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Review article

Implications of biosensors and nanobiosensors for the eco-friendly detection of public health and agro-based insecticides: A comprehensive review

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ABSTRACT

Biosensors, in particular nanobiosensors, have brought a paradigm shift in the detection approaches involved in healthcare, agricultural, and industrial sectors. In accordance with the global expansion in the world population, there has been an increase in the application of specific insecticides for maintaining public health and enhancing agriculture, such as organophosphates, organochlorines, pyrethroids, and carbamates. This has led to the contamination of ground water, besides increasing the chances of biomagnification as most of these insecticides are non-biodegradable. Hence, conventional and more advanced approaches are being devised for the routine monitoring of such insecticides in the environment. This review walks through the implications of biosensors and nanobiosensors, which could offer a wide range of benefits for the detection of the insecticides, quantifying their toxicity status, and versatility in application. Unique eco-friendly nanobiosensors such as microcantilevers, carbon nanotubes, 3D printing organic materials and nylon nano-compounds are some advanced tools that are being employed for the detection of specific insecticides under different conditions. Furthermore, in order to implement a smart agriculture system, nanobiosensors could be integrated into mobile apps and GPS systems for controlling farming in remote areas, which would greatly assist the farmer remotely for crop improvement and maintenance. This review discusses about such tools along with more advanced and eco-friendly approaches that are on the verge of development and could offer a promising alternative for analyte detection in different domains.

1. Introduction

Chemical fertilizers and insecticides are one of the cornerstones crop improvement and control of insects, including mosquitoes for maintaining the health of the population. The world population is expected to grow by nearly 2 billion people, i.e., from 8 billion in 2023 to 9.7 billion in 2050, and approximately half of the population will be at risk of tropical disease and food availability (https://

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www.worldometers.info/world-population). Because of the expected exponential population growth, it is a challenging task for nations to provide adequate nutrition and advanced health facilities to the population [1]. To meet the demands of the increasing population, there has been an increase in the use of insecticides for enhancing the agricultural sector and to provide better public health facilities [2]. This has led to the indiscriminate usage of insecticides [3,4]. Several techniques have been devised for insect control, such as biological control, transgenic plants, host plant resistance, cultural controls, and bioinsecticides, many of which are at the nascent stage of application [5].

Insecticides are substances or mixtures used for preventing, destroying, or controlling insects, including vectors of human and animal diseasethat impede food production, processing, storage, or that might be applied to animals to suppress insect populations, such as mosquitoes, and agricultural pests including beetles, aphids, bugs, locusts, and caterpillars [6]. Although the use of insecticides improves production and enhances insect resistance, continual use of such agents eventually permeate soil and groundwater, causing environmental pollution and a wide range of diseases, allergies, and physiological disorders, such as skin redness, swelling, blistering, wheezing and cough among the common forms, and could also enhance neurodegenerative disease like Parkinson's disease [7]. Such prolonged use of insecticides has led to the development of resistant insects, such as organochlorine resistant and pyrethroid resistant mosquitoes. Because insecticides have been used for decades, selective pressures have minimized the effectiveness of vector control measures [8], which can result in the resurgence of vector-borne diseases. Because of the indiscriminate use of insecticides, such as organochlorines, pyrethroids, carbamates etc., there have been continuous threats to the environment safety as most of these chemicals are recalcitrant, and can pass through ground water into food chains of organisms, leading to chronic disease. Therefore, detection of such insecticides in various hotspots of the environment is important for environmental risk monitoring.

There is a considerable challenge in maintaining a proper balance between the usefulness of such insecticides and the associated health risks [9]. A vital aspect of risk assessment related to environmental exposure including occupational exposure involves biomonitoring, which provides data on the total dose absorbed and indirect information on the concentrations at the target sites [10]. A biomonitoring technique is a scientific approach that provides direct information about the impact and the corresponding toxicities of the contaminants in the environment [11]. Current researches have focused on developing new approaches to detect insecticides in water, soil, and food. Conventionally, there are four widely used sensing methods: gas chromatography (GC) [12], high-performance liquid chromatography (HPLC) [13], electrophoresis [14], and mass spectroscopy [15]. Several demerits of these techniques make them difficult to use in some cases, such as, HPLC is time-consuming, requires highly purified samples, and has high maintenance costs [16]; GC has a low detection limit, and is incompatible with polar insecticides, in addition to being expensive [17,18]; and mass spectrometry is very expensive and requires technically skilled personnel [19]. There have been many attempts to develop better methods for the detection of insecticides that are fast, sensitive, specific, accurate, and user-friendly. In this regard, biosensors and nanobiosensors offer a great promise, as they are highly specific, biologically stable, low application dose, and possess a rapid mode of action [10]. Biosensor is an analytic device that converts a biological response into an electrical signal through the simultaneous coordination of three basic components; biocatalyst: converts the substrate to the product; transducer: determine the biocatalyst reaction and converts it to an electrical signal; and an electronic system: amplifies the signal and records the data [20]. A whole-cell-based biosensor (WCB) is an analytical device that incorporates a living organism and can detect a wide range of analytes including pesticides. WCBs can operate in a broad range of conditions, such as at different temperatures and pH levels [21]. These devices have been used successfully in fields for environmental monitoring, food analysis, pharmacology, and drug screening because of their high sensitivity, selectivity, and high throughput in situ detection capabilities. Algal-based biosensors are one type of WCBs for detecting herbicides in water and food, with high sensitivity, cost-effective cultivation, ease of genetic manipulation, sustainability, and versatility for integration into microfluidics or multiplexing devices [22]. As a result of their adaptability to diverse environments, algae are less susceptible to physicochemical changes than other bioreceptors. Another example of WCB is a free-living soil nematode, *Caenorhabditis elegans*-based biosensor that offers many experimental advantages because of its small size, transparency, rapid life cycle, large brood size, etc., and has been consistently used for ecotoxicity monitoring in different environments [23]. Similarly, the water-filtering organism *Daphnia magna* is very sensitive to changes in environmental conditions and toxic substances, and has been utilized in certain WCBs for ecotoxicological monitoring [24]. Furthermore, insects have also been used for designing certain types of WCBs because of their strong olfactory response that is highly dependent on chemical cues and is capable of detecting a wide array of volatile molecules in the environment [25,26]. Studies have shown that certain insect receptors are very selective and sensitive to indole and skatole, exhibiting fast response in electrophysiological whole-cell measurements, thereby having potential for environmental toxic chemical monitoring [25]. A more advanced form of biosensor is the nano-biosensor that utilizes specific cell component-nanoparticle labelled nano-conjugates, such as nano-enzymes, nano-subcellular entities, nano-cellular complexes, which could be detected using a simple digital reader [27]. Nanobiosensors are more environment-friendly compared to nanosensors, which utilize nano-conjugates of nano-metal based complexes that are non-biodegradable and persist in the environment for long time [28]. Such nanobiosensors are currently been developed and are being deployed for the detection of a range of insecticides for crop improvement and controlling the mosquito populations [29].

