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Review

Potential Strategies in the Biopesticide Formulations: A Bibliometric Analysis

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Abstract: Biopesticides are pest and pathogen management agents based on living microorganisms or natural products (botanical origin). Due to their natural origins, they stand out as an environmentally friendly tool, since they quickly decompose and minimize pollution problems produced by synthetic pesticides. However, these products present significant challenges that affect the bioactivities of the active components, due to the degradation of the biomass or bioactive metabolite by factors such as air, light, and temperature. Therefore, in this study, a systematic search of the Scopus database was conducted and scientometric tools were used to evaluate formulation techniques and approaches that seek to improve the bioactivities of natural preparations. The results showed that published research on biopesticides has significantly increased by 71.24% in the last decade (2011–2021). Likewise, the bibliometrics showed, through temporal flow analysis, and in the period from 2010 to 2021, investigations evolved have toward the use of nanotechnology, with the purpose of improving and potentiating the formulations of biopesticides. Consequently, nanotechnology tools can be classified as current strategies of interest that allow the increase and protection of bioefficacy to a greater extent than traditional biopesticide preparations. This review constitutes an important contribution to future research and expands the panorama in relation to biopesticide formulations for the control of agricultural pests.

Keywords: biopesticides; bibliometric analysis; formulation; pests; biological activity

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1. Introduction

The accelerated growth of the global population is a trend that impacts the agricultural and food sectors. It is estimated that humanity will reach 9.8 billion inhabitants by 2050. Therefore, an increase in the use of pesticides for the control of agricultural pests that affect crop yields has been projected [1].

For decades, synthetic pesticides have been used in food production as pest and plant disease control agents. However, the extensive use of pesticides generates health problems in non-target organisms, which include alterations in hormonal systems, vascular and liver diseases, cancer, and cognitive disorders, among others [2,3]. Additionally, it is known that most of the chemical compounds used as pesticides are non-biodegradable, which favors the contamination of soils and water sources [4,5]. In this context, there is a need to implement sustainable and environmentally friendly strategies, such as biopesticides, in order to provide crop protection in a safe and competitive manner.

Biopesticides are pest and pathogen management agents based on living microorganisms or natural products. In addition, they offer great promise in controlling yield loss, reducing the demand for energy, and restoring the efficiency of agroecosystems [6].

Due to their natural origins, they stand out as an environmentally friendly tool, since they quickly decompose and minimize pollution problems. Likewise, they are characterized by their specificity for target organisms and promote the reduction of environmental and health problems associated with synthetic pesticides [7–9]. Additionally, they represent economic gains; in 2013, the world market was valued at 3 billion dollars, and by 2023 it is projected that values greater than 4.5 billion dollars will be reached. Therefore, the characteristics and economic trends biopesticides present place them as a potential strategy for the comprehensive management of agricultural pests [10,11].

Biopesticide formulations are important processes that must ensure a minimum negative effect on unwanted organisms, while providing the maximum effect of the active ingredient [12]. Although biopesticides make up an important sector of new products that contribute to agronomic safety, there are still challenges in the formulations due to the degradation of the biomass or bioactive metabolite, due to factors such as air, light, and temperature, as well as the development of these products must guarantee easy handling, application, and production viability [13–15]. For this reason, this work aims to present a comprehensive review of the different technological developments that enhance the effectiveness of natural preparations. Furthermore, unlike many conventional literature reviews that only focus on the biological activities of metabolites, this review provides a bibliometric analysis of biopesticides and their formulations, in which quantitative and statistical descriptors are used to establish trends on the most important pests, impact on agriculture, sources of biological control, novel methodologies, and the current state of biopesticide formulations. The analysis presented makes a significant contribution to the bibliometric approach that could be positive in the development of technological advances in the formulation of biopesticides, and provides some suggestions to researchers working on the subject.

2. Bibliometric Analysis of Biopesticide Formulations

Biopesticides are known as an ecological alternative that helps mitigate pollution and health effects caused by synthetic pesticides. However, the preparations of products based on bioactive organic compounds must be analyzed, and for this reason, it is pertinent to evaluate through scientometric tools the technological advances related to the improvement of biopesticide formulations. Consequently, a systematic search was carried out in the Scopus scientific database under search criteria established by means of Equations (1) and (2). It should be noted that the term "botanical insecticides" was incorporated into the search equations, due to use of biopesticides as the only term for the bibliography search may exclude important information of biopesticide research that deals with the control of insect pests by plant-derived substances.

The compiled information was refined in order to avoid the repetition of terms with abbreviations and hyphens [16]. The bibliometric parameters total number of citations, average number of citations per article, and categorization of publications with the highest citation were calculated using Bibiometrix software (University of Naples Federico II, Naples, Italy) from R commander (×64. 4.1.0) [17]. The types of software used were VOSviewer 1.6.16 version (Leiden University, The Netherlands) and CorText Manager (INRAE, Noisy-le-Grand, France) to develop bibliometric networks, such as Co-occurrence and Co-authorship maps, a historical map, a contingency matrix, and a Sankey diagram.

TITLE-ABS-KEY ("biopesticides" OR "botanical insecticides") AND (LIMIT-TO (DOCTYPE, "ar") OR LIMIT-TO (DOCTYPE, "re")). (1)

TITLE-ABS-KEY ("biopesticides" OR "botanical insecticides") AND ("encapsulation" OR "hydrogels" OR "nano" OR "formulation" OR "emulsion")) AND (LIMIT-TO (DOCTYPE, "ar") OR LIMIT-TO (DOCTYPE, "re")). (2)

2.1. Scientific Production

The analysis of scientific production on biopesticide formulations demonstrated the trend of publications per year on biopesticide studies (information compiled with Equation (1)); it was observed that published research showed a significant increase of 71.24% over the last decade (2011–2021) (Figure 1). The increasing trend is possibly related to economic support from government programs, since funding for innovative, sustainable, and ecological research is being considered to meet the demand for food and mitigate environmental pollution.

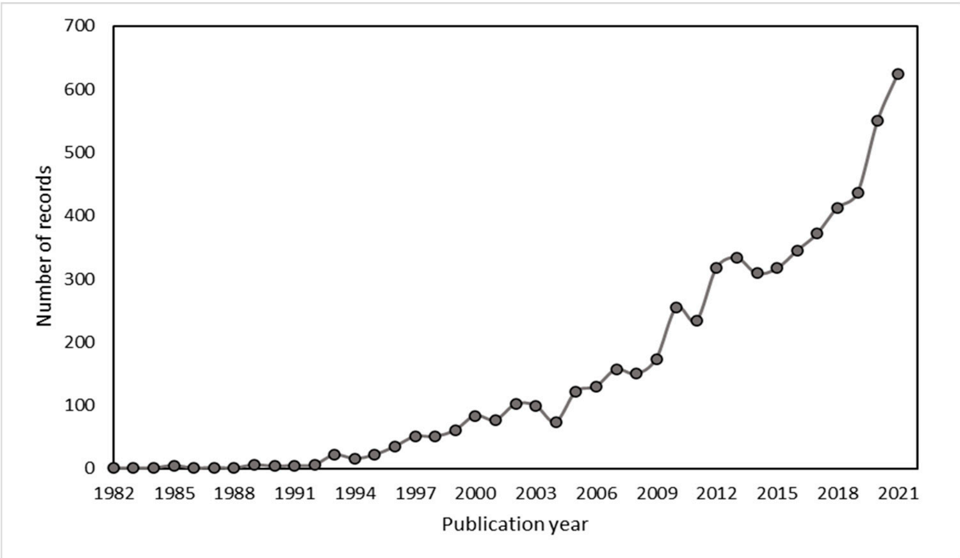


Figure 1. The trend of publication increases concerning biopesticide.

It is known that biopesticide formulation strategies are essential in the efficient management of pathogenic agents; therefore, it was necessary to incorporate into the systematic search, through Equation (2), the keywords: encapsulation, hydrogels, nano, formulation, and emulsion. Consequently, the results allowed us to analyze the relevance of the published research, finding the categorization of the leading countries in article publications on the subject (Table 1); where the United States presented the greatest contribution in number of citations (4080), followed by from India (3491). Furthermore, these showed the highest number of documents, with 157 and 172, respectively. Therefore, the impact of these publications in the study area and their probable use as important references for other research is evident.

Table 1. Leading countries in publications on biopesticides formulations.

Rank	Country	Number of Citations	Average Article Citations	Number of Publications
1	United States	4080	25.98	157
2	India	3491	20.29	172
3	Brazil	2198	21.76	101
4	Canada	1730	27.46	63
5	Italy	1709	26.29	65
6	United Kingdom	1106	29.10	38
7	Spain	884	24.55	36
8	France	847	24.91	34
9	Czech Republic	772	42.88	18
10	Germany	720	28.8	25

The most cited publications related to biopesticide formulations were also analyzed, and it was found that most of the documents listed corresponded to review articles, converted into key reference works on this subject, finding the contribution with the greatest impact made by authors from research centers (Table 2). India had 567 citations and 47.25 citations per year [18]. In this study, potential tools of nanotechnology for the development of precision agriculture were provided. The authors suggested the use of amorphous silica nanoparticles for the formulation of biopesticides with safe characteristics for humans [19]. Conversely, the results showed an original research article was used for its significant contributions in research on biopesticides of microbial origin, with 237 citations and 7.90 citations per year [20]. In this work, the efficacy of formulations based on *Metarhizium flavoviride* conidia for the control of *Schistocerca gregaria* was evaluated. The results showed superior performance of the cottonseed oil-based preparation compared to the water-based suspensions with values LD_{50} of 8.9×10^3 and 1.4×10^6 espores/insect, respectively Therefore, the authors suggested that the oil formulation improved the efficacy of *Metarhizium flavoviride* in agricultural crops.

Table 2. Documents with the most citations in biopesticides formulations research.

