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REVIEW ARTICLE

Neoteric Advances in Pesticide Formulations for Environmentally Benign and Sustainable Vegetable Pest Management

Preeti Dhanker1, Sushil 1 , Pooja Sharma1, Digamber2, Rahul Dhankar3
1Department of chemistry,2Department of S.S.T, 3Department of Agronomy
CCS Haryana Agricultural University, Hisar
Haryana-125004

ABSTRACT

In the way to minimize the production losses and to maintain the quality of vegetables harvest, a variety of agro-chemical protectants are used. Out of these, various pesticides are used in combination with other pest management techniques during cropping to wipe out pests and arrest innumerable diseases. Anyhow, the use of pesticides during production often leads to the presence of pesticide residues in vegetables after harvest. Inflated doses and continual exertion of prosaic formulations lead to accrue pesticide residues in vegetable commodities along with environmental pollution. With the increasing awareness of toxic effects of conventional formulations, there is a significant trend towards switching over from such pesticide formulations using petroleum and organic solvent based constituents to user and environment friendly water based pesticide formulations. The developed world has progressed substantially in this regard to develop eco-friendly formulations which are safer to vegetable and the environment. These formulations would not only replace toxic, non-degradable ingredients/adjuvants of the conventional formulations but also increase the bio-efficacy of the products through incorporating latest technologies including size reduction (Wettable Powder to Suspension Concentrate, Soluble Concentrate to Microemulsion), increased coverage of applied surface area (EC to ME/Nano-formulations), reduced wastage (Dust/WP to Controlled Release Formulations) and dose rates of applied same pesticides to improve food quality with minimum pesticide residues.

Keywords: *Microemulsions, pesticide formulation, solubilized system, stabilityer gave macroemulsion and microemulsion respectively, which were stable over an extended period of time.*

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INTRODUCTION

Indian economy is greatly based on agriculture, as our country is very well known for possessing its own rich and diverse knowledge about various cultivation practices involved in agriculture. Agriculture sector supports a large portion to the nation's GDP. Now also, agriculture is the leading dependent sector for providing self-employment to rural population, whose average farm size continues to decline with population growth and they contribute to approximately 68% of population of the country [1].

Food is considered as the most fundamental human need. It provides adequate nutrients for the body's growth, maintenance, repair and reproduction. India is the second most populous country in the world and its economic scenario is dominated primarily by agriculture sector. Nearly 64% of its population is dependent on agriculture6. India stands second in vegetable production in the world [1, 2]. Vegetables are chief components of the human diet since they provide essential nutrients necessary for most of the reactions occurring in the body. Regular consumption of fresh fruits is greatly healthy for the body. Fruits are enriched in all the required vitamins and minerals which fulfills the body's need. But how safe and healthy are these fruits and vegetables? We think that eating provides our body the essential nutrients that it requires when we consume fresh fruits and vegetables. This might be surprising to some of the people but most of the foods contain extremely contaminated pesticides residue on them. Food security is one of the major concerns for India, where the diverse agro climatic conditions necessitate different approaches for cultivation and crop protection. With the limitation of expansion of land area under cultivation, most of the gains in agricultural production have come from increased productivity through two major inputs i.e. fertilizers and pesticides.

So, with the view of reducing the yield losses and quality of vegetables, pesticides are introduced during cropping in addition to the many other management practices for pest killing and preventing pest

diseases. However, the presence of residues is also a major problem with the use of pesticides after harvest [6]. Pesticides are used to protect the crops from insects, germs and rodents when the plants are growing up. Residual amount of these chemicals are retained on the food when it gets to the grocery store. The pesticide residue cannot easily be removed with plain water. When you consume a fruit, the pesticide residue goes into the body as they get stuck and can make you sick.

In most of the developing countries pesticides are used as dusts, EC's, solutions and many more for pest management in fruits and vegetables. But with the advancement in formulations the above mentioned forms of pesticides are considered as "classical" or "traditional". However, traditional pesticide formulations have several limitations disadvantages, such as high organic solvent contents, dust drift, and poor dispersibility, wherein most of the pesticide is lost to the environment and less than 1% remains on the target. This low effectiveness contributes to serious environmental pollution [44, 48]. They need higher dosed of pesticide and hence, resulted in great residues in plants and vegetables. But, with the awareness towards residual effects of conventional formulations, the need of new and advanced formulations was felt which lead to the present day formulations. This started with the smooth shift from petroleum and volatile organic solvent to much user friendly and environmentally benign formulations. Numerous eco-friendly pesticide formulations, safer to vegetable and the environment [17] are being produced with the advancement in formulation technologies which reduces size, increased coverage area, reduced dosage, declined wastage and least residues with infalted yield and improved quality.

