Biopesticide Formulations, Possibility of Application and Future Trends

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SUMMARY

Biopesticides are the formulated form of active ingredients based on microorganisms such as bacteria, viruses, fungi, nematodes or naturally-occurring substances, including plant extracts and semiochemicals (e.g. insect pheromones). Application of biopesticides is still limited to only a few percent of all pesticides used for crop protection. There are many factors contributing to that situation, such as expensive production methods, poor storage stability, susceptibility to environmental conditions, efficacy problems, etc. Some of these problems can be overcome by formulation improvements. With many pressures on product performance formulation is becoming the most important area to enhance and extend the activity of biopesticides. In this paper we reviewed different types of biopesticides existing on the market and discussed possibilities for their application and current status. The expected future trends in formulation development of biopesticides are explained.

Keywords: Biopesticides; Formulations; Semiochemicals

INTRODUCTION

Pesticides provide significant benefits to people by controlling pests that invade agricultural crops. However, there are many risks associated with their use because of their potential to cause adverse effects. Consequently, there is an increasing public pressure to replace them, if possible, with safer alternatives for crop protection. Plants at all stages of their growth, as well as harvest products in storage, are susceptible to attacks by many pathogens that cause severe damage to plant products. Biopesticides based on microorganisms may represent an alternative path in crop protection because of their safety to humans and non-target organisms, both in individual applications and within integrated pest management (IPM). IPM includes a minimum use of chemical pesticides to maintain crop health and biopesticides may have an important place in that strategy (Chandler, 2011). There are different kinds of biopesticide active ingredients and each has specific properties and can be formulated in a variety of products (Burges, 1998; Knowles, 2005, 2006).

Products containing living and biologically active ingredients have been commercially available for agricultural uses for many years. The most common biological product for plant protection is based on *Bacillus* *thuringiensis* and used for insect control. In Serbia, several products have been registered: Biobit-WP, D-Stop (WP), Foray 48-B (WP), Novodor-FC (SC) and Wormax-Of (WP). Viruses (*Zucchini Yellow Mosaik Virus*) and fungi (*Ampelomyces quisqualis, Candida oleophila, Trichoderma atroviride, T. asperellum*, etc.) have also been shown to be useful in crop protection programs (EU Pesticides database, 2013). The products Polversum (*Pythium oligandrum* – WP) and F-stop (*B. subtilis* – SC), based on microorganisams, are used for disease control in Serbia (Janjić and Elezović, 2010).

Biological products are highly target-specific and their use is highly desirable but acceptable formulations are very difficult to develop. The reason for this is that, apart from the required good physical properties and convenience in use, the formulated product must also keep its biological agent functional throughout storage and during application (Woods, 2003).

Commercial biopesticides should be economical to produce, have persistent storage stability, high residual activity, be easy to handle, mix and apply, and provide consistently effective control of target pests. Different formulations of biopesticides should be introduced to overcome problems relating to their efficacy and their degradation and to be convenient during handling and application (Boyetenko, 1998). This paper reviews different types of biopesticide formulations that are available on the market, and shows the expected future trends in formulation development of biopesticides.

BIOPESTICIDE FORMULATIONS

Active ingredients of biopesticides are formulated in the same way as synthetic pesticides in most cases. This is most convenient for users as it allows them to use the same equipment for different treatments. Many biopesticides are based on living organisms. The viability of these organisms will have to be maintained at acceptable levels during the formulation process and storage. At the time of application, the organisms must revive from their dormant state in order to be active. Problems in formulating biopesticide products are considerable and thorough fundamental understanding of the processes causing loss of viability is necessary for further progress (Seaman, 1990; Boyetenko, 1998). The formulation process leads to a final product by mixing the microbial component with different carriers and adjuvants for better protection from environmental conditions, greater survival of the biological agent, controlled rates, as well as improved bioactivity and

storage stability. Current work is focused on enhancing spray retention, selecting droplet size and deposition on the leaf that are most important for the efficacy of any agent. The most important functions of the developed formulations are: stabilization of microbial agent during distribution and storage, easier handling and application of the product, protection of the bioagent from adverse environmental conditions and enhancement of the bioagent's activity by increasing contact and interaction with the target pest. These functions can be achieved by formulating bioagents in different ways (Seaman, 1990; Mollet, 2001).

