The Potential and Green Chemistry Attributes of Biopesticides for Sustainable Agriculture

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Review

Abstract: Chemotherapy has advanced modern agriculture with costly side effects such as the extinction of beneficial species, resistant pest resurgence, environmental pollution, tainted food consumption, and health implications. Attention is now focused on biopesticides as a solution to the abovementioned disadvantages. Additionally, there is a growing need to understand the range and relative effectiveness of biopesticides in controlling pests and promoting sustainable agriculture. The latter is the major driver of the Sustainable Development Goals (SDGs). In comparison to synthetic pesticides, biopesticides offer nearly similar protection against the most notorious pests, except *Albugo candida* (oomycetes), *Ustilago maydis* (fungi), *Phytomonas* spp. (protozoa), *Nacobbus aberrans* (nematode), and *Cyperus rotundus* (weed). This study shows that viruses are more vulnerable to essential oils, nematodes and weeds to natural enemies, herbivorous insects to biochemical insecticides, and plant pathogens to plant-incorporated protectants and microbial pesticides. This work also demonstrates that it is preferable to use plant-derived biopesticides in a field concurrently. Incorporating these findings into large-scale farming via the integrated pest management method would improve the outcome of sustainable agriculture (SA), which connects 11 of the 17 SDGs. Despite their proven efficacy and sustainable attributes, biopesticides have some deficiencies, such as slow action and a short shelf life span, which can be improved by omics, RNA interference, and nano-based technologies. This field of technologies provides relevant prospects for improving existing biopesticides and discovering and developing new bio-controlling agents (BCA).

Keywords: bio-controlling agents; synthetic pesticides; RNA interference; pest management; scope of effectiveness; SDGs

1. Introduction

Biopesticides are green pesticides that adhere to the 12 Green Chemistry Principles (GCPs), as opposed to synthetic pesticides (SPs). The GCPs propose that (1) safe production processes begin with renewable resources and are powered by minimal energy; (2) waste is prevented or reduced, and (3) end products are harmless [1]. Biopesticides adhere to the Green Chemistry criteria by protecting plants, being innocuous to the environment, being safe to non-target organisms, and being effective in small amounts. The minimal energy condition of the GPCs is met through the use of transaminases, reductases, oxidases, and other biocatalysts in a production process [2]. Thus, biopesticides bridge the gap between green technology and sustainable agriculture (SA), a concept understood as large-scale farming that causes less environmental damage while being socially and economically viable. Crop productivity is lowered by pests; hence, they represent the main adversaries of (sustainable) agriculture. These pests include small vertebrates, nematodes, parasitic plants, microorganisms, pathogens, and insects; and act as biotrophs, necrotrophs, and hemibiotrophs [3]. Their impacts result in a decreased nutritional value, interference with
biomass development, the generation of toxic metabolites, decreased market value, unfitness of food for ingestion, decreased yield, destruction of farmlands, widespread epidemics, mass displacement of humans, and economic loss [4–9]. The reversal of these pest-imposed constraints and the quest for food sufficiency and economic growth led to the intensive use of synthetic pesticides (SPs) during the Green Revolution in the 20th century. Notable examples of effective SPs used in this industrial era are dichlorodiphenyltrichloroethane (DDT), carbofuran, aldicarb, fenobucarb (carbamates), atrazine, simazine (triazines), and deltamethrin (pyrethroids), all of which work primarily by neurotoxicity [10]. Despite the proven efficiency of these SPs, they have drawbacks that are antithetical to sustainability. This calls for the use of biopesticides as alternative pesticides.

Biopesticides are now recognised as the future of agriculture. This is because of the many advantages they have over SPs, including but not limited to productivity, health promotion, and environmental promotion. These factors have led to increased efforts in the development of various biopesticides. The number of commercially available biopesticides is estimated to be 1400 worldwide, with similar efficacy to SPs, particularly in the management of insect pests [11]. Despite their advantages, it has been shown that biopesticides are not as effective as their conventional counterparts [12]. The efficiency of biopesticides relies on their multiple mechanisms of action (MoA).

These multiple MoA restrict the development of resistant pests, which are very common in the overuse of SPs. The strategic relevance of biopesticides has made them essential components of pest management (PM) systems. The Integrated PM (IPM) system promotes the adoption of joint solutions that cause the least disruption to agroecosystems and promote the safety of the environment and its receptors, including humans [13]. It is important to mention that biopesticides cover more than 75% of the IPM pyramid and offer the following benefits: they are innocuous to biofertilizers and pollinators; they promote agro-productivity, producing healthy food; and tend to ecosystem conservation, which are all integral parts of SA [14]. Biopesticide-linked SA is connected to 11 of the 17 Sustainable Development Goals, including SDG 1 (closing the global poverty gap), SDG 2 (ending hunger), SDG 3 (improving nutrition), SDG 6 (water supply), SDG 8 (economic engagement), SDG 12 (eliminating waste of produce), SDG 14 (aquaculture farming), and SDG 15 (land farming) [15]. Though biopesticides play significant roles in SDGs, their full potential has yet to be reached. This frontier can be exploited via nanotechnology, omics technology, gene editing and RNA interference (RNAi) technology.

The implication of biopesticides in SDGs and SA is due to their many benefits and advantages. However, it is important to review the varying level of efficacies and scope of the different categories of existing biopesticides, and the best methods for using them to achieve better outcomes. To achieve this goal, we explore current papers on biopesticides to understand their range of scope and effectiveness over 60 plant pests (excluding vertebrate pests), extracted from the plant pathology database. In addition, this study touched on areas in which the limitations of biopesticides can be improved. This review does not attempt to delve into biopesticide control of a particular group of plant pests. The outcome of this work shows that biopesticides offer a broad range of scope over plant pests with microbial pesticides ranking first and the most effective among the different categories of biopesticides. By the same measure, essential oils ranked second, followed by botanicals, then by biochemical pesticides, PIPs and finally natural enemies. However, the effectiveness of biopesticides against Albugo candida (oomycetes), Ustilago maydis (fungi), Phytomonas spp. (protozoa), Nacobbus aberrans (nematode), and Cyperus rotundus (weed) are poorly understood. This study also demonstrates that some biopesticide categories are preferred over others in the removal of pests. Natural enemies, such as biopesticides, can be paired preferably against nematode pests and weeds. Similarly, biochemical pesticides can be paired against insect pests, PIPs against specific phytopathogenic microbes, essential oils against viruses, and microbial pesticides against a wide spectrum of pathogens. These biopesticide categories do not, however, have a monopoly on effectiveness against their
partnered pest group(s). When combining biopesticides to improve efficacy, it is best to apply essential oils with other plant-derived pesticides simultaneously.