2. Public health agro-based insecticides and detection approaches

Insecticides are chemical agents that kill insects or prevent their destructive behavior. A variety of methods have been used to classify insecticides, based on their chemistry, toxicological action, and mode of penetration. Another recent approach classifies insecticides according to the mechanism of absorption through the digestive tract (stomach poisons), inhalation (fumigants), or through the skin (contact poisons). Chemically, insecticides are classified into four groups: organic, synthetic, inorganic, and miscellaneous [30]. Organic pesticides are derived from natural sources, such as pheromones, gibberellic acid, nicotine, *Bacillus thuringenesis*, neem extract, cinnamon oil, and certain minerals such as copper and sulphur-based compounds. Inorganic pesticides include non-carbon elemental compounds such as metal-based compounds, such as bismuth, arsenic, boric acid, silica gel, etc. [31]. They are highly effective and easily penetrate the body wall of insects; however they are non-biodegradable and render environment pollution. Miscellaneous insecticides comprise hybrid compounds or more complex chemical compounds such as methoxyacrylates–-fluacrypyrin, naphthoquinones–acequinocyl, pyrimidanines–pyrimiifen and benzenedicarboxamides–flubendiamide; which are advanced forms of insecticides, and have been under continuous field trials for conventional application [32]. Synthetic or chemical-based insecticides are the compounds that have been consistently used globally for agro-based and public health activities and can be categorized into five different types (Table 1): Organophosphates, carbamates, organochlorine, pyrethroids, and sulfonylurea compounds.

World Health Organization (WHO) has outlined the classification of insecticides based on acute and/or chronic toxicity imposed by them. Briefly, WHO classifies insecticides by acute/chronic dermal and oral toxicity based on the estimated lethal doses of LD50 (the dose of the insecticide needed to kill 50% of the organisms, when the insecticide is ingested or applied topically). More recently, insecticides have been classified by the hazard posed based on WHO recommendations under the Globally Harmonized System (GHS) Acute Toxicity Hazard Categories (WHO, 2019) (Fig. 1) [33].

Based on the toxicity and formulation of the technical compound, the classification distinguishes between the more and less hazardous forms of each insecticide. The technical-grade active ingredients in the insecticides that are classified as extremely hazardous (Class Ia) including carbamate, organochlorines, and organophosphorus compounds. In addition, pyrethroids and all insecticide ingredients under Class Ia are also included in the category of highly hazardous group (Class Ib). Furthermore, moderately hazardous (Class II) group consists of specific insecticides like certain carbamates and sulfonyl urea compounds. The slightly hazardous (Class III) group comprises insecticides, such as specific types of organophosphorus compounds, carbamate and pyrethroids. A few of the organochlorines, pyrethroids, and carbamates belong to the last category (Class IV) of insecticides that do not impose any acute hazards upon normal application. Besides posing a threat to living organisms, insecticides are also detrimental to the environment. Therefore, detection of insecticides in different setting and with a high sensitivity is required for the monitoring of environmental safety.

Traditionally, insecticide residues in the soil are determined using a solid-liquid separation procedure followed by a clean-up procedure [34]. Utilizing other extraction techniques developed recently can reduce the disadvantages associated with traditional methods, such as the need for copious amounts of solvent as well as the time it takes [35]. Different techniques have been used for this purpose, including supercritical fluid extraction (SFE) [36], solid-phase extraction (SPE) [35,36] and microwave-assisted extraction (MAE) [37,38]. Additionally, researchers have developed a method to prepare soil samples by sonicating small columns of soil. The method can be used as a sensitive and fast indicator of herbicides, insecticides, or fungicides [35,39–41]. Numerous chromatographic methods have been developed to determine the concentration of insecticides in soil. Analyzing insecticides qualitatively and quantitatively is routinely accomplished using GC, which is driven by the difference between the partition coefficients of a liquid stationary phase and a gaseous mobile phase [30,42,43]. GC can be used to analyze insecticide residues with a variety of detectors, such as Pulse Flame Photometric Detector (PFPD) [44,45], Mass Spectrometer (MS), Microwave Emission Detector, Electron Capture Detector (ECD), Flame Ionization Detector (FID), Nitrogen Phosphorus Detector (NPD), Capillary, etc. [46].

