanotubes (CNTs)

Nanotubes are elongated, hollow and tubular nanomaterials characterized by varying lengths and diameters ranging from nanometers (nm) to millimeters (mm). CNTs are carbon structures having sp^2 hybridization made up of graphene sheets structured into molecular tubes. CNTs and halloysite nanotubes (HNTs) have been used extensively due to their large surface area and distinct properties such as chemical and thermal stability, high elasticity, conductivity and tensile strength (91). Pesticide detection is now feasible due to the tendency of these nanotubes to alter their surface. Thakkar *et al.* (91) successfully developed AChE immobilized multiwall carbon nanotubes (MWCNTs) modified with carboxylic groups via amide bond. These modified MWCNTs were put on a glassy carbon electrode and used for detecting OPP pesticides with lowest (3.55×10^{-14} ppm) and highest (1.77×10^{-8} ppm) detection limits of the sensor. The presence of amide bonds between the modified carbon nanotubes and AChE restricts the use of any cross-linker material, which disabled the interference of electron transfer resulting in increased sensitivity of pesticide detection. This sensor exhibited good stability, recovery and 0.1 nM detection limit for paraxon pesticide.

Graphene

Graphene is a hexagonally flat carbon sheet and it is widely used in catalyst fields, chemical sensors, hydrogen storage and gas emitters due to its specific characteristics. Different surfaces are prevalent in graphene, its analogues (always 2630 sqm g^{-1}), good electron mobility, thermal conductivity at room temperature (always 5-113 Wm^{-1} K^{-1}) and strong chemical stability (towards 7200 Sm^{-1}), excellent optical clarity, high strength (130 %), high mechanical strength (130 GPa), Young's-1200 GPa modulus and high mechanical efficiency (1300 GPa) (92). Graphene is a 2-dimensional (2D) material (a sheet of sp^2 hybridized carbon atoms) and because of its outstanding conductivity and biocompatibility, it has attracted considerable interest (93). The high surface-to-volume ratio of graphene intensified the interaction of electrode surface and target analyte, resulting in good sensitivity and selectivity. Moreover, its improved electron transfer properties help in electrochemical biosensing using redox reaction. The functionalized graphene can also be used to provide binding sites for attaching and detecting the target pesticide. Graphene oxide (GO) is used widely to produce nanocomposite for the indemnification of pesticides with various metal and metal oxide NPs. The mechanism behind GO's strong adsorption behavior to different pesticides is the strong P-P interaction with the aromatic ring of the organic contaminant. It has been reported that an ultrasensitive and precise carbamate pesticide sensor based on fluorescent sulfur-doped graphene quantum dots (S-GQDs) was developed, which exhibited LOD of 4.5×10^{-3} ppm for carbofuran and 1.6×10^{-2} ppm for thiram. To create a flexible solid-state fluorescence-sensing platform, S-GQD was also added to the poly vinyl alcohol (PVA) matrix. S-GQD endowed the polymer film with fluorescent qualities and as a result, the film displayed solid-state fluorescence. PVA/S-GQD flexible film had an LOD of 0.06 ppm and 0.21 ppm for carbofuran and thiram, respectively (94). Chitosan modified graphene nanofragments and AChE-coated glassy carbon electrode-based sensor was developed to detect the presence of dichlorvos pesticide. The developed sensor showed good sensitivity with LOD of 54 pM and linear concentration range of 0.1-100,000 nM (95).

Carbon quantum dots (CQDs)

CQDs are distinct and innovative carbon-based nanostructures with less than 10 nm thickness developed using core carbon atoms and functional surface (organic or bio-molecular components). CQDs have an amorphous nucleus which is primarily sp^2 hybridized in the carbon atoms (96). In past decades, the optical properties of CQDs have gained significant attention in fluorescence emissions. CQDs have superior characteristics like water solubility, ignorable cytotoxicity, simple synthesis, easy operation, chemical inertness, excellent fluorescence emission and resistance to photobleaching (97). An ultrasensitive electrochemiluminescence sensor based on the ternary nanocomposites CuS/CQDs/g-C3N4NS has reportedly been developed for the monitoring of the diazinon pesticide with LOD of 7.81×10^{-12} ppm and linear range of 3.55×10^{-11}-1.77×10^{-3} ppm (98). Flumioxazin pesticide was detected in real agricultural samples using azide functionalized CQDs, developed by conjugating 4-azidoaniline based fluorescent nanosensor with LOD of 2.7×10^{-4} ppm and linear concentration range of 0-0.0354 ppm (99). Hazardous ethyl paraoxon (EP) and methyl parathion (MP) were detected using recombinant organophosphorus acid anhydrolase (OPAA) enzyme and CQDs immobilized on thin film-based sensor developed by hydrothermal method. The developed sensor can detect both the pesticides EP and MP with LOD of 0.18 and 0.69 ppm and detection range of 0-100 µM, respectively. Sensor was tested on water samples with good recovery and accuracy (100).

