


REVIEW

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Conventional agrochemicals towards nano-biopesticides: an overview on recent advances

Danial Abdollahdokht¹, Yunhao Gao², Sanaz Faramarz³, Alireza Poustforoosh⁴, Mojtaba Abbasi¹, Gholamreza Asadikaram¹ and Mohammad Hadi Nematollahi^{5*} 

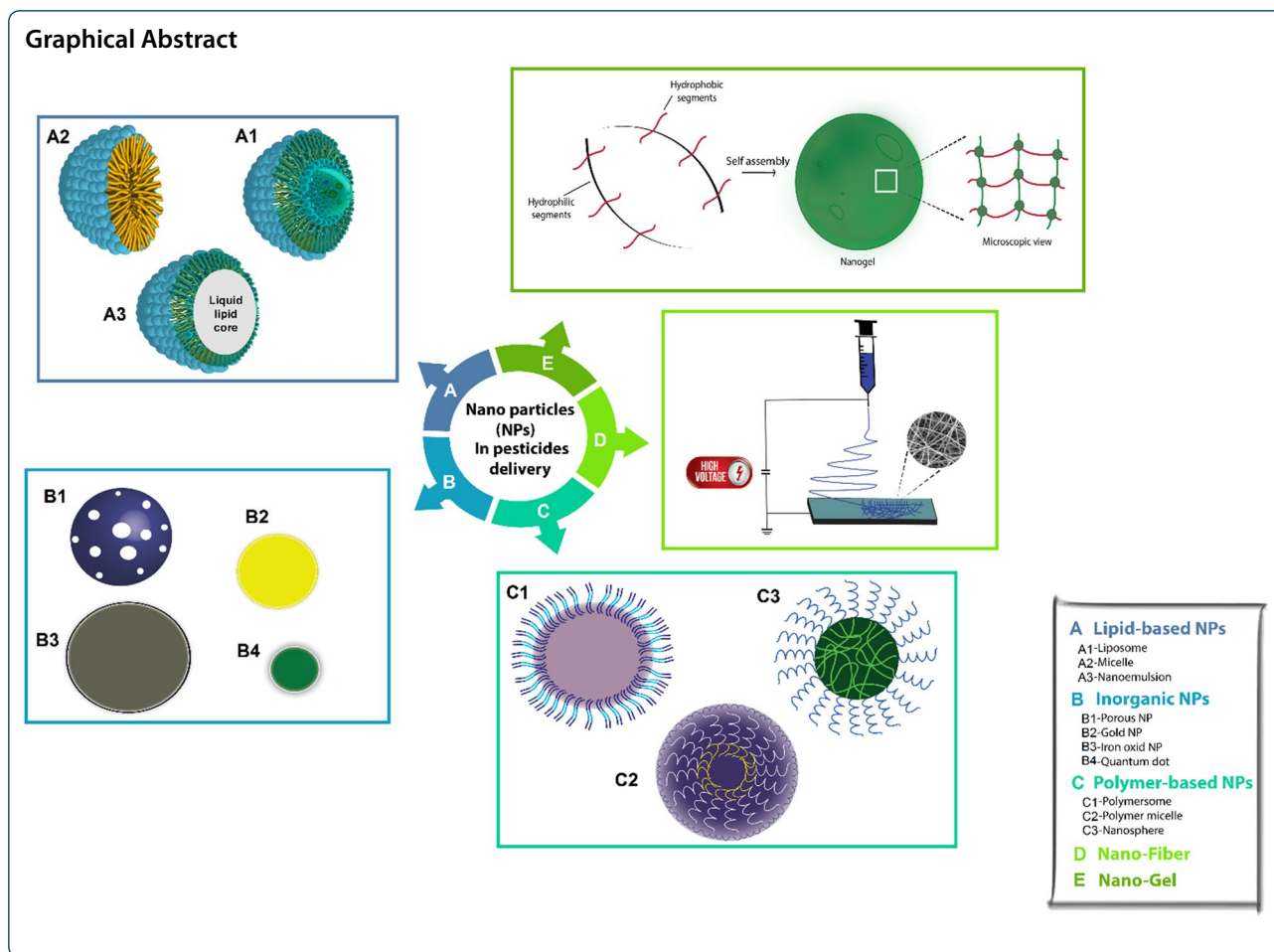
Abstract

Pesticides are classified into several groups based on their structure, including fungicides, insecticides, herbicides, bactericides, and rodenticides. Pesticides are toxic to both humans and pests. For pest control, a very small amount of pesticides reach their target pests. Therefore, nearly all pesticides move through the environment and exert adverse effects on beneficial biota and public health. These chemicals pollute the water, soil, and atmosphere of the ecosystem. Agricultural workers in greenhouses and open fields, exterminators of house pests, and workers in the pesticide industry are occupationally exposed to pesticides. Pesticide exposure in the general population primarily happens through the consumption of food and water contaminated with pesticide residues; however, substantial exposure can also occur outside or inside the house. Currently, intelligent, responsive, biodegradable, and biocompatible materials have attracted considerable interest for the formulation of green, safe, and efficient pesticides. It was indicated that utilizing nanotechnology to design and prepare targeted pesticides with an environmentally responsive controlled release via chemical modifications and compounds offers great potential for creating new formulations. Furthermore, biopesticides include microbial pesticides, which are naturally happening biochemical pesticides. In addition, pesticidal substances generated by plants with added genetic materials, i.e., plant-incorporated protectants (PIPs), have emerged. Based on the foregoing evidence, various types of pesticides are summarized in this review for the first time. Here, new pesticides including nano-pesticides and biopesticides are discussed while focusing on the most recent findings on targeted and safe nano-formulated biopesticides and nano-pesticides.

Keywords: Pesticide delivery, Environment, Pollution, Targeted delivery, Nano-pesticide, Biopesticide

*Correspondence: mh.nematollahi@yahoo.com

⁵ Herbal and Traditional Medicines Research Center, School of Pharmacy, Kerman University of Medical Sciences, Kerman, Iran
Full list of author information is available at the end of the article



Introduction

Pesticides are chemicals that can be used to control pests and prevent plant diseases. Organophosphates, chlorinated hydrocarbons, carbamates, and carbamide derivatives are the most common active ingredients (AIs) in these substances [1]. These compounds are commonly used in veterinary medicine, agriculture, and health. They can harm humans and animals via skin absorption, inhalation, and dietary intake, as well as contaminating the environment [2]. Improper use of pesticides in agriculture leads to changes in the level of antioxidant and oxidant enzymes in the human body, and thus results in the development of diseases caused by oxidative stress [2–5].

Traditional pesticide formulations have a variety of limitations, including high organic solvent content, dust drift, low dispersibility, the ability to last in the soil for an extended period, and other similar drawbacks. Due to these limitations, the majority of pesticides are released into the air, with only 1% remaining on surfaces. This inefficiency leads to severe pollution of the

environment. Therefore, pesticide waste, manufacturing costs, and environmental emissions should all be minimized in addition to extending the period in which pesticides are active on crops [6].

Some pest-control researchers are concentrating their efforts on creating non-toxic alternatives to synthetic chemicals for pest and disease control. One of these alternative methods is the use of biopesticides [7]. Biopesticides, also known as "biological pesticides", are used to control plant pests as an alternative for chemical pesticides [8–10]. The following are the key advantages of biopesticides as natural compounds over traditional pesticides: (i) lower toxicity; (ii) exclusively affecting the pest in question and closely related species; (iii) high potency in small doses; (iv) rapid decomposition; and (v) low exposition with almost no emission issues [11].

Another topic of debate regarding biopesticides is the use of nanotechnology, which has given new properties to old materials [8, 10, 12–14]. Nano-materials have significant applications in fields such as pharmacology

and biology, because their physical and chemical properties differ from those of macro-materials. Nano-materials are distinguished by their surface properties, small scale, and quantum size effects. The use of nano-materials and the developments in pesticide formulations have increased significantly in recent years [13]. Nano-carrier materials also prevent AIs from degrading and allow for a controlled release [15].

Pesticides

Types of pesticides

The purpose of pesticide production is to remove pests and weeds. Farmers use pesticides to protect and enhance the quality of their crops [16]. As shown in Fig. 1, pesticides are divided into five groups based on their structure: fungicides, herbicides, insecticides, rodenticides, and bactericides [17].

Fungicides

Fungicides are pesticides that protect plants against fungal diseases by killing or incapacitating fungi. From

1940 to 1970, fungicides with new chemical structures were introduced (Fig. 2), including dithiocarbamates and phthalimides (organic chemicals), which were more active, less phytotoxic, and easier to prepare than the previously known inorganic fungicides. The fungicides mancozeb and chlorothalonil, known as protective fungicides, were also made during this period. Systemic methods as well as foliar and seed treatment were developed in this decade. Experiments were switched from in vitro to in vivo, and new products were tested in vivo [18].