Title	Journals	Authors Affiliation Countries	Number of Citations	Number of Citations Per Year	References
Perspectives for nano-biotechnology enabled protection and nutrition of plants	*Biotechnology advances*	India	567	47.25	[18]
Biological control of locusts and grasshoppers	*Annual review of entomology*	Canada, Benin, United Kingdom	353	16.04	[21]
Geraniol-A review of a commercially important fragrance material	*South African Journal of Botany*	South Africa	299	23.00	[22]
Biological control of *Bermisia tabaci* with fungi	*Crop Protection*	Brazil, United States	248	11.27	[23]
Nano-based smart pesticide formulations: Emerging opportunities for agriculture	*Journal of Controlled Release*	India, Italy, United States, South Korea	244	61.00	[24]
The enhanced infectivity of *Metarhizium flavoviride* in oil formulations to desert locusts at low humidities	*Annals of Applied Biology*	United Kingdom	237	7.90	[20]
Application of nanotechnology for the encapsulation of botanical insecticides for sustainable agriculture: Prospects and promises	*Biotechnology Advances*	Brazil, India	232	25.77	[25]
Microbial inoculation of seed for improved crop performance: issues and opportunities	*Applied Microbiology and Biotechnology*	New Zealand	188	26.85	[26]
The science, development, and commercialization of postharvest biocontrol products	*Posthasvest Biology and Technology*	Israel, United, States, Spain, Italy, Belgium	180	25.71	[27]
Development, registration, and commercialization of microbial pesticides for plant protection	*International Microbiology*	Spain	179	8.95	[28]

2.2. Co-Occurrence and Co-Authorship Analysis

The keyword co-occurrence map showed seven different interrelated clusters (Figure 2). The grouped themes are associated with types of pests, among which are *Helicoverpa argimera*, *Spodoptera litura*, *Stodoptera frugiperda*, and *Lepidoptera*, as well as biological activities such as bioherbicide, larvicide, bioinsecticide, biofungicide, and entomotoxicity. In the same way, sources were identified for biological control, such as *Bacillus thuringiensis*, *Pseudomonas fluorescens Metarhizium anisopliae*, *Beauveria bassiana*, Baculovirus, nucleopolyhedrovirus (VPN), nematodes, entomopathogenic fungi, and essential oils, and formulation strategies, such as nanoparticles, nanoemulsions, microencapsulation, controlled release, and spray drying. Therefore, the bibliometric network provided an overview of the pest trends with greater study and affectation in agriculture. In addition, it provided significant information on the microorganisms used as potential sources of biological control; among these, the genus *Bacillus* and *Beauveria* is widely studied for its biological activities. Additionally, the analysis showed a focus on technological advances with nanotechnology tools, which are used to improve the efficacy and application of biopesticides, because they increase the surface area of the particles and affect properties such as physical strength, chemical reactivity, magnetism, electrical conductance, among others [29]. On the other hand, the main keywords reported were determined based on their co-occurrence, where biopesticides (264), formulation (80), biological control (76), *Bacillus thuringensis* (73), and botanical insecticides (59) were the words used with greater proximity in published documents according to data extracted from Scopus.

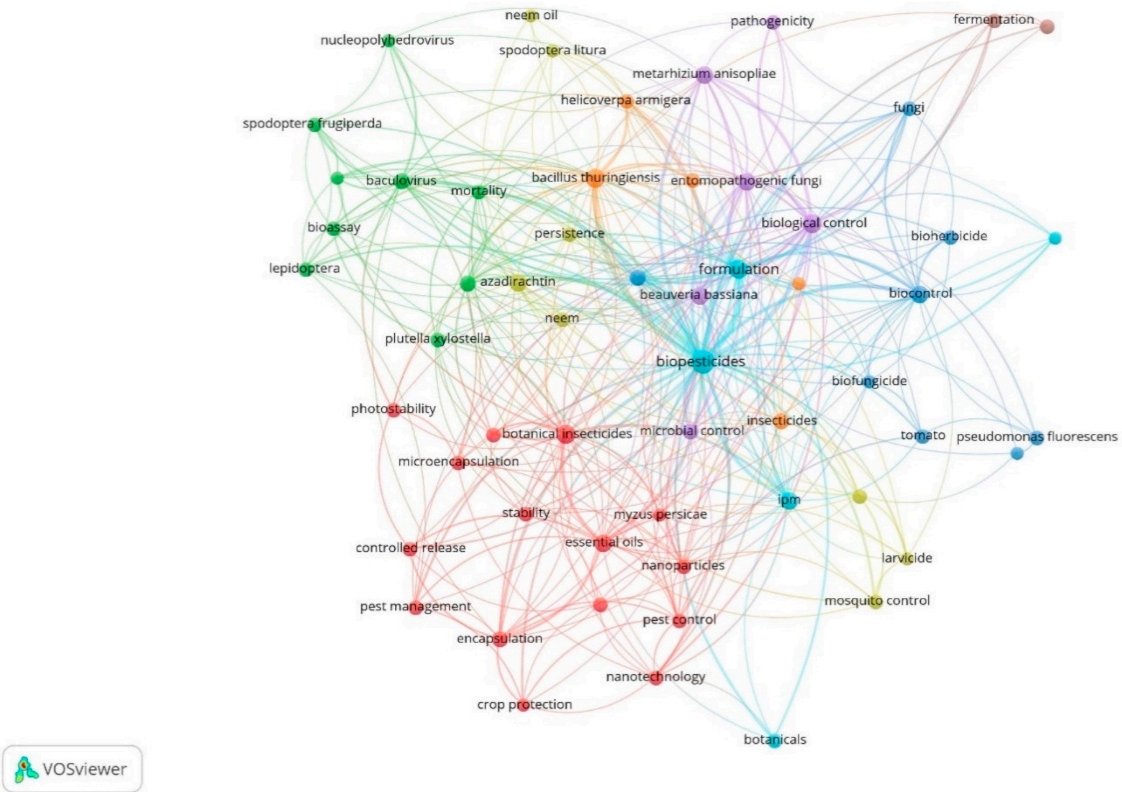
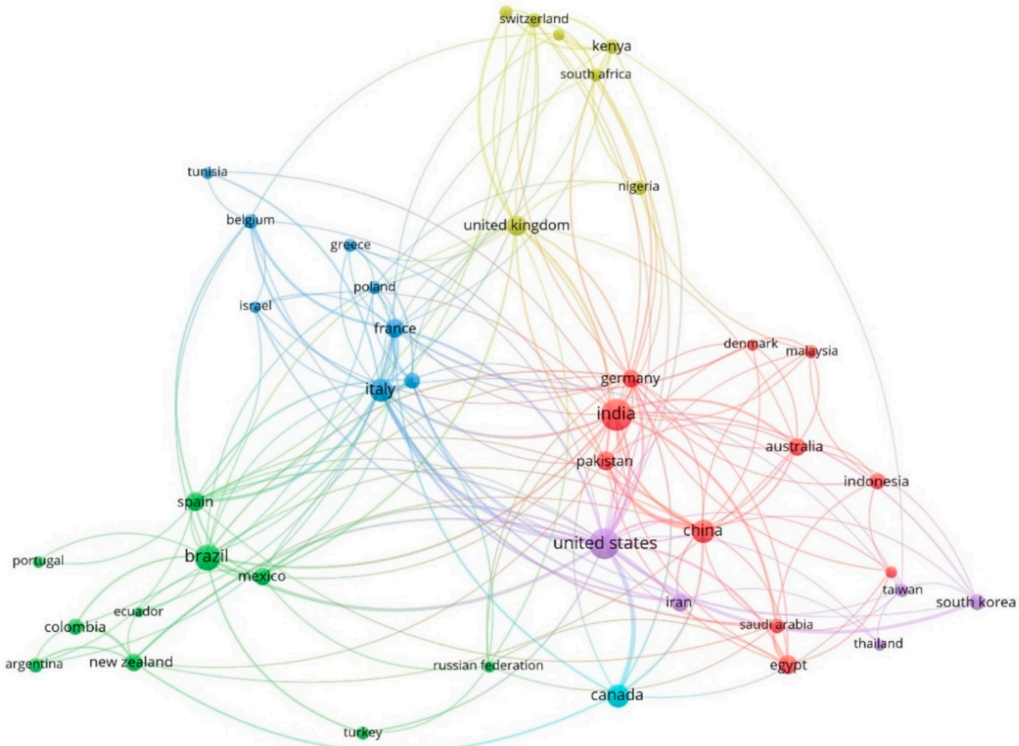
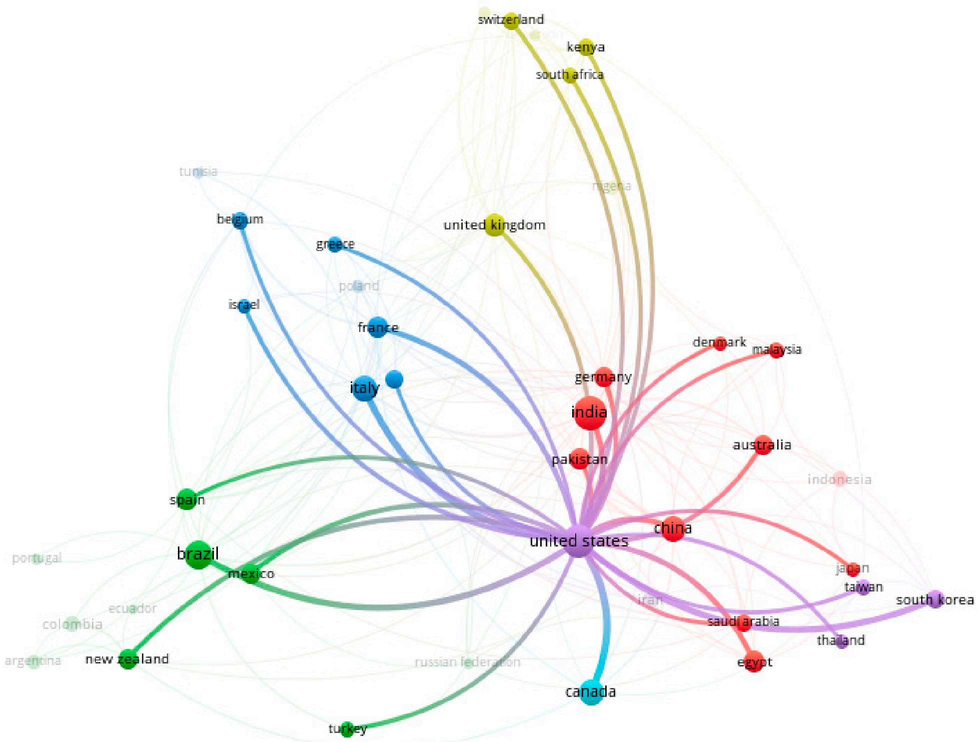


Figure 2. Bibliometric network of author keywords in publications on biopesticide formulations. Note: seven theme groups: yellow, blue, green, purple, red, orange, and sky blue. Information extracted from Equation (2).