Challenges and future aspects

The development of innovative materials, hybrid materials, nanomaterials and novel manufacturing processes of micro/ nanostructures for pesticide detection should continue to be useful to enhance sensitivity and as a result, reduce the LOD of sensing devices. Optical biosensors such as colorimetric, fluorescence-based sensors, etc. are currently being developed and examined in laboratories for the real time detection of pesticide and residue in agriculture sectors. The fabrication of more standardized fluorescence sensors using nanomaterials such as carbon dots and lab-on-chip sensors are still in high demand for commercial and industrial food applications such as food safety, food security and rapid and real-time detection of pollutants and other toxins in less time with better efficiency as compared to conventional methods. Additionally, the development of low cost and scalable portable nano sensors-based kits, strips and filter sheets should be required for easy and real time detection of pesticides and other toxic pollutants. On contrary, the high sensitivity and lower chemical stability of the immunoassay and enzyme-based electrochemical sensors restrict their use in the agriculture sector for onsite detection of pesticides. The working efficiency for pesticide detection of the sensor will be validated using the conventional methods including GC-MS, HPLC, etc. Therefore, novel research should be required on non-destructive technology for the validation of sensing methods for pesticide detection. Non-destructive technology is the analysis of samples without affecting the quality, integrity of the samples for future use of the specimen. Non-destructive methods such as Near Infrared Spectroscopy (NIRS), Internet of Thing (IoT), electronic nose (E-nose), etc. are suitable methods for qualitative and quantitative detection of pesticide in agriculture produce. These innovative non-invasive methods are simple, low cost, reliable, eco-friendly and can improve safety and prevent accidents, thus, reducing downtime, ensuring quality control, reducing environmental risk and being precise for the rapid detection of pesticides, while being used as validation method for sensors. These methods also help in the compliance of the regulatory aspects.

However, to overcome the disadvantage of conventional methods of pesticide detection, application of bio-sensing methods requires more in-depth elaboration in the future to achieve high rapidity, accuracy, sensitivity, integration and miniaturization. Despite the advantages of bio sensing methods, one of the primary challenges associated with the fabrication of nano-sensors is the integration of larger systems, scalable production and efficient material synthesis. During fabrication, it is crucial to reduce errors and contamination, while simultaneously preserving sensitivity, selectivity and stability. Ecological hazards, regulatory ambiguities and elevated expenses impede advancement. Advancements in precision methodologies, materials science and interdisciplinary collaboration are necessary to resolve these challenges. In addition, the presence of various types of chemicals and microorganisms may disrupt the detection of the pesticide residual in fruits and vegetables. Therefore, further research should be carried out on the combined technology of biosensing with biochips and electronic tongue technology for the detection of pesticide residual with better accuracy at low cost and time.

Conclusion

In the present review, the use of pesticides in the agriculture sectors for improving their productivity along with their drawbacks and sensing technologies as alternatives to conventional methods for the detection of pesticide residue in agriculture sector is summed up. This review article summarizes the usage of pesticides in the agriculture sector to enhance productivity, as well as the associated drawbacks. It also discusses sensing technologies as potential alternatives to conventional methods for detecting pesticide residue in agriculture. Based on the previous literature, it may be concluded that pesticides and other contaminants can be determined by analytical methods integrated with nanotechnology as they give outstanding performance. The advantages of nano-sensors over conventional methods are better performance, advanced efficiency, improved sensitivity, selectivity and accuracy. Nanotechnology has potential for use in several aspects of the food supply chain, such as enhancing food safety, quality assurance and developing innovative food components and additives. The present review has discussed the development and improvement of various pesticide detection methods along with the studies of the detection limits of each approach. Biosensors have been shown to be a flexible approach for pesticide detection along with their sensitivity, mobility, dependability and cost-effectiveness. These biosensors can easily overcome time-consuming stages and the demand for skilled staff, which is difficult to avoid in traditional instrumental approaches. Numerous advancements in bio-sensing methods (electrochemical, potentiometric, amperometric, calorimetric, optical biosensors and immunosensors) and their fabrication techniques have opened new vistas for the creation of nanomaterial-based nano-sensors with desirable detection capabilities and miniaturization in recent years. Among all the bio-sensing methods, optical biosensors, especially biosensors based on SPR, are the most well-established with reasonably high sensitivities. Immunosensors operate based on the highly selective and sensitive interaction between antibodies and antigens, but their high specificity can be a disadvantage. Enzyme -based biosensors allow the detection of an extensive range of contaminants. Therefore, they frequently provide a general toxicity index, but do not provide precise details about a specific pesticide. Nanomaterials like AgNPs, AuNPs, BNPs, QDs, CNTs and AChE-enzyme based detection are discussed with their detection efficiency and detection limits. Nanoparticles possess a large specific surface area and good electrical conductivity, which can significantly enhance the sensitivity of detection by functioning as nano-enzymes and electrocatalysts. Nanoparticle-based detection mechanisms have been established by conjugating identification units such as antibodies, aptamers or MIPs to these nanoparticles for detecting pesticides. Nano-sensors are widely accessible for detecting insecticides; however, there have been limited studies on detecting fungicides and herbicides. As we know, fruits and vegetables retain a diverse range of pesticides. However, most detection techniques are limited in their ability to detect only a small number of pesticides simultaneously. Henceforth, it may be essential to integrate nanomaterial-based methods with high-throughput chips to achieve the concurrent detection of multiple pesticides.