Regarding their physical state, biopesticide formulations can be divided into liquid and dry formulations. Liquid formulations can be water-based, oil-based, polymer-based, or combinations. Water-based formulations (suspension concentrate, suspo-emulsions, capsule suspension, etc.) require adding of inert ingredients, such as stabilizers, stickers, surfactants, coloring agents, antifreeze compounds, and additional nutrients. Dry formulations can be produced using different technologies, such as spray drying, freeze drying, or air drying either with or without the use of fluidized bed. They are produced by adding binder, dispersant, wetting agents, etc. (Tadros, 2005; Brar, 2006; Knowles, 2008). Each formulation type is produced in a specific way.

Biopesticides are usually formulated as: dry formulations for direct application – dusts (DP), seed dressing formulations – powders for seed dressing (DS), granules (GR), micro granules (MG), dry formulations for dilution in water – water dispersible granules (WG), and wettable powders (WP); liquid formulations for dilution in water – emulsions, suspension concentrates (SC), oil dispersions (OD), suspo-emulsions (SE), capsule suspensions (CS); ultra low volume formulations (Knowles, 2005, 2006).

Dusts (DP) are formulated by sorption of an active ingredient on finely ground, solid mineral powder (talc, clay, etc.) with particle size ranging from 50-100 μ m. Dusts can be applied directly to the target, either mechanically or manually. Inert ingredients for this formulation are anticaking agents, ultra violet protectants and adhesive materials to enhance adsorption. Concentration of active ingredient (organism) in dust is usually 10%. Although they have positive effects under certain circumstances, they also pose serious inhalation hazard for users. This is an old formulation type that had been used for many years before granules were developed and they became restricted on the account of their adverse health impact on users. Other dusts are manufactured

very simply and they are still used today in many parts of the world (Knowles, 2001).

Powders for seed treatment (DS) are formulated by mixing an active ingredient, powder carrier and accompanying inert to facilitate product adherence to seed coats. This type of formulation is applied to seeds by tumbling seeds with the product designed to adhere to them. Powders for seed treatment are a very old type of formulation, a traditional product form for coating seeds, and they also contain a red pigment as a safety marker for dressed seed (Woods, 2003).

Granules (GR) are similar to dust formulations, except that granular particles are larger and heavier. Coarse particles (size range 100-1000 microns for granules and 100-600 microns for micro granules) are made from mineral materials (kaolin, attapulgite, silica, starch, polymers, dry fertilizers and ground plant residues) (Tadros, 2005). Concentration of active ingredient (organisms) in granules ranges from 5-20%. The active ingredient either coats the outside of the granules or is absorbed into them. Granule products are very simply manufactured, their active ingredient is processed by mixing a powder blend with a small amount of water to form a paste which is then extruded and dried if necessary. Another way of production is applying a liquid active ingredient to coarse absorptive material. After that granules can be coated with resins or polymers to control the rate of effectiveness of active ingredient after application. Granular biopesticides are mostly used to apply products to soil in order to control weeds, nematodes, and insects living in soil, or for plant uptake by root. Once applied, granules release their active ingredient slowly. Some granules require soil moisture to release their active ingredient (Knowles, 2005; Lyn, 2010).

Wettable powders (WP) are dry, finely ground formulations to be applied after suspension in water. Wettable powders are produced by blending an active ingredient with surfactant, wetting and dispersing agents and inert fillers, followed by grinding to a required particle size (about 5 microns). These products can raise serious health and safety issues for manufacturers because of their dustiness, which can cause inhalation and skin and eye irritation problems if strict safety precautions are not taken. For these reasons and because of their dustiness during application, wettable powders are gradually suppressed by suspension concentrates or water dispersible granules, which have been the most widely used pesticide formulations (Knowles, 2005).