Additionally, the co-authorship analysis enabled the construction of the collaboration network of countries regarding studies of biopesticides and their formulations (Figure 3a), finding six interconnected groups (red, blue, green, yellow, purple, and sky blue), with the United States as the country with greater cooperation in the investigations carried out; it forms the strongest collaboration network with 29 countries and is positioned as the main node (Figure 3b). India was also found to constitute the second largest collaboration network, with 21 countries (Figure 3c). Notably, India was the country with the highest number of published documents (172), so it was expected that it would be located as the main node of the cooperation network. The results presented show the relationship that exists between researchers and their respective institutional affiliations; therefore, scientific cooperation in the search for sustainable and ecological strategies that facilitate crop protection in a competitive manner is highlighted.

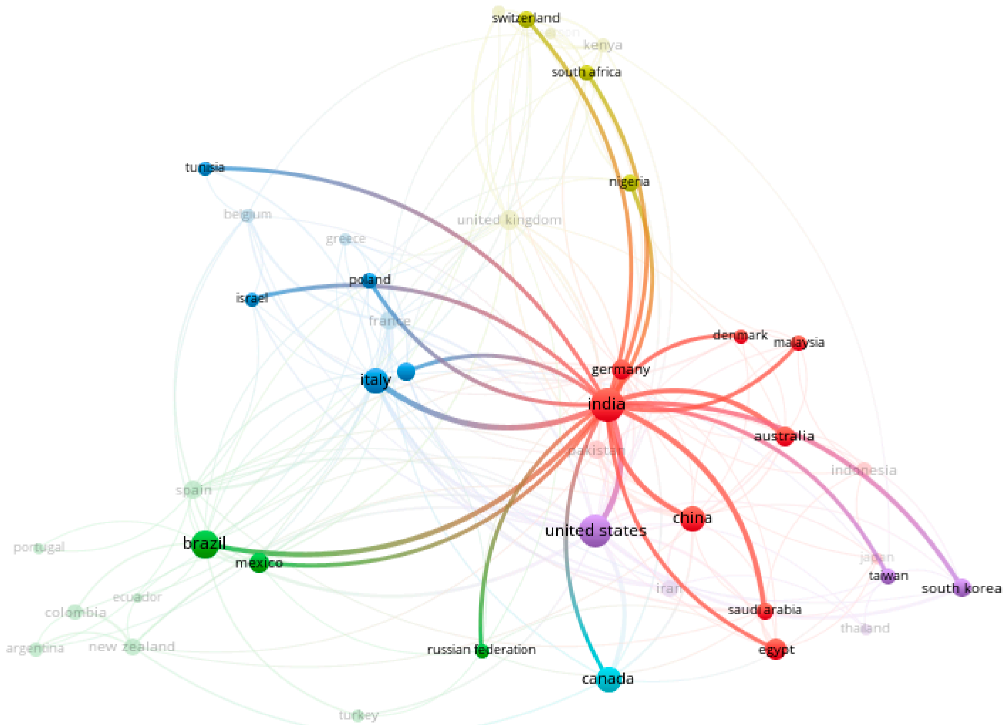


(**a**)



(**b**)

Figure 3. *Cont*.



(c)

Figure 3. Collaboration network of countries in publications on biopesticide formulations, (**a**) general collaboration network, (**b**) United States network, (**c**) India network. Note: five groups of countries: red, green, purple, yellow, and blue. Information extracted from Equation (2).

2.3. Contingency Matrix, Sankey Diagram, and Historical Map

The CorText Manager scientometrics platform was used to perform the contingency matrix, Sankey diagram, and historical map analyses. The contingency matrix consisted of a map, in which the colors indicated the degree of correlation between two variables under the measure of a statistical metric of Chi-square co-occurrence. On the numerical scale, the value of -6 showed that the observed co-occurrence result was 600% lower than expected; on the other hand, the value of 6 indicated that the observed co-occurrence was 600% higher than the expected value [30]. Additionally, the matrix presented negative correlations through blue cells, while the red cells meant a strong relationship; likewise, the white cells indicated that the variables had no relationship (neutrality) [31]. Figure 4 shows the correlations between the most relevant journals and countries in the scientific production of biopesticides and formulations. The analysis indicated that the United States had a correlation of 4 with the Journal of Economic Entomology (Q1–Q2); that is, there are four times more articles assigned between these factors than would be expected if the distributions of co-occurrence and semantic groups were independent [32]. Likewise, India presented correlations of 5 and 6 with the Journal of Biopesticides (Q4) and Pestology (Q4), respectively. It should be noted that the Journal of Economic Entomology is a journal of the Entomological Society of America, and is published in association with Oxford University Press, while the Journal of Biopesticides and Pestology belongs to Indian institutions. This analysis allowed us to infer about the quality of the published studies and will help future researchers in the possible selection of journals in the respective fields of research.

The temporal flow of the keywords was analyzed using a Sankey diagram, and the transformations in the combinations of keywords over time were identified. The diagram showed the interrelated keywords by flows of gray color, where the thickness represented the co-occurrences of the two keywords (Figure 5); the proximity of the words in the posts [33]. In the period from 2002 to 2012, combinations of keywords were identified:

"bicontrol & formulation" and "rhizobacteria & disease control", which were later divided into "aflotoxins & biocontrol" and "phyto-toxicity & milastin-k". This indicated that in a period of 6 years (from 2012 to 2018) disease control evolved towards the prevention of aflatoxins and the use of the commercial product Milastin-k in agricultural crops. Additionally, the period from 2012 to 2018 showed the converging current of the combinations "fungi & ipm" and "aflotoxins & mycotoxins" in "diatomaceous earth & formulations". Similarly, in the period from 2018 to 2021, the evolution of the theme towards the study of nanotechnological tools in pest control was observed; for example, the keyword currents "nanotechnology & nanobiopesticides", "*Bacillus thuringensis* & cry1ac", "essential oil & nanoemulsions", and "aflotoxins & biocontrol" converged into "pest control & biological control", "environment & microbial control", "integrated pest management & insecticide", and "biopesticide & nanotechnology". The divergence and convergence of currents, as well as the transformation of keywords, showed the dynamic evolution of the research field over time [31].

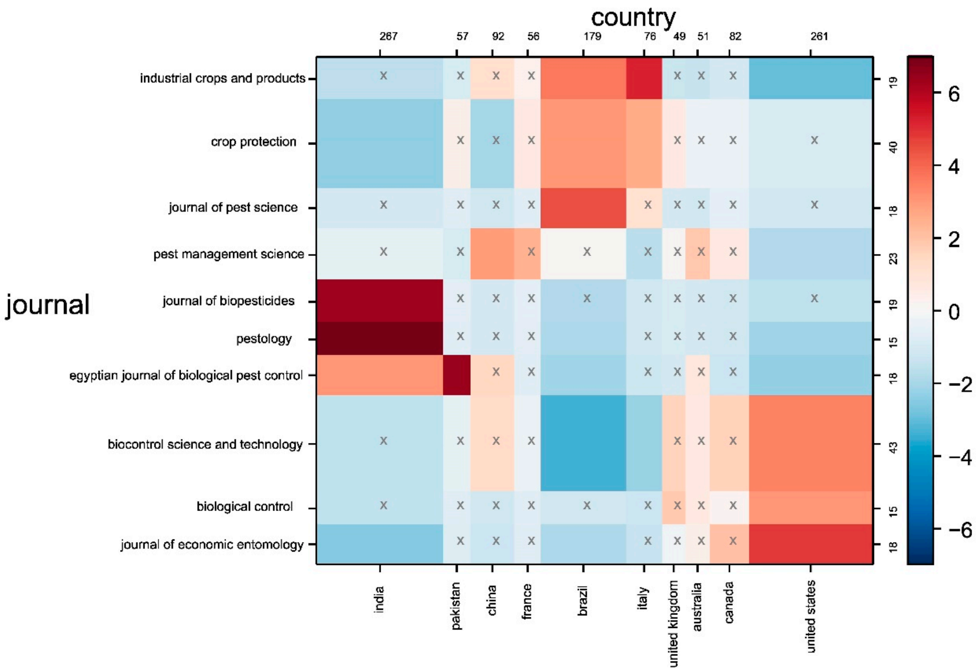


Figure 4. Contingency matrix on the relationship of journals and countries in publications on biopesticide formulations. Information extracted from Equation (2) (cells with x indicate that the model deviation is not statistically significant).

Figure 6 shows the historical map of keywords, which reaffirms the trends observed in the Sankey diagram. The analysis was developed in a time range from 2010 to 2021 and presented the relationships between the keywords, which historically evolved towards the use of nanotechnology to improve and enhance biopesticide formulations. Additionally, pests and sources of microbial biological control and of plant origin, that stood out for their importance in the subject, were identified. This map provides an overview over time of the technological advances on the subject, where nanotechnology is positioned as the tool to be called upon to overcome limitations in biopesticide formulations.