Acknowledgements

Authors acknowledged National Institute of Food Technology Entrepreneurship and Management, Kundli, Sonipat, Haryana 131028 for providing the research facility and infrastructure. The first authors (Aishwarya Dixit) wish to express gratitude to University Grant Commission (UGC-SRF) for providing funding for research work and fellowship.

Authors' contributions

All authors contributed to the study conception and design. The authors indicated in parentheses made substantial contributions to the following tasks of research: conceptualization (AD, NK, SS and AU), writing - original draft (AD and NK), writing - revised, investigation, methodology (AD, NK, YC, YY, YSH, VKB, SS and AU), supervision (SS and AU). All authors read and approved the final manuscript.

Compliance with ethical standards

Conflict of interest: Authors do not have any conflict of interest to declare.

Ethical issues: None

References

1. Thakur RK, Sharma S. Impact of pesticides used in agriculture: Their benefits and hazards. AIP Conference Proceedings. 2024 (Vol. 2986, No. 1). AIP Publishing. https://doi.org/10.1063/5.0193979
2. Kaur R, Choudhary D, Bali SV, Bandral SS, Singh V, Ahmad M, Kumar M, Singh TG, Chandrasekaran B. Pesticides: An alarming detrimental to health and environment. Sci Total Environ. 2024; 915:170113. https://doi.org/10.1016/j.scitotenv.2024.17 0113
3. Cheng M, Cui Y, Yan X, Zhang R, Wang J, Wang, X. Effect of dual-modified cassava starches on intelligent packaging films containing red cabbage extracts. Food Hydrocoll. 2022;124:107225. https://doi.org/10.1016/j.foodhyd.2021.107225
4. Kamalesh R, Karishma S, Saravanan A. Progress in environmental monitoring and mitigation strategies for herbicides and insecticides: A comprehensive review. Chemosphere. 2024;141421. https://doi.org/10.1016/j.chemosphere.2024.141421
5. The Food and Agriculture Organization Q & A on Pests and Pesticide Management,2021. https://www.fao.org/newsroom/detail/Q-A-on-Pests-and-Pesticide-Management/en.
6. Bustamante-Torres M, Torres O, Abad-Sojos S, Pardo S, Bucio E. Application of genetically modified microorganisms for bioremediation of polluted environments. In Genetically Engineered Organisms in Bioremediation. 2024;18-51. CRC Press.
7. Dey S, Adak S, Dhar A, Jana S, Sarkar S, Chatterjee S. How Pesticides Can Harm You and Your Environment: A Review of Drift Exposure Routes and Health Risks 2024.
8. Cuenca JB, Dreij K, Tirado N. Human pesticide exposure in Bolivia: A scoping review of current knowledge, future challenges and research needs. 2024;21(3):305. https://doi.org/10.3390/ijerph21030305
9. Faraj T K, El-Saeid MH, Najim M, Chieb M. The impact of pesticide residues on soil health for sustainable vegetable production in arid areas. Separations. 2024;11(2):46. https://doi.org/10.3390/separations11020046
10. Ramos VCP, Quináia SP, Torres YR, De Lima LS, Machado CS. Development and validation of a method to determine pesticides in river water using QuEChERS combined with UHPLC-MS/MS. Rev Ambiente Água. 2024;18:1-10. https://doi.org/10.4136/ambi-agua.2940
11. Kadadou D, Tizani L, Alsafar H, Hasan SW. Analytical methods for determining environmental contaminants of concern in water and wastewater. MethodsX. 2024;24:102582. https://doi.org/10.1016/j.mex.2024.102582
12. Huang W, Wang X, Xia J, Li Y, Zhang L, Feng H, Zhang X. Flexible sensing enabled agri-food cold chain quality control: A review of mechanism analysis, emerging applications, and system integration. Trends Food Sci Technol. 2023a;133:189-204. https://doi.org/10.1016/j.tifs.2023.02.010
13. Chimene D, Queener KM, Ko BS, McShane MJ, Daniele MA. Insertable Biosensors: Combining Implanted Sensing Materials with Wearable Monitors. Annu Rev Biomed Eng. 2024;26(1). https://doi.org/10.1146/annurev-bioeng-110222-101045
14. Abdel-Karim R. Nanotechnology-Enabled Biosensors: A review of fundamentals, materials, applications, challenges and future scope. Biomedical Materials & Devices. 2024;2(2):759-77. https://doi.org/10.1007/s44174-023-00147-z
15. Kim Y, Jeon Y, Na M, Hwang S, Yoon Y. Recent trends in chemical sensors for detecting toxic materials. Sensors. 2024;24(2):431. https://doi.org/10.3390/s24020431
16. Vidal C, Govan J. Machine learning techniques for improving nanosensors in agroenvironmental applications. Agronomy. 2024; 14(2):341. https://doi.org/10.3390/agronomy14020341
17. Dippong T. Innovative nanomaterial properties and applications in chemistry, physics, medicine, or environment. Nanomater. 2024; 14 (2):145. https://doi.org/10.3390/nano14020145
18. Jiang Z, Zhang Y, Guo S, Sohan ASMMF, Yin B. Advances in microfluidics techniques for rapid detection of pesticide residues in food. Foods. 2023;12(15):2868. https://doi.org/10.3390/foods12152868
19. Thorat T, Patle B, Wakchaure M, Parihar L. Advancements in techniques used for identification of pesticide residue on crops. Journal of Natural Pesticide Research. 2023;4:100031. https://doi.org/10.1016/j.napere.2023.100031
20. Gupta P. Pesticides (agrochemicals). Illust Toxicol. 2018;165-194. https://doi.org/10.1016/b978-0-12-813213-5.00005-5
21. Rapini R, Marrazza G. Biosensor potential in pesticide monitoring. Comp Anal Chem. 2016;74:3-31. https://doi.org/10.1016/bs.coac.2016.03.016
22. Abubakar Y, Tijjani H, Egbuna C, Adetunji CO, Kala S, Kryeziu TL, Ifemeje JC, Patrick-Iwuanyanwu KC. Pesticides, history, and classification. Natural Remedies for Pest, Disease and Weed Control, Academic Press. 2020;29-42. https://doi.org/10.1016/b978-0-12-819304-4.00003-8
23. Akhtar K, Baig JA, Solangi IB, Afridi HI, Khalid A, Solangi SA, Perveen S, Bhanbhro P, Hussain S. Biosynthesis of Titanium oxide-Aluminium oxide Nanocomposites for Electrocatalytic Detection of 2,4,6-Trichlorophenol. Mater Today Commun. 2024;38:108137. https://doi.org/10.1016/j.mtcomm.2024.108137
24. Bernardino PN, Luo A, Andrew PM, Unkel C, González MI, Gelli AC, Lein PJ. Evidence implicating blood-brain barrier impairment in the pathogenesis of acquired epilepsy following acute organophosphate intoxication. J Pharmacol Exp Ther JPET. 2024;388(2):301-12. https://doi.org/10.1124/jpet.123.001836
25. Zheng Z, Zhou Y, Li X, Liu S, Tang Z. Highly sensitive organophosphorous pesticide biosensors based on nanostructured films of acetylcholinesterase and CdTe quantum dots. Biosens Bioelectron. 2011;26:3081-3085. https://doi.org/10.1016/j.bios.2010.12.021
26. Yan X, Song Y, Zhu C, Li H, Du D, Su X, Lin Y. MnO2 nanosheet-carbon dots sensing platform for sensitive detection of organophosphorus pesticides. Anal Chem. 2018;90:2618-2624. https://doi.org/10.1021/acs.analchem.7b04193

