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REVIEW

Smart farming approach using nanotechnology: an inevitable role in the application of pesticides

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Abstract

Food and crops are sourced primarily from agriculture, and due to the enormous growth in population, agricultural goods are in great demand, while farmland is being developed for residences. Therefore, certain chemicals, like pesticides, are being overused and have become unavoidable to increase crop productivity and storage. Excessive release of pesticides into the environment and food chain may pose a health risk. Food and agricultural products need routine analyses to monitor the level of pesticide residuals. As pesticide detection techniques are labor-intensive and require highly qualified professionals, an alternative technique must be developed, such as analytical nanotechnology. The most commonly used nanomaterials for pesticide delivery, enrichment, degradation, detection, and removal are metals, clays, polymers, and lipids. In colorimetric analysis of pesticides, metal nanoparticles are widely used which are quick, easy, and do not require any sample preparation. This manuscript compiles the latest research on nanotechnology in pesticide formulation and detection for smart farming.

Keywords: colorimetric detection, facile detection of pesticide, nanoagroproducts, nanopesticides, nanotechnology in agriculture, smart farming

Introduction

Pesticides are substances intended to eliminate and control the growth of weeds and pests. They are widely used in agricultural fields to protect crops from diseases caused by pests and weeds. They also play a vital role in the prolongation of crop storage, productivity, etc. A pesticide can be a chemical, an antimicrobial agent, a disinfectant, a biological agent, etc. (Casida and Durkin 2017). Since the world's population is enormously increasing every year, it is believed that the availability of agricultural land will be too low, and insufficient to satisfy the needs of the citizens. This is a serious economic concern of every country across the globe. Hence, several practices have led to an increase in farmers' efforts to increase the productivity of agricultural goods (Narenderan *et al.* 2019). This includes frequent usage of pesticides for bulk production of agricultural products at lower prices. Hence, the use of chemicals as pesticides in agriculture has significantly increased around the world (Casida 2012). Pesticides are usually composed of two major ingredients, active and inert materials. The active ingredient in pesticides is involved in destroying or preventing infectious pests. The inert ingredients are added intentionally by order of federal law, and they play a vital role in the improvement of product performance and usability. Active ingredients are sometimes insoluble, and due to this, the inert ingredients are added to act as a solvent for better penetration into plants' leaf surfaces (Mojiri *et al.* 2020). According to federal laws, it is not necessary to give the amount or any details about the inert ingredient since they are confidential. It just has to be approved by the EPA (Environmental Protection

Act) before use. Furthermore, the identity does not need to be specified in the product label (Tefera *et al.* 2019). As per research, pesticides can be classified into various categories such as fungicides, insecticides, and herbicides, which include carbamate, pyrethroids, organophosphorus, sulfonylureas, and organochlorine. Biopesticides are living microorganisms or materials obtained from living organisms that are capable of killing insects and pests (Kosamu *et al.* 2020). Biopesticides are classified into three major groups – microbial pesticides, plant-incorporated-protectants (PIP), and biochemical pesticides (Bharti and Ibrahim 2020). Microbial pesticides include microorganisms e.g., bacteria, fungi, protozoa, viruses, and algae. The most prominent bacteria, *Bacillus thuringiensis,* is used to control insects in several crops. On the other hand, PIPs are plant generated pesticidal materials like pesticidal protein whose genes are introduced into the plant gene to be protected from pesticidal attack. Biochemical pesticides include mainly plant extracts or some specific fatty acids or pheromones that function in a nontoxic manner. Pesticides can also be categorized according to their properties like toxicity and biodegradability. Most chemical pesticides used for agriculture are toxic and non-biodegradable. This leads to environmental toxicity. Among the class of pesticides, insecticides are considered to be extremely toxic to the environment and also to human health (Thornburg 1971). And so, a gold-standard technique should be developed to detect the level of toxic substances in consumer products. Thus, nanotechnology holds a promising position in agriculture. This manuscript provides detailed insight into pesticide classification, their effects, and recent studies that are being conducted on nanotechnology.

Methodology

Articles providing in-depth knowledge about the role of nanotechnology in pesticide based applications were used to make cumulative data. Databases like Google scholar, PubMed, Scopus, etc., were used to evaluate the current research status on nano-based application of pesticides. The article search was focused on keywords such as nano-based applications in pesticide, nanopesticides, nano-based pest management and smart farming. Articles published from the year 1994 including original and review articles were gleaned to prepare this manuscript. A total of 250 publications were chosen during the literature search. Of these, 57 papers were excluded during the screening of abstracts. Another 76 papers were omitted while screening the full text and extracting data. The final analysis was comprised of 117 articles that are relevant to the topic of the manuscript. An article published in 1971 was chosen outside the search criteria due to the immutable information it provided.

Classification of pesticide

Pesticides can be classified according to various bases, such as target organism, chemical structure, entry route, toxicity, mode of action, site of action, origin, physical state, etc. (Weiss *et al.* 2004; Kolesnyk *et al.* 2019; Zhang *et al.* 2020b).

Classification based on target organism

Pesticides classified under this category are specified based on the organism or pest they target (Table 1). They are specifically designed to target an organism or pest to control, harm, kill, mutate, repel or mitigate them (Kolesnyk *et al.* 2019).

Classification based on chemical structure

Classification of pesticides based on their chemical structure is one of the common and useful ways to choose the best for specific applications. The chemical structure can be altered to change the function of the pesticides. The pesticides are categorized into four major groups according to chemical structure: organophosphorus, organochlorines, pyrethrin, and carbamates. These chemicals belong to the organic group of insecticides (Fig. 1) (Torrens and Castellano 2014).

Classification based on the entry route

Route of entry of pesticides into a pest can be used for classification to classify them. The mode and site of action also depend on the route they enter. The entry route alters the effectiveness of the pesticides (Table 2). Most pesticides for the field are chosen in accordance with the entry route into the pest. The most prevalent pest in that particular area is evaluated, and pesticides are chosen according to it (Turusov and Rakitskiĭ 1997).

Classification based on toxicity

Classification based on the toxicity level is an important factor to be analyzed before selecting the pesticide for fieldwork. Toxicity caused by pesticides remains for a while leading to environmental pollution, and the effect can persist for several generations. Hence the usage of certain pesticides is limited. The levels of hazardous chemicals are listed in Table 3 (Al-Saleh 1994).

Table 1. Pesticide classification based on their target organism

Sl. No.	Pesticide	Target organism	Function	Examples
1.	Acaricides	mites and ticks	disruption in their growth and development	chlorinated hydrocarbons, carbamates, pyrethroids, etc.
2.	Algicide	algae	kill or inhibit growth	cybutryne, dichlone, nabam, oxyfluorfen, etc.
3.	Avicides	birds	kill	strychnine, DRC-1339 avitrol., chloralose, etc.
4.	Bactericides	bacteria	chemicals isolated or produced by a microorganism or artificially developed to kill or inhibit bacteria in plants or soil	ningnanmycin, cresol, xinjunan, etc.
5.	Chemosterillant	insect	interferes with the reproduction system and makes them infertile, thereby damaging chromosomes	tepa, metepa, apholate, etc.
6.	Fungicides	fungi	prevent the growth of fungi on food crops	captafol, maneb, ziram, etc.
7.	Herbicides	weeds	chemicals used to specifically kill weeds	paraquat, glyphosate, dinoseb, etc.
8.	Insecticides	insect	kill, repel, and mitigate any species of insects	aldrin, malathion, toxaphene, etc.
9.	Larvicides	insect (larval life stage)	affect the larvae of an insect	DDT (dichloro-diphenyl-trichloroethane), methoprene, etc.
10.	Ovicides	insects and mites	particularly targets the eggs of insects and mites	teflubenzuron, benzoxazin, etc.
11.	Piscicides	fish	used to eliminate the dominant species of fish	antimycin, niclosamide, etc.
12.	Rodenticides	rats (other related animals)	kill mice, rats, and other rodents	warfarin, red squill, white arsenic, etc.
13.	*Silvicide*	woody plants	designed to kill woody plants or brush or trees or the entire forest	cacodylic acid, tebuthiuron, etc.
14.	Termiticides	termites	repellent to termites	fiproni, termidor foam, etc.
15.	Virucide	virus	destroy or deactivate viruses	PAA, ribavirin

