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Bimetallic Nanomaterials-Based Electroanalytical Methods for Detection of Pesticide Residues

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Abstract: The application of bimetallic nanoparticles-based electroanalytical techniques in forensic science for pesticide detection residues in various exhibits are the emphasis of this review paper. Although many pesticide detection methods have been developed, nanomaterial-based electroanalytical methods have several benefits, including rapid analysis, cost-effective analysis, downsizing to increase performance, and field deployability. Bimetallic nanoparticles such as gold, platinum, palladium, nickel, and iron-based nanomaterials have been widely used as electrode modification agents for electrocatalytic activities and the synergistic impact of two different metals in a single probe. This review first outlined the applicability of electroanalytical techniques based on the bimetallic sensor for detecting pesticide residue. To assess existing applications and use of bimetallic nanoparticles for pesticide detection, selected studies with sensitivity, the limit of detection (LOD), and analytical application were examined. Finally, the existing difficulties and possible prospects in pesticide detection employing electroanalytical methods were explored.

Keywords: pesticide; bimetallic nanoparticles; electroanalytical; forensic applications.

1. Introduction

Forensic science deals with the recognition, identification, individualization, and reconstruction of physical evidence collected from the crime scene and finding the truth on the alleged matter by applying theories, principles, laws, and techniques of all the basic sciences in crime scene investigation [1]. Forensic technology is the study, inspection, and identification of clue materials at crime scenes that establish clear connections to offenders and facilitate their quick capture. Forensic evidence is crucial for identifying offenders through examinations at crime sites and related forensic exhibits before a court ruling. Additionally, it's a better way to maintain accurate records of the clue materials against the accused [2].

The majority of forensic technology is used to gather biological clue materials that can be used to identify offenders. Some scientific disciplines applied in criminal investigations include dactyloscopy, entomology, psychiatry, pathology, toxicology, anthropology, and odontology [3]. Ballistics and forensic botany are widely employed in conjunction with technological breakthroughs in various forensic research fields. Forensic technologies include those that analyze handwriting, earprints, sound profiles, and fingerprints. Forensic technology is a different branch of science that has been extensively employed to help law enforcement officials identify criminals and solve crimes. As a result, forensics technology is among the most crucial tools used to catch criminals and guarantee that justice is administered promptly [4].

Forensic technology in crime scene investigation and sample analysis is essential to helping a panel of lawyers and attorneys offer proof against offenders in a court of law. Forensic technology research has considerably benefitted analytical forensics chemistry, including various analytical tools for basic research. Among these, basic research necessitates forensic technology proficiency and medical uniformity. New improvements are required as forensic investigative methods already in use become less dependable and efficient. Even though the forensics analytical approach has settled in forensic technical skills study, this is still the case. Bloodstains, fingerprints, hair, gunshot residues, fabrics, fiber, glass, and paint are some of the most common types of evidence substrates encountered in the forensic analysis [5].

Paint chips or scratch marks are examined as forensic evidence in the case of vehicular road injuries [6]. Forensic clue materials used to identify criminals are mostly bloodstains and fingerprints, which are analyzed using spectroscopic methods. Transmission electron microscopy (TEM), Dynamic light scattering (DLS), Raman microscopy (RM), Scanning electron microscopy (SEM), and atomic force microscopy (AFM) are among the techniques used [7-9]. These are related to the identification of nanosized particles and various clue materials in forensic technology.

The population of the world is increasing at a startling rate every year. Agriculture produces the vast majority of things produced by humans globally, including important dietary crops, energy, textile, and raw materials. Because of a scarcity of natural resources such as land, water, and soil and low crop productivity, there seems to be an increasing demand for advanced agronomic practices that are cost-effective and environmentally feasible. As a result, the usage of pesticides is steadily rising to increase crop output. Chemicals known as pesticides are frequently used in agricultural operations to control pests [10,11]. Pesticides are utilized to prevent structural damage to buildings, keep pests out of residential, personal, and commercial landscaping, and get rid of disease vectors. As per a 2010 study, pesticide use in non-agricultural sectors is 3 to 8 times greater than in agricultural ones [12,13]. The term pesticide includes all of the following: herbicide, avicide, rodenticide, animal repellent, antimicrobial, bactericide, insecticide, nematicide, molluscicide, pesticide, insect repellent, animal repellent, antimicrobial, and fungicide.

The many pesticides and the risks they represent are unknown to farmers and those who come into touch with them. Therefore, it is advantageous for the environment and public health to have a good understanding of pesticide categorization so that exposure, excessive use, and toxicity can be reduced by using it sparingly [14]. When classifying pesticides, the World Health Organization (WHO) has solely recognized acute toxicity. Based on an estimated equivalent lethal dose of LD_{50}, the WHO divides pesticides into two categories: oral dose and acute skin toxicity (pesticide dosages needed to destroy half of the samples once introduced into the body through the oral or dermal route). It is recommended that pesticides be classified into "certain WHO Hazard classes" according to the widely used "WHO approved classification of pesticides by hazard." These classifications were updated in 2009 to correspond with the "Globally harmonized system (GHS) acute oral toxicity hazard categories" [15]. Table 1 shows the World Health Organization's suggested classification of "Pesticides by Hazard," as well as the globally harmonized system (GHS)-amended pesticide classification in Table 2.

Table 1. World Health Organization's suggested classification of Pesticides by Hazard. (Reproduced with permission, WHO, 2009) [16].

WHO Class		LD_{50} for rats (Mg/kg body wt.)		Examples
		Oral	Dermal	
Ia	Extremely Hazardous	< 5	< 50	Phorate, Parathion, Dieldrin
Ib	Highly Hazardous	5 - 50	50 - 200	Dichlorvos, Aldrin
II	Moderately Hazardous	50 - 200	200 - 2000	Chlordane, DDT
III	Slightly Hazardous	Over 2000	Over 2000	Malathion
U	Unlikely to present acute hazard	5000 or higher	-	Cycloprothrin, Carbetamide

Table 2. Globally Harmonized System amended pesticide classification. (Reproduced with permission, WHO, 2009) [16].