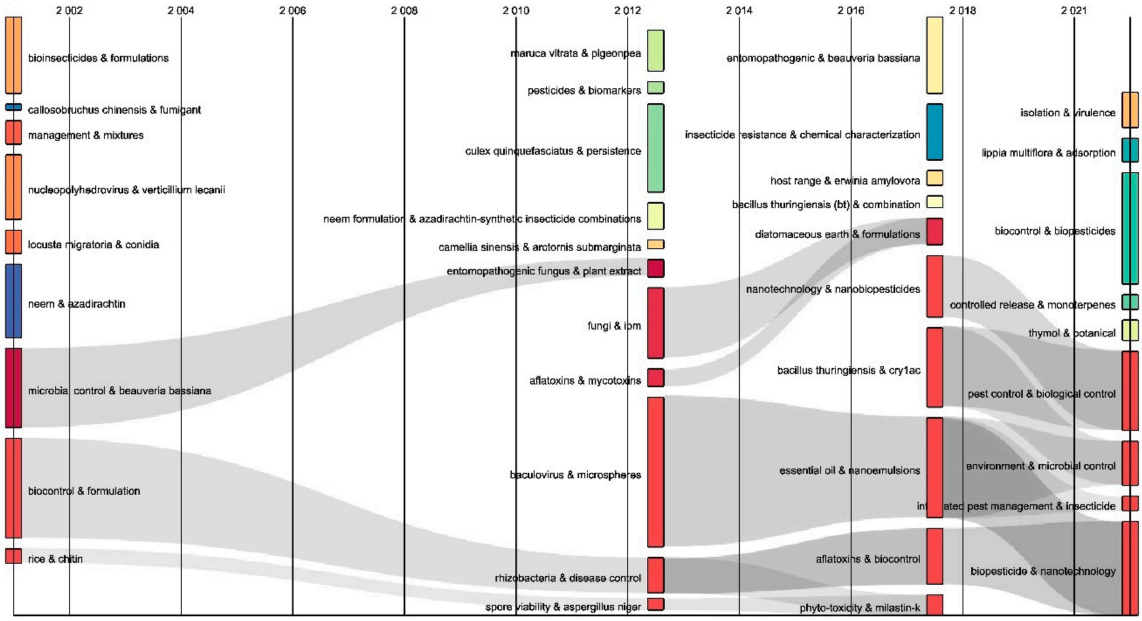


Figure 5. Sankey diagram of author keywords in publications on biopesticide formulations. Information extracted from Equation (2).

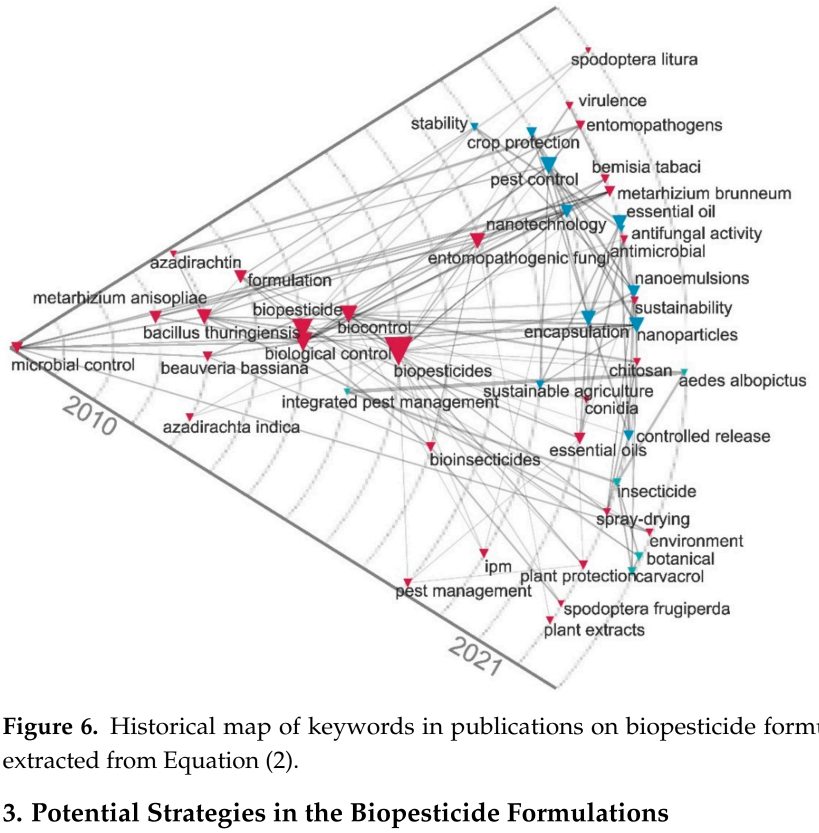


Figure 6. Historical map of keywords in publications on biopesticide formulations. Information extracted from Equation (2).

3. Potential Strategies in the Biopesticide Formulations

3.1. Microbial and Botanical Biopesticides

Microbial biopesticides are biological control products that have been used in the world for more than 60 years and are characterized as the fastest growing segment in the biocontrol industry [34]. Among the different microbial agents is the bacterium *Bacillus thuringiensis*, which corresponds to the most produced and successful microbial control agent due to its toxicity against different species of insects of the order Lepidoptera, Coleoptera, Diptera, and Hymenoptera. Its biological activity is due to the ability to synthesize protein crystals

(Cry) that cause the lysis of epithelial cells in the intestine, which causes the death of the larvae [35]. In the literature, there have been several reports indicating that *B. thuringiensis* is used as a biopesticide with a broad spectrum of action [36–39]. For example, Wu [40] reported a new toxin, Xpp81Aa1, from *B. thuringiensis* strain HSY204 with a thioredoxin domain with toxicity to *Aedes aegypti* larvae. The evaluated biological activity of Xpp81Aa1 had a significant response in *A. aegypti* larvae with LC50 of 156.86 ng/mL, being lower compared to that shown by the Cry2Aa toxin with 435.95 ng/mL. Therefore, the newly identified toxin can contribute toward the control of mosquitoes that cause diseases such as Zika virus, yellow fever, dengue, and chikungunya.

Furthermore, there have been reports of other species of the *Bacillus* genus that are presented as sources of biological control; among them, the *Bacillus cereus* Bc-A strain isolated from *Ricinus communis* roots. This showed activity against *Clavibacter michiganensis* in tomato plants under greenhouse conditions. According to the results, the severity of the disease caused by *C. michiganensis* significantly decreased by 50% with the application of Bc-A, higher than the effect shown by the chemical control Terra-Cu-Oxymet that presented a 25% decrease in bacterial canker disease [41]. On the other hand, Kulimushi [42] evaluated the inhibition of *Rhizomucor variabilis* in the presence of *Bacillus amyloliquefaciens*. In this study, a reduction in the severity of the disease of 4.2 ± 0.9 was determined in maize plants treated with the S499 strain, greater than compared to plants not treated with *Bacillus* strains whose value was 2 ± 0.7 according to the scale disease reduction index (DRI). In addition, fengycin metabolites were identified as those responsible for the antagonistic activity on *R. variabilis*.

Entomopathogenic fungi are also species that are used as pest control agents; currently, around 90 genera of fungi with pathogenicity in insects are known, belonging to the phyla Ascomycota, Chytridiomycota, Basidiomycota, and the subphylum Entomophthoromycotina [43]. Among these is the species *Beauveria bassiana*, a fungus that is characterized by its potential use as a bioinsecticide due to its important infection process that consists of three general stages, such as adhesion of the arthropod, penetration of the cuticle, and colonization of hemoceles. In each stage of infection, the fungus adapts by varying its structure in order to efficiently alter host defenses [44]. Similarly, it has been highlighted that *B. bassiana* biosynthesizes secondary metabolites, such as bassianolides, oosporeins, beauverolides, beauvericin, isarolides, and tenelins, responsible for cytotoxicity in insect cells [45]. An example of the insecticidal capacity of *B. bassiana* is reported by Biryol [46], regarding a biological control study of *Myzus periscae* from oil-based formulations. According to the results, the AFIDISIDAL-OD Bbas-TR61 formulation developed with the KTU-24 strain had the highest mortality effect on *M. persicae* nymphs in leaf-disc and pot experiments in a climatic chamber with values of $82.52 \pm 1.44\%$ and $84.33 \pm 1.20\%$, respectively. Notably, these values were higher than those shown by the Nostalgist-BL control (commercial formulation), for which mortality percentages were $77.33 \pm 1.20\%$ and $73.33 \pm 1.66\%$; so the oil-based formulation with the KTU- 24 can be considered for comprehensive pest management.

The genus *Metarhizium* is highly pathogenic against insects, and it has various well-known species, such as *M. album*, *M. anisopliae*, and *M. flavoviridae*. The most widely used biological control agent in the genus *Metarhizium* is *M. anisopliae*. This strain is an opportunistic pathogen and causes the death of its host by depleting nutrients, damaging tissues, and releasing toxins [47,48]. Riaz [49] reported the impacts of *M. anisopliae* on the mortality of *Trogoderma granarium*. Toxicity of *M. anisopliae* was assessed in terms of LC50 by exposing larval *T. granarium* to five concentrations; i.e., 1×10^8, 1×10^7, 1×10^6, 1×10^5, and 1×10^4 conidia/mL suspensions for 7, 14, and 21 days. The increased concentration of conidial suspensions and prolonged exposure time were responsible for higher mortality.