SELECTIONS RULES/CRITERIA FOR FORMULATIONS

In order to use or select the most relevant formulation for specific vegetable pest management, a very detailed as well as keen analysis of the following factors is required as explained by Cooping [8]:

1. **Safety of applicator:** Applicators are most easily prone to pesticide hazards, via inhalation or skin penetration. So, this is the most vital criteria to be taken in consideration while selecting a formulation.
2. **Environmental factors:** There are a number of formulations that are prone to off target hazards like drifting in air, or residues in water bodies which can cause serious problems. So, Special provisions are required with such formulations. These off target residues cause detrimental causes to wildlife to varying degrees, birds may be attracted by granules, zooplanktons and phytoplanktons.
3. **Biology of Pest:** The growing habits and survival strategies and the life cycle of a pest is an important point to be considered to determine which formulation is suitable.
4. **Equipment:** Availability of specific and proper equipment for application is also important for designing the formulation**.** Some pesticide formulations require specialized handling equipment, including application equipment, safety equipment, and spill control equipment.
5. **Surfaces to be protected:** Proper attention must be paid to the point that certain formulations can stain fabrics, discolor linoleum, dissolve plastic, or cause foliage burn.
6. **Cost efficiency:** Product prices may vary substantially, based on the ingredients used and the complexity of delivering active ingredients in specific formulations.
7. **Formulation types of agrochemicals:** Different types of pesticide formulations can be identified considering the mode of application, acceptability by customer and regional market requirements. At present, most agrochemical companies attempt to formulate a product in a form that can be accepted globally [34]. This presents a challenge to the formulation scientists who not only needs to understand the basic and fundamental principles in such formulation types, but also should be able to produce formulations that can be applied worldwide.

Formulations are classified as solids or liquids on the basis of their physical state in the container at the time of purchase. A formulation can contain more than one active ingredient and many have to be further diluted with an appropriate carrier (e.g., water) prior to use. Different types of solid, liquid and gaseous formulations are provided in the table below.

Table. 1 classification based on their physical state in the container at the time of purchase

SOLIDS	LIQUIDS	GASES
Dust or powders, Granules, Pellets, Dry flowables, Tablets, Particulates or Baits, Wettable powders, Ear tag/, Vapour strips, Seed treatment WDGs	Suspensions Concentrate (Flowables), Solutions, Emulsifiable concentrates, Aerosol, Gels, Microemulsions, Suspoemulsions, Ultralow volume concentrates	Fumigants sold as liquids or solids

DOWNSIDEOF CONVENTIONAL PESTICIDE FORMULATIONS

1. **Granules (GR):** Granular pesticide formulations are similar to dust formulations, but are distinguished according to their mesh size, granules being larger and heavier (the mesh size starts from 4 mesh to 80 mesh). Also, they resemble in the fact that they are water insoluble-just like dusts. The active ingredient is either coated or impregnated into an absorptive element. Pesticide granules are generally free flowing and don't form caky batches, when stored. Additionally, the problem of drift and handling is also very less with granular formulations. Therefore, it can be concluded that granules are, the largest of all solid pesticide formulations (except tablets) and their large size virtually eliminates drift leading to much less loss of pesticide than with powder and liquid formulations [16].
   Disadvantages: A very frequent calibration of application equipment is required. Also, these don't stick to uneven surfaces as well as foliage, so can't be used in case of contact pesticides. Non-targeted hazards are also observed with the use of granules.
2. **Pellets (P or PS**) Most pellet formulations are very similar to granular formulations in their uses, advantages, and disadvantages. However, in pellet formulations, all the particles are more or less the same weight and shape. They are produced by incorporating the active ingredient with inert materials to form a "slurry" —a thick liquid mixture. This mixture is then extruded under pressure. As a result, pellets are round in cross section and cut to a specific length. Because pellet particles are more uniform, you can apply them with precision. However, in many cases, pellets are applied as spot treatments. A few fumigants are formulated as pellets and are clearly labeled as such to avoid confusing them with non-fumigant pellets.
3. **Wettable powders (WP):** Wettable powders are dry and finely-divided solid pesticide formulations which are applied after dilution and as a suspension in water, with the help of wetting and/or dispersing agents. They generally, contain 5% to 95% active ingredient. In the form of suspension, they need regular agitation to keep them suspended. They are highly effective against most of the pests and go well with most type of appliances and spray equipment. These particles are larger than the droplets produced by EC (emulsifiable concentrate) formulations. It is this factor, coupled with the lack of solvent, which gives wettable powders lower biological activity than most liquid formulations. However, this also makes them less likely to cause phytotoxicity to crops [19].
   Disadvantages: Wettable powders are quite difficult to mix in spray tanks and also show very poor compatibility with other formulations. Drift hazards during manufacture / application and inhalation hazards during measuring and mixing the concentrated powder. Additionally, a good, constant mechanical agitation is required, in the spray tank and quickly settle out if agitation ceases.
4. **Emulsifiable concentrates (EC):** Emulsifiable concentrates are well known for high active ingredient concentration but in addition contains surfactants/emulsifier and are very soluble in non-polar solvents. EC formulations are easy to use and, when diluted in water, should give a stable "milky" emulsion with very little creaming and no oil separation. EC formulations must also be compatible with spray tank water covering a range of water hardness from very soft water up to about 1,000 ppm of hardness. EC's are the most versatile and convenient form of formulation, used against agricultural pests, food processing, public health and livestock. Also, they are compatible with different types of appliances and equipment including small, portable sprayers to hydraulic sprayers, low-volume ground sprayers, mist blowers, and low-volume aircraft sprayers.
   Disadvantages: Emulsions may damage plants, vegetable crops, absorbed through skin of humans or animals causing health problems. Plastics and rubbers in spray applicators may also get affected resulting in, equipment "wear and tear." These may also cause pitting or discoloration of painted or other treated surfaces. These are flammable so should be used and stored away from heat or open flame.
5. **Soluble concentrates (SL):** A clear solution applied as a solution after dilution in water is called soluble concentrate. These are either water based or a solvent mixture which are completely miscible in water. These are the simplest of all the formulation types and merely require dilution into water in the spray tank [52]. However, the number of pesticides which can be formulated in this way is limited by two factors, the solubility and hydrolytic stability of the active ingredient in water. Water based solution concentrate formulations often carry a surfactant (being hydrophilic), in order to assist wetting.
   Disadvantages: These often requires surfactant/wetting agents for good spreading on vegetable leaves. These have very low temperature stability and are very corrosive to metals.