GHS Category	Classification Criteria			
	Oral		Dermal	
	LD_{50} (mg/kg bw)	Hazard Statement	LD_{50} (mg/kg bw)	Hazard Statement
Category 1	< 5	If consumed, it is fatal.	< 50	In skin contact, fatal
Category 2	5 - 50	If consumed, it is fatal.	50 - 200	In skin contact, fatal
Category 3	50 - 300	If consumed, it is toxic.	200 - 1000	In skin contact, toxic
Category 4	300 - 2000	If consumed, it is harmful.	1000 - 2000	In skin contact, harmful
Category 5	2000 - 5000	If consumed, it may be harmful.	2000 - 5000	Skin contact may be harmful

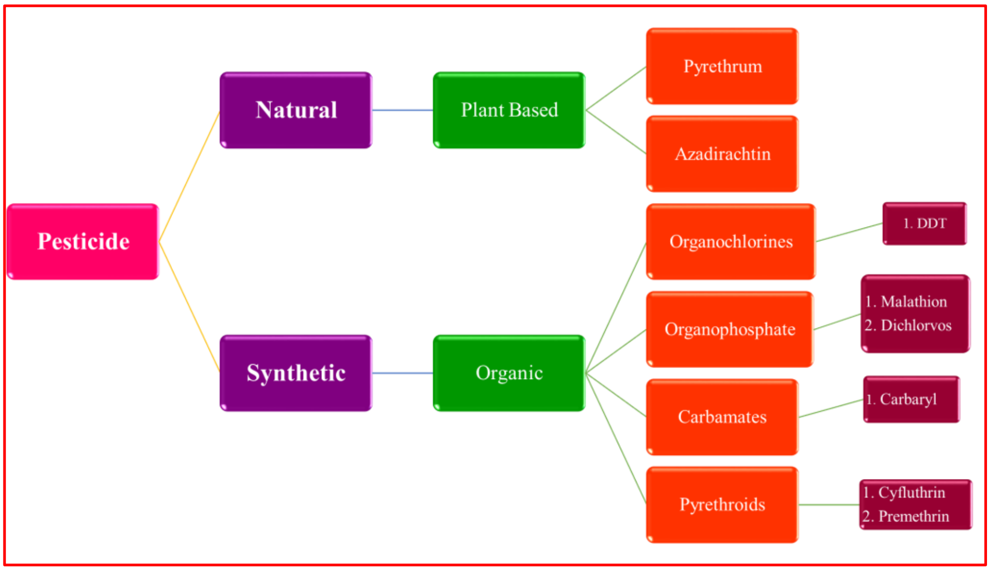

Figure 1. General classification of pesticides.

Pesticides are also categorized based on the pest organisms they kill and the pesticide function (use), which is shown in detail in Table 3 [17,18]. Pesticides can be biodegradable, meaning they disintegrate into harmless molecules when microbes and other organisms come into contact with them, or persistent, meaning they take several months to break down. Pesticides are classified into the following categories based on the pests they kill: Rodenticides that can kill Rodents (rats and mice), Insecticides that can kill Insects, Bactericides that can kill bacteria, Fungicides that can kill fungi, Herbicides that can kill plants, and larvicides which can kill larvae. Broadly, pesticides can be categorized as either synthetic or natural. The classification of pesticides is shown in Figure 1 [19]. One category of the most commonly used artificial compounds in the current world is pesticides. In reality, a wide range of chemicals falls under the name "pesticide."

Table 3. Pesticides are classified based on the pesticide function and the pest organisms they destroy.

Sr. No.	Type of Pesticides	Example	Target Pets (Killed or Inhibits the Growth/Production)
1.	Virucide	Ribavirin	Kill the virus
2.	Termiticides	Fipronil	Kill termites
3.	Synergists	Piperonyl butoxide	Increase the lethality of pets
4.	Silvicides	Tebuthiuron	Kill woody vegetation.
5.	Rodenticides	Strychnine, Warfarin	Kill rats
6.	Piscicides	Rotenone	Kill unwanted fishes
7.	Nematicides	Chlorpyrifos, Carbofuron	Kill nematodes
8.	Molluscicides	Thiadicarb, Metaldehyde	Kill slugs and snails
9.	Mating disrupters	Gossyplure, Disparlure	Prevent insects from breeding
10.	Larvicides	Methoprene	Restrict the larvae's growth
11.	Insecticides	Malathion, Chlorpyrifos	Kill insects
12.	Insect attractant	Gyplure, Gossyplure	Entices pests to enter traps
13.	Herbicides	Alachlor, Paraquat	Destroyed unwanted herbs
14.	Herbicide softener	Cyometrinil, Benoxacor	Inhibits the growth of unwanted herb
15.	Fungicides	Cymoxanil	Chemicals that can kill fungus.
16.	Bactericides	Tetracycline, Streptomycin	Bacteria
17.	Avicides	Fenthion and Strychnine	Birds
18.	Algicide	Diuron, oxyfluorfen	Algae
19.	Acaricides	Dicofol, DDT, chlorpyrifos	Mites and ticks.

Pesticides cover many products, including fungicides, herbicides, horticultural chemicals, residential disinfectants, and rodenticides. On the other hand, these pesticides have different physical and chemical properties [20]. Drum recommends three possible ways for categorizing pesticides used in large quantities. These classes comprise (i) the pesticide's entry route, (ii) the pesticide's chemical structure, and (iii) the pesticide's effect and the species it kills. Bactericides and Fungicides, among several other pesticides, held the highest market proportion in 2015, according to a market survey (41.76 %). The global pesticide market was worth $ 56 billion in the year 2012. According to studies, the pesticide market is predicted to increase at a Compound Annual Growth Rate (CAGR) of 5.15 % between 2016 and 2021. According to predictions, the global pesticide market is expected to reach $ 70.57 billion by 2021 [21]. While pesticides have various benefits, such as improving crop productivity, their overuse has negative consequences for humans and the environment. While occupational, agricultural, or residential pesticide usage are the most common sources of human pesticide exposure, other important elements include the soil, flora, food chain, air, fauna, and water.

Pesticides commonly affect humans through the dermal, oral, ocular, and respiratory systems. As a result, the kind of pesticide exposure is the most important element in determining the harmful health impacts on humans. Pesticide exposure causes respiratory illnesses, neurological disorders, cancer, diabetes mellitus, oxidative stress, and reproductive (sexual) syndromes, among other health issues [22-24]. Pesticides poison nearly 44 % of the world's farming population (a total of 860 million) per year, according to a global study published in BMC Public Health. Pesticides poison around 385 million people each year, primarily agriculture workers and farmers, according to research published by scientists, with eleven thousand deaths yearly. India accounts for roughly 60 % of the fatalities, or six thousand and six hundred deaths annually [25]. Pesticide poisoning by humans has long been considered a serious public health issue [26-29]. A World Health Organization task committee estimated in 1990 that around one million inadvertent pesticide poisonings with severe symptoms occur yearly, resulting in approximately 20,000 deaths [30].

As a result, developing and validating analytical methods for pesticide determination and detection is critical. Furthermore, pesticide analysis is necessary for trading, official control, and human health protection. When it comes to developing methodological approaches for pesticide analysis, it's safe to say that chromatographic methods are the most popular among researchers [31]. Chromatographic techniques have long been the most common method for determining pesticides worldwide. On the other hand, Chromatographic approaches necessitate the sample preparation and extraction of pesticides from various matrices such as foods, soil, and water. These analytical methods are costly and take a long time to analyze. Furthermore, they are unsuitable for use and examination on-site. Traditional spectroscopic approaches for pesticide analysis, such as Fluorescence Spectroscopy and UV-spectroscopy, have drawbacks as well. Non-sensitive and non-selective data is the outcome of overlapping and broad-spectrum bands. Other components or differences in sample preparation could cause spectral discrepancies. Other key elements affecting spectroscopic analysis results include the presence of gas and CO_2 and the turbidity or cloudiness of the samples.