Insecticide residues detected by GC with various systems are:

- **GC-PFPD:** Organophosphates, Acephate, Aldrin, Dicofol, Endrin, Captan, etc.
- **GC-MS:** Trifluralin, Dicholoron, Cypermethrin, Malathion, Cyfluthrin, etc.
- **GC with microwave emission detector:** Parathion
- **GC-ECD/FID and NPD:** Nitrogen–Phosphorus containing Insecticides
- **GC Capillary:** Organochlorines

HPLC is another potential technique to detect insecticides in the environment, especially for insecticides that are thermally unstable. Multiple insecticide residues have been detected from food samples using HPLC and supercritical fluid extraction [47]. Many researchers use spectrophotometry as a way to detect insecticide residues in the environmental samples. This device uses light absorption to calculate the analyte concentration. The amount of light absorbed depends on the analyte concentration. The method can be used to detect toxic chemicals such as malathion, phorate, and dimethoate. An excess of N-bromosuccinimide is used to oxidize organophosphorus insecticides. Spectrophotometric analysis of a decrease in color at 550 nm is performed on the unconsumed N-bromosuccinimide following a reaction with rhodamine B [48]. In some cases, these systems are paired with other sensors as terminal detectors for insecticide detection [47]. In recent years, electroanalytical techniques have become more important in the

Table 1
Classification of insecticides based on their toxicity and biodegradability and exhibiting the mode of entry and action in biological organisms.

Toxicity	Biodegradability	Insecticides types	Mode of entry	Mode of action
Acute	Biodegradable	Organo-phosphates	Systemic	Physical
Chronic	Non-biodegradable	Carbamate	Contact	Protoplasmic
		Organo-chlorine	Stomach poisons	Respiratory
		Pyrethroid	Fumigant	Nerve
		Sulfonylurea compounds	Repellent	Chitin inhibition

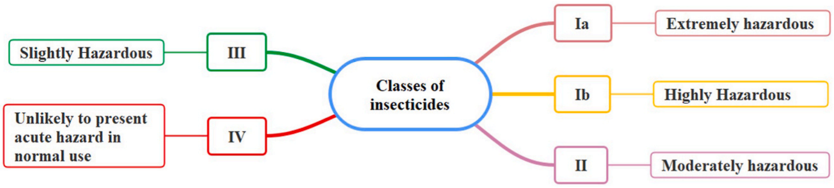

Fig. 1. Types of insecticides based on WHO classification used in public health and for agriculture improvement.

environmental analysis because of their simplicity of operation, sensitivity, selectivity, and portability [49]. Besides, there are several electroanalytical techniques commonly used, such as potentiometry [50], conductometry [51], voltammetry [52], and amperometry [53]. Analytes are quantified by combining amperometry and potentiometry. These techniques are often used in conjunction with other methods such as chromatography, biosensors, flow injection analysis, etc. to determine the presence of insecticides in environmental samples [54] (Fig. 2).

3. Biosensors and nanobiosensors for public health agro-based insecticide detection

Several newer and effective methods have been developed in order to overcome the limitations of classical methods for the detection of public health and agro-based insecticides. In this regard, the use of biosensors, integrated with biorecognition elements that utilize various detection methods have been developed. Such biosensors can be used on-site to measure the extent of pollution levels almost immediately [55]. An analytical device, the biosensor converts a biological response into an electrical signal through the simultaneous coordination of three basic components: Biocatalyst: converts the substrate to the product, which involves a microorganism or cell-based products; Transducer: includes physical components such as electrochemical, optical, thermal or gravimetric techniques that converts one form to energy to another, and could detect the biological reaction and converts to an electrical signal; and Electronic system: amplifies, records, and visualizes the signal [56] (Fig. 3). A more advanced form of biosensor is nano-biosensor that further limits the use of whole organisms as biocatalyst, wherein specific cell component-nanoparticle labelled nano-conjugates can be prepared, such as nano-enzymes, nano-subcellular entities, nano-cellular exudates, etc., and could be read using a simple digital reader [57]. Nanosensors, on the contrary, utilize nano-conjugates of metallic compounds or chemical compounds that are not environment-friendly, and could render environment pollution as they persist in the environment for long time, though the detection ability using nanosensors is quite precise [30].