Fungicides have evolved since the 1970s. During this period, more attention has been paid to the environment and human health, and in 1993, the European Union passed a law, according to which the produced fungicides had to be certified safe by the Union. A list of these fungicides is given in Fig. 3 [19].

During 2005–2021, attempts were made to produce fungicides that reduce the negative effects of artificial factors such as waste, resistance, and environmental pollution. In this regard, fungicides that was made may be selective effective, biodegradable, and less

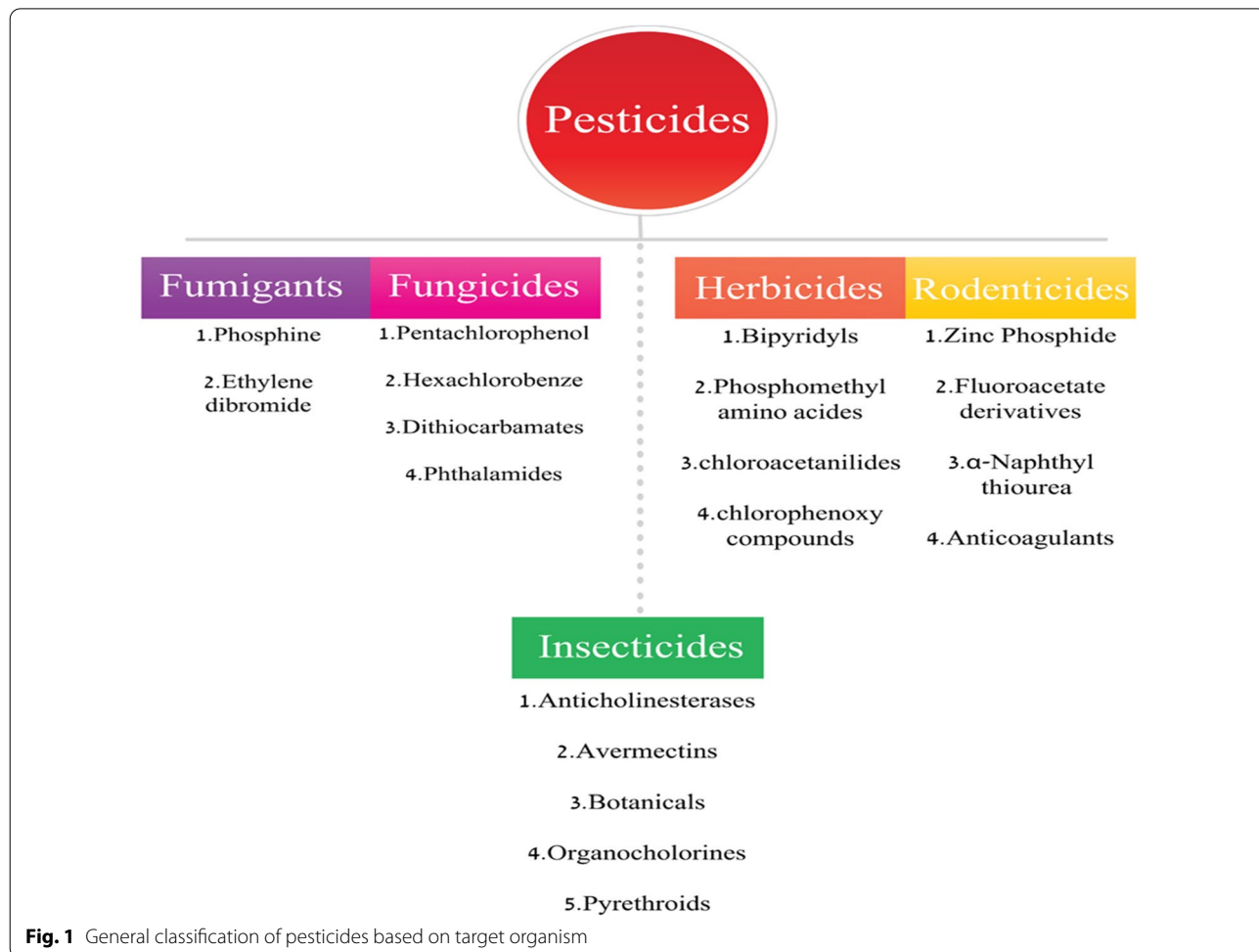


Fig. 1 General classification of pesticides based on target organism

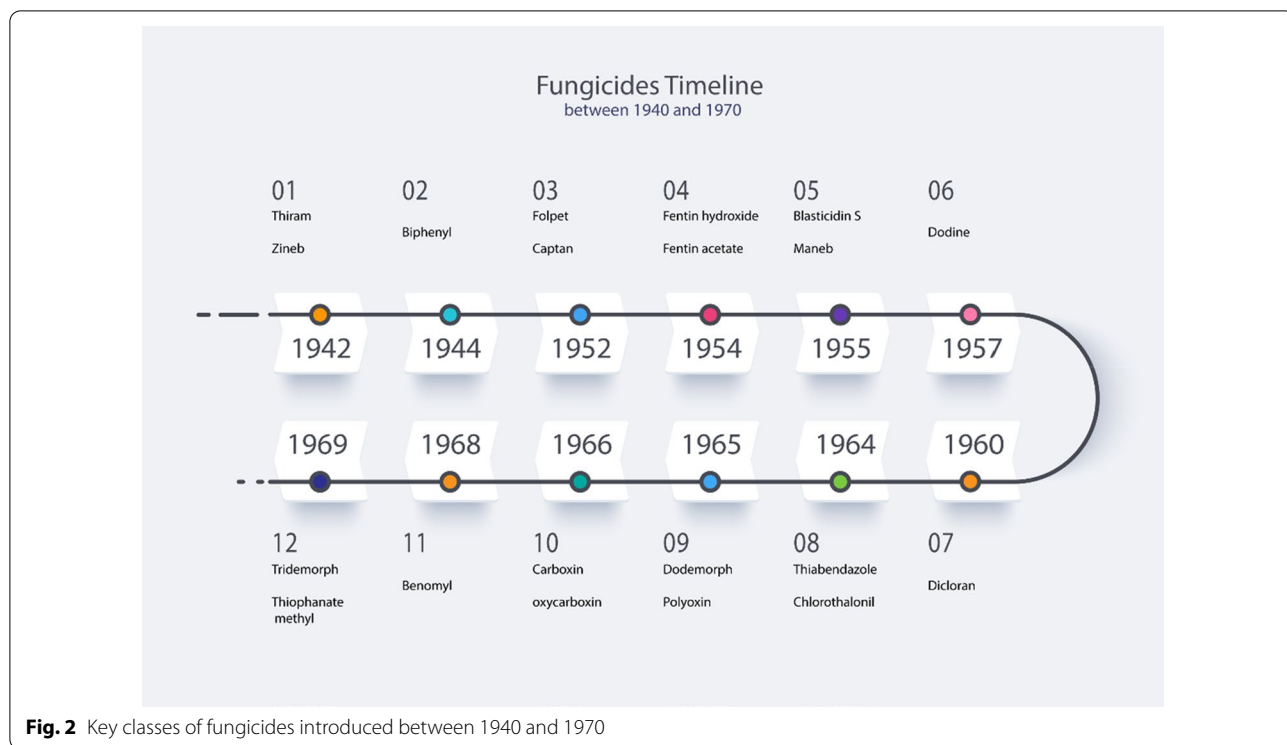


Fig. 2 Key classes of fungicides introduced between 1940 and 1970

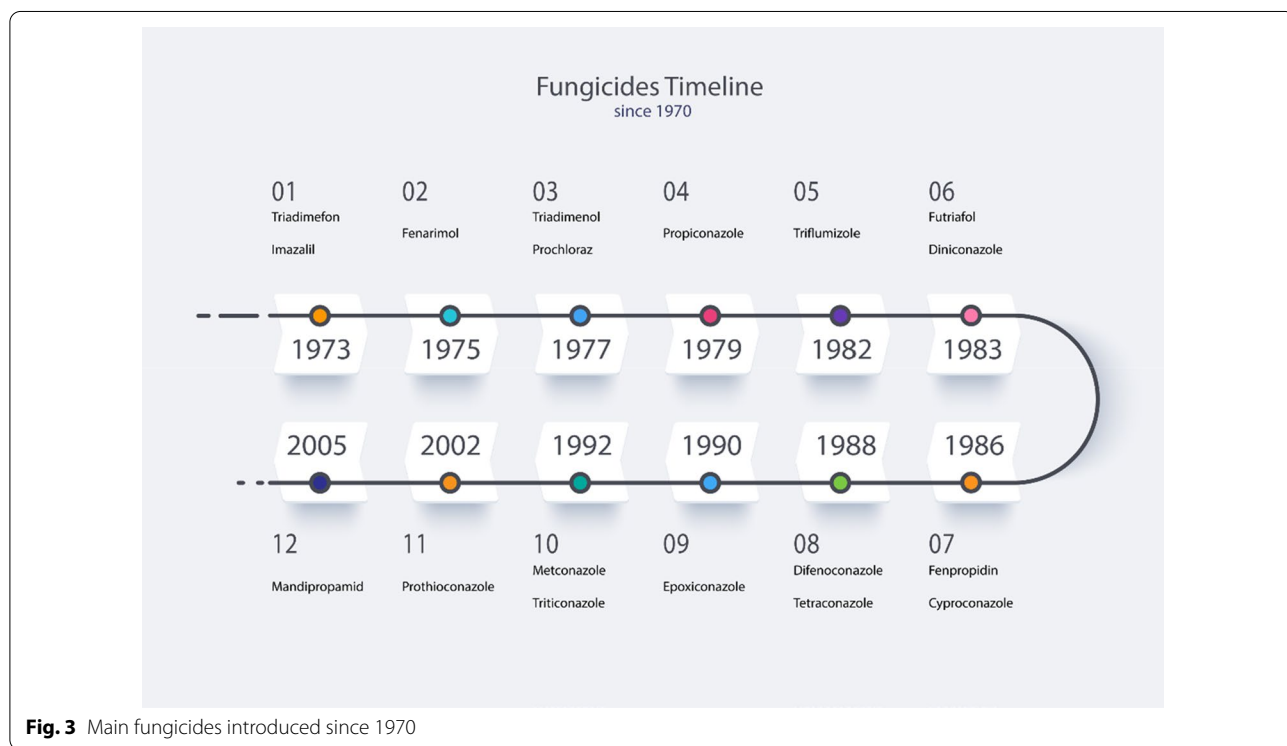


Fig. 3 Main fungicides introduced since 1970

environmentally toxic [20]. Several classes of fungicides introduced in this period. For instance, multi-site inorganic salts, organic compounds with protectant action,

and single-site systemic fungicides with curative activity [21]. However, the latest discovery is succinate dehydrogenase inhibitor (SDHI) fungicides. SDHI are active

components that used in fungicides to control certain fungi. SDHIs inhibit their growth by blocking the enzyme involved in cellular respiration [22]. In the next few years, biopesticides will probably completely replace current pesticides, because they are completely harmless to the environment and humans [23]. A list of these fungicides is given in Fig. 4.

Herbicides

Herbicides are used to eliminate weeds. A weed is a plant that interferes with the growth of crop plants and causes significant problems for farmers. In the early days when humans discovered agriculture (10,000 BC), weeds were removed by hand. Over time, in about 6000 BC, primary hand tools were used to remove weeds. In 1000 BC, oxen and horses that pulled harrows were employed for this purpose. Since 1920, with the development of the agricultural industry, cultivators have been used, and in 1930 and 1947, biological and chemical herbicides were developed, respectively [24]. A mode of action is a functional or anatomical change that occurs when a living organism is exposed to a substance. According to some articles, the mode of action is limited to the cellular level. A mechanism of action, on the other hand, explains such changes at the molecular level [25]. Herbicides are divided into the following groups based on their mechanism of action:

Acetyl-coenzyme A carboxylase (ACCase) inhibitors These herbicides inhibit the activity of the enzyme ACCase and are used to control weeds during the culti-

vation of broadleaf plants [26]. Aryloxyphenoxypropionates (FOP) [27], cyclohexanedione (DIM) [28], and phenyl pyrazoline (DEN) are a few examples of these herbicides [29].

Acetolactate synthase (ALS) inhibitors ALS is an enzyme that is involved in the synthesis of branched-chain amino acids (leucine, isoleucine, and valine) and the suppression of this enzyme causes the plant to wither and eventually die [26].

Root growth inhibitors These herbicides inhibit cell division, thus preventing root growth and development. The purpose of these herbicides is to block the polymerization of microtubules, which disrupts the process of chromosome segregation during mitotic division, resulting in cell death [26].

Plant growth regulators This group includes hormonal herbicides (synthetic auxins), which are used to protect wheat and corn against broadleaf grasses. This group of herbicides targets the ATP protein pump. By activating this pump, the metabolism of nucleic acids and the integrity of the cell wall are compromised. These herbicides are also called indole acetic acid (IAA) imitators [26].

Photosynthesis/photosystem II (PSII) inhibitors The target of these herbicides is the photosynthetic pathways (especially the photosystem II pathway). As a result of the loss of chlorophyll and other pigments such as carotenoids

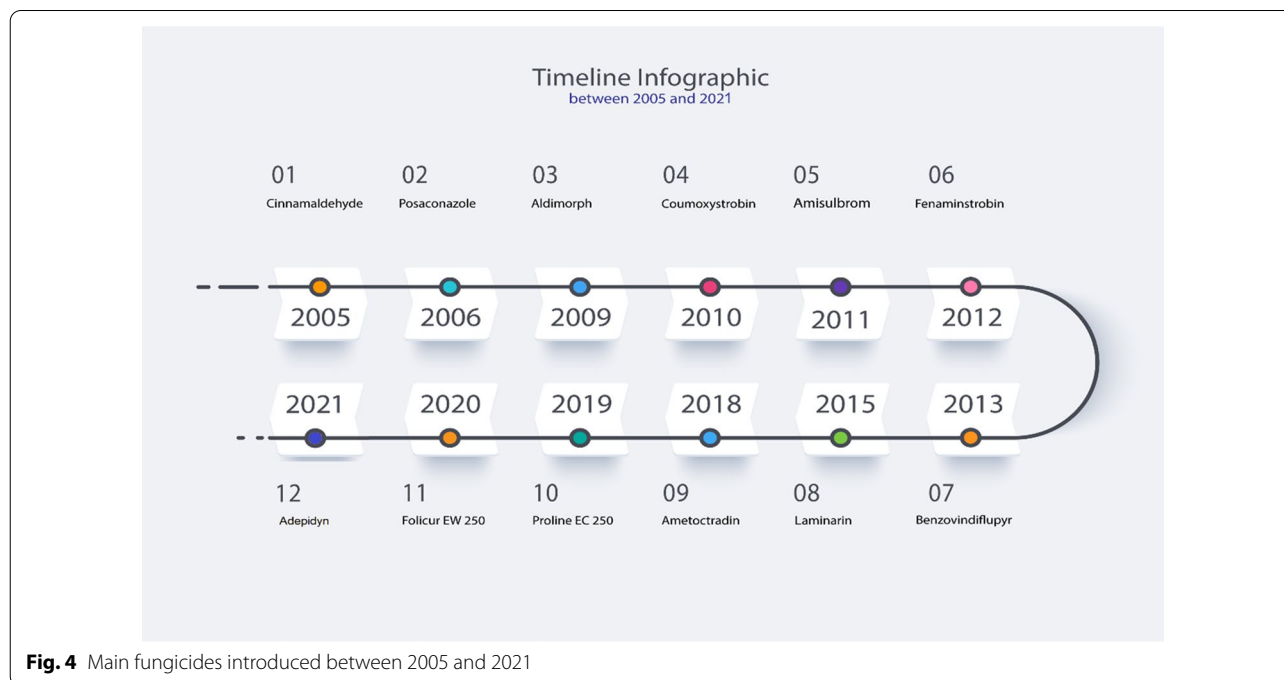


Fig. 4 Main fungicides introduced between 2005 and 2021

from the cell membrane, the production of NADPH₂ and ATP, which are essential for plant growth, is disrupted, eventually leading to plant death [26].

Shoot-growth inhibitors These herbicides are applied to the soil prior to the emergence of the weeds. The functional site of these herbicides is on very long-chain fatty acids (VLCFA) [26].

Aromatic amino acid inhibitors This group of herbicides inhibits the synthesis of amino acids. This action is specific to glyphosate. These herbicides destroy any plant they come in contact with, although they are only licensed for corn, cotton, canola, and soybeans. Glyphosate inhibits the enzyme essential for the production of 5-enolpyruvylshikimate 3-phosphate (EPSP), resulting in a decrease in aromatic amino acids, i.e., tryptophan, tyrosine, and phenylalanine, and eventually cell death [26].