Another important fungus used as a control agent is the genus *Trichoderma*, which has been recognized since the 1920s for its fungicidal capabilities against soil-borne diseases caused by *Botrytis cinérea*, *Verticillium* spp, *Rhizoctonia solani*, *Armillaria* spp, *Sclerotium* spp, and *Sclerotinia sclerotiorum* y *Phytophthora*. [50]. Additionally, *Trichoderma* has been investigated for the control of pathogenic bacteria, such as *Ralstonia solanacerum*, a species that is characterized by infecting more than 450 plant species and producing bacterial wilt [51]. An example of the antibacterial activity of *Trichoderma* is the evaluation of the extracts of three strains: *T. harzianum*, *T. virens* and *T. koningi*, which found plants treated with metabolites of *T. harzianum* had the lowest level of severity of the wilting disease with a value of AUDPC 400 (value of the area under the progressive curve of the disease), while the maximum value of AUDPC of 1750 was determined in plants grown in soil treated with *T. koningi*; therefore, the metabolites of *T. harzianum* emerge as a possible effective tool against *R. solanacerum* [52].

Similarly, Table 3 shows nematode species and their respective formulations that are used for comprehensive pest management. For example, the genera *Heterorhabditis* and *Steinernema* are used to control pests of Japanese beetles, leafminers, termites, and cutworms, among others [53,54]. Recently, the species *H. bacteriophora* and *S. feltiae* have been studied to control potato tuber moth *Phthorimaea aperculella*, showing for the case of *H. bacteriophora*, LC50 values of 98 IJs in the prepupa life stage and 721.47 IJs for pupa, while that from *S. feltiae* LC50 of 5.92 and 569.86 IJs were determined for prepupa and pupa respectively. Consequently, LC50 concentrations showed that *S. feltiae* was more virulent than *H. bacteriophora* in the two life stages of the moth. This evidences the spectrum of action that nematodes can present as tools for pest control [55]. On the other hand, baculoviruses have also been studied as important agents against pests; specifically, they are successfully applied throughout the world to control lepidoptera pests in soybean crops [56], among these are Nucleopoliedrovirus from *Rachiplusia*, VPN from *Drosophila* C, VPN CrPV, FHV, VPN from *Spodoptera frugiperda*, and VPN from *Anagrapha falcifera*.

Table 3. Formulations of microbial biopesticides.

Microorganism (Strain)	Target Pests	Formulation	References
Bacteria			
Bacillus cereaus	*Clavibacter michiganensis*	Aqueous suspension	[41]
Bacillus thuringiensis	*Ephestia kuehniella*	Encapsulation	[57]
Leuconostoc pseudomesenteroides	*Drosophila suzukii*, *Drosophila melanogaster*, *Acyrthosiphon pisum*	Suspensions	[58]
Pseudomonas fluorescens	*Rhizoctonia solani*, *Cnaphalocrosis medinalis*	Suspensions	[59]
Bacillus thuringiensis	*Phyllocnistis citrella*	Emulsion	[60]
Bacillus subtilis Vru1	*Rhizoctonia solani*	Nanoencapsulation	[61]
Bacillus amyloliquefaciens FZB42	*Xanthomonas oryzae*	Suspensions	[62]
Bacillus thuringiensis	*Artogeia rapae L. Trichoplusia ni*, *T. ni Hübner*, *Plutella xylostella L.*, *Autographa californica Spreyer*	Encapsulation	[12]
Pseudomonas fluorescens (VUPF5 and T17-4 strains)	*Fusarium solani*	Nanoencapsulation	[63]
Bacillus velezensis RC218	*Fusarium*	Spray drying	[64]

Table 3. *Cont.*

Microorganism (Strain)	Target Pests	Formulation	References
Fungi			
Beauveria bassiana	*Myzus persicae*	Emulsion	[46]
Beauveria bassiana	*Helicoverpa armigera*	Encapsulation	[65]
Beauveria, *Metarhizium*, *Isaria*, and *Lecanicillium*	*Duponchelia fovealis*	Suspensions	[66]
Purpureocillium lilacinum and *Trichoderma spp*	*Meloidogyne javanica*	Suspensions	[67]
Beauveria bassiana and *Metarhizium anisopliae*	*Diatraea saccharalis*	Encapsulation	[68]
Metarhizium anisopliae	*Plutella xylostella*	Nanoparticles	[69]
Beauveria bassiana	*Musca domestica*	Encapsulation and emulsion	[70]
Beauveria bassiana	Nor reported	Hydrogel	[71]
Metarhizium brunneum	*Annual Bluegrass Weevil*	Hydrogel	[72]
Trichoderma harzianum	*Sclerotinia sclerotiorum*	Encapsulation	[73]
Trichoderma viride	*Helicoverpa armigera*	Nanoparticles	[74]
Trichoderma asperellum TV190	*Rhizoctonia solani*	Emulsion	[75]
Pochonia chlamydosporia	*Meloidogyne incognita*	Emulsion	[76]
Nematodes			
Steinernema carpocapsae	*Rhynchophorus ferrugineus*	Encapsulation	[77]
Steinernema carpocapsae	*Agrotis ipsilon Hufnagel*	Encapsulation	[78]
Steinernema carpocapsae	*Leptinotarsa decemlineata*	Encapsulation	[79]
Heterorhabditis bacteriophora, *Steinernema carpocapsae*, and *Steinernema websteri*	*Ixodes scapularis Say*	Emulsion	[80]
Heterorhabditis bacteriophora	*Diabrotica balteata*	Encapsulation	[81]
Virus			
Nucleopolyhedrovirus of *S. frugiperda* (SfMNPV)	*Spodoptera frugiperda*	Encapsulation	[82]
Helicoverpa armigera nuclear polyhedrosis virus (HaNPV)	*Helicoverpa armigera*	Encapsulation	[83]
VPN of *Spodoptera frugiperda*	*Spodoptera frugiperda*	Viral suspensions	[84]
VPN SfCH15, SfCH32	*Spodoptera frugiperda*	Viral suspensions	[85]
VPN of *Anagrapha falcifera*	*Cydalima perpectalis*	Viral suspensions	[86]

Compounds synthesized by plants, called secondary metabolites, have been studied as an alternative to synthetic pesticides [87], focusing on the biological activities that it presents when used as essential oils, extracts, or both. Plants that produce bioactive substances against agricultural pests include the families *Lauraceae*, *Myrtaceae*, *Rutaceae*, *Asteraceae*, *Sapotaceae*, *Lamiaceae*, *Cupressaceae*, *Caesalpinaceae*, *Apiaceae*, *Solanaceae*, *Piperaceae*, *Zingiberaceae*, *Sapotaceae*, *Poaceae*, and *Liliaceae* [88]. The secondary metabolites explored belong to the families of terpene, alkaloid, flavonoid, and phenolic compounds, among others [89], and are characterized by different modes of action against fungi, insects, nematodes, viral pathogens, and bacteria; for example, they act as inhibitors, protein denaturation agents, and repellents, among others [90].

Botanical compounds for pest control have been continuously investigated in the agricultural sector; an example is the azadirachtin molecule, a triterpenoid that is isolated from the Neem tree (*Azadirachta indica*) and belongs to the class of limonoids [91]. Commercial production of azadirachtin started in 1997 and was effective against more than 200 pest species [92]. It stands out for its low toxicity in mammals, with a tolerable intake in humans of 15 $mg.kg^{-1}$ $bw.day^{-1}$ and LD50 of 5000 $mg.kg^{-1}$ in rats. Its mode of action is characterized by regulating the growth of insects through the effect on the activity of ecdysone [93]. Moreover, the action of azadirachtin on intestinal flora, brain neurons, and intestinal content in *Spodoptera litura* larvae has been investigated. Qin [94] reported that azadirachtin is related to the negative regulation of CREB gene and protein expression in the brain. In addition, azadirachtin affects the arrangement and distribution of intestinal epidermal cells, leading to apoptosis of intestinal epidermal cells and inability to break down and absorb food. This inhibits the breakdown and utilization of fatty acids, glucose, and proteins, as well as reducing the absorption and use of alkanes and other compounds in the intestinal tract, and the absorption and transmission of energy is inhibited.

Other metabolites of botanical origin are shown in Table 4, and were explored for their ability to present bioactivities for the control of agricultural pests. For example, the production of sesquiterpenes in tomato glandular trichomes that contribute to the resistance of the host plant against pests has been reported. Wang [95] evaluated a collection of *Solanum habrochaites* accessions with the potential to obtain sesquiterpenes that affect the potato aphid *Macrosiphum euphorbiae*. The identified chemotypes showed that the compounds β-caryophyllene, α-humulene, α-bergamotene/β-bergamotene, and α-santalene consistently and negatively affected aphid feeding behavior. In addition, the repellent activity of the elucidated terpenes showed an effect on the choice of the host plant by *M. euphorbiae*. Flavonoids are also used to control agricultural pests [96]; for example, the insecticidal activity exhibited by the flavone pinocembrin against Epilachna paenulata (*Coccinelidae*, *Chrysomelidae*), *Spodoptera frugiperda* (*Lepidoptera*, *Noctuidae*), and *Xanthogaleruca luteola* (*Coleoptera*, *Chrysomelidae*). This compound was isolated from an ethanolic extract of *Flourensia oolepis* and showed strong antifeedant activity with an antifeedant index (AI%) against *E. paenulata*, *S. frugiperda*, and *X. luteola* of 90, 91, and 94%, respectively [97]. Similarly, alkaloids make up a group of compounds with structural diversity and biological activities of interest in the agricultural sector [98]. Kokkrua [99] evaluated the efficacy of berberine in the control of foliar diseases of rice. Berberine is a benzylisoquinoline alkaloid that is isolated from plants such as *Coptis*, *Berberis*, and *Coscinium* [100]. The authors indicated that berberine showed antifungal activity against the pathogens *Rhizoctonia solani*, *Bipolaris oryzae*, *Pyricularia oryzae*, and *Curvularia lunata* with a minimum inhibitory concentration (MIC) of 125 µg/L. Additionally, berberine at 10 mg/mL reduced the percentage of severity of rice blast (*P. oryzae*) by 49.81%, which was similar to the action of mancozeb and difenoconazole.