2. Biopesticides’ Definition and Suitability as Green Chemistry Agents

Biopesticides are organisms or natural formulations that control or eliminate pests via diverse modes of action (MoA). They cover a wide range of products and formulations, such as predatory and parasitic species, biochemical compounds (and their chemical equivalents), and plant-incorporated protectants (PIPs) [16]. Organic extracts from shells, crustaceans, and algae function as signal molecules to trigger a defensive response in plants and animals, producing long-lasting effects against biotic infections. These substances are known as semiochemicals [17,18]. So, biopesticides include semiochemicals and biochemical analogues. However, if an organic product exerts its toxicity on pest neurological systems, it becomes a poison [19]. Based on this criterion, rotenone, nicotine, sabadilla, and pyrethrins are regarded as poisonous substances even though they are effective botanicals [20]. As green compounds, biopesticides are of great interest to the 12 Green Chemistry Principles (GCPs).

The overarching 12 GCPs were articulated by Anastas, P. and Warner, J. C. in 1998. These principles are the universal gold standard for developing environmentally friendly processes and products (Figure 1). Green Chemistry advocates methods that lessen the use of dangerous substances and minimise the development of toxic intermediates during chemical transformations. The 12 GCPs require that products are made from renewable feedstock (the focus of Principle 7) under the following conditions:

1. Synthetic processes are safe, green, and use minimal energy;
2. The final products are environmentally friendly;
3. Wastes are prevented or minimized.

![Figure 1. A simplified presentation of the production of a green product concerning the 12 Green Chemistry Principles (GCP). GCP 7: Renewable feedstock; GCP 3: Less harmful chemical synthesis; GCP 5: Benign solvent and auxiliary; GCP 6: Energy efficiency; GCP 8: Reduce derivatives; GCP 9: Catalysis; GCP 10: Degradation design; GCP 12: Inherently safer process; GCP 4: Safer chemical design; GCP 10: Design for degradation; GCP 1: Waste prevention; GCP 2: Atom economy; GCP 11: Real-time analysis.](image)

According to Fenibo et al. [21], the first condition is connected to the 3rd, 5th, 6th, 8th, 9th, and 12th GCPs. The second condition is addressed by Principles 4 and 10, while Principles 1, 2, and 11 ensure waste prevention and minimization (condition three). The surest means of securing condition three is to ensure that the starting materials are integrated into the finished product [22]. As a green product, biopesticides are effective at low concentrations, biodegradable, and harmless to non-target biota. The use of reductases, transaminases, oxidases, hydrolases and other biocatalysts not only meets the minimum
energy requirement but also benefits the environment and the economy. In this sense, biopesticides align with green technology and SA. The latter is characterised by the responsible consumption of resources, biodegradability, and productivity [23]. One important outcome of resource consumption in agriculture is the eradication of pests, as shown in Table 1. The conscious attempt to maintain these sustainable attributes implies integrating green chemistry principles into agricultural practices that previously relied on synthetic pesticides (SPs) for pest eradication.

Table 1. Notable examples of plant pests.

| Pests | Hosts | Impact | Reference |
|-------|-------|--------|-----------|
| **Weeds:**  
 Annual: Ambrosia artemisiifolia, Abutilon theophrasti, Chenopodium album (Baconweed), Amaranthus spp. (Pigweeds), Digitaria spp.  
 Biannual: Ailanthus altissima (Tree-of-heaven), Cirsium vulgare (Bull thistle),  
 Perennial: Convolvulus arvensis, Rubus spp. (Blackberries), Smilax spp. (Greenbrier), Phytolacca Americana (Pokeweed), Toxicodendron radicans (Poison Ivy). | Varieties of crops including grains, wheat, rice, maize, beans, chickpeas, potatoes, vegetables, and cotton. | • Reduces sunlight to crops;  
 • Aggressively competes for water and nutrients;  
 • Tends to grow faster than crops and crowd out actual crops;  
 • Can produce certain chemicals that are toxic to crops or grazing animals. | [24–27] |
| **Nematodes:**  
 Heterodera spp. and Globodera spp., (Plant-parasitic nematodes (PPN), Meloidogyne spp. (root-knot nematodes), Pratylenchus spp., Heterodera and Globodera spp. (cyst nematodes), Bursaphelenchus xylophilus (pine wilt nematode), Aphelenchoides bessei, Radopholus similis (burrowing nematodes), Xiphinema index (virus vector nematode), Ditylenchus dipsaci, Nacobbus aberrans, Rotylenchulus reniformis (reniform nematode). | Varieties of crops including peaches, nectarines, tomato, pepper, cucumber, almonds, squash, eggplant, okra, sugarcane, beetroot, and pineapple. | • They attack plant roots and other below-ground parts and sometimes manipulate the gene regulation and metabolism to their advantage;  
 • They also attack stems and leaves reducing photosynthetic and water and nutrient translocation. | [28–30] |
| **Insects**  
 Aphids, Mexican fruit flies (Anastrepha ludens), grasshoppers, whiteflies, spider mites, silkworms, desert locust (Schistocerca gregaria), migratory locust (Locusta migratoria), screw-worm fly (Cochliomyia), tsetse flies (Glossina), uzi fly (Exorista bombicis), potato beetle, Banana-spotting bug (Amblypelta lutescens), European corn borer (Pyrausta nubilalis), Japanese beetle (Popillia japonica), alfalfa weevil (Hypera postica), alfalfa aphid (Theroaphis maculata. | Varieties of crops including sugar beets and potatoes, maize, peanuts, chickpeas, and cotton. | • They cause both direct and indirect injuries to growing crops;  
 • Direct injury is caused by the insects eating the leaves, reducing photosynthetic activities and burrowing holes in shoots and stems which reduce nutrients and water translocation, burrowing holes in fruits and or/roots, thereby reducing product quality. | [31–33] |
| **Small vertebrates:**  
 Field mice, house mice, rats, feral cats, bats, foxes, wild dogs, pigs, rabbits, snakes, dogs, pigeons. | Varieties of crops including potatoes, grains, sugar beets, citrus and succulent fruits, peaches, plums, pears, strawberries, grapes, potatoes, and carrots. | • Bites on fruits and root crops are entryways for pathogenic and spoilage microorganisms;  
 • Their excrement and urine on food could be a source of poisoning and diseases;  
 • Cause injury and kill cultivated plants. | [34–36] |
| **Fungi**  
 Pythium and Phytophthora infestans (Fungal-like organisms), Fusarium spp., Fusarium graminearum, Fusarium oxysporum, Rhizoctonia solani, Tilletia spp., Plasmodiata vitisola, Puccinia graminis var. tritici, Gaumannomyces graminis var. tritici, Blumeria graminis, Mycosphaerella graminicola, Botrytis cinerea, Ascochyta spp., Ustilago maïdis, Aspergillus spp., Magnaporthe oryzae, Puccinia spp., Colletotrichum spp., Sclerotinia sclerotiorum, Verticillium dahlia, Armillaria spp., Melampsora lini, Phakopsora pachyrhizi Blumeria graminis. | Variety of crops including grains, rice, wheat, sorghum, potatoes, cassava, tomatoes, bananas, cucumber, grapes, strawberries, coffee, cacao, spices, mangos, and several nuts. | • Fungi play reverse roles of being pathogenic agents of diseases and some species are used as biopesticides;  
 • Destruction of mature and senescent tissues of dicots including stored grains;  
 • The growth of fungi on crops, fruits and tubers causes spoilage in the form of seedling damping-off, chlorosis, wilts, rots, rust, brown spots, black spots, smuts, mildew and dusty powder. | [37–39] |
Table 1. Cont.