Glutamine synthetase inhibitors These herbicides suppress the activity of glutamine synthetase, which is involved in the conversion of glutamate and ammonia to glutamine, thus increasing the level of ammonia and lowering pH on both sides of the cell membrane. This activity disrupts various cellular functions, especially the uncoupling of photophosphorylation [26]. One example of these herbicides is glufosinate [30].

Pigment synthesis inhibitors These herbicides destroy chlorophyll, which is essential for photosynthesis in plants. As a result, they cause the plant tissues to turn white, which eventually causes the weeds to die [26]. Some examples include isoxazolidinone and isoxazole [31].

Protoporphyrinogen oxidase (PPO) inhibitors These herbicides damage cell membranes by inhibiting the enzyme PPO. This enzyme is implicated in chlorophyll and heme biosynthesis. Lipid peroxidation occurs following the inhibition of this enzyme, which destroys cell membranes and leads to plant death [26].

Insecticides

Insecticides are substances used to kill insects and are widely used in medicine, agriculture, and industry. Before 1900, only a few chemicals were used as pesticides; however, in the early 1940s, as the Second World War raged on, the insecticide DDT was produced. These insecticides were game-changers. Since then, farmers have been using an ever-expanding list of insecticides to protect their crops. Their use has undoubtedly resulted in substantial increases in agricultural output and a decrease in disease transmission, but it has also resulted in major challenges, including health concerns for pesticide consumers and

the general public, the rise of pesticide resistance, and environmental issues [32].

Insecticides mainly attack three targets in the nervous system: acetylcholinesterase, which is a vital enzyme in nerve impulse transmission (organophosphates and carbamates), voltage-gated sodium channels through the nerve membrane (pyrethroids and DDT), and the acetylcholine receptor (neonicotinoids) [33]. Selective insecticides, such as juvenile hormone mimics (fenoxycarb and pyriproxyfen) [34], ecdysone agonists, and chitin synthesis inhibitors (diflubenzuron), impede insect reproduction and growth by acting on insect-specific targets [35]. Azadirachtin, a feeding deterrent and insect growth regulator, derived from the Indian neem tree, suppresses fecundity, pupation, molting, and adult emergence [36]. Modern insecticides used in pest control include imidacloprid, acetamiprid, and thiamethoxam, which selectively act on the insect's nicotinic acetylcholine receptor (neonicotinoids) [37]. Avermectins are microbial insecticides that target GABA-gated chloride channels, while the ryanodine receptor is targeted by diamide insecticides [38]. Spinosyns are a new generation of insecticides derived from actinomycetes, which exhibit high specificity and low mammalian toxicity while also being environmentally friendly [39].

The destructive effects of pesticides on humans and the environment

Pesticides have negative effects on both human health and the environment [40]. Pesticide poisoning causes around 1 million deaths and chronic diseases worldwide per year [41]. Production workers, formulators, sprayers, mixers, loaders, and agricultural field workers are among the high-risk groups exposed to pesticides. Pesticide compounds can pollute tissues of nearly any living organism on the planet, as well as air, oceans, the fish that live in the oceans, and even the birds that consume the fish [42]. Some pesticides have negative health effects through mimicking or antagonizing natural hormones in the body, and it has been suggested that long-term, low-dose exposure is progressively linked to hormone disruption, immune suppression, reduced intelligence, cancer, and reproductive defects [43]. Some pesticides (carbamates, organophosphates, organochlorines, and pyrethroids) also have neurological effects and are linked to diseases such as Alzheimer's and Parkinson's [44].

Safe target delivery of pesticides

In recent years, the limitations of conventional pesticide formulations have prompted new research focusing on carefully controlled release. On farmlands, controlled pesticide release systems are used to specifically control a target pest by choosing a suitable and applicable output

path. Using a smart design that delays and monitors pesticide release, this strategy aims to reduce the demand for pesticides in crops, allowing for more efficient pesticide application over time [45].

New pesticides

According to the World Health Organization (WHO), pesticides are a major threat to the environment and humans [46]. For this reason, new pesticides with novel natural and synthetic components are developed, which are less toxic, specific to a target pest, effective in small quantities, and decompose more quickly than conventional pesticides [47]. New pesticides are divided into two categories: biopesticides and nano-pesticides.

Biopesticides

Biopesticides are pest-control agents made from microorganisms, plants, and animals. Synthetic pesticides continue to strongly protect agricultural products, but their long-term use has negative effects such as carcinogenicity, long-term stability in the environment, and other similar consequences. To address these issues, the production of new pesticides became necessary [48]. Biopesticides were considered, since they are safe and eco-friendly.

Fungal spores were first used as a biopesticide in the late 1800s to control insect pests. In 1835, Agostine Bassi demonstrated that spores of the white muscardine fungus (*Beauveria bassiana*) could protect silkworms from

diseases. This was one of the first documented cases of biopesticide use. Since then, the application of biopesticides has been continuous throughout modern agricultural history, although it has remained minimal compared to conventional crop protection. The primary distinction between biopesticides and synthetic pesticides is their mode of action. While most synthetic insecticides, if not all, are neurotoxic to pests, many biopesticides have other modes of action, such as anti-feeding, mating disturbance, desiccation, and suffocation. Biochemical, microbial, and plant-incorporated protectants (PIPs) are the three types of biopesticides identified by the US Environmental Protection Agency (EPA) (Fig. 5). Recent reports of the various properties of biopesticides are presented in Table 1 [49].

Microbial pesticides

Microorganisms such as viruses, bacteria, fungi, protozoa, and yeasts are used to produce biopesticides. Microbial pesticides are a more effective alternative to chemical insecticides. Their pathogenicity to the target pest varies depending on the species [67]. The effect of microbial pathogens is induced by the invasion of the pathogen through the skin or the gut of the insect, which results in pathogen multiplication and the death of the host, i.e., the insect. Insecticidal toxins produced by pathogens are critical in their pathogenesis. The majority of toxins produced by microbial pathogens are recognized as peptides, but their structure and toxicity vary considerably.