According to the EPA (Environmental Protection Agency), pyrethrin is the botanical biopesticide with the largest number of registrations in the United States, with approximately 30 registered products. In addition, eugenol has the largest number of suppliers in the United States (95), followed by D-limonene (70), osthole (46), and matrine (46). The European Union has also promoted the accelerated development of biopesticides based on pyrethrins, azadirachtin, and spinosins A and D (Spinosad), among others. Similarly, in China, authorizations were registered for a total of 28 biopesticides in 2019 with the participation of 177 companies. Among them, there are more than 15 registered companies related to the production of matrine, pyrethrin, azadirachtin, osthole, rotenone, and camphor [101].

Table 4. Formulations of botanical biopesticides.

Compounds	Botanical Sources	Target Pests	Formulation	References
Terpenes				
β-caryophyllene, α-humulene, α-bergamotene/β-bergamotene, and α-santalene	*Solanum habrochaites*	*Macrosiphum euphorbiae*	Leafs extracts	[95]
Azadirachtin	*Azadirachta indica*	*Drosophila melanogaster*, *Myzus persicae*, *Spodoptera litura*, *Bactrocera dorsalis*, *Anticarsia gemmatalis*	Emulsions	[102–106]
Azadirachtin	*Azadirachta indica*	Not reported	Nanoemulsion	[107]
Azadirachtin	*Azadirachta indica*	Not reported	Encapsulation	[108]
α-pinene, linalool	Various spice plants	*Spodoptera litura*, *Achaea Janata*	Nanoparticles	[109]
Eugenol	clove essential oil	*Sitophilus zeamais*	Suspensions	[110]
Eugenol	Not reported	Sf9 cell line (*Spodoptera frugiperda*)	Suspensions	[111]
β-caryophyllene	Not reported	*Hypothenemus hampei*	Aqueous suspension	[112]
Limonene	Orange essential oil	*Tribolium confusum* and *Cryptolestes ferrugineus*	Nanoemulsions	[113]
Limonene and α-pinene	*Baccharis reticularia*	*Tribolium castaneum*	Nanoemulsions	[114]
Carvacrol, geraniol, eugenol, thymol	Not reported	*Ditylenchus dipsaci*	Biomass extracts	[115]
Sabinene, β-caryophyllene, terpinolene, pinene, limonene	*Hyptis suaveolens*, *Hyptis spicigera*	*Sitophilus granirius*	Emulsions	[116]
Oxygenated monoterpenes	*Mentha pulegium*, *Mentha suaveolens*	*Toxoptera aurantii*	Biomass extracts	[117]
β-caryophyllene, caryophyllene oxide, epiglobulol	*Atalantia buxifolia*	*Tribolium castaneum*, *Lasioderma serricorne*, *Liposcelis bostrychophila*	Biomass extracts	[118]
Flavonoids				
Naringenin, hesperidin	Not reported	*Xylella fastidiosa*	Syringe application	[119]
Pinocembrin	*Fluorensia oolepis*	*Epilachna paenulata*, *Xanthogaleruca luteola*, *Spodoptera frugiperda*	Ethanolics extracts	[97]
Miricitine, naringenina, quercetina	*Cynara carduncLos*	*Trifolium incarnatum*	Emulsions	[120]
Flavonoids from roots, stalks and fruits	*Withania somnífera*, *Terminalia chebula*	*Furarium oxysporum*	Biomass extracts	[121]
Naringine, naringenine, hesperidine and its Cu^{2+} complexes	Not reported	*Spodoptera frugiperda*	Suspensions	[122]

Table 4. *Cont.*

Compounds	Botanical Sources	Target Pests	Formulation	References
Tetrahydrocurcumin	Curcuma	*Fusarium graminearum*	Encapsulation	[123]
Quercetin, chlorogenic acid, rutin	Not reported	*Helicoverpa argimera*, *Spodoptera lutira*	Oral Infection	[124]
Flavonoids from plant tissue	*Calotropis procera*	*Callosobruchus chinensis*	Methanolic extracts	[125]
Alkaloids				
Lupanine	*Lupinus*	*Arion vulgaris*, *Arion rufus*, *Deroceras reticulatum*	Oral Infection	[126]
Berberine	*Berberis*	*Bipolaris oryzae*, *Curvularia lunata*, *Pyricularia oryzae*, *Rhizoctonia solani*	Aqueos extracts	[99]
Matrine	*Sophora flavescens*	*Diaphorina citri*, *Panonychus citri*, *Sitophilus zeamais*, *Spodoptera frugiperda*	Emulsions	[127]
Alkaloides N-Phenilsulfonylmatrinics and N-bencilmatrinics	Organic synthesis	*Mythimna*, *Aphis citricola*	Organic solvents Extracts	[128]
Sarmentine, sarmentosina	*Piper sarmentosum*	*Echinochloa crusgalli*, *Amaranthus retroflexus*	Emulsions	[129]
Berberine	*Cotis chinensis*	*Bidens pilosa*	Aqueos extracts	[130]
Palmatine, Jatrorrizine	*Tinospora capillipes*	*Colletotrichum gloeosporioides*, *Fusarium oxysporum*, *Mycosphaerella sentina*, *Pestalotia mangiferae*, *Cercospora kaki*, *Gymnosporagium haraeanum*, *Rhizoctonia solani*, *Colletotrichum graminicola*	Aqueos extracts	[131]
Tylophorine, tylophorinine, isotylocrebrine	*Tylophora indica*	*Helicoverpa armígera*	Organic solvents Extracts	[132]
Flindersine	*Toddalia asiatica*	*Helicoverpa armígera*, *Spodoptera litura*	Organic solvents Extracts	[133]

3.2. Emulsions

Emulsions consist of colloidal dispersions with droplet sizes of 0.1–10 µm that have optical transparency, low viscosity, and thermodynamic stability conditions [134,135]. Oil-in-water (O/W) systems are a type of emulsion that allows the combining of the protection provided by the hydrophobic environments created inside the droplets with the greater dispersion of the metabolites in an aqueous medium. This characteristic favors the handling of active compounds because the degradation of molecules is limited without affecting biological activity [136]. Currently, the use of O/W emulsions that include essential oils and semiochemicals is of interest and they have been investigated as a potential alternative to improve the penetration, diffusion, and dispersion of natural compounds. Furthermore, these types of water-based formulations are not only environmentally friendly, but also less toxic to plants and can easily scale due to simple preparation processes. Likewise, they can be considered as release systems to load and release hydrophobic substances [137].

Essential oils exhibit significant antimicrobial activities, since they have a high percentage of phenolic compounds, such as thymol, eugenol, carvacrol, and monoterpenes with tertiary alcohols; for example, the essential oil extracted from *Lippia alba* was evaluated by O/W emulsions for the control of *Rhizoctonia solani* in seedlings of *Ocimum basilicum* and *Plantago ovata*. The formulations were made in water and Tween 80 (0.1%), and showed improvements in seedling survival up to 92 and 98% in pots treated with *P. ovata* and *O. basilicum*, while pots not treated with the oil emulsions presented 15 and 20%, respectively. It is noteworthy that the essential oil of *L. alba* contained 73.8% of monoterpenic alcohols; consequently, the presence of these metabolites had an impact on the biological action against *R. solani* [138].

Thermodynamic stability is an important factor in the development of emulsions, since an emulsion is a thermodynamically unstable system due to the natural tendency of the mixture to decrease interfacial tension [139]. Therefore, equipment such as homogenizers, rotor-stator systems, and pipe flows that supply energy must be used to reach the new thermodynamically stable condition [140,141]. For example, the stability of Neem oil-based O/W emulsions has been investigated by using a high-shear mixer. Iqbal et al. [142] reported that the variation of the stirring time at 3600 RPM had an effect on the droplet size in formulations based on Neem oil, and found that during 15 min of stirring the droplet size was 6.70 µm and at 60 min it reduced to 1.20 µm. Additionally, emulsion shaken for 60 min showed greater stability after 14 days of storage and higher mortality at a concentration of 500 ppm of 99.70% in Aedes aegypti larvae compared to the less shaken emulsions. Notably, droplet size has an impact on emulsion properties such as stability, long persistence on the applied surface, dispersion in aqueous medium, and bioefficacy of the active ingredient [143].

Water-in-oil (W/O) emulsions are also of interest in the formulation of biopesticides, due to present advantages over granular formulations, as the oil traps water around the organism and delays evaporation of the water once applied. This is especially beneficial for organisms that are sensitive to desiccation [144]. For example, Yakook [145] reported the development of W/O emulsions for the formulation of *Bacillus thuringiensis serovar aizawai* (BtA) for pest control. In this research, the Pickering emulsion method was used to obtain W/O emulsions. This method uses solid particles as emulsifiers, instead of surfactants, and formulations are considered superior to conventional emulsions in terms of release rate control, droplet size, and stability over time of the incorporated microorganisms. The studied BtA/emulsion system exhibited a mortality rate of 92% against *Spodoptera littoralis*. However, the non-formulated BtA has shown 71% mortality, and the emulsion alone resulted in only 9% mortality.

3.3. Suspension Concentrates

Suspension concentrates are stable suspensions of solid pesticides in a fluid generally intended for dilution with water before spray. The active ingredient in these formulations is a solid that does not dissolve in either water or oil. There are requirements of particle size to ensure proper bioactivity, chemical activity, etc. If the particles are pre-milled to the required size, they are easily dispersed in the liquid phase. Like wettable powders, when suspension concentrates are sprayed onto a sorptive surface, the insecticidal particles remain on the surface of the substrate where they are readily available to the target pest [146]. For example, Vineela [147] evaluated the improved bioefficacy of *Bacillus thuringiensis* var. *kurstaki* against *Spodoptera litura* by formulation as a concentrated suspension. The results showed that the LC50 value of the suspension concentrate formulation developed with 559 nm Bt particles was 2.84 µL/mL containing only 0.95 mg Bt. Field evaluation of the suspension concentrate formulation against *S. litura* on castor revealed the highest percent of larval reduction, 92.4% and 96.2%, at concentrations of 2.5 and 3.0 mL/L, respectively.