| Pests                          | Hosts                                                                 | Impact                                                                                                                                       | Reference |
|-------------------------------|----------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| Protozoa: Phytomonas leptovasorum, Phytomonas stahelii, Phytomonas française, Phytomonas serpens | Variety of crops including, coffee beans, Coconut palm, oil palms, cassava, tomatoes.                                                        | • These protists can cause phloem necrosis, hampering the transport and distribution of organic nutrients in plants. Visible symptoms are yellowing, drooping leaves, foliage desiccation, root die-back and eventual death of the tree. [40,41] |           |
| Bacteria: Xanthomonas campestris, Psuedomonas syringae, Pseudomonas corrugate, Clavibacter michiganensis, Pseudomonas spp., Erwinia spp., Ralstonia solanacearum, Rhizomonas suberifaciens, Erwinia carotovora, Agrobacterium tumefaciens, Spiroplasma citri | Variety of crops including, lettuce, cucurbits, cucumber, pumpkin, melon, tomatoes, chilli, potatoes, eggplant, rice, beans. | • Bacterial infection occurs at points of injury on plants and is aided by free water; • They cause a variety of symptoms including, scabs, blights, soft rot, lesions, wilt, cankers, discoulouration, disagreeable odours, and necrosis on infected areas. [42,43] |           |
| Viruses: Cassava mosaic begomovirus, Citrus Tristeza closterovirus, Barley yellow dwarf luteovirus, Plum pox potyvirus, Potato leafroll polerovirus, Cacao swollen shoot badnavirus, Potato potexvirus X, Tobacco mosaic tobamovirus, Turnip crinkle carmovirus, Tomato spotted wilt virus, Cucumber green mottle mosaic virus, Pepino mosaic virus | Variety of crops including, cassava, citrus fruits, barley, cucumber, lettuce, tomatoes, peppers | • Viruses can initially be symptomless, or their symptoms may resemble other diseases of known aetiology making it difficult to differentiate and treat; • Some observable symptoms include chlorosis, mosaic leaf pattern, crinkled leaves, yellowed leaves. [44–46] |           |

3. Effectiveness of Synthetic Pesticides and Their Disadvantages

For 60 years, farmers have consistently applied SPs in agriculture based on economic considerations. The application of pesticides started with sulphur, dating back to earlier than 2000 BC, to control rodents, insects, and fungi. In the 15th century, heavy metals such as lead, arsenic, chromium, cobalt, and nickel were also used. In 1940, Paul Muller received the first chemical pesticide patent for dichlorodiphenyltrichloroethane (DDT) [47].

Pesticides are compounds or materials that can inhibit, prevent, kill, or reduce pests of farmland and livestock. They are categorised as microbicides, herbicides, insecticides, nematocides, and rodenticides based on the domain of pests they eliminate or control. Synthetic pesticides are essential components of commercial agriculture that control farm pests, which diminish production, cause diseases, and compromise food quality. DDT is an effective organochlorine insecticide that eliminates a wide range of pests. DDT harms the insects’ nervous systems when they come into contact with it. The active compound binds to the voltage-gated sodium channel proteins in neurons, keeping them constantly open, leading to the excessive diffusion of sodium ions ($\text{Na}^+$) through the phospholipid membrane, causing hyperpolarization and, eventually, spasms that can be fatal [48,49].

Organophosphates (phosphoric acid esters) and carbamates ($N$-methyl carbamic acid esters) are also widely used to target insects. Examples of organophosphates are malathion and parathion, while carbaryl and propoxur are examples of carbamates. They function by inhibiting acetylcholinesterase, thereby preserving the continuous increase in neurotransmitter concentration, duration, and function, which causes neurotoxicity and death to (non-) target insects [49]. Other carbamates (cyclodienes, phynylureas, and thiocarbamates) inhibit $\text{CO}_2$ generation in soil respiration by acting as 2,4-dinitrophenol analogues that shunt oxidative phosphorylation in microbial aerobic cellular respiration. Triazoles are a class of pesticides that are sensitive to a wide range of pests, including mildew, leaf spot, and rusting fungal diseases. Triazoles’ efficacy is attributed to their capacity to block the cytochrome P450-dependent sterol 14-demethylase enzyme, a vital component of the sterol biosynthesis pathways, leading to the creation of ergosterols thought to be essential in the regulation of membrane fluidity and structure. The absence of ergosterols causes the reduction of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$, which in turn disrupts sterols needed for cell wall synthesis [50], leading to the ultimate death of insects. Two independent investigations show triazole to
be very effective in suppressing *Botrytis cinerea* at a 50% concentration (EC50). Itraconazole [51] and tebuconazole [52] effectively inhibited the fungus’s radial growth on PDA in these studies.

Although SPs have been effective in reducing crop pestilence and improving productivity, they cause pollution with characteristic long-term persistency in the ecosystem and on ecological receptors [53]. A study found that aldrin, dieldrin, and endosulfan were the most persistent pesticides in soil [54,55]. Pentachlorophenol inhibits microbial activities, damages soil fertility, distorts nutrient cycling, causes mutation, and has neurotoxic effects on aquatic organisms [56,57]. Cancer, respiratory conditions, Parkinson’s disease, and death are some of the consequences of being exposed to SPs [58]. The classification of these pesticides and their pest-controlling impacts are reflected in Table 2. It is pertinent to note that the impact of exposure is proportional to the increase in the concentration of the SPs. This was demonstrated in a study carried out in Southern India (Vellore) involving 100,000 people, which revealed that observable health impact effects were evidenced when farmers sprayed pesticides at mean peak flow rates of 346 L/min and 390 L/min [59]. Overall, traditional pesticides place the environment, diversity, plants, animals, and humans at risk (Figure 2). Thus, the call for the minimal use of SPs and the diversion to safer and more sustainable alternatives. Implementing large-scale farming in the context of alternative pesticides would help to define SA and its attendant benefits, including profitability, environmental protection, and social acceptability. The surest way to achieve this is by relying on biopesticides, which have the potential to fill the gaps associated with SPs.