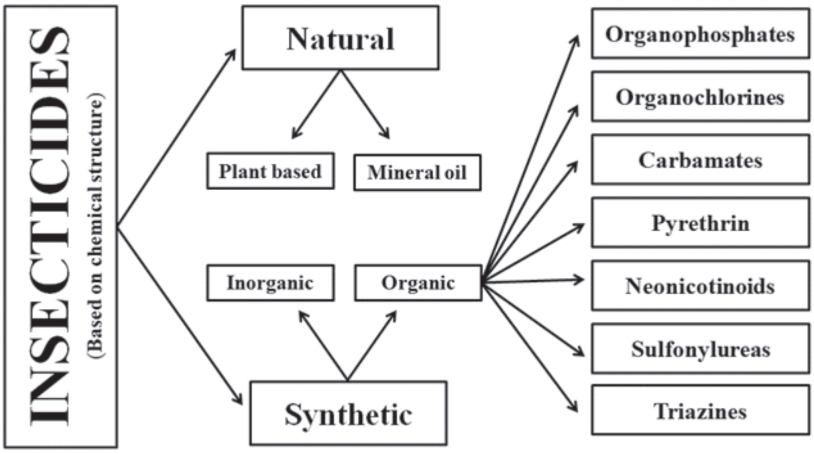


Fig 1. Schematic representation of the classification of insecticides

Table 2. Pesticide classification based on its entry route

Sl. No	Pesticide	Mechanism of action	Examples
1.	Fumigants	vaporize and enter the tracheal system of the pest.	methyl bromide, Iodoform, formaldehyde, etc.
2.	Stomach poisons	enter the digestive system of the pest through the mouth.	melathione, sulfur
3.	Contact poison	attacks the pests when they come in contact	paraquat, diquat, DDT
4.	Systemic poison	absorbed and distributed throughout the plant to offer protection	macrotraphus, 2,4-D, glyphosate

Table 3. Pesticide classification based on the level of toxicity

Sl. No.	Hazard level	Name of chemical	Chemical family
1.	Extremely hazardous	phorate	organophosphate
2.	Highly hazardous	monocrotophos	organophosphate
		profenofos and cypermethrin	combination pesticide
		carbofuran	carbamate
3.	Moderately hazardous	dimethoate	organophosphate
		qunalphos	organophosphate
		endosulfan	organochlorine
		carbaryl	carbamate
		chlorpyrifos	organophosphate
		cyhalothrin	pyrethroid
		ddt	organochlorine
		fenthion	organophosphate
4.	Slightly hazardous	malathion	organophosphate
5.	Unlikely to present acute hazard with normal use	carbendazim	carbamate
		artizine	triazine

Effects of pesticides

There has been a long history of using chemicals to prevent the growth of pests and weeds. However, during the Second World War the use of pesticides grew to prominence and was seen as advantageous because crops needed to be protected and their storage enhanced. As a result, the synthetic pesticide was formulated and used without knowing the risk factor. Since then, pesticides have become an inseparable part of the agricultural sector. Hence their prolonged use has led to multiple problematic situations, such as a decline in neurobehavior and cognitive activity, also increased risk of some chronic disorders, namely, diabetes, hypertension, etc. (Kim *et al.* 2017). The impact of pesticides is on both environmental and human health. In addition to the effects that animals may experience when consuming plant-based food, some chemicals may be absorbed into the soil, causing contamination of the soil and groundwater. This can affect marine organisms. Some chemicals are volatile, which may lead to air pollution. All these effects can ultimately reach humans. Thus, pesticides are considered to have an impact on both the environment and human health (Suratman *et al.* 2015).

Effect of pesticides on the environment

'Environment' is a very general term involving an immeasurable number of species. Any small change in the environment may trigger many changes. The primary target of pesticides as a pollutant is the environment since it is exposed during both production and application. The ultimate destination of environmental pollutants is humans. The impact of pesticides on the environment can be in different areas, including soil, air, water, organisms, plants, etc., even though the intended effect is different (Mauffret *et al.* 2017). Pesticides, if mixed in bodies of water, may travel beyond the aimed area, leading to an ineffective effect of pesticides on pests. Under federal laws, the usage percentage must not be beyond the recommended level (Prudnikova *et al.* 2021). Pesticides contaminate the soil via various sources, such as spray drift during field treatment, release from treated plants, or pesticides being sprayed into the soil to treat pests (Damalas and Eleftherohorinos 2011). The uptake of pesticides solely depends on the chemical, physical and biological properties of the soil. Some pesticides may degrade in the soil, causing no toxic effect, whereas some might settle and persist for a long time. This affects the growth of the plants cultivated in that area. This can directly affect plant-eating animals and may also cause toxicity to human health (Maroni *et al.* 2006).

Most pesticides are manufactured as water-soluble to achieve the desired effect, but this becomes a major issue. Pesticides can settle in soil and leach into bodies of water, making them contaminated. When this contaminated water, comes in contact with living organisms, it can cause various health issues, including cancer, immunotoxicity, neurotoxicity, etc. The contamination of water disrupts the life of marine organisms, and consequently, the food chain also gets disrupted (do Carmo *et al.* 2020). The contamination of groundwater is a more serious concern than surface water. Pesticides have a high degree of degradability until they are present in surface water. At the groundwater level, the oxygen rate is very low. Hence, bacteria living under such conditions are less prone to degrade the chemicals, thereby greatly decreasing the degradability rate. This causes the pesticide residues to remain for a long time in groundwater. They can also be transported farther away from the destination, causing issues elsewhere (Motoki *et al.* 2016).

Persistent organic pollutants (POPs) are also referred to as "forever chemicals". The existence of such pesticide residues is of major concern due to the low vapor pressure of pesticides. POPs in the air are capable of bioaccumulation and biomagnification. They affect non-target organisms (Onwona-Kwakye *et al.* 2020). Aerial spraying is one of the main causes of air contamination. Air pollution is responsible for major health issues in humans. The inhalation of pesticide residues in the air greatly impacts the disruption of endocrine, respiratory and reproductive systems. Thus, pesticides need to be applied following IPM (Integrated Pest Management) regulations recommended by EPA (Yadav *et al.* 2015).

Effect of pesticides on human health

The effect of pesticides on human health is not a surprising topic to be discussed. Since the environment can become completely polluted, it influences human health (Fig. 2). The effects on human health can be classified into acute and chronic. This depends on the route of exposure and duration of exposure (Souza *et al.* 2017). People who are in contact with a pesticide are prone to acute effects, which are treatable. Some common acute effects are nausea, giddiness, anorexia, abdominal pain, etc. There is strong evidence provided by the WHO (World Health Organization) that about 1,000,000 people worldwide are affected by acute poisoning of pesticides every year (Matysiak *et al.* 2016). Long-term effects are due to regular exposure to pesticides, and multiple studies have examined the long-term effects of pesticides (Tudi *et al.* 2022). Continuous exposure to pesticides can cause long-term effects like respiratory issues, reproductive issues, neurological disorders, cancer, etc. Certain pesticides which are classified as neurotoxins are still in use. Frequently pesticide handlers are not very aware of their effects. Researchers have found an association between pesticide