Biosensors are easily disposable, environment-friendly, selective, reliable, can be produced in large quantities, can be miniaturized for efficient use, and can detect very low volume of target analyte [58]. Currently, most nano biosensors are not easy to operate under all conditions owing mainly to the biological component such as cell, enzyme or other biological component tagged to the nano-detector, which requires ambient conditions of pH, temperature, humidity, and skilled personnel for operation. Additionally, during miniaturization, there is increased risk of manipulation and care, and hence, it needs to be modified in such a way that it can be robust and field-deployable. A proper design of this device can minimize its limitations, and can be used conveniently by coupling it with an electrochemical sensor. The cell-based biosensors that use *Escherichia coli* [59], *Pseudomonas putida* [60], *Moraxella* sp. [61], *Chlorella vulgaris* [62], etc., are capable of detecting insecticides such as Paraoxon, Parathion, Methyl parathion, Diazinon, Triazines, Carbamides, and Organophosphates. An enzyme-based biosensor typically measures either enzyme activity or inhibition through an enzyme substrate mechanism. An example of the former is the broad substrate specificity of organophosphorus hydrolase (OPH). For

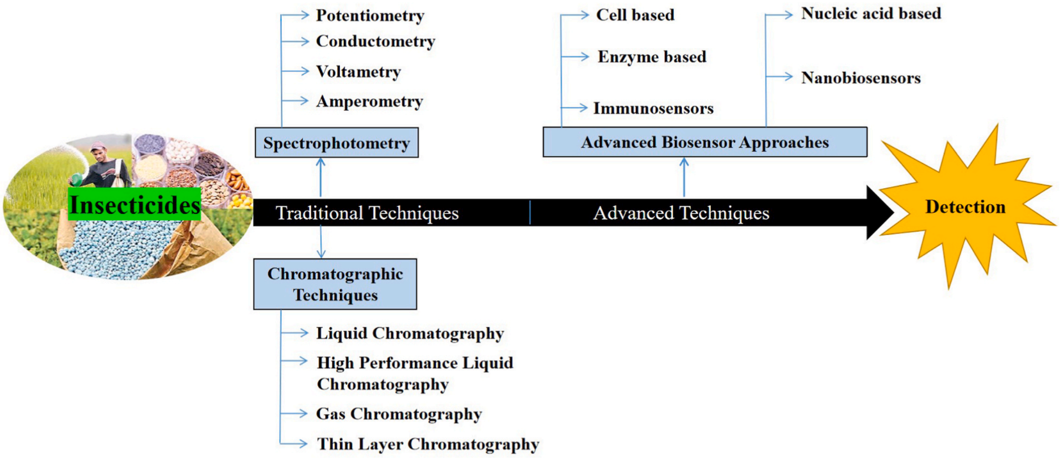

Fig. 2. Outline of different conventional and modern techniques involved in the detection of insecticides.

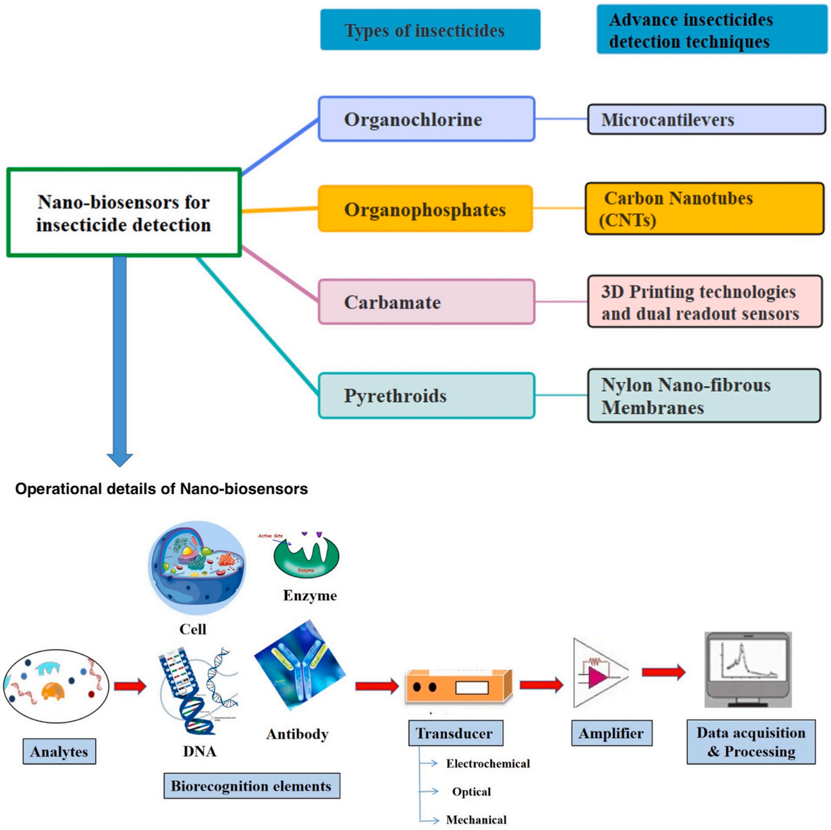

Fig. 3. Different kinds of nano-biosensor detection approaches for detecting various insecticides of public health importance, along with their basic operational mechanism (Below).