Furthermore, the instrument and sample presentation methods significantly impact these procedures [32, 33]. Electroanalytical methods now have several advantages over other methods. Compared to chromatographic and spectroscopic approaches, these methodologies are simpler and less expensive. The total number of compounds, as well as their reduction/oxidation stages, can be calculated. The sample preparation steps are simple and allow you to work with significantly less sample volume. Electroanalytical procedures' precision, sensitivity, accuracy, and selectivity are all quite good [34].

Furthermore, the surface of electrodes can be changed in these procedures to achieve more sensitive results. Researchers have been producing both inorganic and organic nanopowders using physical, chemical, and biological processes for diverse forensic applications, including pesticide detection, for the past two decades. Figure 2 shows a generic diagram of nanotechnology's potential applications in forensic research. The qualities, shapes, and sizes of nanoparticles (NPs) are used to classify them into different groups. Among the many groups are fluorescent NPs, ceramic NPs, fullerene, polymeric NPs, and metal NPs. Nanoparticles have unique chemical and physical properties due to their nanoscale size and enormous surface area. Because of absorption in the visible area, their optical characteristics are considered to be size-dependent, resulting in varied colors. In addition, their particular shape, size, and structure influence their toughness, reactivity, and other qualities. These characteristics make them good candidates for various forensic uses, such as the detection of pesticides.

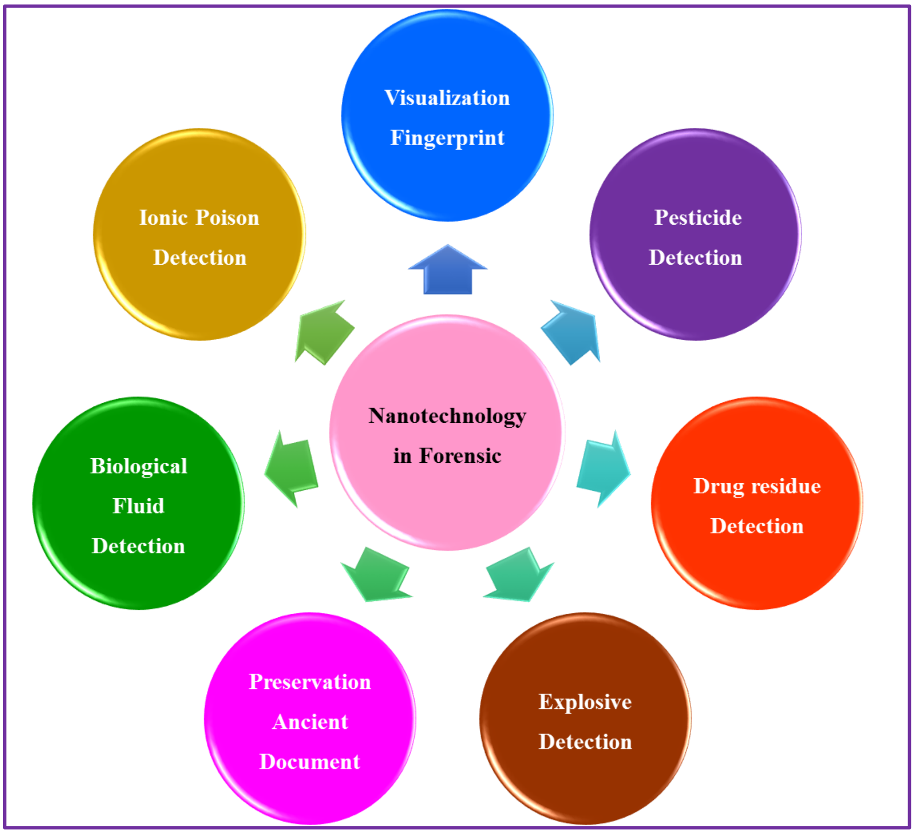

Figure 2. Overview of general potential nanotechnology in forensic science.

In electrochemical nanosensor studies, various nanoparticles, such as quantum dots, metal, magnetic, carbon-based, metal oxide, and polymeric, are commonly used for signal enhancement [35,36]. Bimetallic nanoparticles and their nanostructured materials have received a lot of interest in recent years among these nanomaterials in research & development studies [37]. The annual improvement in electrochemical detection based on bimetallic nanoparticles demonstrates the importance of these nanomaterials. Bimetallic nanomaterials, as the name implies, are made up of two separate metallic elements. New bimetallic nanostructures with profoundly different characteristics than their bulk form and the previous generation of monometallic nanomaterials are produced when two metal components are joined at the nanoscale. The synergistic interplay of the two metals' unique features can result in a bimetallic nanocomposite with remarkable physical, electrical, and chemical capabilities.

Bimetallic nanomaterials increase sensitivity and stability due to the combined interactions between two metallic components [38]. Different metal sizes and structures can be used to alter the characteristics of bimetallic nanostructures. They also allow for optimizing the strength of plasmon absorption and the metals mixture, resulting in a versatile biosensing instrument [39]. Platinum, iron, palladium, copper, nickel, and gold-based nanomaterials are preferred because of the composition of bimetallic nanoparticles, which have distinct electrochemical properties [40]. As a result of their synergistic effects, electrodes modified with bimetallic nanomaterials provide very sensitive electrodes. Bimetallic nanomaterials are also used as nano-enzymes because they have extremely selective enzyme-like activity. Furthermore, their biocompatibility and lack of toxicity are significant advantages.

The utilization of nanomaterials as modifying materials and pesticide detection have been the subject of several review articles in the literature. For example, Wang *et al*. reviewed nanoparticle-based electrochemical sensors to detect pesticides [41]. On the other hand, Rhouati *et al*. published an article that examined nonenzymatic electrochemical nanostructures for pesticide detection [42]. Rajeev *et al*. examined bimetallic nanomaterials-based electrochemical sensors for detecting hydrogen peroxide, glucose, dopamine, ascorbic acid, and uric acid. At the same time, Stephanie *et al*. published a study on the usage of bimetallic nanoparticles for biosensing applications [43].

The current article offers a detailed and comprehensive overview of electroanalytical approaches for pesticide detection based on bimetallic nanoparticles. Given the benefits of bimetallic nanoparticles, this review aimed to explore electroanalytical methods based on these particles for pesticide detection. In addition, a thorough analysis of pesticide applications covers current problems and potential advancements in this area.

2. Bimetallic Nanoparticle-based Electroanalytical Methods for Pesticide Detection

With the development of nanotechnology, more research is being done on electroanalytical methods based on nanomaterials to improve pesticide analysis results. Bimetallic nanoparticles have more sophisticated physical and chemical features than the monometallic nanoparticles that gave rise to them, as evidenced in various applications. The ability to detect pesticides with extreme sensitivity makes these attractive nanomaterials candidates. Bimetallic nanomaterials have several benefits over equivalent monometallic ones, including stronger catalytic activity, improved catalytic selection, and high resistivity to deactivation.