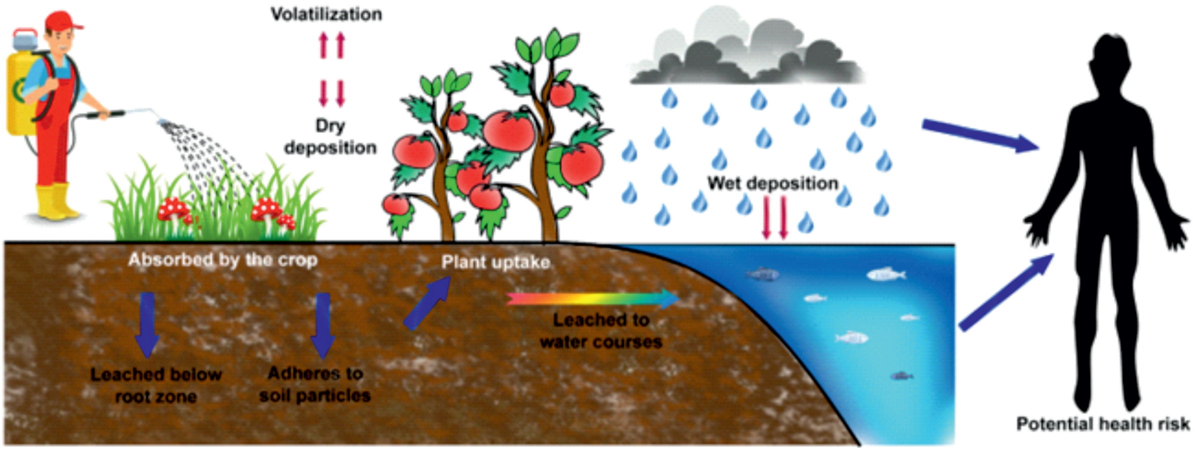


Fig 2. Pictorial representation of the effect of pesticides

exposure and cancer which can be due to both occupational and residential exposure. It has been found that there is an increased probability of birth defects and abnormal fetal development due to long-term exposure (Keifer and Firestone 2007; Costa *et al.* 2008; Matysiak *et al.* 2016).

Importance of registration toolkit

Presently the use of pesticides has become unavoidable in consideration of the production and storage of crops. But it is essential to ensure that the pesticides do not have any poisonous effects on both humans and nature. The Food and Agricultural Organization (FAO) of the United Nations has developed a four-step registration toolkit for any pesticide to be registered on the market (Fig. 3). The registration of a pesticide is done in four phases: 1 – pre-registration, 2 – registration, 3 – post-registration, and 4 – review of existing registrations (Haggblade *et al.* 2022). An approved pesticide needs to contain a label of the measurable amount to be used. With this, pesticide handlers can use certified standards to check whether the pesticide meets the quality and required specifications in order to function efficiently without any harmful consequences. Even though pesticides are used according to regulations framed by the EPA, their residues on the plants have become inevitable. In order to avoid undesirable effects, a testing kit for pesticide presence should be developed to determine the amount of pesticide residues on the plant before consumption (Handford *et al.* 2015).

Detection techniques and their limitations

According to FAO, China is the leading consumer of pesticides around the globe. Europe and America are the leading importers of pesticides and other agrochemicals throughout the world (Sharma *et al.* 2019). Pesticides are the most important elements for both productivity and storage of cultivated goods. However, excessive and improper usage leads to various health hazards, primarily to humans and all other living organisms. Therefore, routine analyses are required to detect the presence of toxic pesticide residuals in both food and agricultural products. There are several detection techniques that are already available. Most of

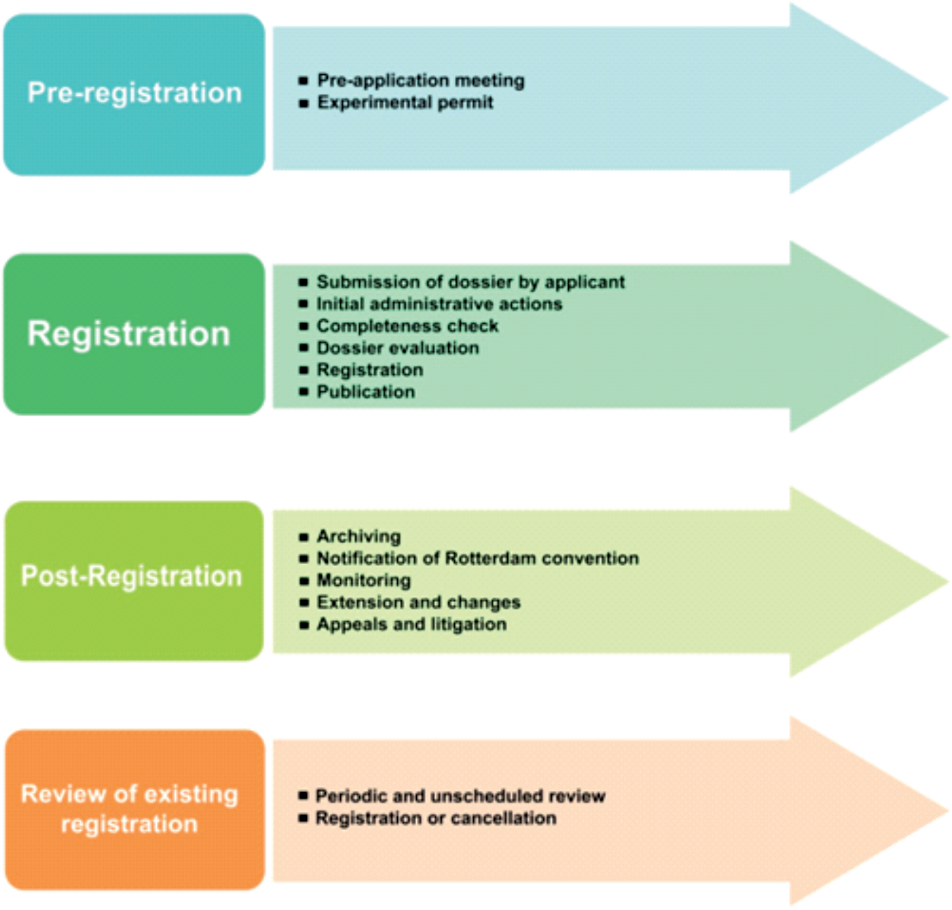


Fig 3. Schematic representation of registration toolkit introduced by FAO

the techniques are based on analytical methods. Before the advent of nanotechnology in analysis, detection was performed with various techniques like HPLC, GC-MS, and other chromatography-based techniques (Haggblade *et al.* 2022).

HPLC, commonly known as high-pressure liquid chromatography or high-performance liquid chromatography, is usually used in analytical chemistry for the separation of components in a mixture. At times it can also help in the identification, quantification, and purification processes of every individual component in a mixture after the separation process. Thus, HPLC is frequently used for the detection of pesticidal residues in food and crops. Usually it is coupled with mass spectrophotometry (MS) for characterization. The combination of HPLC-MS is the most preferred detection technique used. The major problem associated with this technique is the sample preparation. Preparation of the sample for detection involves multiple steps, which are considered to be burdensome. To avoid this, several other techniques are being developed (Takahashi 2006; Sur and Sathiavelu 2022). Unlike HPLC, they provide both qualitative and quantitative data on the residues of the sample simultaneously. This technique needs to be combined with specific detectors for detection. They are more selective for the organophosphate group of pesticides. The efficiency, precision, and accuracy of GC are good at the nanogram to microgram level of residues. The only problem associated with GC is the selection of suitable detectors for specific detection (Matisová and Hrouzková 2012).

Immunological assays have been used for a long time and are an antigen-antibody binding-based analytical tool used as an alternative to mechanical tests in pesticide detection (Suri *et al.* 2009). Antibodies are proteins that are naturally produced within the animal, whereas antigens are foreign substances. Antibodies produced by animals are highly specific and capable of binding only to closely related chemical configurations (antigen). The goal of antibodies is to protect an animal from any disease-causing toxic compounds or organisms. Therefore, an immunoassay can be developed by the production of an antibody that is complementary to the chemical structure of a pesticide by considering the pesticide as an antigen. This can be detected and monitored by an appropriate indicator system. Thus, a developed immunoassay can detect the concentration of pesticides less than 1 ppb (Table 4). Immunoassay provides better benefits than the traditional mechanical test. It is very precise and can detect the concentration of a pesticide even if it is less than one ppb, which can be noticed by visual color change. Pesticides are primarily detected by providing a "yes" or "no" response rather than accurately determining their concentrations using immunoassays. In addition, the storage of the immunoassay kits is arduous, which may affect their accuracy (Gabaldón *et al.* 1999; Jiang *et al.* 2008; Zhang *et al.* 2020a).