**Figure 2.** Negative impacts linked to the toxicological distribution chain of chemical pesticides. 

$D =$ Deposition, $P =$ Percolation, $L =$ Leaching, $Pr =$ Precipitation; Red lines = Negative impacts.
| Chemical Group | Trade Name | Pest Controlled | Plant Protected | Toxicity | Reference |
|----------------|------------|-----------------|----------------|----------|-----------|
| **Carbamates** |            |                 |                |          |           |
| Aldicarb       | Temix, Standak, Namex | Effective against: thrips, aphids, nematodes | Cotton, potatoes, soya beans | Acute, environmental | [60] |
| Fenobucarb     | Wardam, Knock, BioStadt | Effective against: hoppers | Rice field, cotton | Irritant, environmental | [61] |
| Carbofuran     | Furadan, Curaterr, Carbosip | Effective against: Mites, nematodes | Corn, soybeans, potatoes | Acute, environmental | [62] |
| **Organochlorine** |            |                 |                |          |           |
| Aldrin         | Aldrec, Altox, Octalene | Effective against: Termite, weevil, hoppers | Corn, potatoes | Acute, health, environmental | [63] |
| Lindane        | Agrocide, benexane, Isotox | Effective against: Beetles, ants, locust | Corn, rice, seeds | Irritant, acute, health, environmental | |
| DDT            | Anofex, Cezarex, dicophane | Effective against: Armyworms, mites, soil larvae | Cowpea, cotton | Irritant, acute, health, environmental | [64] |
| **Chlorothalonil** |            |                 |                |          |           |
| Bravo, Daconil, Nopaxide | Effective against: Mold, mildew, algae | Vegetables, trees, ornamental crops | Corrosive, irritant, acute, health, environmental | [65] |
| **Organophosphates** |            |                 |                |          |           |
| Chlorpyrifos   | Brodan, Scout, Nufos | Effective against: Borers, hoppers, termites | Apples, soybeans, broccoli | Acute, environmental | [66] |
| Dichlorvos     | Vapona, Dicogreen | Effective against: Beetles, aphids, larvae | Grains, mushrooms, citrus | Irritant, acute, environmental | [67] |
| Diazinon       | Basudin, Gardentox, Dazzle | Effective against: Mites, aphids, worms | Vegetables, nuts, fruit trees | Irritant, environmental | [68] |
| **Triazines**  |            |                 |                |          |           |
| Atrazine       | Aatrex, Fenamin, Prozine | Effective against: Weeds, borers, termites | Corn, sugarcane | Irritant, health, environmental | [69] |
| Simazine       | Aquazine, Primatol, Simade | Effective against: Weeds | Seedlings | Health, environmental | [70] |
| **Pyrethroids** |            |                 |                |          |           |
| Cypermethrin   | Ammo, Basathrin, Arrivo | Spiders, scorpions, bugs | Lettuce, cotton, cowpea | Irritant, environmental | [71] |
| Fenvalerate    | Sumicidin, Devifen, Pydrin | Mites, tobacco budworms | Cotton lettuce | Irritant, acute, environmental | [72] |
| Deltamethrin   | Decis, Kordon, Sadethrin | Millipedes, fleas, silverfish | Strawberries, ornamental gardens | Acute, environmental | [73] |
| **Phenoxy-derivatives** |            |                 |                |          |           |
| 2,4-D          | Hi-Dep, Weedar 64, Weed RHAP | Dandelions, clover, and chickweed | Variety of plants | Corrosive, irritant, environmental | [74] |
| 2,4,5-T        | Dacamine, Inverton 245, Forron | Broadleaf weeds | Monocotyledinous plants | Irritant, environmental | [75] |
| Carbofuran     | Furadan, Curaterr, Carbosip | Mites, nematodes | Corn, soybeans, potatoes | Acute, environmental | [76] |
| **Dipyridyl-derivatives** |            |                 |                |          |           |
| Paraquat       | Gramoxone, Helmqaut, Firestorm | Weeds | Seedlings | Corrosive, irritant, acute, health, environmental | [77] |
| Glycine derivatives |            |                 |                |          |           |
| Glufosinate    | Basta, Rely, Ignite | Weeds | Seedlings | Irritant, health | [78] |
4. Biopesticides as a Substitute for Conventional Pesticides

The performance of any pesticide is dependent on its effective pest-controlling and eradicating potential. For this section, SPs effectiveness is taken as a standard. With this in mind, we can compare biopesticides with SPs from many angles. More than 55,000 plant pests have been subjected to SPs, with fungi accounting for up to 50,000 [79]. Rajput et al. [80] suggested that the efficacy of biopesticides is comparable to traditional pesticides in terms of insect management (Figure 3). Biopesticides have also performed well in controlling weeds and pathogens [81]. Tripathi et al. [82] revealed that the available biopesticides on the market amount to approximately 1400 (see Table 3), with commensurate pest management success.

Figure 3. Susceptible target points of insect pest, mode of action and applicable biopesticide. EP = Entomopathogenic.

The efficacy of biopesticides depends on their pest elimination and control potential. This in turn depends on the multiple MoA and synergy. The performance of biopesticides over the top 60 plant pests (from the plant pathology database) showed that they possess the ability to eliminate a wide range of harmful biotic factors, excluding vertebrate pests. Microbial pesticides ranked first among the various biopesticide groups. Essential oils came second, followed by botanicals, biochemical biopesticides, PIPs, and natural enemies. However, not many studies have been made public to prove the efficacy of biopesticides over *Cyperus rotundus* (weed), *Nacobbus aberrans* (nematode), *Albugo candida* (oomycetes), *Ustilago maydis* (fungi), and *Phytomonas* spp (protozoa). Hence the need for research in this direction.
Though biopesticides control a good number of pests, there are instances where certain biopesticide groups are preferred over others. As illustrated in Figure 4, natural enemies eliminate weeds and nematode pests better than other classes of biopesticides [83]. Hence, they will be more useful as bioherbicides and bionematicides. As mentioned in the literature, herbivorous insects are more sensitive to biochemical pesticides and their chemical analogues. Plant viruses are better controlled by essential oils, while phytopathogens are more vulnerable to PIPs and microbial pesticides [84–86]. However, microbial pesticides cover a broader scope. When a combination of biopesticides becomes necessary, it is better to use plant-based pesticides simultaneously for a synergistic result. Combining a plant-based pesticide and any of the microbial pesticides, entomopathogenic nematodes, or natural enemies will not yield a synergistic result because of the multiple MoA inherent in phytochemicals. However, if they must be used together, the application of plant-based pesticides should come first.

Figure 4. Biopesticides coverage against plant pests with preferred categories.

Biopesticides display multiple mechanisms of action, as shown in Table 3. Photo-bleaching, growth inhibition, protein content reduction, dry mass reduction, phytotoxicity, allopahy, and necrosis are used against weeds. Bioinsecticides act through parasitism, gut solubilisation, resistance induction, gene disruption, disruption of a life cycle, ovicidal activity, oviposition deterrence, antifeedants, growth mal-regulation, repellence, electron transport inhibition, and neurotoxicity in controlling insect pests [87,88]. Antibiosis, hyperparasitism, antagonism, competitive exclusion, biostimulation, cellular wall disruption, hypersensitivity response, resistance gene activation, and lipid peroxidation are some of the mechanisms employed by biofungicides and bio-bactericides [89,90]. Mechanisms by which bionematicides protect plants against pests are egg parasitism, root colonization, physicochemical barricade, chemotoxicity, and resistance induction [91]. The control of viruses is achieved through particle inactivation, cytotoxicity, protein masking, and envelope structure modification [92,93]. Natural enemies adopt parasitism and predation. Plant-incorporated pesticides confer protection via gene transformation, suppression of pest resistance, target gene silencing, biological barricade, larval mortality, and viral replication obstruction [94]. The multiple MoA exhibited by biopesticides make it difficult for pests to develop resistance, which is common with SPs [95]. According to Dammos et al. [96], there are more than 500 resistant pests globally connected with conventional pesticide overuse. These problematic resistant pests are also susceptible to biopesticides.