2.1. Nanosensors-based bimetallic nanomaterials for pesticide detection.

A sensor is an analytic tool that details the composition of various analytes in the immediate environment, whether that environment is a liquid or a gas. The sensor is referred to as a nanosensor if the analyte is detected using nanoparticles. In recent years, more research using electroanalytical techniques based on nanosensors has been conducted in an attempt to enhance pesticide analysis performance.

In their 2015 study, Mansouriieh *et al*. used Fe/Ni bimetallic nanoparticles as a catalyst to degrade profenofos. In the decomposition of the insecticide, zero-valent iron (nZVI) nanoparticles acted as a reducing agent. Ni helped to hasten the reaction by halting surface corrosion on the nZVI particles. The amount of Fe/Ni NPs, pH, and starting profenofos concentration all had a role in the investigation's findings regarding the degradation process. The greatest removal rate was achieved at pH 5.12 with a profenofos concentration of 1.4 mg/L and a catalyst concentration of 13.83 gm/L (94.51 %) [44]. Fe/Ni Nanoparticles have also been used in the study carried out by Nascimento *et al*. in the year 2016 to dechlorinate sulfentrazone. Figure 3 depicts the Mechanism of sulfentrazone degradation by Fe/Ni nanoparticles. The highest dechlorination was achieved at pH 4 and 1 gm/L of NPs. The insecticide was completely dechlorinated after 30 minutes. Through dechlorination, the catalyst's active sites assisted in lowering the pesticide. The toxicity test of the dechlorination product on *Daphnia similis* showed that it is less dangerous than the pesticide [45].

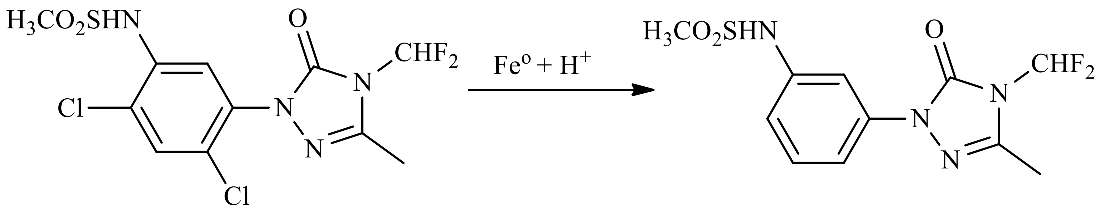

Figure 3. Degradation of sulfentrazone by Fe/Ni nanoparticles.

Unique dual-function AuNPs were created by Gao *et al*. in their research conducted in the year 2017 by covering standard AuNPs with an extremely thin platinum surface at ten atomic planes (Au@Pt NPS). The nuclear energy source of Au@Pt NPS has an extremely high catalytic activity triggered by the Pt shell while retaining the initial plasma activities of the AuNPs. About 2 ng/mL was the optical detection limit for LFAs [46]. As shown in Figure 4, in the 2016 research carried out by Wang *et al*., authors doped Fe_3O_4 nanoparticles with gold nanoparticles to create Au@Fe_3O_4 hybrid nanoparticles using a one-step solvothermal technique. The peroxidase-like activities of Au@Fe_3O_4 NPs were significantly increased by the synergistic interactions between Fe_3O_4 NPs and AuNPs. Based on these findings, they created a colorimetric sensor with a detection limit of 30 pg/mL for ochratoxin A [47].

A simple approach for the preparation of bimetallic palladium and gold nanoparticles covered on nanosheets (Au-Pd/rGO nanocomposite) has been described by Jahromi *et al*. in their paper from 2019. It was also looked into if this nanocomposite might be used to modify a Carbon Paste Electrode (CPE) for the electrochemical detection of parathion in an aqueous solution. FT-IR spectroscopy, X-ray diffraction, SEM, Thermogravimetric Analysis, and ED-X-ray spectroscopy were used to characterize the synthesized Au-Pd/rGO (EDS). Using SWASV and cyclic voltammetry, the improved electrode's electrochemical performance toward PAR was evaluated. The parameters, such as time, accumulating potential, and pH, that can influence the Au-Pd/rGO/response CPEs to the pesticide's identification were optimized. The electrode responds linearly from 0.01 to 11.2 M with a detection limit of 0.008 M under ideal circumstances. Au-Pd/rGO/CPE displayed great selectivity for PAR detection when the effects of various putative samples on the electrochemical sensing of PAR were studied. The modified electrode was then used to calculate the PAR of several spiked real samples, including tap water, groundwater, and cucumbers. The results show that the proposed sensor has a good potential for sensing PAR in actual samples, and the recovery rate supports this [48].

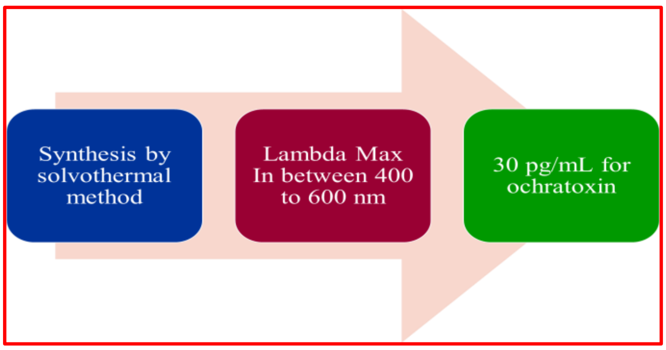

Figure 4. Au@Fe_3O_4 hybrid nanoparticles detection for ochratoxin pesticide residue.

2.2. Biosensors-based bimetallic nanomaterials for pesticide detection.

A biosensor is a type of analytical device which uses biological sensing to identify a specific analyte molecule. Biosensors can be used in various sectors, including biomedicine, environmental monitoring, forensic science, and food safety. Nanobiosensors are innovative nanobiotechnology-based, non-invasive, robust, and well-designed [49]. Real-time reaction signals produced by nano-biosensors are very simple to gather and analyze [50, 51]. The nano-biosensors use a variety of nanomaterials, including nanoparticles, nanocrystals, nanotubes, nanocomposites, and nanowires. Applications for nano-biosensors could include monitoring the presence of natural resources in ecosystems, such as fertile soil and accessible groundwater, as well as the identification of biological fluids, explosives, and pesticides [52, 53]. The nano-biosensor consists of a biological probe with affinity-based components such as nucleic acid interactions, cell-based interactions, antibody-antigen interactions, and enzyme-substrate interactions, a data capture unit with data transfer and storage capabilities, and a transducer that transforms biological signals into digital data ones. [54].