3.4. Encapsulation

Encapsulation is defined as a physical process in which an active substance or material, called a core, is completely or partially isolated by an encapsulating agent or wall material. This makes it possible to improve the stability of biopesticides, reducing the reactivity and volatility of the core, while maintaining viability against biotic and abiotic stress conditions [148]. Likewise, encapsulation makes it possible to formulate biopesticides from microbial agents (microorganism cells), which guarantees metabolic activity and bioefficacy during storage and application [149].

Encapsulation systems are generally based on droplet formation of capsules from liquids using wall or coating materials, such as biopolymers; additives, such as surfactants, oils, and oxide-minerals; and production methods, such as emulsification, coacervation, spray drying, gelation, thermal ionic gelation, precipitation, and coating (Figure 7). The encapsulation of nuclei of interest as essential oils has been studied; for example, the essential oil of clove *Syzygium aromaticum* was encapsulated by emulsification with the purpose of improving the bioefficacy of the active ingredient, and found a significant improvement through prolonged efficacy of up to 14 days against *P. operculella* compared to the unencapsulated pure oil which lost bioactivity against insects after the first day of application. Encapsulation was performed by emulsifiable concentrate using zeolites due to their ability to control emissions and adsorption of low concentrations of volatile organic compounds. Tween 80 and gelatin were also used as an additive and polymeric matrix, respectively [150].

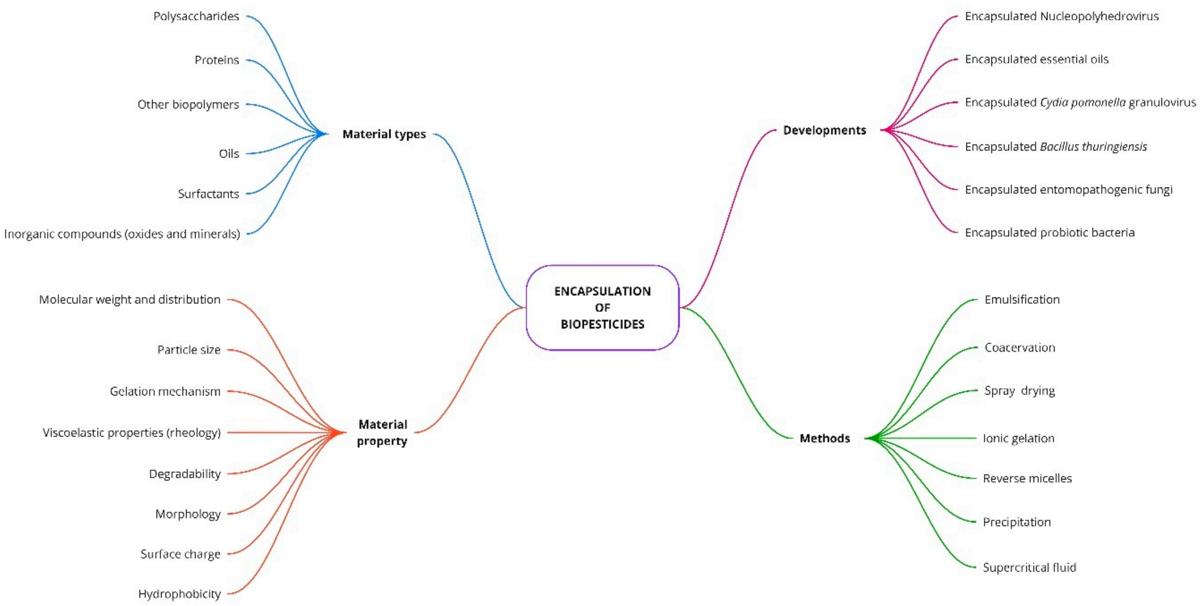


Figure 7. Schematic representation of the criteria for the encapsulation of biopesticides.

It is known that the most widely used microbial biopesticides are formulated from conidia. These microorganisms must remain ungerminated before application in the field. This means that the conidia must be encapsulated in the oil phase of the emulsion, since the chemical nature of the surface of most conidia is hydrophobic, which results in their disposition in the oil phase. Therefore, the encapsulation of conidia in O/W emulsion systems may have significant potential for the development of new biopesticide formulations [151]. Amar Feldbaum [152] reported the encapsulation of the entomopathogenic fungus *Metarhizium brunneum* by Pickering O/W emulsion. The authors evaluated the UV protection capacity for conidia formulations prepared by Pickering O/W emulsions that were stabilized with TiO_2 nanoparticles. Emulsions that demonstrated successful single cell encapsulation showed an average droplet diameter close to the size of conidia cells (4.5–8.0 μm). In addition, it was found that the encapsulation improved the germination of the conidia, finding that the germination rate of the Pickering emulsion preparations in treatments exposed during outdoor UV radiation (sunlight) was higher (90.50 $\pm$ 3.50%), compared to the conidia in the control (Triton X-100 solution), which did not germinate in the presence of UV radiation. Notably, when biopesticides are applied in the field, exposure to UV radiation (290–400 nm) significantly decreases biological activity, because the conidia of entomopathogenic fungi and bacterial spores are sensitive to UV radiation, thus affecting the germination and viability of natural preparations [153].

Additionally, biopesticide encapsulation systems have been developed using supercritical fluid technologies. These methods have advantages compared to other conventional processes, such as the reduction of the use of toxic organic solvents, easy solute/solvent separation, and adjustable density [148]. Pemsel [154] reported the encapsulation of the *Cydia pomonella* granulovirus (CpGV) for the control of the codling moth (*Cydia pomonella*). The formulations were made using the particulate gas saturated solution (PGSS) technique and showed no loss of virulence compared to the commercial CpGV product. The PGSS process may be suitable for the encapsulation of viruses since the carbon dioxide supercritical fluid used is chemically inert; the temperatures used do not allow the virus proteins to denature, and the organic solvents that can negatively affect the biological material are reduced.

3.5. Hydrogels

Hydrogel products constitute a group of polymeric materials, whose hydrophilic structure makes them capable of retaining large amounts of water in their three-dimensional networks while presenting resistance to dissolution arising from cross-links between the network chains [155]. Hydrogels vary according to the preparation methods and are classified into homopolymeric, copolymeric, and interpenetrating polymeric (IPN) hydrogels (Figure 8). In addition, these present functional characteristics such as high absorption capacity, photostability, high biodegradability, maximum durability, and stability in swelling environments [156]. In material science, there has been interest in hydrogels due to their excellent biocompatibility, easy preparation, and versatile applications; in particular, they have been used in nutrient/drug delivery, tissue engineering, bioadsorbents, and separation systems [157].

In the agricultural sector, hydrogel systems are developed with the purpose of increasing crop production by supplying water, micronutrients, and fertilizers in a controlled manner to the soil [158,159]. Additionally, these materials have been investigated for the formulation of pest control products; for example, Nasser [160] prepared k-carrageenan-based hydrogels for the delivery of *Bacillus thuringiensis israelensis* (Bti). The formulations were made with the purpose of avoiding degradation and enhancing the biological action of the microbial agent against Aedes aegypti. The hydrogels showed an absorption capacity greater than 100% without alterations in their shape, even after seven months of being submerged in water; thus demonstrating the stability of the hydrogels. In addition, it was found that the material produced was effective in the gradual release of Bti during the 11 weeks analyzed, providing a larval mortality rate of 100%. Moreover, the widely known bioinsecticide azadirachtin was incorporated into alginate granules in the presence of bioabsorbents, such as lignin, humic acid, and olive pomace. The presence of bioabsorbents was found to decrease the rate of metabolite release. In addition, the formulations improved stability to photodegradation, which turns out to be an important factor in enhancing the bioefficacy of the active ingredient due to UV protection. Notably, the prepared hydrogels were homogeneous materials with a high azadirachtin trapping capacity [161].

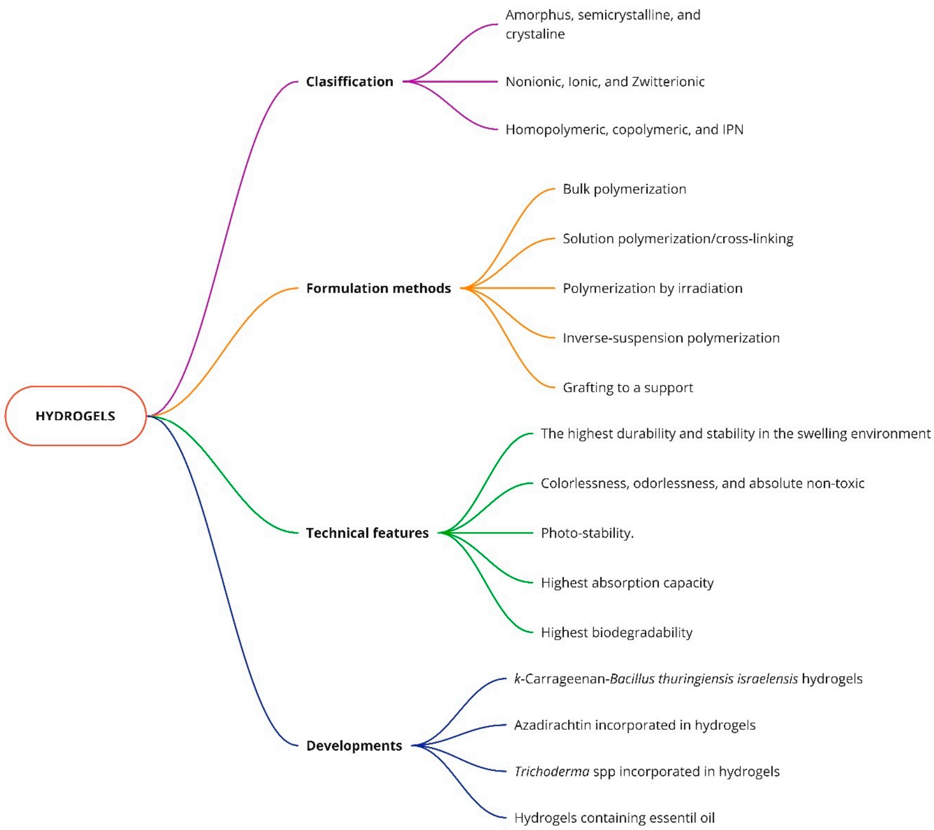


Figure 8. Schematic representation of hydrogels in the formulation of biopesticides.