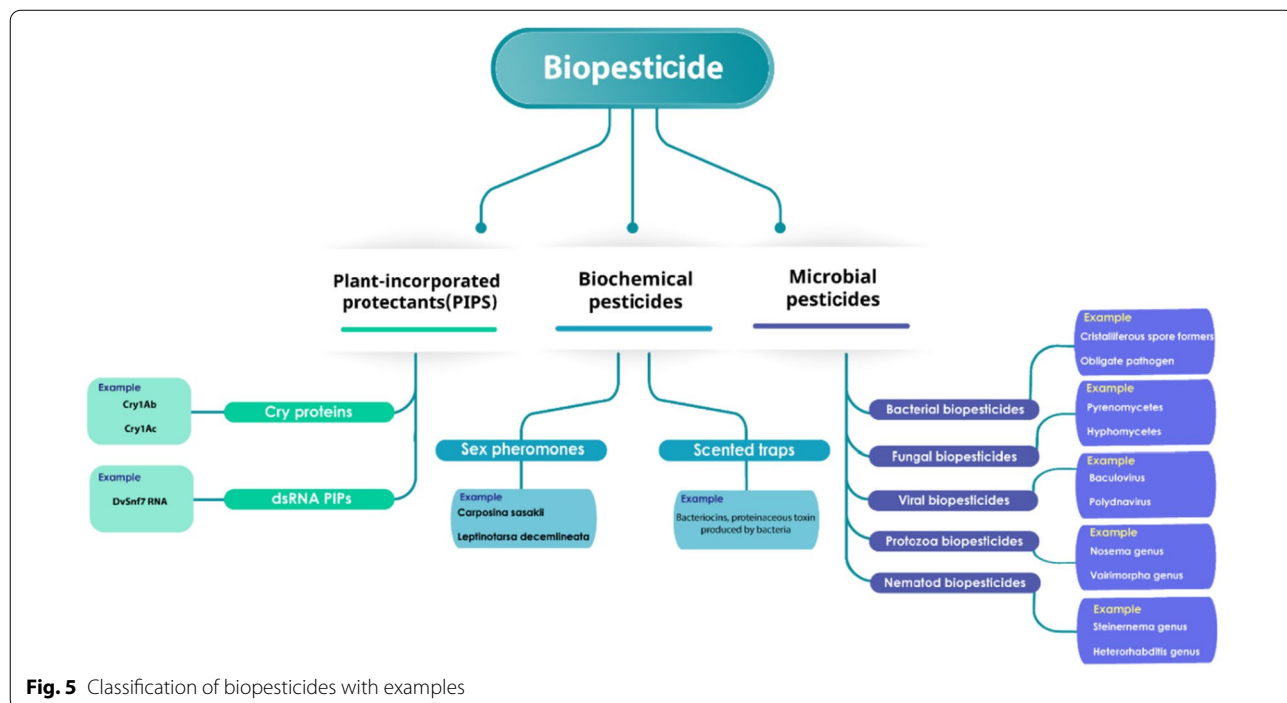


Fig. 5 Classification of biopesticides with examples

Table 1 Recent reports of various substances with biopesticide properties

Biopesticide	Target pest	Action	References
Oxathiapiprolin	<i>Plasmopara obducens</i>	Fungicide	[50]
<i>Beauveria bassiana</i>	Arthropod pests	Fungicide	[51]
<i>Alternaria destruens</i>	<i>L. sinense</i>	Herbicide	[52]
<i>Myrothecium vaerrcaria</i>	Ticks	Insecticide	[53]
<i>Heterorhabditis bacteriophora</i>	<i>Otiorhynchus sulcatus</i>	Insecticide	[54]
<i>Heterorhabditis</i> species	<i>Helicoverpa armigera</i>	Insecticide	[55]
Micro-encapsulated baculoviruses	Insect crop pests	Insecticide	[56]
Hydrolate derived from <i>A. absinthium</i>	<i>Meloidogyne javanica</i>	Nematicide	[57]
Biopesticide methionine	Honey bees	Insecticide	[58]
Spider venom neurotoxin	Hive beetle	Insecticide	[59]
Cordycepin	<i>C. militaris</i>	Fungicide	[60]
Crucifalexins	Fungi	Fungicide	[61]
<i>Chromobacterium</i> sp. Panama	Larval mosquito	Insecticide	[62]
<i>B. pumilus</i> chitinase	<i>R. solani</i> <i>T. harzianum</i>	Fungicide	[63]
Triflumezopyrim	Rice planthoppers	Insecticide	[64]
SK gene	<i>Tribolium castaneum</i>	Insecticide	[65]
D-limonene	Fungi	Fungicide	[66]

Humans and other non-target species can benefit from the effectiveness and safety of the pesticides. These pathogens leave their meals with little or no residues [68]. Microbial pesticides are ecologically safe and remove threats from other natural pests, resulting in increased biodiversity in managed ecosystems. As a result, microbial agents are highly specific against target pests, allowing beneficial insects to thrive in treated crops. This is the reason why, over the last 3 decades [69], microbial insecticides have been introduced as biological control agents. Different pests can be controlled using different microorganisms as the AIs, such as bacteria, fungi, viruses, or protozoa; however, each active ingredient is relatively specific for its target pest. Some fungi, for example, control certain weeds, while others kill particular insects. As another example, *Bacillus thuringiensis* toxin may be more effective against *Aedes aegypti*, while the *sphaericus* strain is effective against a variety of insects, including *Culex quinquefasciatus* [70].

Biochemical pesticides

Biochemical pesticides are substances naturally occurring in the environment, which control pests via a non-toxic mechanism. The mechanism of action of biochemical pesticides is different from that of traditional pesticides. Traditional pesticides directly affect and destroy their target, but biochemical pesticides act indirectly. For example, they disrupt the sexual function of their targets. Natural plant-derived products such as terpenoids,

alkaloids, phenolics, and other secondary chemicals may be used as biopesticides. Pesticidal properties have also been discovered in certain vegetable oils, such as canola oil [71].

PIPs

PIPs are pest-control substances made by plants and the genetic material needed for the plant to make the substance [72]. The majority of pesticides in use are synthetic organic compounds with low molecular weights (LMWs, less than 500 g/mol or 0.5 kDa). These pesticides' environmental and analytical chemistry, as well as their potential effect on human and environmental health, have been thoroughly investigated. While LMW-synthetic pesticides have dominated the market, biopesticides are becoming an increasingly important part of the overall pesticide market [73]. The global market for all biopesticides is currently estimated to be worth \$34 billion, accounting for approximately 6% of the total pesticide market. PIPs are biopesticides that are expressed directly in the tissue of genetically modified (GM) crops to protect them from pests such as insects and viruses. Because of the widespread use of insecticidal PIPs around the world, as well as the recent emergence of new PIPs targeting insect pests, this section focuses on PIPs developed against insects [74]. Insect pests consume PIPs when feeding on the transgenic crop tissue. Cry protein and double-stranded ribonucleic acid (dsRNA) PIPs in the insect gut affect

insect development or cause insect mortality in various ways [75]. Cry protein PIPs interact with specific receptors on epithelial cells in the insect midgut, insert into the cell membrane, and eventually form transmembrane pores, which lead to cell lysis and pest death. There are several types of Cry proteins, each with a specific structure and toxicity that is unique to certain insect orders. Lepidoptera (e.g., the corn borer) is poisoned by Cry1 proteins, while Coleoptera (e.g., the corn rootworm) is poisoned by Cry3 proteins.

Cry proteins were the first-generation insecticidal PIPs. The next-generation dsRNA PIPs have been recently approved. Following ingestion, the dsRNA PIPs in the pest insect are transported into a target cell. dsRNA is cleaved into small interfering RNA molecules (siRNA, 20 nucleotides) within the cell, which guides the insect's endogenous RNA interference (RNAi) machinery to degrade the complementary mRNA. The degradation of the targeted mRNA prevents it from being translated into basic pest insect proteins, causing sublethal effects (e.g., decreased growth) or pest mortality (Fig. 6). The first dsRNA PIP to be approved by the FDA targets the corn rootworm (*Diabrotica virgifera virgifera*) by interfering with the synthesis of the Snf7 protein, which is an important vacuolar sorting protein [76].

Nano-pesticides

Engineered nanoparticles are now being used, or have the potential to be applied, as novel carriers for pesticide delivery. A range of formulation types has been suggested, including nano-emulsions, nano-encapsulations, nano-vesicles, nano-gels, nano-fibers, etc., which can be used to improve the efficacy of existing pesticide AIs or to enhance their environmental safety profiles, or both [77]. The most common nanoparticles are illustrated in Fig. 7.

Nano-emulsion

Nano-emulsion is a biphasic dispersion system formed by mixing surfactants; AIs dissolved in the oil phase and the water phase [78]. The nanometer-sized droplets (~20–200 nm) make this system kinetically stable and give it a transparent or translucent appearance [79, 80]. Nano-emulsion of pesticides is an oil-in-water (O/W) dispersion, which can dissolve poorly water-soluble pesticides into small oil droplets and greatly improve their bioavailability and efficacy [81, 82]. In addition, nano-emulsion significantly reduces the use of organic solvents and surfactants compared to traditional pesticide formulations, and has attracted considerable attention from researchers in recent years [83, 84]. For example, Jiang et al. presented a nano-emulsion system that