27. Li X, Jiao HF, Shi XZ, Sun A, Wang X, Chai J, Li DX, Chen J. Development and application of a novel fluorescent nanosensor based on FeSe quantum dots embedded silica molecularly imprinted polymer for the rapid optosensing of cyfluthrin. Biosens Bioelectron. 2018a;99:268-73. https://doi.org/10.1016/j.bios.2017.07.071

28. Umapathi R, Rani GM, Kim E, Park S, Cho Y, Huh YS. Sowing kernels for food safety: Importance of rapid on-site detction of pesticide residues in agricultural foods. Food Frontiers. 2022; 3(4), 666-76. https://doi.org/10.1002/fft2.166

29. Tang X, Zhang Q, Zhang Z, Ding X, Jiang J, Zhang W, Li P. Rapid, on-site and quantitative paper-based immunoassay platform for concurrent determination of pesticide residues and mycotoxins. Anal Chim Acta. 2019;1078:142-50. https://doi.org/10.1016/j.aca.2019.06.015

30. Chen X, Wang D, Li J, et al. A spectroscopic approach to detect and quantify phosmet residues in Oolong tea by surface-enhanced Raman scattering and silver nanoparticle substrate. Food Chem. 2020b;312:126016. https://doi.org/10.1016/j.foodchem.2019.126016

31. Lu X, Lü T, Song D, Li Y, Gao F. Bimetallic Pd@Au nanorods based ultrasensitive acetylcholinesterase biosensor for determination of organophosphate pesticides. Sens Actuators B Chem. 2018;255:2575-581. https://doi.org/10.1016/j.snb.2017.09.063

32. Wu S, Li D, Wang J, Zhao Y, Dong S, Wang X. Gold nanoparticles dissolution based colorimetric method for highly sensitive detection of organophosphate pesticides. Sens Actuators B Chem. 2017;238:427-33. https://doi.org/10.1016/j.snb.2016.07.067

33. Luo Q, Li Y, Zhang MQ, Qiu P, Deng Y. A highly sensitive, dual-signal assay based on rhodamine B covered silver nanoparticles for carbamate pesticides. Chin Chem Lett. 2017;28:345-49. https://doi.org/10.1016/j.cclet.2016.10.024

34. Liao Y, Cui X, Chen G, Wang Y, Qin G, Li M. Simple and sensitive detection of triazophos pesticide by using quantum dots nanobeads based on immunoassay. Food Agric Immuno. 2019; 30:522-32. https://doi.org/10.1080/09540105.2019.1597022

35. Arkhypova V, Soldatkin O, Soldatkin A, Dzyadevych SV. Electrochemical biosensors based on enzyme inhibition effect. Chem Rec. 2024;24(2):e202300214. https://doi.org/10.1002/tcr.202300214.