Table 4. Immunoassay kits available for specific pesticides

Sl. No.	Type of pesticide	Immunoassay kits
1.	Herbicides	atrazine cyanazine (Bladex) paraquat simazine (Princep)
2.	Insecticides	aldicarb (Temik) heptachlor parathion
3.	Fungicides	benomyl (Benlate) metalaxyl (Ridomil, Apron)

Among other pesticide groups, organophosphate (OP) is the most widely used due to its increased productivity. To detect the presence of OP, spectroscopic analyses are usually preferred. OP has a special capability of binding to metals; hence different data retrieved by multiple spectroscopic techniques are adequate. Techniques like UV-visible, fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), Raman spectroscopy, and mass spectroscopy (MS) are commonly used (Akiyama 2004). UV-visible spectroscopy plays a crucial role in the detection and interaction between metal ions and organic ligands (Soylak *et al.* 2021). FTIR has direct access to monitoring the stretch of the phosphoryl group and can quickly identify undiluted residues in the sample. They are used to obtain both qualitative and quantitative results (Sánchez *et al.* 2010). NMR spectroscopy is considered more important for the study of structure elucidation than other spectroscopic techniques. NMR provides complete information on the number of atoms that are magnetically distinct. NMR has great utility in the detection of OPs and related fragments. Many nuclei can be studied with NMR, like ^{1}H, ^{15}N, ^{13}C, ^{19}F, ^{31}P, etc. For the detection of OPs, numerous nuclei have to be studied, especially ^{31}P (Tonogai 2004). Raman scattering has an excellent feature with simple pretreatment of samples, fast spectral measurement, weak signal inference of water, etc. Thus Raman spectra are mostly used for detecting pesticide residues in water samples.

Mass Spectroscopy is performed to determine the mass-to-charge ratio after the ionization of a molecule using various techniques. MALDI-TOF (Matrix-Assisted Laser Desorption/Ionization-Time Of Flight), GC-MS (Gas chromatography-Mass Spectroscopy), SPAMS (Single Particle Aerosol Mass Spectrometry) are some of the MS techniques used. They are often combined with an analytical technique to obtain better results.

Even though spectroscopic analysis produces better and quicker results than analytical techniques, the detection cannot be performed onsite since it requires a laboratory and sample treatment. Pre-sample treatment is strenuous work in spectroscopic analysis (Hatakeyama *et al.* 2006; Watanabe *et al.* 2013). These techniques are highly reproducible, reliable, and sensitive, but are labor intensive, expensive, and require trained professionals. In consideration of the issues involved in conventional techniques, an alternative technique that is simple, rapid, accurate, highly sensitive, and with high reproducibility must be designed (Tuzimski 2012).

Biomonitoring

Biomonitoring is an important scientific approach to the assessment of the environment by calculating the amount of chemicals which have entered and accumulated in an organism. It is commonly performed by assessing the tissue or fluid of an organism. With these calculations, biomonitoring provides data on the potential effect and toxicity of pollutants. In this technique, the presence of pollutants and their toxicity level can be measured using a biological indicator (Sessink 2019). There are two general approaches regarding biomonitoring, active and passive. In passive monitoring, depletion of the ecosystem, exclusion of sensitive species, and minimization of biodiversity are some of the adverse consequences of pollution, and regarding an individual, the buildup of toxic substances in organs and tissues and other characteristics of pollution in the environment can be investigated. Whereas, in active monitoring, the reaction of synthetic populations, neurophysiological characteristics of specimens, specific mechanisms of organs, muscular movement, reproduction, respiration, and cognitive behavior, along with cellular and subcellular functions, can be studied under the influence of toxic compounds. For biomonitoring, various biosensors are being developed (Tranfo 2020).

Nanotechnology in agriculture (smart farming)

In recent years nanotechnology has gained enormous attention due to its wide applications in various fields like medicine, drug development, catalysis, energy, and materials (Girigoswami *et al.* 2018; Haribabu *et al.* 2019; Haribabu *et al.* 2020; Pallavi *et al.* 2022). The property of nanoparticles with small size (1–100 nm) to large surface area is the major reason for the potential medical, industrial, and agricultural applications (Sharmiladevi *et al.* 2019; 2021a; 2021b; Nagaraj *et al.* 2021). Researchers have worked towards the synthesis of nanoparticles in different ways, including chemical, physical and biological methods (Sharmiladevi *et al.* 2017; Harini *et al.* 2022a; 2022b; Poornima *et al.* 2022). Nanotechnology in agriculture has gained intense attention with an abundance of funding received for the development of agricultural sectors (Fig. 4). This can be attributed to novel farm production and storage

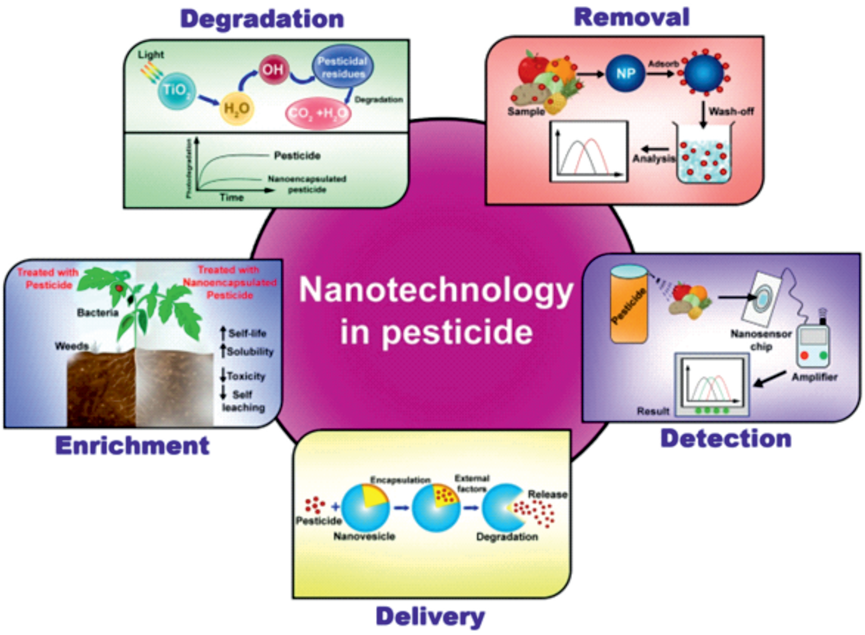


Fig 4. Different applications of nanotechnology in pesticides

techniques, which function as open systems where energy and matter are exchanged freely. Nanobased sensors can be developed which are inexpensive and portable, providing rapid and real-time detection of pesticides (Bayda *et al.* 2019). Several studies have been undertaken to explore the application of nanotechnology in agricultural sectors to improve crop production, growth, detection of pesticides, and storage of crops (Sereni 2016). Incorporating the idea of nanotechnology in pesticides can minimize the potential hazards that are associated with excessive use. Nanobased technologies can interfere with five different applications of pesticides (Fig. 4) such as delivery, enrichment, degradation, removal, and detection. Certain nanomaterials are critically being used as pesticides themselves. The chemistry behind these applications of nanomaterials can be explained by two techniques: homogenous and heterogeneous chemistries. Homogenous chemistry defines the nanoparticles being directly used in sensing or remediation, whereas heterogeneous chemistry is about the nanoparticle being applied on a supportive material before its application.