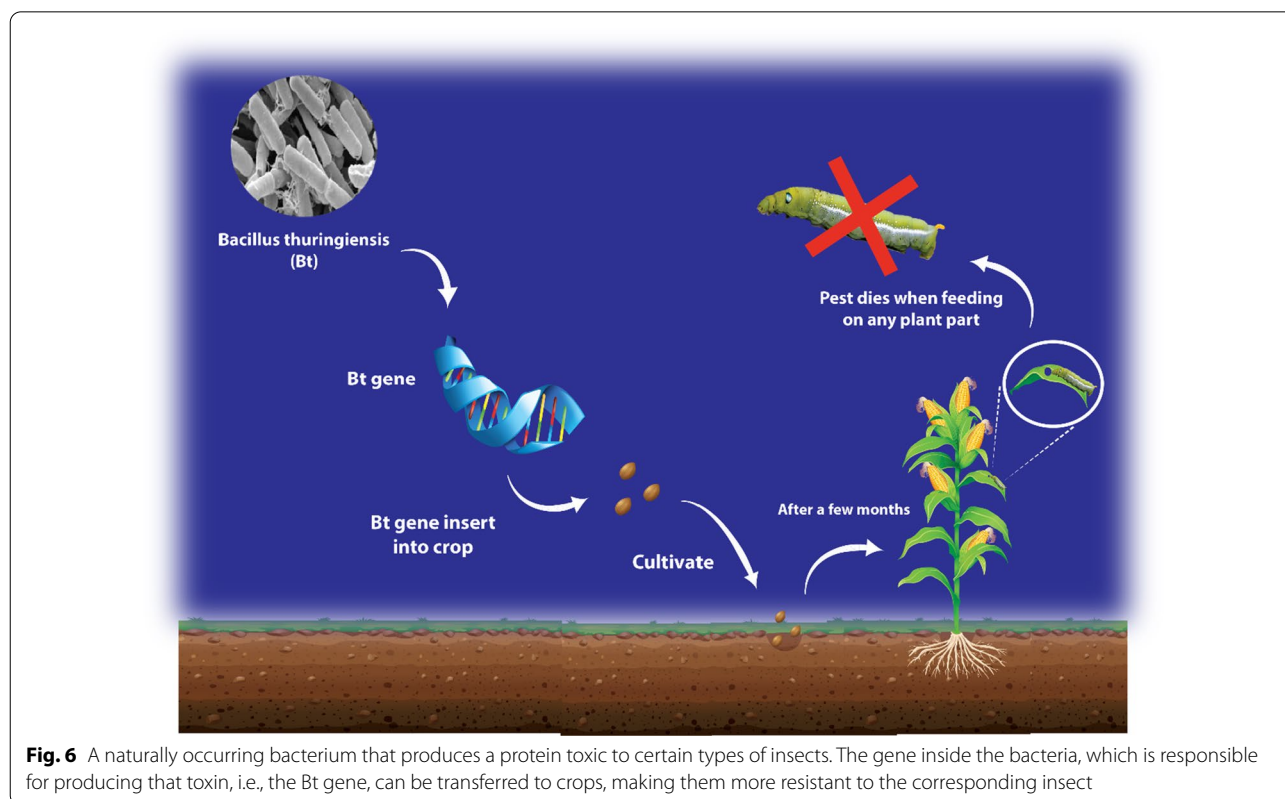
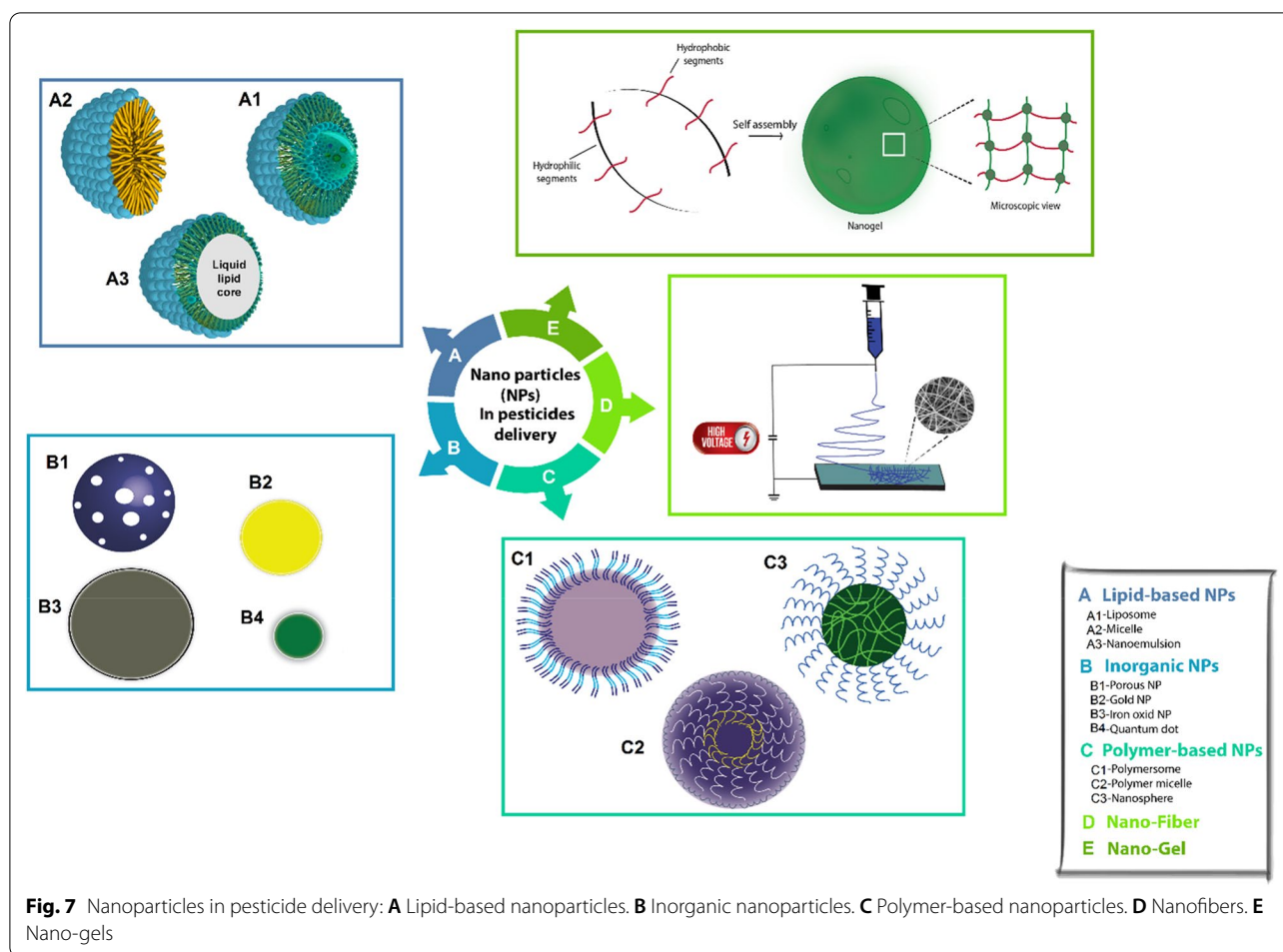


Fig. 6 A naturally occurring bacterium that produces a protein toxic to certain types of insects. The gene inside the bacteria, which is responsible for producing that toxin, i.e., the Bt gene, can be transferred to crops, making them more resistant to the corresponding insect



encompassed environmentally friendly surfactants, esterified vegetable oils, and 41% (w/w) herbicide glyphosate isopropylamine [85]. This nano-emulsion had a small particle size (<200 nm) and lower surface tension than the commercial cationic surfactant system (Roundup®), which would cause the droplets to be deposited uniformly on leaves with lower contact angle and increase the wetting, spreading, and permeation. Visual injury assessment indicated that the nano-emulsion formulations showed significantly lower effective dose 50 (ED₅₀) than Roundup®, suggesting that they exhibited higher biological efficacy. In another study, Feng et al. developed an abamectin (Abm)-loaded nano-emulsion containing 2% Abm, 5% castor oil polyoxyethylene, and 7.5% hydrocarbon solvent, which conformed to the quality indicators of the Food and Agriculture Organization (FAO) [86]. Compared with commercial oil/water emulsions (EW) and microemulsions (ME), the nano-emulsion exhibited various advantages such as a smaller dynamic contact angle on cabbage leaves, higher insecticidal activity, and lower cytotoxicity. Although a nano-emulsion of pesticides with remarkable physical stability can be readily obtained, the

most common approach is high-energy emulsification, and the oil phase and emulsifiers may still be toxic [87, 88]. To overcome these challenges, green nano-emulsions and low-energy methods (e.g., self-emulsification, phase transition, phase inversion temperature methods, etc.) are promising strategies [89, 90]. Du et al. developed a green nano-emulsion of β -cypermethrin using renewable fatty acid methyl ester (methyl laurate) as the oil phase, "green surfactant" alkyl polyglycoside, and the non-ionic surfactant polyoxyethylene 3-lauryl ether (C₁₂E₃) as the mixed surfactant [89]. The nano-emulsion incorporating β -cypermethrin had a nearly monodisperse droplet size distribution (polydispersity index (PDI) < 0.2 Mw/Mn), which indicated excellent wetting and spreading properties on the hydrophobic surface compared with the commercial β -cypermethrin nano-emulsions, suggesting a biocompatible strategy for pesticide delivery.

Nano-encapsulation

Nano-encapsulation of pesticides is a delivery method in which AIs are encapsulated in various nanomaterials and released in a controlled way [91]. Encapsulation by

nanomaterials can protect AIs from premature degradation (e.g., photolysis, hydrolysis, biodegradation, etc.) and unnecessary losses by leaching and volatilization, and it is more effective in practical applications than traditional pesticide formulations [92, 93]. After the rational design, nanomaterials can also enable the encapsulation system to exhibit sustained release behavior to prolong the control period or give it stimulus-responsive release properties to achieve precision control [94–96].