DNA, enzymes, antibodies, biomimetic materials, and aptamers are examples of biological components. Synthetic receptors have taken the role of natural biological components to duplicate the functions with a faster and more focused detection range [55]. Combining biological probes with different nanoparticles, including magnetic, graphene oxide, metallic, carbon nanotubes, and quantum dots can detect analytes. Amperometric, potentiometric, voltammetric, and optical signals, such as colorimetric, metallic fluorescence, surface plasmon resonance, and optical fibers, are electrochemical signal transducers [56, 57]. As seen in figure 5, many types of cutting-edge materials have been used in nanosensing applications to create nano-biosensors. SWCNTs and MWCNTs, two carbon nanotube-based nanomaterials, have been employed in creating nanosensors. Nanomaterials with a carbon foundation have been shown to be the best surfaces for immobilizing biological components in biosensors [58].

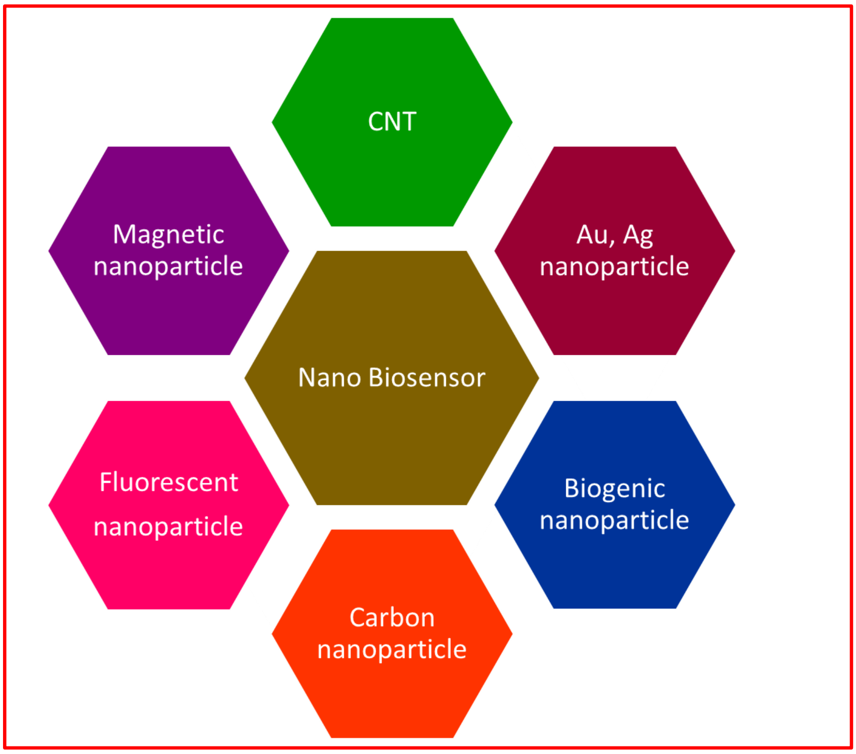

Figure 5. Outline of nanomaterials used in nano biosensors.

Using just a customized screen-printed carbon electrode with graphene, gold nanocage, as well as chitosan nanocomposite for chlorpyrifos detection, Yao *et al*. published an electrolytic biosensor based on AChE suppression in their 2019 work. As illustrated in Figure

6, the chlorpyrifos concentration is as low as 3 ngL^{-1} and displayed significant electrocatalytic performance for the oxidation of thiocholine produced by enzymes [60].

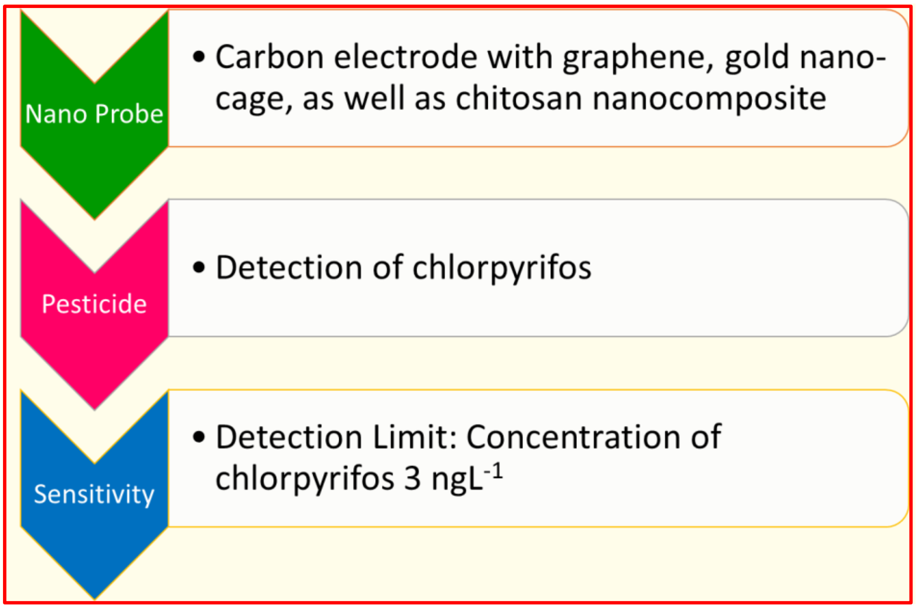

Figure 6. The AChE base biosensor for effective detection of chlorpyrifos pesticide.

In a similar vein, Bao *et al*. created a biosensor for malathion determination in their 2019 study, employing a 3-D graphene-copper oxide nanoparticles electrode, and were able to acquire a broad linear relation to malathion concentration ranging from 3 pM to 46.665 nM with a fictitious limit of detection at 0.92 pM [61]. Through adsorbing AChE on chitosan, rGO-based many-fold matrix, and TiO_2 sol-gel, Cui *et al*. validated a steady electrochemical AChE biosensor for identification of dichlorvos, with a linear range differing from 0.036 M to 22.6 M, a limit of detection of 29 nM, and an average detection time of about 25 min [62].

A very sensitive AChE amperometric sensor based on Ag-rGO-NH_2 composite and the conjugated polymer was created by Zhang *et al*. in 2019 along similar lines. The process the group utilized to create the electrodes was a little different. The 4, 7-di (furan-2-yl) benzothiadiazole was electrochemically polymerized on the electrode surface before the Ag-rGO-NH_2 nanocomposite was applied. The biosensor is demonstrated to be extremely effective and biocompatible with a linear range of 0.001 g L^{-1} for trichlorfon and 0.099 to 9.9 gm L^{-1} for malathion [63]. A biosensor for the detection of chlorpyrifos was also created by Mogha *et al*. in 2016 using rGO-supported zirconium oxide immobilized AChE, as illustrated in Figure 7. Two linear ranges, one from 10^{-13} to 10^{-9} M and the other from 10^{-9} to 10^{-4} M, were used to identify the chlorpyrifos [64].