the enzymatic biosensors, several enzymes are often used, including choline esterase (CE), acid phosphatase, tyrosinase, ascorbate oxidase, acetolactate synthase, aldehyde dehydrogenase, etc. Most often, activated silica gel is used in these systems to immobilize acetylcholine esterase (ACE) [63]. As carbamate and organophosphate insecticides inhibit the activity of ACE, the method relies on enzyme inhibition. ACE hydrolyzes neurotransmitters to produce choline and acetic acid. The carbamate insecticide inhibits this enzyme reversibly, whereas the organophosphate insecticide inhibits it irreversibly [64]. Another kind of biosensor is immunosensors for quantifying the host immune response with insecticide application. Sensing elements in immunosensors can be antibodies (Abs) or antigens (Ags) that are immobilized on a transducer. Analyte binding to Ab can be measured directly if Ab is immobilized. In the case of immobilized Ag, the analyte and a fixed amount of Ab work together to detect the presence of the analyte. There are four main types of immunosensors described so far [65]: piezoelectric, optical, electrochemical, or thermometric. Piezoelectric immunosensors are predominantly used because of their ability to detect atrazine, parathion, and other insecticides. By using an Ag or Ab coating on a piezoelectric crystal, the change in mass caused by binding the analyte can be correlated with its concentration [66,67]. Optical immunosensors are based on Surface Plasmon Resonance (SPR) devices. The SPR device can detect this change in refractive index when the Ab coated on the metal sheet is bound up with the analyte. This method is also used in automatic optical immunosensors. An optical immunosensor based on the total internal reflection fluorescence (TIRF) is also available. They can detect substances such as terbutryn, atrazine, parathion, polychlorophenol, and similar insecticides [67]. The nucleic acid biosensors are based on the oxidation property of guanine, a nucleic acid base [68]. Insecticides interact with DNA molecules in the nucleic acid biosensors. Changes in redox potential can be detected as a result of such reactions. It is feasible to measure these using electrochemical sensors, such as voltammetry and potentiometry (here, DNA is immobilized on electrodes). Monitoring can also be done on electroactive analytes intercalated on DNA layers [69].

Nanotechnology assesses and manipulates matter at the atomic or molecular scale, wherein materials with smaller scales exhibit unpredictable characteristics and behaviors compared to materials of the same type with larger scales (e.g., silver, copper, iron) [USEPA, 2007]. Nanoscale is defined as one billionth of a meter or 1–100 nm. In general, nanoparticles (NPs) are divided into three groups based on their physical characteristics: natural, incidental, and engineered. Clays, weathered minerals, organic matter, and metal oxides are examples of naturally occurring NPs [70]. As a result of fuel combustion, manufacturing, agricultural practices, vaporization, and weathering, NPs are released in an uncontrolled manner into the environment [71]. NPs that are manufactured to possess specific properties are usually known as engineered Nps and are found in the environment as a result of industrial processes and environmental applications. They have specific shapes, sizes, surface properties, and chemistry [72]. In recent years, engineered nanoparticles (e.g., silicon dioxide, titanium dioxide, cerium oxide, and iron oxides) have become an important part of the modern economy. The industrial sector has used engineered NPs in a variety of applications, including pharmacy, cosmetics and electronics, as well as consumer goods [73].

Insecticide detection is becoming an increasingly important concern, which has prompted researchers to seek out innovative approaches involving nanomaterials. The usage of nanoclusters has increased due to the ease of synthesis routes [74]. Many advantages can be attributed to it, including low toxicity, ease of operation, immediate reaction time, compatibility, and solubility [75]. Nanosensors are atomically sized devices designed to collect data and transmit it to an external computer for analysis. For example, they can examine chemical and physical phenomena in areas that are hard to reach, analyze cellular biochemistry, and measure nanoparticles in the environment and industry. The sensors are highly sensitive chemical or physical detectors that can detect viruses and also detect small concentrations of substances that may be harmful. The last few decades have seen tremendous progress in nanotechnology, leading to the development of biosensors based on functional nanostructures. As a result of their design, a new generation of sensing systems has replaced conventional systems and offered not just better sensitivity, but also refinement and multiplexing ability [76]. Medical research and basic science benefit greatly from biosensors. New sensing technologies facilitate scientific breakthroughs in this area, which allows researchers to study previously unstudied biological phenomena [77]. Several nanobiosensors have been recently developed for the detection of different categories of insecticides (Fig. 3) as outlined below:

4. Organochlorine

A class of organic compounds containing atoms of chlorine is called organochlorine insecticides (OCPs). The majority of OCPs are hydrophobic and lipophilic, therefore, exhibit high resistance to degradation, remaining in the environment for decades or even centuries following their initial use [78]. As a result, groundwater, surface water, food products, the air, and soil become contaminated. In light of the significant health risk associated with OCP in the environment, they are primarily categorized as persistent organic pollutants (POPs). Initial reports listed nine organochlorine pollutants, including aldrin, chlordane, dieldrin, endrin, dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), mirex, toxaphene, and heptachlor, among the 12 initial POPs referred to as the dirty dozen (Stockholm Convention, UNEP). For monitoring organochlorine insecticide exposure, immunochemical techniques have replaced the time-consuming and expensive chromatographic techniques. Using BSA-conjugated synthetic haptens and monoclonal antibodies specific to them [79], nanomechanical biosensors were successful used for the first time for the detection of dichlorodiphenyltrichloroethane (DDT) [80]. Nanomechanical biosensors differ from most other biosensors in that they produce signals that are proportional to the concentration of the target. Nanomechanical sensors analyze adsorption differences at two opposite edges of a cantilever, with one end (top) functionalized for receptors. If nonspecific adsorption occurs on the bottom, the recognition of molecules on the top side may be impaired. The effects of modulating the buffer solution ionic strength and pH can be reduced by modulating targets or receptors in the assay [81]. Recent research studies found that 3D-nanostructures on the top surface of the cantilever enable nanomechanical movements to be more effective, thereby minimizing the impact of nonspecific adhesive penetration at the bottom [82]. In addition, if the binding of the target to the functionalized cantilever side is considered, the surface stress change may not always coincide with target concentration. In contrast to most biosensors, nanomechanics provide a more complex and richer response. In the majority of instances, recognition molecules produce a downward cantilever bend as well as negative surface stress. Basically, the bound target molecules repel each other due to intermolecular interaction forces, where these forces are mostly electrostatic and steric. Deflection of the cantilever is approximately proportional to target centering. Nevertheless, surface stress variations on a longer timescale can be indicative of changes in the structure of the molecules adsorbing on the biological surfaces [83]. Furthermore, when two opposing forces interact, the nanomechanical response can be reversed [84]. These modified designing suggest nanomechanical biosensors are capable of having a high level of sensitivity without being labelled with fluorescent or radioactive molecules. In contrast to other biosensors that do not require labels (such as the surface plasmon resonance biosensor ($\sim$mm^2) and the quartz crystal microbalance ($\sim$cm^2), nanomechanical biosensors are the most rapid and sensitive for detecting insecticides based on immunoreactions because of their small reaction areas ($\sim$100 μm^2) [85]. Developing nano fluidics and miniaturization of cantilevers will enable femtomolar sensitivity with minimal reagent usage in the future [86]. Moreover, microcantilevers can be manufactured using standard silicon technology, which permits high-throughput testing through the use of clutches of cantilevers, low costs, and portability of the devices [87].