Steps for the synthesis of this diagram. The first ten pests of each category (excluding weeds) are taken from the molecular plant pathology database. Then, the 60 plant pests are crosschecked for biopesticides sensitivity using open-access publications. However, the routine and prolonged use of a particular biopesticide can lead to pest resistance [97]; however, resistance will not be as intense as SPs. To avoid such a
phenomenon, a change of management approaches should be encouraged since there is more than one biological option for controlling a particular pest or pests.

Table 3. Selected examples of commercially available biopesticides.

| Product       | Manufacturers                          | Active Agent                           | Mode of Action                                | Controlled Pest                                | Protected Crop                        | Reference |
|---------------|----------------------------------------|----------------------------------------|------------------------------------------------|------------------------------------------------|--------------------------------------|-----------|
| Biochemical   |                                        |                                        |                                                |                                                |                                      |           |
| Aza-Direct    | Gowan (USA)                            | Azadiractin                            | Growth and moulting disruption                 | Egg, larvae and pupae of beetles and sucking insects | Cotton, Papua, vegetables            | [96]      |
| Timorex Gold  | STK Stockton (Israel)                  | Tea tree oil (1,8-cineole and terpinen-4-ol) | Antifeedant, disruption of the fungal cell wall and curative activities | Black Sigatoka, a leaf-spot fungal disease | Bananas, strawberries, tomatoes, grapes, lettuce. | [99]      |
| Regalia MAXX  | Marrone Bio Innovations (USA)          | Extract of Reynoutia sachalinensis      | Broad-spectrum antimicrobial activity, resistance against disease | Fungi and bacteria                             | Hemp, cannabis, tomatoes, apples, blueberries | [19]      |
| Nema-Q        | Brandt Consolidated (USA)              | Saponins                               | Nematicidal effects,                           | Root-knot nematodes                            | Berries, Citrus, Pome Fruit Grapes, Nut Crops | [100]     |
| Microbials    |                                        |                                        |                                                |                                                |                                      |           |
| Lipel         | Agri-Life (India)                      | Bacillus thuringiensis                 | Lethal action against eggs and larvae of diamondback moth | Diamondback Moth                              | Cruciferous vegetables; Collard greens, cauliflower | [101]     |
| Cordalene     | Agrichem (Australia)                   | Bacillus thuringiensis                 | Killing of midgut cells by Cry toxins through signal transduction | Lepidoptera insect pests                       | Maize, sugarcane, soybeans, peanuts, flax | [102]     |
| Daman         | International Panacea Ltd. (India)     | Beauveria bassiana                    | Growth inhibition and larvicidal activities    | Larval, pupal and nymphal stages of Spodoptera | Rice, maize, sorghum                   | [103]     |
| MeloCon WG    | Certis (USA)                           | Paecilomyces lilacinus                 | Colonization of plant roots, egg mass of nematodes and incapacitating second-stage instars | Nematodes                                     | Vegetables, citrus strawberries, grapevines, tomato | [104]     |
| Grasshopper Spore | ARBRICO Organics                     | Nosema locustae                        | Infects insects at the moulting stage           | Grasshopper                                   | Vegetables, fruits,                   | [105]     |
| Littovir      | Andermatt Biocontrol AG (Switzerland)  | SpliNPV *                              | Induction of adult, pupa and larval malformation | African cotton leaf worm (Spodoptera littoralis) | Okro, onion, groundnut, beetroot, cabbage |           |
| PIPs          |                                        |                                        |                                                |                                                |                                      |           |
| Bt-cotton     | Chinese Academy of Agricultural Sciences. | Cry1Ac, Cry2Ab toxins                | Act as gut poison leading to pore formation    | Diptera, beetles, H. armigera                 | Cotton                                | [106]     |
| 5345          | Monsanto (USA)                         | Cry1Ac gene                            | Kills insects by pore insertion into gut membranes | Lepidopteran pests: Fruitworm, pinworm, hornworm | Tomatoes                              | [107]     |
| At^-Potato    | Research-limited                       | RNAi                                   | Causes post-transcriptional silencing target genes responsible for infection and maintenance | Phytophthora infestans                        | Potatoes                              | [108]     |
### Table 3. Cont.

| Product Manufacturers | Active Agent Mode of Action | Controlled Pest | Protected Crop | Reference |
|-----------------------|-----------------------------|-----------------|----------------|-----------|
| Mealybug Destroyer; Convergent Lady Beetles; Whitefly Predator; Spider Mite Destroyer; Scale Predator; Fungus Gnat Predator | Great Lakes IPM, Inc. (Vestaburg, MI, USA) | Cryptolaemus montrouzieri; Lady beetle; Delphastus; Stethorus; Cybocephalus nipponicus; Rove beetle (Atheta coriaria) | Predation | Citrus, corn, ornamentals, vegetables, sweet potato | [109,110] |

| Chinese Mantid; Green Lacewings; Aphid Predator Midge; Predatory Mites | Crop King, (Lodi, OH, USA) | Tenodera aridifolia; Chrysoperia spp. larva; Aphidoletes aphidimyza larva; Phytoseiidae | Predation | A broad range of insects including aphids, Pea, cabbage, cowpea, cucurbits, crucifers, eggplants, okra, lettuce | [111,112] |

* Spodoptera littoralis nucleopolyhedrovirus; Agrobacterium tumefaciens.

The most suitable, effective, and flexible method that can address the drawbacks of conventional farming is the integrated pest management (IPM) system. IPM is a management approach that combines and implements dimensions and guidelines in sequence to lessen the impact of pests and produce healthy crops with minimal disruption to the agroecosystem. The first two IPM system processes are pest characterization and pest load quantification. The latter determines the economic thresholds at which pests begin to affect the micro-economy (farm) and macro-economy (country’s GDP). Pest characterization can be accomplished through a molecular approach, which provides more reliable details than morphological identification techniques [113]. Currently, drone technology [114], image technology [115], and an artificial intelligence system combined with a pest database [116] are used to identify arthropods. The pest destruction guidelines are carried out in the following order: cultural practice, monitoring, decision-making, physical treatment, bioaugmentation, application of least toxic pesticides, and the use of SPs [117]. In reality, pest elimination tactics are pyramidal (Figure 5) and use biopesticides, except in the decision-making component. For example, kairomone- or pheromone-baited traps can serve the purpose of monitoring resistant cultivars and natural enemies for cultural techniques, while garlic soap and diatomaceous earth (biochemical biopesticide examples) application can assist in the physical approach [118]. Recently, climate-smart pest management (CSPM) has been used in IPM management to identify the ideal seasons for the cultivation of particular crops and pest prevention [48]. Additionally, laser-based technology (a physical technique) has recently been used to eradicate aphid species such as Acyrthosiphon pisum and Rhopalosipham padi [119].