Regarding solid biopesticide formulations, much attention has been focused on WPs because of their long storage stability, good miscibility with water and convenient application using conventional spraying equipment (Brar, 2006).

Water dispersible granules (WG) have been developed to overcome problems of dustiness of powder formulations. Water dispersible granules are designed to be suspended in water, i.e. granules break up to form uniform suspension similar to that formed by a wettable powder. Compared to powder products these WGs are relatively dust-free, and with good storage stability. Water dispersible granules can be formulated using various processing techniques, such as extrusion granulation, fluid bed granulation, spray drying, etc. The products contain wetting agent and dispersing agent similar to those used in wettable powders, but the dispersing agent is usually at higher concentration. Water dispersible granules are usually more expensive than older types of formulations (dusts, wettable powders) but their safety and greater convenience regarding application make them still desirable for many users (Knowles, 2008).

Emulsions consist of liquid droplets dispersed in another immiscible liquid (dispersed phase droplet size ranges from 0.1 to 10 µm). Emulsion can be oil in water (EW), which is a normal emulsion, or water in oil (EO), an invert emulsion. Both products are designed to be mixed with water before use. To avoid instability the proper choice of emulsifiers for stabilization is extremely important. In the case of invert emulsions, losses due to evaporation and spray drift are minimal because oil is the external phase of the formulation (Brar, 2006). However, lower shelf stability and occasional phytotoxicity may affect the overall performance of emulsions. Studies are currently being conducted to screen a variety of oils and emulsifying agents in order to improve initial invert emulsion formulations for biopesticides (Verner, 2007).

Suspension concentrate (SC) is a mixture of a finely ground, solid active ingredient dispersed in a liquid phase, usually water. The solid particles are not dissolved in liquid phase, so that the mixture needs to be agitated before application to keep particles evenly distributed. The composition of suspension concentrate is complex and it contains wetting/dispersing agents, thickening agents, antifoaming agents, etc. to ensure a required stability. They are produced by a wet grinding process and have particle size distribution ranging from $1-10 \,\mu$ m. During the grinding process, inert ingredients adsorbed onto particle surfaces prevent re-aggregation of small particles. These small particles often exhibit improved bioefficacy in use because greater particle surface area offers easier access of the active ingredient to plant tissues. Because they are water-based, they offer many advantages, such as of pouring and measuring, safety to the operator and the environment, and economy. Therefore they are becoming a very popular type of formulation (Woods, 2003; Knowles, 2005).

Oil dispersions (OD) are dispersions of solid active ingredients in non-aqueous liquid intended for dilution before use. The non-aqueous liquid is most often an oil, the best choice is some kind of plant oil. In that way retention, spreading and penetration can be improved. Oil dispersion provides several important characteristics, such as an ability to deliver water sensitive active ingredients and an ability to use an adjuvant fluid instead of water which can increase and broaden pest control. This formulation is produced in the same way as suspension concentrate. Inert ingredients for this type of formulation should be carefully selected to prevent instability problems (Vernner, 2007).

Suspo-emulsions (SE) can be considered as a mixture of suspension concentrate and emulsion. The product is very demanding to formulate because it is necessary to develop a homogenious emulsion component simultaneously with a particle suspension component which will remain stable in the final formulation of the product. Careful selection of appropriate dispersing and emulsifying agents is necessary to overcome the problem of heteroflocculation between solid particles and oil droplets. In addition, extensive storage stability testing of this formulation is necessary (Knowles, 2008). In spite of the complexity of this formulation, the use and importance of suspo-emulsions has been remarkable and will continue to increase.