36. Rana JS, Jinda Mariyappan V, Sundaresan R, Chen S, Ramachandran R, Al-Sehemi AG, Jeevika A, Wu W. Constructing a novel electrochemical sensor for the detection of fenitrothion using rare-earth orthophosphate incorporated reduced graphene oxide composite. Process Saf Environ Prot. 2024;1:185:726-38. https://doi.org/10.1016/j.psep.2024.03.013

37. Dincer C, Bruch RC, Costa-Rama E, Fernández-Abedul MT, Merkoçi A, Manz A, Urban G, Güder F. Disposable sensors in diagnostics, food and environmental monitoring. Adv Mater. 2019;31(30). https://doi.org/10.1002/adma.201806739

38. Zahirifar F, Rahimnejad M, Abdulkareem RA, Najafpour G. Determination of Diazinon in fruit samples using electrochemical sensor based on carbon nanotubes modified carbon paste electrode. Biocatal Agric Biotechnol. 2019;20:101245. https://doi.org/10.1016/j.bcab.2019.101245

39. Mariyappan V, Sundaresan R, Chen S, Ramachandran R, Al-Sehemi AG, Jeevika A, Wu W. Constructing a novel electrochemical sensor for the detection of fenitrothion using rare-earth orthophosphate incorporated reduced graphene oxide composite. Process Saf Environ Prot. 2024;1:185:726-38. https://doi.org/10.1016/j.psep.2024.03.013

40. Uru ŞK. A critical perspective on the applied potential in amperometric phosphate biosensors. J Water Proc Engineering. 2024;58:104886. https://doi.org/10.1016/j.jwpe.2024.104886

41. Mashuni, Ritonga H, Jahiding M, Kurniawati D, Hamid FH, Khaeri AM. The electrode optimization of biosensor based on carboxymethyl cellulose/glutaraldehyde membrane and its application for carbaryl pesticide analysis. Nucleation and Atmospheric Aerosols, The 9th international conference of the indonesian chemical society ICICS 2021: Toward a Meaningful Society. 2022; 2638:050004. https://doi.org/10.1063/5.0104374

42. Kamel AH, Abd-Rabboh HSM. Imprinted polymer/reduced graphene oxide-modified glassy carbon electrode-based highly sensitive potentiometric sensing module for imidacloprid detection. Microchem J. 2024;197:109789. https://doi.org/10.1016/j.microc.2023.109789

43. Modak N, Friebe VM. Amperometric biosensors: Harnessing photosynthetic reaction centers for herbicide detection. Curr Opin Electrochem. 2023;42:101414. https://doi.org/10.1016/j.coelec.2023.101414

44. Patel H, Rawtani D, Agrawal YK. A newly emerging trend of chitosan-based sensing platform for the organophosphate pesticide detection using Acetylcholinesterase - a review. Trends Food Sci Technol. 2019;85:78-91. https://doi.org/10.1016/j.tifs.2019.01.007

45. Martoni LV, Gomes NO, Oliveira Jr ON, Machado SA, Raymundo-Pereira PA. Low-cost photoelectrochemical sensor sensitized with carbon spherical shells and cobalt (II) phthalocyanine for fast acetaminophen determination. Microchem J. 2024; 197:109780. https://doi.org/10.1016/j.microc.2023.109780

46. Zheng Y, Hua T, Sun D, Xiao JJ, Xu F, Wang F. Detection of dichlorvos residue by flow injection calorimetric biosensor based on immobilized chicken liver esterase. J Food Eng. 2006; 74:24-29. https://doi.org/10.1016/j.jfoodeng.2005.02.009

47. Qin J, Guo N, Yang J, Wei J. Recent advances in metal oxide nanozyme-based optical biosensors for food safety assays. Food Chem. 2024;139019. https://doi.org/10.1016/j.foodchem.2024.139019

48. Bilal S, Tariq A, Khan SI, Liaqat M, Andreescu S, Hong-Xia Z, Hayat A. A review of nanophotonic structures in optofluidic biosensors for food safety and analysis. Trends Food Sci Techno. 2024;104428. https://doi.org/10.1016/j.tifs.2024.104428

49. Zhou J, Qi Q, Wang C, Qian Y, Liu G, Wang Y, Fu L. Surface plasmon resonance (SPR) biosensors for food allergen detection in food matrices. Biosens Bioelectron. 2019;142:111449. https://doi.org/10.1016/j.bios.2019.111449

50. Pundir CS, Malik A, Preety P. Bio-sensing of organophosphorus pesticides: A review. Biosens Bioelectron. 2019;140:111348. https://doi.org/10.1016/j.bios.2019.111348