Various nanomaterials including organic materials (e.g., synthetic and natural polymers [97–102], lipids [103, 104], plant-derived nanoparticles [105–107], etc.), and inorganic materials (e.g., silica-, carbon-, calcium-, and clay-based nanoparticles, etc.) have been applied for nano-encapsulation of pesticides [95, 108]. AIs are often encapsulated into nanocarriers via incorporation, electrostatic complexation interactions, or covalent bonding, which will improve uptake, dispersibility, mobility, adhesion, and controlled or target release, thus leading to increased bioavailability and a longer effective lifetime of AIs. Due to their excellent biocompatibility and biodegradability, as well as their abundant functional groups, various forms of polymer-based nano-encapsulated pesticides, including nano-capsules, nano-spheres, nano-micelles, nano-gels, and nano-fibers, have been extensively investigated [100]. Lipid-based nano-encapsulation of pesticides not only can lead to effective encapsulation of hydrophobic or hydrophilic AIs without the need to use organic solvents but also can enhance their penetration and absorption in insect epidermis, resulting in an increased insecticidal activity. More recently, several published articles have demonstrated that the nano-encapsulation of the pesticides based on plant viral nanoparticles (red clover necrotic mosaic virus, tobacco mild green mosaic virus) could increase the mobility or distribution of Abm, a nematocide, within the soil compared to the free Abm, leading to enhanced crop protection against plant-parasitic nematodes in the soil [106]. Although nano-encapsulation of pesticides based on low-cost organic materials has been widely investigated, many challenges still need to be addressed, such as physicochemical instability and acid monomers formed by polymer degradation leading to the decomposition of AIs. Deteriorative reactions occur when polymers are subjected to heat, oxygen, and mechanical stress, and during the useful life of the materials when oxygen and sunlight are the most important degradative agencies. Moreover, degradation may be induced by high-energy radiation, ozone, atmospheric pollutants, mechanical stress, biological action, hydrolysis, and many other influences [109].

Porous inorganic materials such as silica and calcium carbonate are ideal carriers for pesticides because of their large surface area, tunable pore size, high loading

capacity, and good biocompatibility [110–116]. The controlled release properties and anti-photolysis ability of AIs are significantly enhanced after encapsulation in those materials. Some articles have reported that the release behavior of encapsulated AIs could be regulated through controlling the pore structures (e.g., 2D hexagonal channel, 3D open network structure, single large pore, etc.), thus further improving the efficacy in practice [117, 118]. In addition, some inorganic materials with specific shapes or structures have been reported for controlling the encapsulated AI loss. For example, the Wu group reported a high-energy electron beam (HEEB)-modified natural nano-clay that could effectively encapsulate chlorpyrifos and increase its adhesion on crop leaves through the 3D network structure [119]. In another study, Sharma et al. used graphene oxide decorated with copper selenide nanoparticles for the encapsulation of chlorpyrifos, which led to enhanced adhesion to cauliflower leaf due to the resistance of graphene oxide to aqueous runoff, the ability of carbon to bind to the organic surface, and the piercing effect by a sharp sheet on the plant leaf [120].

In general, nano-encapsulated pesticides have two typical release behaviors: (i) sustained (slow) release and (ii) stimuli-responsive release. For the sustained release of nano-encapsulated pesticides, AI concentrations remain within an effective control window against pests for a long period, avoiding frequent pesticide application. To achieve optimal control efficacy, developing stimuli-responsive nano-encapsulated pesticides that can precisely deliver AIs to the target is crucial. So far, various stimuli-responsive (e.g., pH-, enzyme-, temperature-, redox-, light-, ionic strength-, and humidity-responsive) nano-encapsulated pesticides have been reported for promoting the smart release of AIs in response to biotic (plant pathogens, insects, and weeds) or abiotic (temperature, sunlight, drought, soil texture, flooding, and salinity) stimuli, and have been discussed in detail in the previous reviews [94, 121–126]. These controlled release properties indicate the potential of nano-encapsulated pesticides for improving pesticide-use efficiency.

Vesicles such as liposomes and niosomes are versatile drug vehicles that are composed of various phospholipids or non-ionic surfactants [127, 128]. In general, they could carry both lipophilic and hydrophilic drugs anchored into their bilayer or encapsulated in their cavity, respectively. These vesicles have the potential to be used as carriers for pesticide delivery. Some studies have utilized vesicles for pesticide delivery. Kang et al. examined the impact of the nanoform of pyrifluquinazon on the destruction of the green peach aphid, *Myzus persicae*. The nanotype of pyrifluquinazon was constructed using liposomes and was subsequently covered with chitosan to make the unstable

core materials more durable [129]. Moreover, to decrease the toxicity of paraquat, which is a widely used herbicide, photo-responsive and user-friendly vesicles loaded with paraquat were utilized. In this formulation, paraquat could only be released upon UV or sunlight irradiation [130]. Zhang et al. used liposomes to deliver the dsRNA of the P0 gene to the tick *Rhipicephalus haemaphysaloides* and evaluate the anti-tick characteristics of this system. Their findings revealed that P0 dsRNAs are virtually silenced [131]. Some of the studies that focused on nucleic acid delivery using vesicles in the context of crop protection are presented in Table 2.

Nanoparticles

Nanoparticle-based pesticides discussed herein mainly include two types, nanoparticles directly used as pesticides and pesticide nanoparticles. Organic/inorganic nanoparticles are widely investigated as pesticides for the management of insect pests and bacterial and fungal diseases of plants [140]. For example, some articles have reported the insecticidal activity of silica nanoparticles, nickel nanoparticles, and titanium dioxide nanoparticles against weevils (*Sitophilus oryzae*), cattle tick (*Rhipicephalus microplus*, *Hyalomma anatolicum anatolicum*), mosquito (*Anopheles subpictus*, *Culex quinquefasciatus*, and *Culex gelidu*), and *Haemaphysalis bispinosa* [141–143]. Many metalloids (e.g., gold, silver, copper, platinum, etc.) and metal oxides (e.g., silver oxide, zinc oxide, copper oxide, titanium dioxide, etc.) [144–146], as well as nonmetal nanoparticles (e.g., sulfur [147, 148], reduced graphene oxide [149], and chitosan [150, 151], etc.), can be directly used as nano-pesticides owing to their anti-fungal or antibacterial activity.

In recent years, the use of bottom-up or top-down nanotechnology to formulate pesticide AIs as nanocrystalline particles has shown significant promise

for improving the solubility and dispersion of poorly water-soluble pesticides [93]. After nanosizing pesticides, their solubility, permeability, dispersion, penetration, and bioactivity could be greatly improved [152]. Compared with commercial emulsions in water, nanosuspensions showed increased retention on leaf surfaces, improved anti-photolysis, and enhanced bio-availability. In a study by Wang et al., a pyraclostrobin solid nanodispersion with a mean particle size of 20 nm and zeta potential of -29.3 mV was prepared via the self-emulsifying method which exhibited superior wettability, retention, and storage stability [153]. As a result, the solid nanodispersion showed a greater than fourfold increase in fungicidal activity compared to the conventional water dispersible granule. Owing to their ease of large-scale production and wide applicability for almost all poorly water-soluble pesticides, the use of pesticide nanoparticles is emerging as the key innovative strategy for reducing pesticide consumption.

Nano-gels

Nano-gels have gained considerable interest from researchers as nanoscopic drug carriers and are mainly used for delivering bioactive mediators in a time-controlled or site-specific manner. Using van der Waals forces or covalent bonds, hydrophilic polymers are cross-linked and can absorb high volumes of water. Extensive studies have been conducted on nano-gels as the carriers of essential oils and pheromones [154, 155]. The potential of nano-gel systems for the delivery of AIs in a constant, targetable, and controlled manner has been proven.

Pheromones are environmentally friendly and highly specific biological control agents which require to be protected against decomposition in ambient conditions and released slowly. As evidence has revealed, the evaporation of pheromones is significantly decreased in nano-gel carriers compared with the pure AIs. This extends their efficacy up to 33 weeks compared with that of the pure AIs, which is only 3 weeks [155]. As proposed by Brunel et al., the performance of copper-based antifungal treatments can be improved using pure chitosan nano-gels [156].

The Institute of Pesticide Formulation Technology (Gurgaon) has recently presented a permethrin nano-gel formulation (a synthetic pyrethroid pesticide) for enduring the impregnation of this pesticide in clothes. This formulation protects individuals against mosquito bites while working in forest areas [157]. Another research has developed chitosan nano-capsules containing lemon-grass oil in the form of gel for long-lasting anti-mosquito effects [158].

Table 2 Nano-vesicles employed for the delivery of nucleic acids (dsRNA) in the context of crop protection

Nano-vesicle composition	Target species	References
Lipofectamine	<i>Euschistus heros</i>	[132]
Lipofectamine	<i>Spodoptera frugiperda</i>	[133]
GenJe plus	<i>Blattella germanica</i>	[134]
Lipofectamine	<i>Drosophila suzukii</i>	[135]
Lipofectamine (Cellfectin, DMRIE-C, Transfectin also used in one assay)	<i>Drosophila melanogaster</i> , <i>Drosophila sechellia</i> , <i>Drosophila yakuba</i> , <i>Drosophila pseudoobscura</i>	[136]
Cellfectin	<i>Spodoptera frugiperda</i> Sf9 cell line	[137]
Effectene (Qiagen)	<i>Aedes aegypti</i>	[138]
Effectene (Qiagen)	<i>Aedes aegypti</i>	[139]

Electrospun nano-fibers

Electrospinning has recently emerged as useful nanotechnology for the production of nanofiber materials that can be applied in different biomedical areas [159]. Electrospinning technology can scale up and meet industrial manufacturing requirements. Recently, researchers have studied the nano-fibers generated by electrospinning for plant protection purposes. Although they are still in the early stages of agricultural application, electrospun nanofibers have the benefit of evading release bursts, resulting in the facilitation of the field application of essential oils and pheromones [160].