Nanoinsecticides

To minimize the toxic effects of pesticides, they can be nanoformulated, which decreases the amount to be used, thereby minimizing the toxic effects. Nanopesticides are currently being very intensively researched. The global market of nanopesticides is expected to be $1.6 billion by 2031, as reported by allied market research. Certain nanomaterials like silver nanoparticles contain biotoxic properties and hence, can be used in the place of pesticides. Sap-lam *et al.* (2010) synthesized polymethacrylate-stabilized silver nanoparticles through UV irradiation to evaluate their larvicidal activity. After exposure to *Aedes aegypti* larvae, the concentration of the formulation at 5 ppm showed lower survival rates of larvae of less than 10%. Zinc oxide nanoparticles have been shown to have a strong anti-pathogenic effect and are currently being studied for their effectiveness against phytopathogens (Zhao *et al.* 2022b). Manimaran *et al.* (2021) synthesized titanium dioxide nanoparticles via the green route from *pleurotus djamor*. The prepared particle exhibited effective larvicidal activity against *Aedes aegypti* larvae. The LC_{50} value for the particles was recorded as 4-6 $mg \cdot l^{-1}$ (Zhao *et al.* 2022b). There are many different types of nanoparticles in pesticide applications, including metal, polymer, clay, and lipid-based nanoparticles. Anand *et al.* (2018) synthesized chitosan-based nanoparticles via green synthesis using shrimp shells as the larvicidal agent. Sodium tripolyphosphate was used as the reducing agent for the synthesis of chitosan nanoparticles. The larvicidal activity against *A. aegypti* larvae was observed at LC_{50} as 66.42 $mg \cdot l^{-1}$.

Nano-mediated delivery of pesticides can minimize the amount to be used in a given area. The right amount of pesticide can produce a healthy and high yield. Due to several advantages, nanomaterials are being employed to deliver pesticides. Nanomaterials can help in multiple ways in the delivery of pesticides, such as acting as emulsions, crosslinkers, suspension, or encapsulating agents. The encapsulation of nanoparticles can readily enhance the stability of the active ingredients (AIs). AIs that are prone to photolysis can be protected in nanocapsules, which, in turn, improve their bioavailability. Kumar *et al.* (2014) developed a nanoformulation of pesticides containing imidacloprid as an active ingredient. Sodium alginate nanoparticles were used to encapsulate the AIs. A field study was carried out with synthesized insecticides against leafhoppers. Compared to nano-encapsulated pesticides, other samples showed high growth of the insect beyond the threshold level. The effectiveness of encapsulated formulation was comparatively high, and hence it was concluded that the product developed could serve the purpose better with further research. Many polymeric nanomaterials are being used to deliver the product to the targeted site through translocation. Mendez *et al.* (2022) synthesized lignin nanoparticles via emulsion evaporation as a delivery vehicle to transport and enhance the translocation of methoxyfenozide. The team developed a hydroponic condition with Hoagland medium for soybean plants. The uptake of formulated pesticide mixed in the suspension was found to reach the stems and leaves via roots. Despite the higher translocation efficiency of free methoxyfenozide, the results showed that the concentration of the formulation in leaves and stems was enhanced compared to the free methoxyfenozide.

Smart delivery nanosystem

Stimuli-responsive nanoformulations can release the AIs more precisely corresponding to the biological or environmental demands (Table 5). The amount of pesticides to be released can also be programed and thus can reach the goals of sustainable agricultural practices. The two major factors that affect crop production and declining yield are biotic and abiotic stresses. Biotic stress is caused by pests, weeds, nematodes, and other pathogenic diseases, whereas abiotic stress is caused by environmental conditions such as salinity level, temperature, pH of water, soil condition, poor nutrition, etc. Temperature, redox condition, pH, enzyme, and light are some of the stimuli that are used to deliver pesticides in a controlled manner.

Besides pH, temperature, and light, other stimuli like ultrasound, enzymes, and magnetic properties are

Table 5. Compilation of recent studies on smart nanoparticles in delivering pesticides

Applications	Nanosystem	Nanoparticles	Active ingredients	Trigger group	Target	Activity/ conclusion	Ref.
				Temperature			
Control over nematodes and insects	metal-organic framework [MOF]	carboxyl functionalized zirconium oxide [UiO-66-(COOH)$_2$]	indoxacarb	poly(N-isopropyl acrylamide)	*Spodoptera frugiperda*	the delivery system showed excellent temperature-responsive control over *S. frugiperda* in insecticidal experiments.	(Wan *et al.* 2022)
Pesticide transportation	multi-functional composite nanocarrier	poly(N-isopropylacrylamide) modified graphene oxide	lambda-cyhalothrin	–	–	the carrier system showed controlled release of AI according to the change in temperature and possessed good stability and solubility.	(Wang *et al.* 2021)
Control over parasitic worms and insects	composite nanocarrier	quaternary ammonium chitosan surfactant	avermectin	–	–	the evaluation of the adhesiveness of the system to the leaves showed improved results and enhanced performance at 35°C.	(Chen *et al.* 2022)
				Light			
Control over weeds	composite material	β-cyclodextrin– and azobenzene modified mesoporous silica nanoparticles	hexaconazole	azobenzene	–	the transition of azobenzene from its trans position to the cis position resulted in an irreversible gatekeeper pathway system and responsiveness towards UV light; the system also showed sensitivity towards pH in the release	(Pan *et al.* 2021)
Control over weeds	polymeric nanoparticles	1,1,3,3-tetramethyl guanidine	2,4-dichlorophenoxyacetic acid (2,4-D)	–	–	the release of the AI was increased gradually after exposure to UV light	(Shan *et al.* 2022)
Control over insects	composite nanocarrier	PEG and α-cyclodextrin functionalized hollow carbon microspheres	imidacloprid	–	european corn borer	upon exposure to infrared, the carrier system degraded due to an increase in temperature, and a controlled release was noticed	(Liu *et al.* 2021)
				pH			
Control over phytopathogens	metal-organic framework (MOF)	zeolitic imidazolate	boscalid	oxalic acid	*Botrytis cinerea*	the carrier system exhibited excellent control over the release of AI depending on the pH condition of the system	(Zhang *et al.* 2022)
Control over nematodes and insects	MOF	zeolitic imidazolate (8)	β-cypermethrin	intermediate acid-unstable imidazole organic compounds	*Coptotermes formosanus*	the acidic condition promoted the decomposition of MOF and the release of insecticide	(Ma *et al.* 2022)
Control over fungus	hybrid nanoparticle	chitosan derivative functionalized mesoporous silica nanoparticles	fludioxonil	–	*Fusarium oxysporum* f.sp. *radicis-lycopersici*	the fungicidal activity against the target was better, and the discharge of AI was controlled	(Mosa *et al.* 2022)

also being used to develop smart nanoparticles to actively deliver pesticides. To accurately deliver agents, researchers are also employing dual or tri-stimuli responsive functional groups. Recent studies with multifunctional functional moieties for dual stimuli responsiveness have been tabulated in Table 6.

Nanobased enrichment

The encapsulation of the AIs using nanoparticles not only allows site-specific delivery but also enriches its properties. The major limitations of pesticides are their reliance on their solubility, photostability stability, adhesion, crop yield, and quality. Conventional pesticides can possibly infect non-target organisms via consumption. Nanoscaled materials help to formulate the pesticide with enhanced properties. Due to improved functionalities, the amount of pesticide used can be reduced, which in turn reduces the toxicity. For the enrichment of pesticides, mesoporous silica nanoparticles are being widely employed. Kong *et al.* (2021) discussed the potential applications of nanosilica in the enrichment of active ingredients. Metal-organic frameworks are another class of nanomaterials that are being used in the enrichment of the properties of pesticides.