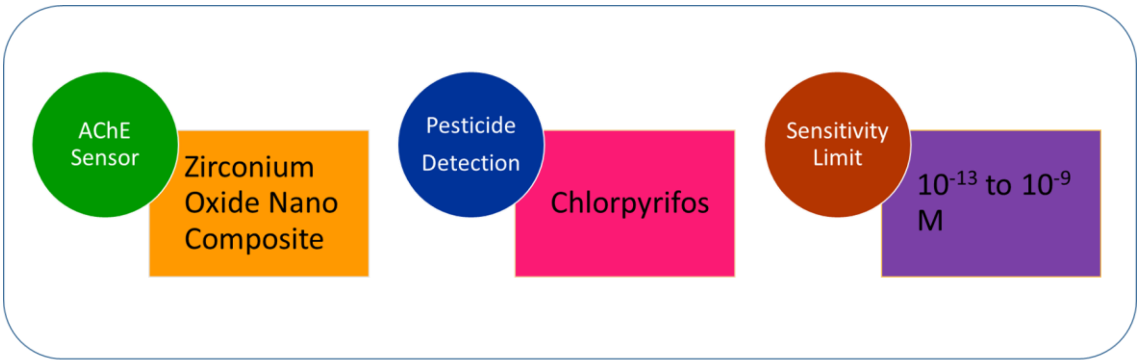

Figure 7. AChE sensor base nanohybrid of zirconium oxide for detection of Chorpyrifis pesticide.

Researchers have created the nonenzymatic biosensor for identifying paraoxon ethyl in the study by Aghaie *et al*. in 2019. The fabrication of a square wave voltammetric-based NiFe bimetallic phospho-sulfide nanocomposite biosensor employs graphene as the basis material. The detection limit for paraoxon methyl is 3.7 nmol L^{-1}, with a linear range of 12.3-10,000 nmol L^{-1} [65].

A simple H_2O_2 biosensor was proposed in the Zheng *et al*. study in 2021 to simultaneously realize sensitivity, simplicity, selectivity, and speed. The *in situ* electropolymerized polypyrroles functionalized with electrodeposited platinum-palladium (PPy-PtPd) nanomaterials were used as the H_2O_2 sensing component. The Pt_7Pd_4 nanoparticles may bind PPy and provide glassy carbon electrodes with excellent electrocatalytic activity to H_2O_2 via an NH-metal interaction. After parameter adjustment, this H_2O_2 biosensor displayed outstanding electrochemical performance toward H_2O_2 reduction. It featured a broader detection range of 2.5-8000 M, high sensitivity of 1360.83 $AmM^{-1}cm^{-2}$, reproductivity, superior anti-interference properties, and exceptional endurance (> 60 days at ambient temperature). It is important that the proposed biosensor proved successful in detecting H_2O_2 in three biological samples. The electrochemical biosensor, which utilizes nanocomposites from electrochemistry, is an easy-to-design and simple-to-use biosensor [66].

2.3. Non-enzymatic-based bimetallic nanomaterials for pesticide detection.

Whether the immediate environment is a liquid or a gas, a sensor is an analytical tool that provides insights into various analytes' structures. If the analyte is detected using non-enzymes, the sensor is referred to as a nonenzymatic sensor. There's been much more interest in nanozymes, nanoparticles with enzyme-like properties, over the last ten years. As a result, numerous studies have been done to examine the usage of synthetic enzymes in place of natural enzymes. Various nanomaterials, including noble metals, metal oxides, metal-organic frameworks, and carbon nanomaterials, have been recently discovered to have enzyme-like properties. High stability, simple production processes, high activity, reusability, cheap cost, and adaptability are just a few of the distinctive qualities of nanozymes [67,68]. In one of the earliest studies, various researchers examined a silver-based alloy to demonstrate the potential of bimetallic nanomaterials as nanozymes. They concluded that the morphology and content of the nanoalloy had an impact on the catalytic and optical characteristics of the bimetallic Ag-based alloy [69].

2019 saw the development of a very accurate nonenzymatic electrochemical sensor by Aghaie *et al*. to detect paraoxon ethyl. This study's electrochemical signal of PE was enhanced using a novel electrocatalytic modifying agent made of Gr-based Ni-Fe bimetallic phospho-sulfide nanocomposite. The presence of iron makes it possible for P to stay on the catalyst surface. Also, Nickel-P production increases the Ni active center's electron density. This makes it feasible to facilitate electron transport. According to study findings, Gr-NiFeSP performs significantly better in SWV peak current than other synthetic composites. Nonenzymatic sensors showed two linear ranges between 1.00-10.00 and μM 0.01-1.00 μM under the ideal stripping circumstances. The limit of detection was determined to be 3.7 nM. Additionally, a newly created sensor was employed to find paraoxon ethyl in samples, including cucumber juice, tap water, and tomato juice [70].

Based on bimetal Au-Pt organic-inorganic hybrid composites with a zirconium hexacyanoferrate layer, Gholivand and Azadbakht created a novel biosensor for hydrazine detection. In this study, organic nanofibers based on tetramethylbenzidine were doped with Pt using a wet chemical method. Then, employing electrodeposition, AuNPs were applied to the organic nanofibers. A few Pt (II) ions in the organic nanowires were converted to metallic Pt during the electrodeposition of AuNPs. As a result, bimetallic inorganic-organic hybrid Au-PtNP/NF nanostructures were created. A bimetallic Au-PtNP/NF-based organic-inorganic hybrid composite underwent one final phase of modification where zirconium hexacyanoferrate (ZrHCF) was electrodeposited on the surfaces of the nanoparticles. When the ZrHCF/Au-PtNPs/NFs/GCE electrode pictures were analyzed with a scanning electron microscope, they showed a very homogenous distribution and a spherical shape. More hydrazine can be absorbed by electrode structure nanoparticles that are smaller. This surface morphology demonstrated that hydrazine could penetrate the holes entirely and reach the inner layer. As a result, the enhanced electrode's surface shape and porosity proved effective for hydrazine electro-oxidation. The newly developed composite material-based sensors have an impressive catalytic activity profile, including hydrazine oxidation and a large efficient surface area. Additionally, the ZrHCF/Au-PtNPs/NFs/GC electrode's sensitivity for amperometric hydrazine detection was greatly enhanced. The sensor produced in this study had a linear range of hydrazine concentrations between 0.15 and 112.5 μM and a limit of detection (LOD) of 0.09 μM. A new sensor, on the other side, simplified applications because it sustained its initial activity under ambient circumstances for more than ten weeks [71].

In the 2019 study by Xie *et al*., the CuO/CeO_2 modified GCE was used as a malathion sensor. Figure 8 provides another illustration of the non-enzyme electrochemical approach. This work uses a decrease in the anode peak current of CuO-CeO_2/GCE after malathion administration as a detection method. By providing numerous more active sites on the electrode materials, the nanostructured CuO/CeO_2 bimetallic nanomaterials had a varied surface area and were able to trap malathion molecules through the coordination interaction between CuO and organic phosphorus. Additionally, the modified electrode's stability and sensitivity are increased by the synergistic reaction between CuO and CeO_2. A large linear range (10 fM-100 nM) and a low detection limit (3.3-0.03 fM) were generated under optimum experimental conditions [72].