As reported by Hellman et al., pheromones can be efficiently incorporated into nano-fibers composed of cellulose acetate or polyamide (approximately 30 wt.%), and a nearly linear release can be obtained over several weeks [161].

Xiang et al. presented an analogous nanofiber network made of cellulose and poly (lactic acid) nanocrystals. The thiamethoxam-loaded fibers were effective against whitefly over 9 days in a glasshouse experiment at 50% of the proposed dose for the pure AIs [162]. Pesticides were delivered in a localized manner by coating seeds with electrospun cellulose diacetate (CDA) nanofibers containing fluopyram or Abm, and it was found that nanofibrous seed coating could be potentially used as an alternate approach for controlling plant pathogens, such as fungi and nematodes [163]. In another study, the authors produced the thiram/hydroxypropyl- β -cyclodextrin inclusion complex nanofiber (thiram/HP β CD-IC-NF) using electrospinning for efficient delivery of the pesticides [164].

Future perspectives

In a future perspective, the development of nanoparticles that can act as fertilizers and pesticides is necessary. Nanotechnology research in agriculture is still at its initial stages, but is developing quickly. The application of nanostructures as agrochemicals for plant growth and protection has to be investigated due to their novel physicochemical characteristics [165]. With clear nano-bio interactions, transport, and fate in the plant and environment, these nanoparticles have sustained release and resistance for plant protection management [166]. The majority of recently supported projects and future study calls seem to be concentrating on producing safer, environmentally friendly nanomaterials for efficient responses [165]. It is expected that the controlled release of pesticides by nanotechnologies will become essential in the near future to promote cropland fertility and protection with the least effect on the environment and human health

[166]. Future studies should be conducted using natural sources rather than standard media and assess the interaction of nano-agrochemicals with other contaminants. Soon, using nanostructured catalysts will be possible, which will enhance the effectiveness of pesticides and herbicides, allowing the use of more moderate doses. Nanotechnology will also guard the environment obliquely by promoting the use of filters or catalysts, which can decrease the contamination in soil and water [167]. Future opportunities for target delivery of crucial nutrients, pesticides, and genetic materials utilizing nanomaterials will provide new prospects for the agricultural revolution [168, 169]. However, several features of nanoparticles are supposedly dangerous to human health. Therefore, these substances must be more cautiously studied. For example, for dry nano-products, the relative ease with which nanopowders are suspendable in the air might lead to potential human inhalation and subsequent health hazards. On the other hand, suspensions of nanoparticles in water used as a soil drench or foliar sprays pose risks such as the transformation of the particles into ions or aggregation into submicrometer- or micrometer-sized particles [170]. Experts should evaluate the influences of nanoparticles on human health and the environment, and improve the approaches used to assess and control any hazards they may pose. Researchers also need to find renewable methods to fabricate nanoscale materials to be employed in agriculture. Moreover, general approaches should be developed in the pioneer institutes or nations to test laboratory-scale nano-products in actual farm settings for more comprehensive technology validation. Finally, educative and developmental initiatives should be established via study plans to bring the users and experts together in addressing possible customer interests.

Marketed safe and target-delivered pesticides

Since the AIs of traditional pesticides are more toxic, the demand for harmless outcomes with a safer performance propelled the development of bio- and nano-pesticides and the growth of their commercialization [171, 172]. Microbial-based pest-control products are gaining recognition and show an influential growth within the market for pest management technologies (Table 3). Despite the possible advantages of nanotechnology applications in agriculture and the increasing trend of patent applications (mainly from agrochemical companies), nano-based pesticide products have limited market reach [173]. Today, two types of nanomaterials have appeared in nano-enabled industrial pesticides accessible in the market (Table 4).

Table 3 Several marketed microbial pesticides

Pathogen	Marketed product	Reference
Bacteria		
<i>Bacillus thuringiensis</i> var. <i>kurstaki</i> (Bt)	Bactur [®] , Bactospeine [®] , Bioworm [®] , Caterpillar Killer [®] , Dipel [®] , Futura [®] , Javelin [®] , SOKBt [®] , Thuricide [®] , Topside [®] , Tribactur [®] , Worthy Attack [®]	[174]
<i>Bacillus thuringiensis</i> var. <i>israelensis</i> (Bt)	Aquabee [®] , Bactimos [®] , Gnatrol [®] , LarvX [®] , Mosquito Attack [®] , Skeetal [®] , Teknar [®] , Vectobac [®]	[175]
<i>Bacillus thuringiensis</i> var. <i>tenebrinos</i>	Foil [®] , M-One [®] , M-Track [®] , Novardo [®] , Trident [®]	[176]
<i>Bacillus thuringiensis</i> var. <i>aizawai</i>	Certan [®]	[177]
<i>Bacillus popilliae</i> and <i>Bacillus lentimorbus</i>	Doom [®] , Japidemic [®] Milky Spore Disease, Grub Attack [®]	[176]
<i>Bacillus sphaericus</i>	Vectolex CG [®] , Vectolex WDG [®]	[176]
<i>Bacillus subtilis</i> strain 713	Serenade [®]	[178]
<i>Bacillus pumilus</i> strain 2808	Sonata [®]	[178]
Fungi		
<i>Beauveria bassiana</i>	Botanigard [®] , Mycotrol [®] , Naturalis [®]	[179]
<i>Lagenidium giganteum</i>	Laginex [®]	[180]
Protozoa		
<i>Nosema locustae</i>	NOLO Bait [®] , Grasshopper Attack [®]	[175]
Viruses		
<i>Gypsy moth nuclear polyhedrosis</i> (NPV)	Gypchek [®] virus	[181]
<i>Tussock moth</i> NPV	TM Biocontrol-1 [®]	[182]
<i>Pine sawfly</i> NPV	Neochek-S [®]	[183]

Table 4 Marketed nano-pesticides

Nano-pesticides	Marketed product	References
Copper-based nano-pesticides	Kocide [®] 3000 (DuPont) and NANOCU	[184]
Silver-based nano-pesticides	Zeroxee [®] , Silver leaf, Zeromix [®] Zerebra Agro [®] WA-CV-WA13B, WA-AT-WB13R, WA-PR-WB13R	[185]

Conclusion

Population growth, the increasing need for food, and restrictions on areas under cultivation have led to pesticide overuse. As a result of climatic changes and continued global warming, the development of all possible pests on crops, fruits, vegetables, and livestock is possible. Pests are migrating to previously unexplored territories, putting farmers, and plants at risk. Therefore, synthetic pesticides are used by farmers to control these pests. However, the widespread use of pesticides causes harm to a wide variety of nonpathogenic species, and there has also been an increase in pathogens in foods, which leads to further deterioration of soil and water quality.

Nanotechnology is a relatively new method of pesticide delivery and application that is becoming increasingly relevant. The use of nanotechnology and modern

nanomaterials is becoming more prevalent in agriculture and the food industry. Nano-based products have improved stability and efficiency/potency due to changed solubility and adhesion to surfaces, permeability across biological membranes, and targeted and controlled release. As a consequence of these altered properties, using lower pesticide concentrations is now possible. Moreover, biopesticides or natural-based chemicals with significant anti-pest effects are currently being manufactured. The vast majority of natural substances have drawbacks such as a short duration of action and poor stability; therefore, nanotechnological approaches have been applied, either for the development of stable biopesticide nano-formulations with long-term effects or for the “green” synthesis of active inorganic nanomaterials that are antimicrobial, antifungal, and antiparasitic.

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Author details

¹Department of Biochemistry, Afzalipour School of Medicine, Kerman University of Medical Sciences, Kerman, Iran. ²College of Plant Protection, China Agricultural University, Beijing, China. ³Student Research Committee, Kerman University of Medical Sciences, Kerman, Iran. ⁴Chemical Engineering Department, Faculty of Engineering, Shahid Bahonar University of Kerman, Kerman, Iran. ⁵Herbal and Traditional Medicines Research Center, School of Pharmacy, Kerman University of Medical Sciences, Kerman, Iran.

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