Nanobased degradation

Nanosized materials can accelerate the degradation of pesticidal residues in samples. The role of pesticides is to destroy any pathogenic agents in the sample. But afterwards, the residues tend to remain, which may lead to toxicity in a non-target organism. To avoid this issue, nanobased materials can be used to encapsulate the pesticides, which will be released later to degrade the residues. There are two ways to degrade pesticides: direct and indirect. Direct agents may degrade the pesticides during their mechanism of action; hence, indirect agents are always preferred. Various classes of nanomaterials are being used for the degradation of active ingredients and their residues. Zhao *et al.* (2022a) prepared a composite nanomaterial consisting of pesticides and plant hormones. The photostability of the particle was studied, and showed improved photostability. The particle developed provided sustained release with accelerated degradation of pesticide residues due to the subsequent release of the plant hormone. Rizo *et al.* (2020) synthesized copper oxide nanoparticles for the degradation of methyl parathion which is known for its neurotoxicity. Copper oxide nanoparticles were prepared via a precipitation reaction using Benedict's reagent. The degradation of methyl parathion was carried out via a hydrolytic pathway and characterized by using various photophysical tools. The degradation was shown to be about 87% without the use of any external probes like light or other chemical species. Das *et al.* (2017) synthesized magnetic nanoparticles functionalized with enzyme laccase. The nanoparticle was prepared by the co-precipitation method, and the surface was modified with carbodiimide and chitosan. The degradation study showed about 99% of the degradation of chlorpyrifos with good reusable potentiality.

Nanobased removal

Organochlorines (OCs) are one of an extensively used class of pesticides. The AIs used in this class of pesticides have a high potential for bioaccumulation and resistance against microbial degradation. Hence, it has become important to remove the residues completely from the sample. Several methods of removal based on chemical, physical and biological methods are being developed. OCs possess complex structures, and so only a few microorganisms have been found to be effective degradation agents. Furthermore, sensitivity in these methods is still lacking. As an alternative, semiconductor-based nanoparticles can degrade and remove the residues photo-catalytically. Liang *et al.* (2021) made 3D composite nanomaterial composed of MOF growth on carbon nanotubes (CNTs). The synthesized product was tested in adsorption experiments to remove the pollutants in the water sample. The results showed that the product developed with CNTs had a stronger adsorption capacity than the MOF alone. The product also exhibited reusability. Mohammed *et al.* (2022) studied the effect of span-80 surfactant in the removal of pesticide residues in the presence of magnetite nanoparticles. The particles were sensitive towards abamectin and removed about 99% of the residues present in the aqueous sample within 10 mins under optimal conditions. Nageswara *et al.* (2021) synthesized a nanocomposite material consisting of ferric oxide and silver oxide doped with titanium dioxide nanoparticles. The material was developed to remove flumioxazin, specifically in a water sample. The photocatalytic activity of the material completely degraded the residues and resulted in absolute removal.

Nanobased detection

Through the potential use of analytical nanotechnology, a new trend is in progress to overcome the above issues, i.e., nanotechnology-based detection techniques. The presence of analytes can be detected by metal nanoparticles with high sensitivity and analytical capability. Nanoparticle-mediated colorimetric detection techniques are widely used for the detection of the presence of environmental pollutants, including heavy metal ions, anions, microbial contaminations, etc. Recently, these techniques have also been applied for the detection of pesticide residues in food samples

Table 6. Compilation of recent studies in multi-stimuli responsive nanoparticles for the delivery of pesticides

Stimuli	Nanosystem	Nanoparticles	Active ingredients	Target	Application	Conclusion	Ref.
Redox/ Enzyme	MOF	pectin nanoparticles	pyraclostrobin	*Magnaporthe oryzae*	control over fungus	the carrier system responded to dual stimuli, and the release of the fungicide was controlled; thus, the system could promote the growth of the plant	(Liang *et al.* 2022a)
Redox/pH/ Enzyme	MOF	MIL-101(Fe)- -carboxymethyl starch nanoparticles	chlorantraniliprole	*Spodoptera frugiperda*–larvae	control over insects	the duration for the control over the insect was enhanced when the AI was nanoformulated	(Liang *et al.* 2022b)
Light/ Temperature	composite material	polymer modified dopamine based mesoporous silica nanoparticles	imidacloprid	–	control over insects	the developed polymer brush features sustained release of insecticide responding to light and temperature	(Xu *et al.* 2022)
Enzyme/pH	composite material	zein-functionalized mesoporous silica nanoparticles	avermectin	–	control over insects and nematodes	the pesticidal effect of the nanoformulated AI was enhanced with improved photostability, high loading efficiency, and great adhesion properties	(Zhong *et al.* 2022)
Redox/pH	composite nanocarrier	bimodal mesoporous silica nanoparticle functionalized with disulfide bond, and β-cyclodextrin s	prochloraz	–	control over fungus	the carrier system exhibited controlled overresponse to pH and redox condition of the biological environment	(Wu *et al.* 2022)

with simple and rapid functions (Samsidar *et al.* 2018). Nanobiosensors are the biological application of nanomaterials that are used for sensing. They can be either physical or chemical agents. Nanobiosensors perform various activities like (1) detecting biochemicals in cell organelles, (2) analyzing the phenomenon of a region, (3) measuring the number of nanoscopic particles in an environment, etc. (Table 7). They are so sensitive that they can detect the target molecule even at a very low concentration. The sensor detects the presence of an electrical impulse produced when the biorecognition element interacts with the target analyte. The biorecognition element can either be an antibody, protein molecule, enzyme or DNA. A wide range of nanomaterials, such as metal nanoparticles (gold, silver, copper), non-metallic nanoparticles, or carbon-based nanoparticles (graphite, graphene, carbon nanotubes), is used for designing nanobiosensors. Other than this, novel nanoparticles like nanoclusters, antibodies, quantum dots, and aptamers are also used in heavy metal detection. The synthesis process can be either chemical or biochemical. The sensitivity and specificity of biosensors are decided by the precursor molecule that they are made of. Multiple studies have shown that metal nanoparticles and carbon nanotubes exhibit excellent properties in conductivity and electron transfer. Biosensors can be classified into two groups based on bioreceptors and transducers (Rawtani *et al.* 2018). The sensitivity and selectivity of a specific biosensor depend on the characteristic of the biorecognition element that is used for analyte binding. Bioreceptors are made up of multiple combinations of elements based on the application. The classification here is based on the biological materials that are used as bioreceptors.

Biological material-based

Aptamers are single-stranded oligonucleotide or peptide molecules at nanodimensions. They can be constructed either from DNA or RNA molecules selected using an *in vitro* technique SELEX (Systematic evolution of ligands by exponential enrichment). Since they have the ability to form various helix structures and single-stranded loops, they are extremely versatile and bind to a target molecule with high specificity and selectivity. Aptamers are basically smaller than other biorecognition elements like antibodies or enzymes. The change in conformation of the aptamer when it binds to a specific analyte is converted to an output signal and is detected by the transducer (Zheng *et al.* 2016). Antibodies, otherwise called immunoglobins, are protein molecules found in the immune system. The primary work of antibodies is identifying and neutralizing pathogenic substances. Antibodies bind to the specific conformation of a pathogenic substance called an antigen. Both types of antibodies, monoclonal and polyclonal, are used in sensor design. Since monoclonal antibodies are made up of single cell type, they are very specific and bind to corresponding antigen molecules, whereas polyclonal antibodies are sensitive and bind to different epitopes on the target analyte. Comparing both, monoclonal antibodies possess high specificity, and polyclonal is highly sensitive (Saini *et al.* 2017).

Transducer-based

The role of the transducer is to convert the physiochemical changes that occur due to the biorecognition event into an optical or electrical signal at a measurable level. Based on the type of transducer used, the biosensor can be classified into several types. Electrochemical biosensors measure the electrochemical signal produced by the biorecognition event. They rely on electrical properties such as capacitance, potential, current, and impendence. They measure the current produced during the reduction and oxidation of an electrolyte. The binding of the analyte to the biorecognition element triggers a change in electrical parameters which result from the oxidation and reduction reaction occurring due to the biological interaction producing an electrical signal which is measured by an electrochemical biosensor (Barthelmebs *et al.* 2011).

The performance of optical biosensors is based on the interaction of the optical field with the biorecognition element. Optical sensing offers direct, rapid, real-time detection. It can be broadly classified into two types: label-free and label-based detection. Label--free enables the generation of detected signals directly by the interaction of sample molecules with the transducer. An example of label-free sensing is SPR (Surface Plasmon Resonance). Label-based sensing involves the use of labels to generate an optical signal. Label-based sensing can even detect simple molecules like glucose using enzymatic oxidation reactions (Agraharam *et al.* 2022; Girigoswami and Girigoswami 2022).