51. Mauriz E, Calle A, Manclus JJ, Montoya A, Escuela AM, Sendra JR, Lechuga LM. Single and multi-analyte surface plasmon resonance assays for simultaneous detection of cholinesterase inhibiting pesticides. Sens Actuators B Chem. 2006;118:399-407. https://doi.org/10.1016/j.snb.2006.04.085

52. Wang K, Wang Y, Li Q, Liu Z, Liu S. A fluorescence and localized surface plasmon resonance dual-readout sensing strategy for detection of acetamiprid and organophosphorus pesticides. Sens Actuators B Chem. 2022;351:130977. https://doi.org/10.1016/j.snb.2021.130977

53. Nawrot W, Drzozga K, Baluta S, Cabaj J, Malecha K. A fluorescent biosensor for detection vital body fluids' agents. Sensors. 2018; 18 (8):2357. https://doi.org/10.3390/s18082357

54. Huang Y, Guo N, Xu C, Xie N, Liang F, Yang S, Lv S. Development and critical evaluation of a novel fluorescent nanosensor based on a molecularly imprinted polymer for the rapid detection of procymidone in ginseng. Anal. 2022; 147:2718-730. https://doi.org/10.1039/d1an02186a

55. Cao J, Wang M, Shao Y, She Y, Cao Z, Xiao M, Jin F, Wang J, El-Aty AMA. Fluorescent sensor for rapid detection of organophosphate pesticides using recombinant carboxylesterase PvCarE1 and glutathione-stabilized gold nanoclusters. Microchem J. 2024;110322. https://doi.org/10.1016/j.microc.2024.110322

56. Ma Y, Hou C, Zheng J, Huang M, Hou J, Luo H, Hou C, Huo D.

Detection of organophosphorus pesticides by a fluorescent sensing assay coupled with enzyme inhibition. J Food Compos Anal. 2024;106139. https://doi.org/10.1016/j.jfca.2024.106139

57. Yang Z, Huang X, Lin L, Guo H, Yang F. Tetraarylimidazole-based fluorescence sensor for halosulfuron-methyl. Dyes Pigm. 2024; 222:111860. https://doi.org/10.1016/j.dyepig.2023.111860

58. Octobre G, Delprat N, Doumèche B, Leca-Bouvier BD. Herbicide detection: A review of enzyme- and cell-based biosensors. Environ Res. 2024;118330. https://doi.org/10.1016/j.envres.2024.118330

59. Verma N, Bhardwaj A. Biosensor technology for pesticides-a review. Appl Biochem Biotechnol. 2015;175:3093-119. https://doi.org/10.1007/s12010-015-1489-2

60. Zhang F, Huang L, Yuan D, Yu X, Wang M, Hua X. Development of gold nanoparticle-based lateral flow immunoassay for the determination of tebufenozide in agro-products. Microchem J. 2024a; 110153. https://doi.org/10.1016/j.microc.2024.110153

61. Ballesteros CA, Mercante LA, Alvarenga AD, Facure MH, Schneider R, Correa DS. Recent trends in nanozymes design: from materials and structures to environmental applications. Mater Chem Front. 2021;5:7419-451. https://doi.org/10.1039/d1qm00947h

62. Kavruk M, Özalp VC, Öktem HA. Portable bioactive paper-based sensor for quantification of pesticides. Anal Methods Chem. 2013;1-8. https://doi.org/10.1155/2013/932946

63. Song G, Zhang J, Huang H, Wang X, He X, Luo Y, Li JC, Huang K, Cheng N. Single-atom Ce-NC nanozyme bioactive paper with a 3D-printed platform for rapid detection of organophosphorus and carbamate pesticide residues. Food Chem. 2022;387:132896. https://doi.org/10.1016/j.foodchem.2022.132896

64. Melendez RG, Moreno KJ, Moggio I, Arias E, Ponce A, Llanera I, Moya SE. On the influence of silver nanoparticles size in the electrical conductivity of PEDOT: PSS. Mater Sci Foru. 2010; 644:5-90. https://doi.org/10.4028/www.scientific.net/msf.644.85

65. Soliman M, Lee B, Ozcan A, Rawal TB, Young M, Mendis HC, Rajasekaran P, Washington T, Pingali SV, O'Neill H, Gesquiere A. Engineered zinc oxide-based nanotherapeutics boost systemic antibacterial efficacy against phloem-restricted diseases. Environ Sci Nano. 2022; 9:2869-2886. https://doi.org/10.1039/d2en00263a

66. Dixit A, Das S, Jyoti A, Kaushik S. Biogenic synthesis of silver nanoparticles and its potential application in prevention of acute ear infections. J Pharm Sci Res 2017;9(1):14-17.