Capsule suspension (CS) is a stable suspension of micro-encapsulated active ingredient in an aqueous continuous phase, intended for dilution with water before use. Bio-agent as its active ingredient is encapsulated in capsules (coating) made of gelatin, starch, cellulose and other polymers. In that way the bio-agent is protected from extreme environmental conditions (UV radiation, rain, temperature, etc.), and its residual stability is enhanced due to slow (controlled) release. The most frequently applied method of encapsulation uses the principle of interfacial polymerization. Encapsulation in microcapsules has been extensively used to give smaller size and high efficiency to fungal biopesticide formulations (Winder, 2005; Brar, 2006). Microcapsule suspensions need to be stabilized with surfactants and thickeners in the same way as suspension concentrate and similar additives are used. Despite clear benefits of this controlled release formulation, its commercial development is rather slow. The

slow progress is partly due to the complexity of formulation and partly to its high production cost (El-Sayed, 2005; Chen, 2013).

Ultra low volume liquids (UL) are formulations with very high concentration of active ingredient which is extremely soluble in crop-compatible liquid (ultra low volume liquid). UL products are not intended for dilution with water before use and often contain surface active agents and drift control additives. Ultra low volume liquids are easy to transport and use. UL liquid biopesticides can be formulated in a similar way using a suspended biocontrol agent as an active ingredient (Woods, 2003).

FUTURE TRENDS

The requirement for safer products intended for plant protection leads to a preference of biopesticide formulations with good efficacy and stability. Biopesticides provide environmentally friendly alternatives to chemical pesticides but they face a number of challenges in their development, manufacture and application. Research of their production, formulation and delivery could greatly assist in commercialization of biopesticides. It seems likely that biopesticides will have a wider use in the future as their application methods improve and better and cheaper choice of different inerts has been identified for various formulations. The use of biopesticides with adjuvants has been shown to enhance their activity and that fact has opened new opportunities for further development in that area. Selection of an appropriate formulation can improve product stability, enhance and extend activity, and may reduce inconsistency of field performance of many potential bio-agents. Biopesticides are seen as a tool for developing a more rational pesticide use strategy and future products should have improved balance between efficiency and cost (El-Said, 2005; Rao, 2007; Glare, 2012; Khater, 2012).

Trends relating to the type of biopesticide formulations would probably go the way from wettable powders and suspension concentrates to water dispersible granules, and from dusts to granules, for safety reasons, and from single component to multi-component formulations. In addition, an increased number of controlled release formulations can be expected to optimize their biological effects, while new types of formulations, such as nanoemulsion, nanosuspension, nano capsule suspension, etc., will result from newly developed nanotechnology (Rao, 2007; Ghoromade, 2011; Glare, 2012). Significant progress has been made in developing formulations and application methods but much work still remains to be done regarding the use of biopesticides for plant protection. Further improvement of techniques and multidisciplinary research of plant pathologists, formulation chemists and agricultural engineers are likely to provide good, safe, effective and inexpensive products for plant protection.

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Formulacije biopesticida, mogućnosti primene i perspektive daljeg razvoja

REZIME

Biopesticidi predstavljaju formulisane proizvode na bazi mikroorganizama kao što su bakterije, virusi, gljive, nematode ili prirodnih proizvoda kao što su biljni ekstrakti i semiohemikalije (npr. feromoni insekata). Udeo biopesticida koji se primenjuju u zaštiti bilja iznosi svega nekoliko procenata od ukupne količine pesticide koja se upotrebljava u te svrhe. Postoji više razloga za ovakvu situaciju kao što su, na primer, skup proizvodni proces, niska stabilnost biopesticida pri skladištenju, osetljivost na klimatske uslove pri kojima se primenjuju, zatim problemi vezani za efikasnost i dr. Neki od navedenih problema mogu da budu prevaziđeni odgovarajućim procesom formulisanja biopesticida. Zahtevi za što kvalitetnijim i efikasnijim proizvodima su sve veći tako da proces formulisanja otvara važan prostor za povećanje i proširenje aktivnosti biopesticida.

U ovom radu razmatrane su različite formulacije biopesticida koje se nalaze na tržištu, mogućnosti njihove primene, prikazano je trenutno stanje u ovoj oblasti i date su perspektive daljeg razvoja.

Ključne reči: Biopesticidi; formulacije; semiohemikalije