Augmentation (which is the same as biointensive pest management), the third stage of the pest eradication guidelines, is accomplished by using entomopathogenic nematodes and microorganisms. A soil moisture between 20 and 60% encourages entomopathogenic microbes to function effectively [120]. The next stage of the pest management guidelines, the employment of least hazardous pesticides, requires the application of biochemical biopesticides, botanicals, and essential oils. Some notable botanicals have neurotoxic properties (e.g., pyrethrins, rotenone, sabadilla, azadirachtin) but can still be used because they are less harmful than SPs [121], which come last in the IPM strategy. Recently, Umetsu and Shirai [122] published novel synthetic chemicals that are safe for the environment and humans. They include fungicides (flupyrimin, flupyradifurone) that inhibit succinate dehydrogenase, demethylation, flupyrmin, flupyradifurone, and quinone. The production of low-toxicity pesticides in commercial quantities can be achieved through the manufacture...
of biochemical pesticide analogues. The eradication of SPs is a possibility on this path, but it depends on financing, research, and time. As we wait for this auspicious moment, SPs remains the last resort in the IPM strategy. A critical examination reveals that biopesticides dominate the IPM pyramid. This demonstrates the importance of biopesticides to agriculture now and in the future. Other components that are key to IPM implementation are knowledge of pest ecology and biology, resources, organization and planning, and communication.

Figure 5. A simplified integrated pest management system. Adapted from [48,113,118]. Key: CSPM: Climate-smart pest management; LTS: Least toxic pesticides; CP: Chemical pesticide.

5. Sustainability Attributes of Biopesticides

There are key parameters that promote agriculture and its related subjects. Constructive manipulations of these parameters in large-scale agriculture translate into sustainable agriculture (SA). The latter is understood as the prudent and continuous use of land and other factors of production in meeting the food needs of the populace and other dimensions such as economic productivity, environmental protection and socio-cultural acceptability. Some of these parameters serve as renewable feedstock and products used in agriculture, including biopesticides. Beyond these roles, biopesticides drive economic productivity and are harmless to non-target organisms, including plant growth-promoting microorganisms and pollinators [123]. These beneficial organisms interact closely with plants for mutual benefits. Plants benefit from the essential nutrients supplied by the microorganisms, which in turn gain energy and protection. In some cases, these rhizomicrobes (rhizobacteria) antagonise soil pests using bioactive substances they produce and metabolise carbon-rich pollutants as an energy source [124]. The majority of these growth-promoting rhizobacteria (PGPR) perform nitrogen fixation, mineral solubilization, generation of active metabolites, and induction of systemic resistance for the advantage of the concerned plants [125]. The assimilation of H₂ during nitrogen fixation improves the growth of the associated plant [126].
Examples of PGPR (biofertilizers) are *Azospirillum*, *Allorhizobium*, *Bacillus*, *Bradyrhizobium*, *Arthrobacter*, *Agrobacterium*, *Mesorhizobium*, *Caulobacter*, *Rhizobium*, *Azotobacter*, *Frankia*, *Erwinia*, *Micrococcus*, *Serratia*, and *Flavobacterium* [127]. Inoculation of PGPR to plants improves yield, and as a practice is becoming popular. The use of biofertilizers (PGPR) and biopesticides is essential to organic farming, conserves biodiversity and increases crop yield.

An increase in crop yield is partly attributed to insect pollination. Pollinators contribute to more than 75% of food crops, and 90% of wild angiosperms found in agro-fields benefit from most insect–plant interactions [128]. In addition, the interaction between pollinators and plants results in genetic variability, yield stability, early reproduction, and strong traits [129]. Adamidis et al. [130] established that honeybee-driven pollination contributed to a yield increase in sesame and cotton by 62%. Other significant pollinators are solitary bees, bumble bees, moths, and butterflies. Studies have shown that pollination services raise crop value by USD 17,174 per hectare, boost worldwide food production by 9.5%, with a net worth of USD 405 billion, and account for 67% of Tanzania’s food crops [131,132]. Apart from food, pollinators also contribute to the production of timber, biofuel, fibre, and medication [133]. Garratt et al. [134] noted that the gains from pollination services can only make sense where fertilisers are not limited. This implies that in the presence of sufficient plant nutrients (biofertilizers) and thinned pests, the many advantages of pollination can be fully realized.

From the preceding sections, it is clear that pests, nutrients, and pollinators are critical factors in agricultural practice. Water, the atmosphere, and humans are also critical factors in agriculture. The involvement of pesticides (biopesticides and SPs) improves agro-yield by mitigating pests. However, the other remaining factors respond differently to pesticides in general. Apart from their pest-controlling efficacy, SPs defile the air, soil, groundwater, and surface water. The polluted state of the environment normally leads to health challenges, the abandonment of natural resources, biodiversity losses, and high costs of remediation. Environmental chemical-instigated health challenges can lead to discomfort, fatigue, Parkinson’s disease, cancer, or even death [135]. Attina et al. [136] revealed that the negative impact of organophosphate pesticides costs the United States USD 44.7 billion/year. Earlier, Nowak and Greenfield [137] estimated damages caused by by SPs in the following sectors: bird losses (USD 2.2 billion/year), crop losses (USD 1.4 billion/year), public health (USD 1.1 billion/year), pesticide resistance (USD 1.5 billion/year), and groundwater pollution (USD 2.0 billion/year). The high degree of soil and surface water contamination leads to abandonment or suspension of usage until remediation is carried out. Chemical remediation can be accomplished through conventional and bioremediation approaches. Though the bioremediation approach is considered the best option, both techniques cost money, time, and effort. The attenuation of a particular pesticide to a safe target level usually requires a period of 12 to 24 months. All these costs and negative effects of using CPs in agriculture could be avoided by utilising biopesticides instead. The application of biopesticides provides a safer environment and improves productivity. These are areas of concern for the sustainable development goals (SDGs).

The SDGs address 17 subject areas, poverty (SDG1), hunger, health, education, gender, clean water, energy, economic growth, infrastructure, inequality, communities, production and consumption, climate, life underwater, life on land, strong institutions and partnership (SDG 17) [138]. However, the ones that are of interest to agriculture are life under water (SDG 14) and on land (SDG 15). Each of them serves as a base for agricultural activities. Land, especially fallowed ones, can be cultivated while water bodies can be used for aquaculture for subsistence and commercial farming. Sustainable agriculture (SA) is driven by the conscious utilisation of water (SDG 6), nutrients, and energy (SDG 7) [14]. Agriculture-based skills and education (SDG 4) and responsible production of agro-products and consumption (SDG 12) optimise the impact and services that SA provides. Examples of services agriculture provide are the reduction of poverty (SDG 1), drastic hunger reduction (SDG 2), nutrient-linked health improvement (SDG 3) and the reduction of global warming.
Vegetation helps reduce greenhouse gases by absorbing CO$_2$. For this reason, research on CO$_2$ capture and sequestration has been given priority attention in recent times to address global warming [139]. Strong institutions (SDG 16), which promote policies, peace, and justice, serve as enablers of SA improvement and support practitioners on an equal gender basis (SDG 5) to engage in agriculture as a decent profession for economic growth (SDG 8). In summary, it is instructive to conclude that SA platforms (SDG 14 and 15) provide services such as hunger eradication (SDG 2), poverty reduction (SDG 1), health improvement (SDG 3), and air purification (SDG 13). These services can be optimised by ensuring education (SDG 4) and judicious production and consumption (SDG 12) habits. Strong institutions serve as essential elements for all aspects. Conclusively, biopesticide-driven large-scale agriculture is linked to 11 of the 17 SDGs and guarantees food security, productivity, and environmental sustainability.