67. He Y, Xu B, Li W, Yu H. Silver nanoparticle-based chemiluminescent sensor array for pesticide discrimination. J Agric Food Chem. 2015;63:2930-934. https://doi.org/10.1021/acs.jafc.5b00671

68. Kodir A, Imawan C, Permana IS, Handayani W. Pesticide colorimetric sensor based on silver nanoparticles modified by L-cysteine. In 2016 International Seminar on Sensors, Instrumentation, Measurement and Metrology (ISSIMM). 2016;43-47. https://doi.org/10.1109/issimm.2016.7803719

69. Luo Q, Lai J, Qiu P, Wang X. An ultrasensitive fluorescent sensor for organophosphorus pesticides detection based on RB-Ag/Au bimetallic nanoparticles. Sens Actuators B Chem. 2018;263:517-523. https://doi.org/10.1016/j.snb.2018.02.101

70. Shrivas K, Sahu S, Sahu B, Kurrey R, Patle TK, Kant T, Karbhal I, Satnami ML, Deb MK, Ghosh KK. Silver nanoparticles for selective detection of phosphorus pesticide containing π-conjugated pyrimidine nitrogen and sulfur moieties through non-covalent interactions. J Mol Liq. 2019;275:297-303. https://doi.org/10.1016/j.molliq.2018.11.071

71. Arain M, Nafady A, Haq MaU, Asif HM, Ahmad H, Khan MA, et al. Selective and sensitive colorimetric detection of endocrine disrupter fungicide carbendazim through secnidazole capped silver nanoparticles. *Spectrochim Acta A Mol* Biomol Spectrosc. 2024;304:123313. https://doi.org/10.1016/j.saa.2023.123313

72. Ali I, Khan S, Shah ZA, Ahmed F, Shah I, Hameed A, Ullah R, Shah MR. Synthesis and Characterization of Silver Nanoparticles Conjugated with Triazole-N-acetamide Thiazole Derivatives for Selective Detection of Cymoxanil in Complex Samples. Chemistry Select. 2024;9(4). https://doi.org/10.1002/slct.202304484

73. Plaisen S, Cheewasedtham W, Rujiralai T. Robust colorimetric detection based on the anti-aggregation of gold nanoparticles for bromide in rice samples. RSC Adv. 2018; 8(38), 21566-1576. https://doi.org/10.1039/c8ra03497d

74. Tan MJ, Hong ZY, Chang MH, Liu CC, Cheng HF, Loh XJ, Chen CH, Liao CD, Kong KV. Metal carbonyl-gold nanoparticle conjugates for highly sensitive SERS detection of organophosphorus pesticides. Biosens Bioelectron. 2017;96:167-72. https://doi.org/10.1016/j.bios.2017.05.005

75. Li Y, Luo Q, Hu R, Chen Z, Qiu P. A sensitive and rapid UV–vis spectrophotometry for organophosphorus pesticides detection based on Ytterbium (Yb3+) functionalized gold nanoparticle. Chin Chem Lett. 2018b;29:1845-848. https://doi.org/10.1016/j.cclet.2018.11.016

76. Abdali M, Ghasemi F, Hosseini HM, Mahdavi V. Different sized gold nanoparticles for array-based sensing of pesticides and its application for strawberry pollution monitoring. Talanta. 2024; 267:125121. https://doi.org/10.1016/j.talanta.2023.125121

77. Sharma G, Kumar A, Sharma S, Naushad M, Dwivedi RP, ALOthman ZA, Mola GT. Novel development of nanoparticles to bimetallic nanoparticles and their composites: A review. J King Saud Univ Sci. 2019;31:257-69. https://doi.org/10.1016/j.jksus.2017.06.012

78. Ma L, Han E, Yin L, Xu Q, Zou C, Bai J, et al. Simultaneous detection of mixed pesticide residues based on portable Raman spectrometer and Au@Ag nanoparticles SERS substrate. Food Control. 2023b;153:109951. https://doi.org/10.1016/j.foodcont.2023.109951

79. Yaseen T, Pu H, Sun DW. Fabrication of silver-coated gold nanoparticles to simultaneously detect multi-class insecticide residues in peach with SERS technique. Talanta. 2019;196:537-45. https://doi.org/10.1016/j.talanta.2018.12.030

80. Mohammadi P, Sheibani H. Evaluation of the bimetallic photocatalytic performance of Resin–Au–Pd nanocomposite for degradation of parathion pesticide under visible light. Polyhedron. 2019;170:132-37. https://doi.org/10.1016/j.poly.2019.05.030

81. Mansouriieh N, Sohrabi MR, Khosravi M. Optimization of profenofos organophosphorus pesticide degradation by zero-valent bimetallic nanoparticles using response surface methodology. Arab J Chem. 2019;12:2524-532. https://doi.org/10.1016/j.arabjc.2015.04.009

82. Wu Z, Zhu J, Wen W, Zhang X, Wang S. Spherical covalent organic framework supported Cu/Ag bimetallic nanoparticles with highly catalytic activity for reduction of 4-nitrophenol. J Solid State Chem. 2022;311:123116. https://doi.org/10.1016/j.jssc.2022.123116

83. Shrivas K, Patel S, Thakur SS, Shankar R. Food safety monitoring of the pesticide phenthoate using a smartphone-assisted paper-based sensor with bimetallic Cu@ Ag core–shell nanoparticles. Lab on a Chip. 2020;20:3996-4006. https://doi.org/10.1039/d0lc00515k