5. Organophosphates

Insecticides that comprise organophosphates (OP) (e.g. paraoxon, parathion, malathion, and temephos) have wide spread application in agriculture and are effective for eliminating insects, however, they exhibit low environmental stability at natural temperatures and humidity. OP insecticides are applied to millions of hectares annually, posing serious health and environment issues [88,89]. A residue from such products can cause eye irritation, stomach pain, seizure, respiratory breakdown, paralysis, and even death in humans when ingested. Their toxic effects are caused by their irreversible binding to acetylcholinesterase (AChE), an enzyme necessary for nerve impulse transmission. OP insecticide can inhibit the acetylcholine chloride (ACh) reaction with AChE by reacting with the OH bond at serine residue of AChE [90,91]. Therefore, OP agents are important targets for detection due to the threats they pose; carbon nanotubes (CNTs) are recently been developed and used for their detection [92].

All CNTs are nanoscale, and have excellent electrical conductivity, chemical stability, and mechanical strength. CNTs have a bunch of intriguing features that make them valuable materials for sensing applications. Glassy carbon electrode (GCE) is coated with a film of multiwalled carbon nanotubes (MWCNTs) dispersed in Nafion solution [93]. Following this, the electrode is used as a parathion amperometric sensor. Compared to the bare GCE, modified MWCNT GCE, and Nafion-modified GCE, the MWCNT/Nafion film electrode display significantly higher redox current. It has been found that the MWCNT/Nafion film demonstrated efficient electrocatalysis toward parathion. Co-immobilization of enzymes can improve the accuracy and acuity of MWCNT- and single-walled CNTs (SWCNT)-modified electrodes [94]. By converting OP compounds into p-nitrophenol, organic phosphorus hydrolase (OPH) presents an interesting method to detect OP compounds, which relies on monitoring the oxidation of p-nitrophenol. It is highly desirable to improve the anodic detection of p-nitrophenol in order to overcome surface fouling and high voltage issues associated with these reactions. A CNT-modified electrode [95] is then used to oxidize the OPH. This has led to the fabrication of an amperometric biosensor utilizing OPH adsorption onto a CNT-modified electrode [64]. These electrodes have CNTs that serve primarily as transducers, effectively transmitting the signals transmitted by active enzyme centers to their substrates. In order to achieve this, several techniques have been developed based on non-covalent or covalent interactions between the enzymes. By adsorbing the OPH layer onto the CNT film, a CNT/OPH biosensor was prepared. In order to prepare the CNT-modified electrode, CNT dispersion was evaporated or cast onto the electrode, and then the enzyme solution containing Nafion was added to the electrode, and allowed to evaporate. The OPH enzyme was immobilized onto a CNT-modified GCE in this manner, resulting in a sensor for organophosphorus compounds. A stable anodic current signal was observed for p-nitrophenol for approximately 60 min using these CNT-modified electrodes. The biosensor is able to detect paraoxon and methyl parathion as low as 0.15 μmol/l under ideal conditions, with respective sensitivity of 25 nA/mmol/l and 6 nA/mmol/l. Thiocholine that is generated via enzymatic means using anodic detection technique yields lower oxidation, and greater acuity when using CNT-modified GCEs due to their edge-plane-like graphite end sites, efficient electron transfer, and large working CNT surface areas [96]. This study serves as a basis for the design of CNT-based biosensors suitable for sensitive, fast, and automatic OP analysis. Researchers developed a disposable biosensor that can be used for the analysis of organic pollutants using carbohydrate chemistry and a coupling agent of 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDC). An amide bond is formed by amine residues on the CNT surface and carboxylic acid groups on AChE and choline oxidase are co-immobilized on the CNT electrode. In the analysis of OP compounds, a biosensor using AChE/CHO enzymes generates high sensitivity, a long linear range, and a small detection limit (0.05 μM). This is because CNTs can catalyze the redox reaction of hydrogen peroxide generated during the enzymatic reaction between AChE/ChO and their substrate [97]. Although nanobiosensors have shown considerable advantages over conventional techniques, they are still in the preliminary stages of being used for the detection of OPs, and many challenges still need to be addressed before they can be practically used at a larger scale.