6. Emerging Frontiers of Biopesticide

The existing classes of biopesticides have their disadvantages, which require improvement to improve their technical performance. Omics technology, nanotechnology, and RNA interference technology are avenues through which these improvements can be made [140]. PIPs are employed to deliver biopesticides during genetic modification, which causes plants to synthesise compounds to ward off pests. It was established in 2014 that PIPs could reduce synthetic pesticide consumption by 37% and increase agricultural output by 22% [141]. Current studies explore omics tools to ascertain potential proteins and metabolites that can be integrated into plants to eliminate bacteria, fungi, viruses, pathogens, and insect pests [142]. Metagenomics, a branch of omics technology, is used to discover novel enzymes and encode genes from microbial communities. For example, a chitinase encoded by the Chi18H8 gene was active against *Rhizoctonia solani* and *Fusarium graminearum* [143]. Additionally, the CfHNN1 gene was active against *Cladosporium fulvum*, a pest of tomatoes and tobacco [144]. Hjort et al. [145] developed a framework for the identification of Chi18H8 genes from soil microbial communities. The protocol involved creating a library by performing PCR amplification and sequencing the Chi18H8 gene in gene pools. These results demonstrate that metagenomics can be utilised to locate pesticidal genes that can endow plants with transgenerational protection. Metagenomics research has also discovered biological control agents in soils.

Metabarcoding, a genomic technique, is described as a method for identifying and labelling organisms within microbial communities with peculiar characteristics. Genomes are amplified and sequenced using specific primers (16S, 27F, and ITS1 and ITS4), thereby aiding the description of host–pathogen interactions and the recognition of phylotypes whose DNA segments are identical to those of a known species [146]. Data collected through these means are instrumental in developing biopesticides and biofertilizers for managing pathogens. Cobo-Diaz et al. [147] used metabarcoding to recognise biocontrol microbes capable of mitigating *Fusarium* spp. disease in maize stalks. *Pseudomonas, Pedobacter, Sphingomonas, Flavobacterium, and Janthinobacterium* (bacteria genera), *Epicoccum, Articulospora, Exophiala, and Sarocladium* (fungi genera) were identified as biocontrol agents. Combined consortia-metabarcoding and co-occurrence network analyses were used to quantitatively ascertain the antagonistic relationship between the biocontrol consortia and *Fusarium* spp. The research also discovered an antagonistic interaction between *F. avenaceum, F. graminearum, Sarocladium* and *Epicoccum*. This report corroborates the results of Kemp et al. [148], who demonstrated how a symbiotic relationship between *Sarocladium zae* and *Fusarium* spp. could discourage head blight disease in wheat. An earlier study carried out by Jensen et al. [149] established the antagonistic effect of the wheat endophyte, *Epicoccum nigrum* on *Fusarium graminearum*. *Epicoccum layuense* is an agent of biocontrol against *Phaeomoniella chlamydospora* and *Fomitiporia mediterranea* in grape vines [150].

The genome editing (GE) technique is currently used for modifying plant immunity in diverse ways by altering targeted genes to create more resistant crop species [151]. Three mutagenesis tools are used to edit genes that confer resistance in plants. CRISPR (clustered
regularly interspaced short palindromic repeats) is one of these. The CRISPR-associated system (CRISPR-Cas) is easier to implement and has a high efficiency in generating mutagenesis [152]. CRISPR-Cas9 has been employed to raise wheat that is resistant to powdery mildew and white rot [153]. The other two are ZFNs (zinc finger nucleases) and TALENs (transcription activator-like effector nucleases) [154]. Chen et al. [155] used CRISPR-Cas9 to transform the cotton genome using an Agrobacterium-delivering medium via the shoot apexes. CRISPR-Cas9 gene editing confers immunity against blight, cotton genniviruses, and viruses [153]. ZFN was used to modify the AaegGr3 gene encoding the heteromeric CO₂ receptor subunit from Ae. aegypti mosquitoes [156], while TALEN was employed to produce mutant mosquitoes that are hyper-vulnerable to Plasmodium parasites [157]. This opens an opportunity for malaria prevention and elimination. Genomics has been useful in the development of transgenic plants and improvement of cultivars by way of introducing resistant genes into plants.

Experiments have proven RNA interference (RNAi) technology as a viable pest control method. It is a post-transcriptional regulatory process in eukaryotic cells in which specific RNAs inhibit gene translation and expression by counteracting targeted mRNA molecules. RNase participates in a series of activation complexes that culminate in the formation of the RNA-induced silencing complex (RISC), a multi-protein complex composed of a micro RNA (miRNA) or small interfering RNA (siRNA) and RNase enzymes [158]. With the right delivery mechanism, the biopesticides’ shelf life in the open environment can be extended [159]. Emerging delivery technologies of RNAi are liposomes, polymeric nanoparticles, viral-like particles, and peptide-based delivery techniques [160]. The application of RNAi for pathogen and pest control is achieved in three different ways. The first approach involves the silencing of host-induced genes (HIG). HIG silencing causes the development of transgenic crops that express double-stranded RNA (dsRNA) specific to pathogens or pests. An RNAi-defined transgenic plant is now available (Tradename: SmartStax) on the market. It targets the snf7 gene of corn rootworm by the elicitation of a hairpin-dsRNA [161]. The second approach is the silencing of spray-induced genes (SIG), which could have a pronounced effect on root adsorption and trunk injections. Sucking and chewing insects can accrue expressed double-stranded RNAs. The final method is the silencing of virus-induced genes (VIG), which requires engineered microbes as vectors for the production of siRNA or dsRNA. Colorado potato beetle, Asian corn borer, brown plant hoppers (insects), alfalfa mosaic virus, tobacco etch virus, pepper mild motile virus, sugarcane mosaic virus (plant viruses), and Fusarium graminearum, Botrytis cinerea, and Sclerotina sclerotiorum (fungi) are all controlled by double-stranded RNA [159]. RNAi is limited by its narrow application range because of its instability, sensitivity variance in insects, and poor risk assessment of the environment, plants, and humans.