84. Malik MA, Alshehri AA, Patel R. Facile one-pot green synthesis of Ag-Fe bimetallic nanoparticles and their catalytic capability for 4-nitrophenol reduction. J Mater Res Technol. 2021;12:455-70. https://doi.org/10.1016/j.jmrt.2021.02.063

85. Gai K, Qi H, Zhu X, Wang M. Preparation of Ag-Fe3O4 nanoparticles sensor and application in detection of methomyl. E3S Web of Conferences. 2019;118:01002. https://doi.org/10.1051/e3sconf/201911801002

86. Nsibande SA, Forbes PB. Fluorescence detection of pesticides using quantum dot materials–a review. Anal Chim Acta. 2016; 945:9-22. https://doi.org/10.1016/j.aca.2016.10.002

87. Fan Y, Liu L, Sun D, Lan H, Fu H, Yang T, She Y, Ni C. “Turn-off” fluorescent data array sensor based on double quantum dots coupled with chemometrics for highly sensitive and selective detection of multicomponent pesticides. Anal Chim Acta. 2016;

916:84-91. https://doi.org/10.1016/j.aca.2016.02.021

88. Carneiro SV, De Queiroz VH, Cruz AA, Fechine LM, Denardin JC, Freire RM, Do Nascimento RF, Fechine PB. Sensing strategy based on Carbon Quantum Dots obtained from riboflavin for the identification of pesticides. Sens Actuators B Chem. 2019; 301:127149. https://doi.org/10.1016/j.snb.2019.127149

89. Nair LV, Nair RV, Jayasree RS. Cadmium selenium quantum dot based nanosensor with femto molar level sensitivity for the detection of the pesticide endosulfan. J Polym Sci Eng. 2024; 6(1), 3208. https://doi.org/10.24294/jpse.v6i1.3208

90. Zhao S, Bai X, Mou M, Duo L. Carbon nanomaterial addition changes soil nematode community in a tall fescue mesocosm. Pedosphere. 2022;32:777-84. https://doi.org/10.1016/j.pedsph.2022.06.013

91. Thakkar JB, Gupta S, Prabha CR. Acetylcholine esterase enzyme doped multiwalled carbon nanotubes for the detection of organophosphorus pesticide using cyclic voltammetry. Int J Biol Macromol. 2019;137:895-903. https://doi.org/10.1016/j.ijbiomac.2019.06.162

92. Nasrollahzadeh M, Nezafat Z, Gorab MG, Sajjadi M. Recent progresses in graphene-based (photo) catalysts for reduction of nitro compounds. Mol Catal. 2020;484:110758. https://doi.org/10.1016/j.mcat.2019.110758

93. Oliveira TM, Ribeiro FW, Sousa CP, Salazar-Banda GR, de Lima-Neto P, Correia AN, Morais S. Current overview and perspectives on carbon-based (bio) sensors for carbamate pesticides electroanalysis. TrAC - Trends Anal Chem. 2020;124:115779. https://doi.org/10.1016/j.trac.2019.115779

94. Nair RV, Thomas RT, Mohamed AP, Pillai S. Fluorescent turn-off sensor based on sulphur-doped graphene quantum dots in colloidal and film forms for the ultrasensitive detection of carbamate pesticides. Microchem J. 2020;157:104971. https://doi.org/10.1016/j.microc.2020.104971

95. Zhang JH, Hu H, Wang P, Zhang C, Wu M, Yang L. A stable biosensor for organophosphorus pesticide detection based on chitosan modified graphene. Biotechnol Appl Bioc. 2021b;69(2):567-75. https://doi.org/10.1002/bab.2133

96. Kumar JV, Rhim J. Fluorescent carbon quantum dots for food contaminants detection applications. J Environ Chem Eng. 2024; 111999. https://doi.org/10.1016/j.jece.2024.111999

97. Molaei MJ. The optical properties and solar energy conversion applications of carbon quantum dots: A review. Sol Energy. 2020; 196:549-66. https://doi.org/10.1016/j.solener.2019.12.036.

98. Kamyabi MA, Moharramnezhad M. A novel cathodic electrochemiluminescent sensor based on CuS/carbon quantum dots/g-C3N4 nanosheets and boron nitride quantum dots for the sensitive detection of organophosphate pesticide. Microchem J. 2022;179:107421. https://doi.org/10.1016/j.microc.2022.107421

99. Panda S, Jadav A, Panda N, Mohapatra S. A novel carbon quantum dot-based fluorescent nanosensor for selective detection of flumioxazin in real samples. New J Chem. 2018;42:2074-080. https://doi.org/10.1039/c7nj04358a

100. Vyas T, Jaiswal S, Choudhary S, Kodgire P, Joshi A. Recombinant Organophosphorus acid anhydrolase (OPAA) enzyme-carbon quantum dot (CQDs)-immobilized thin film biosensors for the specific detection of Ethyl Paraoxon and Methyl Parathion in water resources. Environ Res. 2024;243:117855. https://doi.org/10.1016/j.envres.2023.117855