3.6. Nanoformulations

Recently, biopesticide nanoformulations have been considered as a technology for mitigating pests that cause economic losses in agriculture [162]. Through the development of systems such as nanoemulsions and nanoencapsulations, limitations that traditional biopesticides manifest in terms of production methodologies, costs, performance, and functionalities can be overcome. Nanotechnology has the potential to guarantee a significant increase in dissolution speed, water solubility, and dispersion uniformity in the application of bioproducts, which increases the bioefficacy of natural preparations [163]. Although no chemical alteration of the molecules of interest is carried out, reducing the size of particles at the nanoscale allows the analysis of new chemical, physical, and mechanical properties useful for the production of new products [24,164].

Nanoemulsions are systems that present superiority in terms of physicochemical properties with respect to other types of colloidal systems. Due to droplet sizes ranging from 10–500 nm and low polydispersity [165], these formulations show advantages compared to microemulsions, such as better physical stability against sedimentation, flocculation, and Ostwald ripening; they have also improved bioavailability due to high surface area/volume ratios, they require low doses of emulsifiers, and have improved chemical stability [166,167]. Choupanian [168] reported the improvement of the efficacy of the limonoid azadirachtin, through nanoemulsions of neem oil, against two species of pests: *Sitophilus oryzae* and *Tribolium castaneum*. The formulations showed particle sizes between 208–507 nm and contact mortality after two days of exposure in *T. castaneum* and *S. oryzae*, with values ranging between 74–100% and 85–100%, respectively. Notably, the implementation of nanotechnology in the preparation of Neem oil nanoemulsions generated a significant increase in mortality compared to the commercial formulation Neemix (17% mortality) and unformulated Neem oil (0% mortality). Likewise, nanoemulsions have been made from membrane lipids of *Trichoderma brevicompactum* to control the downy mildew disease caused by the fungus *Sclerospora graminicola*, which affects the seeds of the pearl millet species *Pennisetum glaucum*. The preparations were carried out by the ultrasonic emulsification method using Tween 80 as a surfactant. The study showed results of droplet size of 5–51 nm, and it was found that the seeds treated with the membrane lipid nanoemulsion of *T. brevicompactum* presented a protection of 82.80% and the lowest incidence of the disease, 16.90%, while the control showed the highest incidence of the disease with 94%. Additionally, the prominent molecule of the lipid fraction responsible for the induction of systemic resistance in the host against the downy mildew pathogen was identified [169].

Nanoencapsulation is defined as the technology capable of packaging nanoparticles, which enhances bioavailability, controlled release, and allows a precise orientation of bioactive compounds to a greater extent than microencapsulation [170]. Nanoencapsulation formulations can be developed by using nanospheres and nanocapsules. Nanospheres are defined as matrix systems in which the active ingredient is uniformly dispersed; while nanocapsules consist of vesicular systems in which the active compound is confined in a cavity surrounded by a polymeric membrane [171]. Ebadollahi [172] evaluated the toxicity of essential oils isolated from the leaves of *Thymus eriocalyx* and *Thymus kotschyanus* in *Tetranychus urticae* adults. The essential oils were nanoencapsulated in the mesoporous material MCM-41 and showed particle sizes between 40–100 nm. Nanoencapsulation increased the stability and extended persistence of oils at 18 and 20 days for *T. kotschianus* and *T. eriocalyx*, respectively. In addition, the mortality of *T. urticae* individuals increased from 80 to 230 mites when the *T. eriocalyx* essential oil nanocapsules formulation was used, while the nanocapsules formulated from *T. kotschyanus* increased mortality from 58 to 186 mites. Therefore, compared to pure oils nanoencapsulation improved the bioavailability and bioefficacy of bioactive compounds. Consequently, nanoencapsulated essential oils of *T. eriocalyx* and *T. kotschyanus*, through a widely known mesoporous material, MCM-41, can be a potential method for its application in the management of *T. urticae*.

4. Overall Discussion and Perspectives

Biopesticide formulations are processes that must guarantee the development of products that can be implemented in the field and are potentially marketable. One example is the field trials of *Metarhizium anisopliae* var. *acridum* against *Locusta migratoria manilensi* from oil emulsions. Emulsion implementation was conducted in cage trials in corresponding field plots to accurately estimate mortality; doses of 3.3×10^{12} and 5.0×10^{12} conidia/ha caused 90% mortality between 9 and 13 days. In the ground spray test, 3.3 × 1012 conidia/ha killed >90% of *L. migratoria manilensis* between 11 to 15 days after treatment in a wide variety of vegetation and climatic conditions. In the aerial spray treatment, the final percentage of locust survival was reduced to 10% at 11 and 14 days in the field cage and open field lobsters, respectively [173]. Moreover, in a study in northern Niger, avian predation was evaluated in a locust population aerially sprayed with *Metarhizium acridum* in oil-based formulations (Green Muscle ®) with 107 g conidia/ha. Locusts started dying five days post-spray and the biopesticide reached its maximum effect one–two weeks after the spray, with 80% efficacy at day 21. After spraying, kestrels took significantly more of the larger female (75–80%) than the smaller male (20–25%) locusts. This indicated that avian predation increased the impact of the biopesticide by removing more of the adult female locusts. No direct or indirect adverse side-effects were observed on non-target organisms, including locust predators such as ants and birds. It should be noted that the Food and Agriculture Organization of the United Nations (FAO), based on the recommendations of its Pesticide Referee Group, considers biopesticides based on *M. acridum* to be the most appropriate option for locust control [174].

In addition, single formulations and combinations of *Beauveria bassiana*, *Metarhizium anisopliae*, and *Bacillus thuringiensis* have been applied in greenhouse and field trials against the tomato leaf miner *Tuta absoluta Meyrick* 1917. Formulated suspensions were sprayed with a hand spray nozzle and the highest protections were obtained on leaves (93.4, 89.7, and 90.1%) and fruits (93.5, 94.4, and 95%) with *B. bassiana*-AAUB03, *M. anisopliae*-AAUM78, and *B. thuringiensis*-AAUF6 under greenhouse conditions, respectively. While in the field, the combined treatments improved leaf protection efficacy by up to 95.3% [175].

Although the microbial agents *Beauveria bassiana*, *Metarhizium anisopliae*, and *Bacillus thuringiensis* have been extensively studied for improved bioactivity and implementation against pathogens in laboratory, greenhouse, and field trials, improved formulations of nematodes used as control agents are also known; for example, encapsulation of *Steinernema carpocapsae* has been performed in sodium alginate capsules to control *Agrotis ipsilon Hufnagel*. Notably, entomopathogenic nematodes, like fungi and bacteria, still face significant barriers such as susceptibility to desiccation and solar ultraviolet (UV) radiation, as well as a lack of durable formulations and appropriate application methods. Therefore, encapsulation with sodium alginate shows that the nematodes have better infectivity after 6 months of storage, so that the sodium alginate capsules improved the stability and efficacy of the nematodes [78].

The results obtained from the bibliometric analysis of biopesticide formulations allowed the integration of techniques and approaches that seek to improve the bioactivities of natural preparations. For example, nanotechnology is currently an important tool that has been mainly used in the nanoformulation of essential oils as control agents, among which neem oil stands out. However, it is expected that these nanotechnological methodologies will be consolidated in the large-scale production of biopesticides. In addition, the need to adequately test actual integrated pest management programs, develop better formulations, and improve shelf life of some microorganisms ensures the continued need for research. Therefore, growth opportunities are projected in the biopesticide sector, which is promising from a commercialization and sustainability point of view.

In addition, the progress of genetically modified microorganisms may further increase the number of new products, and it will be interesting to observe the evolution of biopesticides in the global crop protection market and their success will be linked to environmental policies.

5. Conclusions

Research on biopesticides is a field that is constantly growing. Due to their natural origins, advantages are attributed to biopesticides as respectful strategies in the environment, since they quickly decompose and minimize health problems and environmental pollution. Using scientometric tools, this review showed that published research on biopesticides showed a significant increase of 71.24% in the last decade (from 2011 to 2021). Additionally, the bibliometric analysis allowed analysis of scientific productions on the subject, identifying leading countries such as the United States and India, which formed the main networks of scientific cooperation in the search for sustainable and ecological strategies that facilitate the protection of crops in a competitive way.

The bibliometrics presented trends for the formulation of biopesticides, finding preparations made by means of emulsions, encapsulations, hydrogels, and nanoproducts. Notably, biopesticides have limitations due to the degradation of biomass or bioactive metabolites, due to factors such as air, light, and temperature; therefore, it is necessary to encourage the development of processes that guarantee overcoming these limitations. Similarly, the bibliometrics showed, through temporal flow analysis, that in the period from 2010 to 2021 investigations evolved towards the use of nanotechnology, with the purpose of improving and potentiating the formulations of biopesticides. Consequently, nanotechnology tools can be classified as the current strategies of interest that increase and protect bioefficacy to a greater extent than traditional biopesticide preparations. This review constitutes an important contribution for future research and expands the panorama in relation to biopesticide formulations for the control of agricultural pests.

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