In pest management, nanotechnology is an evolving field of study because new properties (high reactivity, uniform conductance, high surface area, etc.) arising from nanosized particles are quite different from the attributes of the bulk/parent material. Jasrotia et al. [162] noted that nanotechnology in plant protection has the following advantages: long-lasting protection of active ingredients (AIs); enhanced physicochemical attributes (solubility, wettability, dispersion, storage stability, penetrability, bioavailability uniformity) of the AIs; controlled release of the AIs; high surface area; improved efficiency, etc. Inorganic compounds, metals, and organic polymers are common materials used for nanoformulations (ending in the form of suspension, spheres, aerosols, particulates, powder, capsule, micelle, gel, fibre, and granules). Often used terminologies with nanoformulations are nanoparticles, nanoemulsion, nanosuspension, nanocapsules, nanoencapsulation, nanogel, and nanofiber [163]. Nanoparticles have a pesticidal effect on plants. For example, copper, silver, platinum, sulphur, graphene oxide, titanium dioxide, silver oxide, copper oxide, and chitosan nanoparticles have been proven to control pests such as weevils, mosquitoes, and fungal and bacterial diseases through their biocidal (oxidative stress, enzyme inhibition, protein synthesis inhibition, ill-developmental changes leading to reproductive failure, gene mal-regulation, insect dehydration, and repellent effect) properties [164]. Nanoparticles
are now obtained from plants, including *Anacardium occidentale* (gold, silver, and copper), *Acorus calamus* (gold and silver nanoparticles), and *Aloe secundiflora* (silver). Nanosizing parent pesticides could have the same improved results. The nanostructuring of biological pesticides represents an advantage of nanotechnology in terms of biopesticides [165]. Nanobiopesticide efficacy has been demonstrated against *H. armegera*, *Anopheles*, insect larvae, bacteria, fungi, and stored grain protection. Thus, nanoparticles and biopesticide nanoparticles serve as emerging areas of interest for practitioners.

Nanoformulations share the following properties: higher specificity, increased persistence, and reduced mass in comparison to free biopesticides, some of which have poor water solubility properties and a predilection for oxidation, volatility, and instability [21]. A nanoemulsion (droplets with a radius of less than 100 nm) is a diphasic system in which its active parts are spread in oil-in-water phases with the aid of surfactants. This suggests that nanoemulsions are oil-in-water dispersions that improve the efficiency of pesticides by dissolving them into very small oil droplets. In addition, nanoemulsions are suitable for both hydrophobic and hydrophilic pesticides. This property of nanoemulsion helps in eliminating the need for toxic organic solvents and synthetic surfactants [166], apart from aiding uniformity. Like synthetic surfactants, nanoemulsion enhances spreadability, wettability, and permeability. Essential oils are a notable subject of interest in nanoemulsion. They exert their pesticidal activities through repellent activity, toxicity attributes, development inhibition, behavioural alterations, sterility properties, and infertility effects [167]. Nanoemulsions of essential oils improve biopesticide delivery in agriculture, especially for phytophagous insects. Palermo et al. [168] formulated eight commercial nanoemulsions of essential oils (anise, fennel, artemisia, sage, garlic, lavender, mint, and rosemary) which showed improved repellency, aerosol/gel, and acute toxicity against *Tribolium confusum* (pest of stored grain). Behara [169] stated that nanoemulsions possess the following advantages: higher pesticidal activity, lower cytotoxicity, smaller dynamic contact angle on leaves, pesticide delivery, and physical stability in comparison to microemulsions and emulsions. Details about the methods of nanoemulsion production can be found in [170,171], but low-energy methods are much greener. Apart from the popular nanoemulsion technique, nanoencapsulation is another popular nanotechnology critical for plant protection advances.

Nanoencapsulation is implemented using polymers and inorganic materials that aid the delivery of the active parts in a controlled manner, either with slow (sustained) or stimulus-response release to abiotic and biotic factors [172]. Apart from protecting the active components from degradation, hydrolysis, volatilization, leaching, photolysis, and hydrolysis, encapsulation prolongs the release duration and affects precision control to yield effective results [173], enhance the mobility and distribution of nematicide against soil parasitic nematodes (plant-viral nanoparticles) [41], and provide good biocompatibility (silica and calcium carbonate) with biopesticides [174]. Thus, nanoencapsulation serves as an effective delivery platform for pesticide delivery and incorporation of particles (nano-pesticides) into plants to increase the effectiveness of biopesticides against pests and pestilence [175]. Regulating nanoencapsulation pore structure enhances the effectiveness of the active agents [176]. Noisomes and liposomes are efficient carriers for pesticide delivery [177]. Nano-gel has a reputation for serving as a carrier for pheromones, which is thus protected from decomposition and decreased evaporation. Nassar [178] demonstrated that chitosan nanogel improves the performance of copper-based antifungal remedies. Similarly, nanofibers improve the efficacy of essential and pheromone molecules by evading release outbursts [179]. For example, thiamethoxam-loaded fibre proved effective against whitefly with a 50% improvement rate [180]. In essence, nanoencapsulation improves pest control via the controlled release of AIs and delivers them to the target pest, thereby increasing specificity.
7. Constraints and Outlook

Despite the many advantages of using biopesticides, they do have their disadvantages, including slow action. This limitation serves as a hindrance to their widespread adoption in commercial farming. Their use is currently popular only among organic farmers who cater to the elite and high-end consumers. Furthermore, these biopesticides are easily influenced by the environment, as demonstrated by controlled versus uncontrolled experiments, with frequent significant variations in outcomes once environmental factors are accounted for in field studies. This research is needed in the areas of stability, delivery methods, shelf-life, and packaging materials that will preserve efficacy. Though most of the limitations are addressed by nanotechnologies, some areas could benefit from further improvement. Nanotechnology improves biopesticide stability, high precision in biopesticide delivery to target pests, controlled release of AIs, and concentration minimization of biopesticide, thereby reducing their possible toxic impact. Some identified areas where improvement is needed in nanotechnology as it relates to pest management are mass production, low selective toxicity, and the non-biodegradability of inorganic nanoparticles. As an evolving technology, questions exist regarding the environmental impact of nanotechnology and its effects on receptors. Thus, further research is needed to provide answers, including for the production of environmentally safer nano-pesticides. The safety of food tainted with nanoparticles is still unknown, and information about the exact precautions to be taken (where necessary) is still lacking. In addition, research centred on ecotoxicity studies of nanoparticles, cheap nanoformulations, and legislative frameworks is urgently needed. Such information would bring to the fore issues of green nanotechnology, which will be of great benefit to SA and is marked by food safety, economic productivity, eco-friendliness, social acceptability, and cost-effectiveness.

8. Conclusions

Biopesticides are emerging pesticides and are a better option than synthetic pesticides due to their unique sustainability and green chemistry attributes. Different types of biopesticides respond preferentially to different pest categories. For instance, phytophagous insects are more susceptible to biochemical pesticides and botanicals. As are plant pathogens to microbial pesticides and plant-incorporated protectants. Natural enemies preferentially eliminate weeds and nematodes. Thus, it is imperative to systematically characterise pests before applying biopesticides. The pest elimination guidelines of integrated pest management (IPM) pave the way for pest characterization and accommodate the use of bio-controlling agents. The implementation of IPM principles in large-scale farming gives rise to sustainable agriculture, which promotes continuity, economic productivity, social acceptability, and environmental sustainability. Sustainable agriculture is the main driver of the Sustainable Development Goals (SDGs), and it is connected to 11 of the 17 SDGs. Consequently, biopesticides connect green chemistry and sustainable development through agriculture. Though the call for the increased use of biopesticides is evident, some shortcomings need to be addressed through nanotechnology, omics technology, and RNA interference (RNAi) technology. When these avenues are fully explored, the use of synthetic pesticides will become an obsolete practice.

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