Piezoelectric sensors are considered to be some of the most sensitive sensors developed to date. Piezoelectric sensing uses the piezoelectric effect and quantifies changes in temperature, pressure, acceleration, or force and converts them into an electric charge. The sensing is based on the principle "The change in frequency is proportional to the mass of absorbed material". When the sample is exposed to laser light, such as quartz, and vibrates under the influence of an electric field, it emits electron waves that are detected at a specific angle of an electron by piezoelectric with the use of gold (Maghsoudi *et al.* 2021).

Colorimetric detection

Colorimetric analysis for onsite visual detection is possible due to the excellent features possessed by LSPR (Localized Surface Plasmon Resonance). Due to LSPR, the colloidal metal nanoparticles exhibit a high extinction coefficient which leads to possessing

Table 7. Compilation of studies that developed nanobiosensors for the detection of pesticides

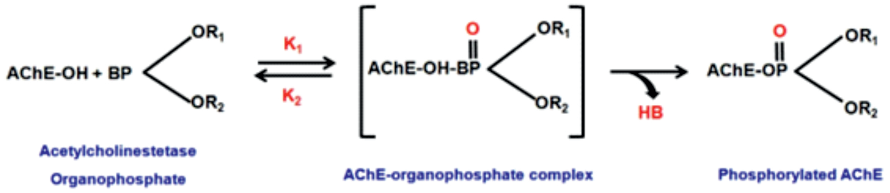
Sl. No.	Nanoparticle	Surface modification	Synthesis method	Detection method	Analyte	Detection matrix	Evaluation mechanism	Detection limit	Ref.
1.	Reduced graphene quantum dots and multi-walled carbon nanotubes	aptamers	citric acid pyrolysis	apta-nanosensor	diazinon	tap water, urine, river water, and agricultural runoff water	quantified by HPLC method	0.4 nM	(Talari *et al.* 2021)
2.	Carbon nanotube	ferrocene-thiophene	click chemistry	electrochemical nanosensor	parathion and chlorantraniliprole	tomatoes, apples, and soil sample	HPLC analysis	0.02–6.50 μmol · l^{-1} and 0.01–7.00 μmol · l^{-1}	(Tümay *et al.* 2021)
3.	Iron oxide and molybdenum carbide micro flowers	graphitic-carbon nitride	hydrothermal method	electro chemical nanosensor	parathion	food samples	–	7.8 nM	(Devi *et al.* 2022)
4.	Carbon nanotubes and silver nanoparticles	pyrolytic graphite electrode	–	amperometric detection	diazinon, malathion and chlorpyrifos	tap water, orange juice, and apple fruit real samples	–	0.35, 0.89 and 0.53 μmol · l^{-1}	(Porto *et al.* 2022)
5.	Tantalum(V) oxide nanoparticles	silver film and silica core	–	fiber–optic nanosensor	fenitrothion	–	spectrophotometric analyis	38 nM	(Kant 2020)
6.	Upconversion nanoparticles and graphene oxide	aptamer	–	apta-nanosensor	diazinon	food sample	fluorescence resonance energy transfer (FRET) method	0.023 ng · ml^{-1}	(Rong *et al.* 2020)
7.	Manganese dioxide nanosheets	–	–	fluorescence polarization (FP) assay	diazinon	real water sample	fluorescence polarization signal	0.01 ng · ml^{-1}	(Qin *et al.* 2022)
8.	Fluorescent carbon dots.	–	–	nanosensor	diazinon	tomato juice	spectrofluorometer	0.038 ± 0.01 μM	(Khaledian *et al.* 2021)
9.	Gold nanoparticles	thiolated aptamers	–	electrochemical aptasensor	diazinon	–	differential pulse voltammetry	0.0169 nM	(Hassani *et al.* 2018)
10.	Vanadium disulfide quantum dots	graphene nanoplatelets/carboxylated multiwalled carbon nanotubes	hydrothermal method	voltammetric and impedimetric aptasensor	diazinon	various real samples	differential pulse voltammetry	1.1×10^{-14} mol · l^{-1}	(Kumar *et al.* 2014)

different colors in the visible region of the spectrum. Hence, any metal nanoparticles can be used to design a colorimetric detection technique, which can eliminate the use of expensive or advanced instruments (Singh *et al.* 2020).

Sensitivity and rapidity are considered the two major advantages of nanotechnology-based colorimetric detection techniques over conventional techniques. The presence of target moiety can be easily detected by color change when nanoparticles interact with the sample. This is achieved through the unique property of the metal nanoparticles, i.e., the SPR. The high extinction coefficient property of the metals is also due to the SPR. Most of the metal nanoparticles have a broad range of absorption spectrum at the visible region, which is the primary consideration for the development of a colorimetric-based detection technique. The size and shape of the nanoparticle have to be properly maintained during the synthesis since most of the properties depend on these two characteristics (He *et al.* 2019).

The color change during interaction is mainly due to the inhibition of acetylcholinesterase (AChE) by the organophosphate group of pesticides (Scheme 1). The mechanism includes the reaction of organophosphate with an OH bond on the serine of AChE. This binding causes an inhibition with acetylcholine chloride. The color change is due to the interaction between nanoparticles and pesticides because they tend to form aggregations. When well-spaced nanoparticles aggregate, it results in color change allowing for visual onsite detection of target moieties. The concentration of the target molecule can be easily quantified using various photophysical tools. In addition, a proper chemical interaction can be monitored and used to design a sensitive assay. Interaction between target moiety and nanoparticles can be mediated via a covalent bond, hydrogen bond, ligand exchange reactions, and donor-acceptor reaction. The most widely used metal nanoparticles are gold and silver (Zheng *et al.* 2016; Ghoto *et al.* 2019b).

There are four possible strategies involved in the aggregation of nanoparticles that aids colorimetric detection (Fig. 5). 1 – target-induced aggregation: The interaction of the nanoparticle with the pesticide causes



Scheme 1. Chemistry that accounts for the inhibition of AChE by organophosphates

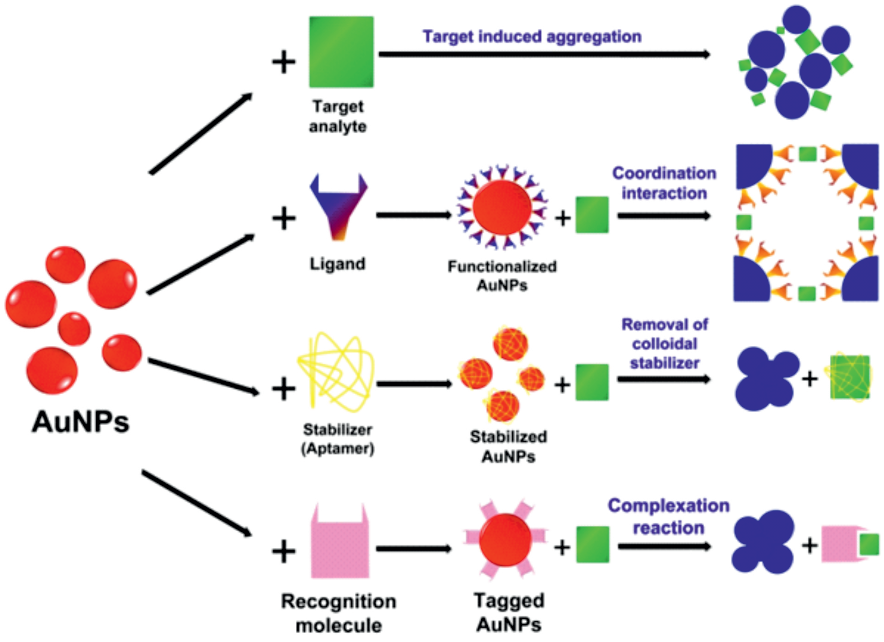


Fig. 5. Possible strategies of aggregation in nanoparticles by target analyte

aggregation as per the above-mentioned principle; 2 – coordination interaction mediated aggregation: depending on the target molecule, the surface of the nanoparticle can be functionalized to actively target the analyte, and this receptor-ligand type of binding causes the color change; 3 – colloidal stabilizer mediated aggregation. The stabilizer of the nanoparticle can be designed in such a way as to bind to the target analyte, and the removal of stabilizer molecules such as aptamer for the nanoparticle can lead to aggregation; 4 – complexation reaction: A recognition molecule complementary to the target analyte can be fabricated and tagged onto the nanoparticle, which will be removed from the nanoparticle after binding to the analyte, causing aggregation.