Figure 8. Bimetallic CuO-CeO_2 composite for effective detection of malathion pesticide residue.

Using an altered PGE combined with a batch injection analysis system with multiple pulse amperometric detection, Porto *et al*. determined the three organophosphorus compounds, including diazinon, malathion, and chlorpyrifos, for the first time using an electrochemical method in their 2022 work. A nanocomposite made of functionalized carbon nanotubes and nanoparticles altered the PGE. The organophosphate samples were directly analyzed on the modified working electrode surface using the BIA-MPA system in Britton-Robinson buffer

0.15 mol L^{-1} at pH 6.0. Two potential pulses were applied successively on modified PGE at 1.3 V (100 ms) and +0.8 V (100 ms), respectively, for the selective detection of all three OPs and working electrode cleaning to detect DZN, MLT, and MPA. The sensor has a linear range of 0.1-20 mol L^{-1} for DZN, 1.0-30 mol L^{-1} for MLT, and 0.25-50 mol L^{-1} for CLPF under ideal circumstances. DZN has LOD and LOQ values of 0.89 and 2.98 molL^{-1}, 0.53 and 1.78 mol L^{-1}, and 0.35 and 1.18 mol L^{-1}, respectively. With values of 0.068, 0.030, and 0.043 mA L mol^{-1}, the suggested approach demonstrated significant sensitivity of DZN, MLT, and CLPF, respectively. [73].

2.4. Enzyme-based bimetallic nanomaterials for pesticide detection.

A sensor is a piece of analytical equipment that provides information on the make-up of different analytes in the surrounding ecology, whether those surroundings are a liquid or a gas. If the analyte is detected utilizing the enzymes, the sensor is referred to as an enzymatic sensor. Biosensors based on alcohol dehydrogenase [74], micro-peroxidase [75], horseradish peroxidase [76], tyrosinase [77], urease [78], and acetylcholinesterase [79] are also well known for their high sensitivity and selectivity. The central nervous system contains the catalytic enzyme acetylcholinesterase (AChE), which catalyzes the breakdown of acetylcholine and choline esters. The presence of many organophosphorus and carbamate insecticides lowers their ability to catalyze, even at low levels. Graphene oxide-based nanohybrids with a large surface area and many active sites can readily be employed to immobilize AChE on their surface for the creation of AChE inhibition-based biosensors. [80].

Although nanosensors show potential as pesticide detection tools, a range of biosensors have been created as viable alternatives that are inexpensive, simple to use, succinct, sensitive, resilient to environmental factors, and able for on-site pesticide detection monitoring. Several pesticides show their effects through a strong enzymatic mechanism in pests [81,82]. As a result of this situation, several enzymatic inhibition-based biosensors for pesticide surveillance have been developed. When the literature is thoroughly examined, it becomes obvious that multiple biosensors, particularly for identifying organophosphorus pesticides, have been constructed using various approaches to inhibit cholinesterase enzymes [83]. Because bimetallic nanoparticles are biocompatible with biological fluids, they are extensively used in clinical applications, including biosensors. Enzymes are frequently used as biosensing elements in transducing systems, and this shows how a biosensor might work in conjunction with them. Bimetallic nanoparticles offer good protein retention and high surface-to-volume ratios, allowing them to enhance rather than impede enzyme loading. They also help to improve accuracy by increasing electron transit between the enzymes and the electrode [84].

To measure paraoxon, Lu *et al*. constructed an AChE biosensor that was concentrated on core Pd-Au NRs. For bare GCE, Pd NRs/GCE, Au NRs/GCE, Pd-Au NRs/GCE, and AChE-Chit/Pd-Au NRs/GCE, the values for electron transfer resistance were 500, 290, 330, 228, and 880; respectively these findings demonstrated the high conductivity of Pd-Au NRs and the successful immobilization of the insulator properties of AChE. Additionally, the constructed sensors were DPV characterized in buffer solution. The Nafion/AChE-Chit/Pd-Au NRs/GCE system was used to quantify the paraoxon's maximum oxidation peak current. This increase demonstrates that Pd-Au NRs are suitable for monitoring enzymatic products. Furthermore, the effects of Pd-Au NRs, in addition to their outstanding biocompatibility and conductivity, are to blame for the significant increase in current. The paraoxon inhibition showed a consistent range between 3.6 pM and 100 nM with a 3.6 pM detection limit under ideal circumstances. The created biosensor was also employed to locate paraoxon in tap water samples [85].

In recent work, Chen *et al*. rejected Au-Ag bimetallic nanomaterials in favor of graphene-bimetallic biosensors with a very low limit of detection (LOD of trace methyl parathion). Using a one-pot method, a more straightforward OPs biosensor was developed on RGO-PDA-AuNPs-AgNPs-AChE-Chit nanocomposite film-modified GCE. To produce the electrodes for this study, a centrifuge tube was filled with 2.0 L of RGO-PDA complex, 2.0 µL of AuNPs distribution, 2 µL of AgNPs dispersion, 0.2 mL of AChE buffer solution, and 1 µL of Chit solution (0.2 percent with pH: 5) then vortexed for 30 seconds. It was then equally drop-cast onto the prepared GCE's surface and allowed to dry at room temperature while covered with a beaker. After 28 storage periods, the response has stayed at 62.0 %, proving the sensors' outstanding storage capabilities. Additionally, the sensor has a linear detection range of 0.076-3040 nM and a LOD of 9.1 pM for methyl parathion. The biosensor performs effectively against interference and has strong reproducibility and stability [86].

In their research to identify organophosphorus pesticides, Kesik *et al*. created a unique amperometric biosensor based on a conducting polymer and an electrode modified with many walls of carbon nanotubes. Acetylcholinesterase (AChE) was effectively immobilized on the improved graphite electrode through covalent bonding. Electrochemical processing functionalized carbon nanotubes. Poly(4-(2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl)benzenamine) (poly(SNS-NH_2)) was electropolymerized to explore the matrix characteristics of a conducting polymer for biomolecule immobilization. This approach effectively promoted acetylthiocholine electrochemical oxidation at a lower voltage (Ag reference vs. +100 mV.) while boosting the rate of electron transfer. Surface morphologies and electrochemical characterizations were monitored using SEM, X-ray photoelectron spectroscopy, contact angle measurements, electrochemical impedance spectroscopy, and cyclic voltammetry (CV) methods. High sensitivity (24.16 A mM^{-1} cm^{-2}), low detection limit (0.09 mM), wide linear range (0.05 mM and 8.00 mM), and quick reaction time were all characteristics of the suggested biosensor design. It was observed that paraoxon, parathion, and chlorfenvinphos inhibit the enzymatic activity of AChE. The built-in biosensor was tested to see if it could find pesticides in samples of treated tap water. It was discovered that the outcomes closely matched those of the HPLC/DAD method [87].