6. Carbamate

Among the most common insecticides are carbamate compounds, which are esters of carbamic acid, and are called N-methylcarbamates. Carbamate insecticides boost agriculture production and also help prevent insect-borne disease when applied appropriately at agricultural fields. Unfortunately, these insecticides can cause poisoning in humans and animals if they are overexposed. Insecticides containing N-methylcarbamates render toxicity through the inhibition of the enzyme AChE. As a result, the toxic signs indicate hypercholinergic activity. N-methyl-d-aspartate receptors are also hyperactivated during carbamate-induced excitotoxicity [98].

Because of their unique chemical or physical properties, novel nanomaterials have the potential to provide improved analytical methods in the newly emerging fields of nanoscience and nanotechnology [99]. The ability to change color based on molecular events allows gold nanoparticles (AuNPs) to be used in colorimetric assays for many types of analytes without the need for advanced devices [82]. Using this optical property and the resulting change in color of the solution, rapid qualitative detection is possible with bare eyes. Because the aggregation of AuNP based sensors is controlled, it has been used as a hot spot for insecticide residue trace detection. Unfortunately, most colorimetric assays based on AuNP lack sufficient sensitivity and consequently, it is difficult to achieve quantitative and qualitative evaluations simultaneously for the same category of insecticides or from a variety of categories [100,101]. As a result, highly sensitive fluorescent materials have been selected that work together with gold nanoparticles for fabricating dual-readout sensors that increased their sensitivity. Moreover, the fluorescent materials have been successfully employed in previous studies for the detection of multiple analytes, including complex proteins, teas, wines, aldehydes and biomarkers [102].

It is notable that 3D printing is capable of rapidly prototyping, optimizing, and producing microfluidic detectors that are versatile, inexpensive, non-toxic, eco-friendly, high-precision, and characterized by their efficiency in detecting insecticides because they have excellent liquid flow control, low reagent consumption, and easy integration with minimal power and space requirements [103,104]. This unique property of 3D printers can be used for prototyping individual precision channels and functional chambers while avoiding expensive master plates or masks necessary for microfluidic chip manufacturing methods such as machining and lithography [105,106]. To accomplish rapid carbamate insecticide discrimination, a convenient and self-regulating dual-readout device was designed [102]. Using 3D printing technology and a dual-readout sensor, a disposable, low-cost microfluidic chip that delivers dual-readout materials and samples, has been developed, which enables carbamate insecticide detection in a highly sensitive manner by applying innovative engineering techniques such as dual-signal assay, machine learning algorithms, and cross-reactive fluorescence fingerprinting. As a result, if the dual-signal database approach was adopted, the generated biosensor could be useful for environmental monitoring and insecticide detection [102].

7. Pyrethroids

As an alternative to OP insecticides, pyrethroids are highly prevalent synthetic insecticides used for agriculture and household applications. There are many harmful effects associated with extremely high pyrethroid exposure. As a result, prolonged exposure to these synthetic insecticides may cause neurological damage, significant harm to male reproduction, and adverse effects on the endocrine system. The most known metabolite of pyrethroid insecticide hydrolysis is 3-phenoxybenzoic acid (3-PBA). 3-phenoxybenzyl alcohol or 3-phenoxy benzaldehyde of these pyrethroids is metabolized by esterases in mammals into 3-PBA. Because of its prevalence, it is widely used as a pyrethroid biomarker [107]. To develop a rapid detection assay for 3-PBA [108], different technologies have been adapted and integrated, including nanofibers, nanobodies, and electrochemical techniques. In order to construct the nanosensor, nylon nanofibrous membranes were surface modified with citric acid and a nanobody alkaline phosphatase fusion protein (Nb-ALP). Using an immobilized 3-PBA membrane coupled to a nylon nanofibrous membrane decorated with CA and Nb-ALP, the proposed immunosensor was constructed onto a screen-printed electrode (SPE). Differential pulse voltammetry (DPV) was used to measure alkaline phosphatase activity [107]. The overall approach was highly sensitive and could detect a low volume of pyrethroids in different settings with high precision.

8. Future directions and challenges

Biosensors and in particular nanobiosensors, are highly appealing tools for insecticides detection because of their preciseness, accuracy, sensitivity, and rapidity of detection. A biosensor reacts with the target and creates a signal for accurate identification; tagging a nanoparticle to a biosensor further enhances the limit of detection and the precision, thereby resulting in a highly sensitive and precise detection tool. In light of the above described methods, it becomes apparent that they play a crucial role in the detection and quantification of insecticides. Commercialized nanoparticles may be used to detect insecticides in the near future when bioelements are incorporated. The recent advances in nanobiosensors have rendered positive and effective results, paving the way for a sustainable future, while giving rise to discoveries and advancements on a wide range of topics. To make nanobiosensors more effective for insecticide trace analysis, their usage must be extended to recognition. Nanobiosensors offer a range of benefits and have also been environment-friendly. The shift to the development and application of organic nanoparticles, carbon based nanoparticles, encapsulated metal nanoparticles, and modified nanoparticles at a minimum dose application for the detection of analyte contribute to faster biodegradation and less persistence in the environment. In addition, researchers have been constantly working on the development of organic and nano-based insecticides that could yield most effective results in a rapid manner and at low dose application that confer great benefits to the environment. Most of these approaches are at the stage of application in developed countries, and could be adopted readily by developing countries for combating the issues of environmental pollution posed by such insecticides. The benefits of the bio recognition element can still be improved by genetically modifying nucleic acids and enzymes, immobilization strategies, and the use of suitable nanomaterials. Additionally, a variety of methods must be developed in order to make nanobiosensors reusable. Research should be conducted on the catalytic activity and stability of nanobiosensors as they are poorly understood. Nano based biosensors could thus lead to a paradigm shift in the monitoring of insecticide at routine level, which could greatly assist in the overall development of the population. Additionally, in order to implement a smart agriculture system, nanobiosensors could be integrated with mobile apps and GPS systems for controlling farming in remote areas. Farmers in remote areas can be benefited through a proper solution for pest control, fertilization and harvesting.