Research evidence of colorimetric detection

As already stated, gold and silver nanoparticles are widely used metal nanoparticles for pesticide residue detection. Li *et al*. (2011) developed a colorimetric probe using surface-modified gold nanoparticles (AuNP) to visualize the organophosphate group of pesticides. The group utilized citrate-coated AuNP to detect methamidophos residues in the vegetable sample. Detection was monitored using an assay based on the principle of catalysis hydrolysis of acetylcholinesterase. The visual color change from wine red to purple was noted upon the addition of AuNP to the vegetable sample denoting the presence of methamidophos residues. In order to further confirm the specific detection, an interference study was conducted and showed no obvious interference of the usual substances like vitamin B_1, B_2, C, Mg^{2+}, Zn^{2+}, etc. The detection limit of the developed probe was found to be $1.40\ ng \cdot ml^{-1}$. Thus, the probe served as a rapid onsite detection of pesticidal residues.

Surface-modified gold nanoparticle with 2-mercapto-6-nitrobenzothiazole (AuNP-MNBT) was developed by Wang *et al*. (2018). Extracts of tomatoes and cherries were chosen as the sample. The presence of deltamethrin was confirmed by the color change. The mechanism underlying this process is the aggregation due to the core-shell structure formation. The AuNP-MNBT takes the core position, and the deltamethrin forms a layer around the core leading to core-shell formation. Thus, the particles accumulate, and a visual color change can be noted. The detection limit was recorded as 0.25 μM. This method can provide rapid detection by not utilizing any sophisticated equipment. Sun *et al*. (2011) developed a colorimetric sensor based on AuNP-coated lipoic acid. Assay analysis based on the principle of catalytic hydrolysis of acetylcholinesterase was carried out in a sample extract collected from apples. The prepared probe, when it came in contact with the organophosphate residues in the apple extract, showed color change providing an onsite detection with the limit of 4.52×10^4 PM. Besides gold, silver nanoparticles (AgNPs) also change color when aggregated. Developing this fact, Xiong and Li (2008) synthesized AgNPs and modified them with p-sulfonatocalix[n]arene through one-pot synthesis to the detection of optunal. The detection limit was found to be 10^{-7} M. To compare the results and to study the sensitivity, the obtained result was compared with the HPLC results. Both results were comparatively the same, showing that surface-modified AgNP can serve as a rapid colorimetric assay similar to sophisticated instruments. Besides AuNP and AgNP, cerium oxide nanoparticle is another metal nanoparticle that is being widely used in colorimetric detection. Zhang *et al.* (2016) developed cerium oxide nanoparticles coated with polyacrylic acid. The principle was based on the catalytic oxidation activity. The particle, upon incubation with organophosphates such as dichlorvos and methyl-paraoxon, showed an increase in the intensity of the blue color. The color change and the chemistry behind this were explained by the action of acetylcholinesterase. The organophosphates can readily form a covalent bond with the active site of acetylcholinesterase, thus inhibiting its activity. Acetylcholinesterase usually acts as a catalyst to convert acetylthiocholine to thiocholine. Here, the prepared particle acted as an oxidase mimic. Inhibiting the action of acetylcholinesterase decreases the production of thiocholine, thus increasing the production of tetramethylbenzidine, which was used as a substrate. This increased production of tetramethylbenzidine accounts for the increased color intensity. The whole experiment was conducted at room temperature showing that the assay can be carried out as an onsite detection technique (Zhang *et al*. 2016). Further experiments conducted in this field have been summarized in Table 8.

Conclusions and future perspectives

Due to the growing number of harmful pollutants in the environment, there is an increasing need for alternative agents and detection tools that are rapid, portable, and inexpensive. There is a growing interest in nanobased pesticidal applications. Nanoparticles are being actively employed as carrier moieties to deliver pesticidal agents to appropriate sites, enrich their properties, as well as degrade and remove the residues in the sample after treatment. Nanobased materials are also widely used in detection techniques. Conventional detection techniques already exist which are rapid but require specialized technicians and are expensive. The use of nanosensors in the field provides rapid, accurate results within seconds. This can be achieved by colorimetric nanosensors. Without using expensive

Table 8. Compilation of studies that developed colorimetric nanosensors for the detection of pesticides

S. No	Nanoparticle	Surface modification	Synthesis method	Analyte	Detection matrix	Observation	Detection limit	Ref.
1.	AuNP	lanthanum (La3+)	turkevitch method and stirring for conjugation	methyl parathion	water and soil sample	color change from red to blue	0.1 nM	(Wang *et al.* 2014)
2.	AuNP	melamine	turkevitch method	pymetrozine	water, apple juice, and tea	color change from red to blue	80–10 nM	(Kang *et al.* 2018)
3.	AuNP	OBA- aptamer	turkevitch method	omethoate	real soil samples	color change from red to blue	0.1 μmol · l^{-1}	(Liu *et al.* 2018)
4.	AgNP	pyrimidine nitrogen and sulfur moieties	–	diazinon	apple, grapes, beans, and potato	color change from yellow to a pinkish-red and redshift of LSPR absorption band in UV-Vis region	7 ng · ml^{-1}	(Shrivas *et al.* 2019)
5.	AgNP	–	green synthesis using clove extract	vinclozolin	real water samples	color changes from yellow to dark brown	21 nM	(Hussain *et al.* 2019)
6.	AgNP	L-cysteine	green synthesis using Diospyros blancoi leaf extract	cypermethrin	stocks of pesticide solutions	color change from brownish yellow to clear and peak absorbance dropped to 0.17 from 1.15	–	(Kodir *et al.* 2016)
7.	Copper nano-particles	cetyltrimethyl ammonium bromide	wet chemical reduction method	dithiocarbamate ziram, zineb, and maneb	environment and juice samples	color change from reddish wine to yellow	97.9–489.3 ng · ml^{-1}, 8.8–44.1 ng · ml^{-1} and 8.4–42.4 ng · ml^{-1} for ziram, zineb and maneb	(Ghoto *et al.* 2019a)
8.	Copper nano-particles	tween 80	wet chemical reduction method	thiram	water sample	color change from dark brown to olive green and colorless	0.17 μM	(Anh *et al.* 2021)
9.	Cerium dioxide nanoparticles	–	ZIF-8 directed templating	organophosphorus pesticides and oxytetracycline	vegetable sample	color change from colorless to blue	7.6 ng · ml^{-1}	(Chen *et al.* 2020)
10.	Cerium dioxide nanoparticles	polymer	–	dichlorvos	food sample	color change from colorless to blue	0.024 μg · l^{-1}	(Wang *et al.* 2016)

tools an immediate color change renders a visual result. The results are obtained onsite instead of conducting a test in the laboratory. Besides pesticidal applications, nanotechnology can be used in various fields of agriculture like crop production, nanoformulations of agrochemicals, storage of crops, food packaging, etc. Hence, the future of agriculture depends on nanotechnology. However, an equal concern must be dedicated to the toxicological aspects of nanoparticles in order to create a sustainable environment for the usage of nanobased products on a large scale. To overcome the exposure of nanoparticles and avoid their adverse effects, a safer working environment and proper personal protective equipment (PPE) must be designed. The toxic concentration of a specific product also has to be studied in detail before performing the experiments. Considering nanosafety, which is a comprehensive term, the specific objectives of research for the study with nanoparticles needs to be well understood to attain effective usage of resources. In this way, nanoscience can be applied on a large scale to focus on the betterment of humankind.

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