In particular, over the past twenty years, using such bimetallic nanoparticles in nanosensor and biosensor-based pesticide assessments has expanded. This paper provides an overview of a few electroanalytical methods based on bimetallic nanoparticles that can be used to identify different pesticides. The analyte, sensor, and detection limit of several electroanalytical bimetallic nanocomposite-based sensors for the detection of pesticides are also listed in table 4.

Table 4. Selected electrochemical sensors for pesticide analysis based on bimetallic nanocomposites.

Sr. No.	Analyte	Sensor	Limit of Detection (LOD)	Reference
1	Profenofos	Fe/Ni	1.4 mg/L	[44]
2	Dechlorinate Sulfentrazone	Fe/Ni	1 g/L	[45]
3	IVD	Au@Pt	2 ng/mL^{-1}	[46]
4	Ochratoxin A (OTA)	Au@Fe3O4	30 pg mL^{-1}	[47]
5	Parathion	Au-Pd/rGO/CPE	0.008 M	[48]
6	Chlorpyrifos	AChE/Au NCs/GO–CS/SPCE	3 ng L^{-1}	[60]
7	Malathion	Graphene-Copper Oxide	0.92 pM	[61]
8	Organophosphorus	CS@TiO2-CS/rGO	29 nM (6.4 ppb)	[62]
9	Malathion	AChE -Ag-rGO-NH2	0.032 µg L^{-1}	[63]

Sr. No.	Analyte	Sensor	Limit of Detection (LOD)	Reference
	Trichlorfon		0.001 μg L^{-1}	
10	Chlorpyrifos	AChE/ZrO2/RGO	10^{-13} M	[64]
11	Paraoxon Ethyl (PE)	Graphene-based NiFe	3.7 nmol L^{-1}	[65]
12	Hydrogen Peroxide	PPy-PtPd	2.5–8000 μM	[66]
13	Paraoxon Ethyl (PE)	Gr-NiFeSP	3.7 nM	[70]
14	Hydrazine	ZrHCF/Au-PtNPs/NFs/GC	0.09 μM	[71]
15	Malathion	CuO-CeO2 /GCE	3.3 fM	[72]
16	Diazinon Malathion Chlorpyrifos	PGE-BIA–MPA	0.35 μmol L^{-1} 0.89 μmol L^{-1} 0.53 μmol L^{-1}	[73]
17	Paraoxon	Nafion/AChE-Chit/Pd-Au NRs/GCE	3.6 pM	[85]
18	Methyl Parathion	RGO-PDA-AuNPs-AgNPs-AChE-Chit	9.1 pM	[86]
19	Paraoxon, Parathion, and Chlorfenvinphos	Amperometric Biosensor	0.09 mM	[87]

3. Discussion

In a forensic investigation, cases related to pesticide poisoning include either homicidal or suicidal crimes. Currently, a complex and advanced technology must be created to examine forensic evidence in cases of this nature. Pesticides have an impact on both target and nontarget creatures, including plants, birds, fish, earthworms, and humans. Numerous scientists have noted that pesticides negatively affect human health and the entire ecosystem. Particularly severe effects are caused by organo-phosphorus insecticides, which comprise over 70% of the pesticide class. They reduce the activity of the acetylcholinesterase enzyme, which is necessary to regulate body nerve transmissions. As an illustration, omethoate residue can have neurotoxic effects on people. Malathion, meanwhile, has toxic effects on cell division, root growth, and the development of cellular abnormalities.

Pesticide residues pose a significant risk to the environment and human health, which has sparked intense interest in creating effective tools and procedures for detecting them. Field applications are surely possible for electroanalytical methods with the benefits of straightforward, large-scale production, low prices, exceptional resilience to harsh environments, long-term storability, and on-demand tailorable performance. Recent advances in electroanalytical approaches, including nonenzymatic sensors, nanosensors, biosensors, and enzymatic sensors for the detection of pesticides, were emphasized in this study. This discipline is undergoing a period of fast growth, as seen by the rising number of publications.

According to studies on pesticide detection, the most common noble metals employed to create bimetallic nanoparticles were Au, Pt, and Pd. Bimetallic nanoparticles alone should not be used as modifying agents. The synergistic effects are enhanced when bimetallic nanoparticles are combined with another material. Bimetallic nanomaterials immobilize more enzyme molecules due to the synergistic interactions between the two metals. As a result, electron transport can be quickened. Therefore, the production of enzyme-based biosensors for pesticide assessments benefits significantly from using bimetallic nanomaterials. Additionally, the green synthetic technique has grown in popularity recently for synthesizing bimetallic nanoparticles due to its low cost, environmentally friendly nature, and nontoxicity. However, bimetallic nanoparticles for pesticide analysis have not yet been produced using this method. Bimetallic green synthesized investigations are therefore anticipated in the future. In addition to the above-mentioned reasons, nonenzymatic bimetallic nanoparticles can be employed to provide visible, low-cost, quick, and extremely sensitive pesticide detection techniques.

Furthermore, bimetallic nanoparticles based on extremely stable sensors can be used in handheld devices for on-site and speedy detection for pesticide screening in forensic evidence. Although several obstacles in the growing field have been overcome, more work is needed to advance electroanalytical method-based pesticide detectors for practical applications.

4. Future Perspective

Although electroanalytical sensors have several benefits over conventional approaches, including high sensitivity, lower detection limits, super selectivity, quick responses, and tiny sizes, their use in pesticide detection is still in its infancy. Several obstacles still need to be cleared before practical application. To increase their sensitivity to pesticides, nanomaterials like CNTs and microparticles should undergo further development in their production process. For instance, identifying OPs at small concentrations will be greatly aided by the synthesized nanomaterials with stable and high fluorescence capabilities. Second, it would be great to discover new kinds of targeted antibodies. OPs come in a wide variety of forms, and there are more and more of their derivatives utilized in agriculture each year. The key to developing OP immuno-sensors is the development of novel antibody types. To rationalize the interface between nanoparticles and biomolecules, new assembly and integration strategies of nanoparticles & biomolecules should be investigated. If the structures and interactions of the nanoparticles or biomolecules in nano-biosensors can be precisely regulated, it may be anticipated that both sensitivity and selectivity will be considerably improved.

5. Conclusions

In conclusion, the field of pesticide detection has seen significant potential for electroanalytical sensors. Commercial nanotechnology items are likely to be used in the detection of pesticides shortly. Bimetallic nanomaterial probes are highly efficient in the examination of pesticide residue in various exhibits related to forensic science, food samples, and environmental-related samples. The bimetallic nanomaterials-based electroanalytical method's prominent features include minimum analysis time, optimum sensitivity, and precise accuracy up to nanogram.

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Conflicts of Interest

The authors declare no conflict of interest.

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