Nanotechnology approaches are promising for the development of nanobiosensors for agricultural applications, such as pesticide detection. Although there exists a substantial amount of scientific publications and patents related to nanobiosensors for pesticide detection, there are many challenges both at the technical and non-technical levels to transform the ideas validated at the laboratory scale into commercial products [109,110]. Some of the following points should be considered while considering the development of nanobiosenors for point-of-care applications: High sensitivity: The detection limit of nanobiosensors should be as low as possible so that it can identify the trait at early stages; Rapid measurements and detection: The nanobiosensors need to be fast in the measurement-to-detection process and able to distinguish between different analyte types within a short period of time; Portability and ease of operation: The sensor should be portable to remote locations for monitoring and should have user-friendly features. Currently, most nanobiosensors are not easy to operate under all conditions owing to the presence of biological component tagged to the nano-detector that requires ambient conditions of pH, temperature, humidity, etc. Therefore, more innovative approaches during nanobiosensor design need to be utilized for rendering it robust and field-deployable; and finally Accessibility: Nanobiosensors should be integrated with information technology systems (such as mobile apps). This will help the agriculture and health authorities to access the field reports even from remote areas in real-time, thereby offering a solution prior to outbreaks of diseases. Another important aspect to consider during the development of a nanobiosensor is cost-effectiveness and affordability that could assist the farmers in rural areas who face a significant challenge related to the cost-effectiveness and affordability. Such cost management depends on the cost of nanomaterial production, their characterization, and the assembly and testing of sensing units. It is also imperative for potential manufacturers to make sure that production costs can be affordable in rural areas. Reusability and long-term stability of nanobiosensors can also reduce cost [111]. Another challenge includes the scaling-up process which ensures that mass productions component for nanobiosenors should have the same properties and working action as verified in the basic laboratory condition. Simultaneously, the sensor performances under practical conditions (for field applications) should also be evaluated thoroughly with different field trials. Another aspect, environment compatibility also plays an important role. As biosensors will be used for various field applications, their impact on the environment should be addressed clearly [112]. In this regard, nanosensors, such as lab-on-chip (LoC) microfluidic platforms are rapidly developing for constructing highly complex, fluid-controlled microchannel networks for effective detection and assessment of eco-toxicity [113]. Nanobiosensors can be incorporated into devices designed for the culture and analysis of cells or tissues to achieve an integrated LoC. A single system can therefore perform cell culture, assays, and read-outs, in contrast to several bulky and expensive instruments found in laboratories. For example, *Heterocypris incongruens*, a freshwater ostracod that is useful as a bioindicator of environmental conditions, was exploited to develop a nanobiosensor [114]. The nanobiosensor examined the ability of the ostracod to discriminate between different colored lights based on behavioral properties; the findings of the study identified and described behavioral ecology and cognition processes in ostracods, paving the way for new research directions on the biological use of LoC systems [114]. Another study demonstrated that sub-lethal behavioral analysis of saltwater crustacean *Artemia franciscana* carried out under microperfusion was capable of providing much more sensitive effect end-points than conventional protocols that use mortality as the primary criterion, thereby implicating the utility of LoCs as rapid aquatic toxicity tests [115]. Hence, technologies such as LoC are opening up new avenues for the rapid and inexpensive assessment of aquatic ecotoxicity [115]. Unicellular organisms like bacteria, algae, protozoa, and yeast have been the most commonly studied organisms used in biosensors for ecotoxicity testing. Because of their high sensitivity and reproducibility, these organisms have been increasingly used to assess the toxicity of aquatic contaminants in recent years. As a result of their small size, these organisms make excellent candidates for devices that use microfluidics to develop nano-fluidic biosensors [116].

Cartlidge et al., 2017 developed microfluidic and millifluidic technologies along with utilizing nanotechnology for automated toxicity testing of marine and freshwater species such as *Allorchestes compressa*, *Artemia franciscana* and *Daphnia magna*, and *Brachionus calyciflorus* [117]. Furthermore, chip-based platforms were developed to analyze the behavior of crustaceans and rotifers exposed to water-borne organic (e.g. caffeine, valproic acid) and inorganic (e.g. copper, cadmium, manganese) toxicants. Such strategies in combination with detector nanoparticles could lead to the development of more effective and robust miniaturized nanobiosensors in future that will greatly aid in the field of nanodiagnostics [117]. Hence, LoC technology is gradually emerging as a potential analytical platform with significant applications in environmental ecotoxicology, chemical risk assessment, and biomonitoring. Microfluidics in combination with nanotechnology can open up new avenues for high-throughput ecotoxicological screening, which is a challenging task while using conventional approaches.Declarations

Author contribution statement

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