TRENDS TOWARDS SAFER FORMULATION TECHNOLOGIES

In developing countries like Asia and Pacific region pesticides are mainly available as dust, wettable powder, emulsifiable concentrates, solutions, etc for vegetable pest management. These types of formulations are considered presently as in "conventional", "old technology", "classical" or "traditional" because of their intensified dose rate or repeated applications to get desired bio efficacy. These inflated doses and recurrent applications lead to aggregated pesticide residues in vegetable commodities accompanying environmental pollution [25]. Conventional pesticides provide innumerable advantages. 26 primary and 31 secondary benefits of conventional pesticides were observed by Cooper and Dobson [7]. The chief merit includes elevated crop yields, surpass food safety, human health, and quality of life, and reduced labor, energy use, and environmental degradation. The use of conventional pesticides over the last few decades has resulted to a range of problems extending from agriculture, environment to human health [47, 15]. In addition to the direct costs, there are numerous indirect or external costs derived from pesticide use, including monitoring and sanitation for contamination of soils, drinking water, or food, and the deleterious effects on non-target organisms such as bees and other beneficial insects, fish, and birds. Also, more precisely, highly concentrated WP formulation pose serious hazards to human and environment, EC formulations use organic solvents which are inflammable and cause toxicity via dermal penetration. To steer clear of these problems numerous newly developed modern formulations are being introduced like Drift less dust, water emulsifiable gel, floating granules, macro and micro encapsulated suspension, hollow fibers, monolithic matrix, laminated structures and many more. Taking the cost efficiency and many other factors in consideration innumerable new pesticide formulations with improved designs, better efficiency and less hazardous are on the way to development. However, a dramatic shift has been observed from WP formulate to WG, from EC to EW and many more. Popularity of SCs have also heightened due to their water based nature, environmental advantages, and ease of application with spontaneous dispersion on dilution into water. [33]. All the above said ideas need keen knowledge and information regarding formulations and their properties. Hence, in the present article, some of the neoteric approach in formulation technology will be discussed**.**

WATER BASED DISPERSION TECHNOLOGY

1. **Suspension concentrates (SC):** In suspension concentrates, pesticide particles are to be suspended in an oil phase, or water. But, water based suspension concentrates are much usual. [34]. This technology is being applied to the formulation of many solid crystalline pesticides since the early 1970s. Numerous surfactants are being used as wetting and dispersing agents, leading to a great deal of research on the colloidal and surface chemistry aspects of dispersion and stabilization of solid/liquid dispersions [17]. Aqueous suspension concentrate formulations are of substantial importance with many advantages such as handling and application ease, high concentration of insoluble active ingredients, operator and environment safety, low cost. It also, allows water-soluble adjuvants to be built-in for inflated biological activity. These are highly preferred by farmers compared to wettable powders because they are non-dusty and easy to measure and pour into the spray tank. Inspite advantages, these do have some disadvantages, notably the requirement to produce formulations which do not separate badly on storage, and also to safeguard the product from freezing which may cause aggregation of the particles. Example: Fipronil 5 SC, Sulphur 52 SC, Hexaconazole 10 SC, Carbendazim 50 SC etc.
2. **O/W emulsions (EW):** An emulsion is defined as a mixture that occurs when one liquid is dispersed (as droplets) in another liquid, and each liquid will retain its original identity. Also, there is needed some degree of agitation to avoid the emulsion from separating. There are different forms of emulsions being used as formulations namely oil-in-water emulsions, suspoemulsions, micro and macro emulsions and many more. Considerable attention is being paid to oil-in-water emulsions with a view to lessen volatile organic solvents (VOCs) for safer handling [49]. As these are water based, oil-in-water emulsions can have significant advantages over emulsifiable concentrates in terms of cost and manufacture safety, transportation as well as use. The key concept is that the active ingredient must have very low water solubility in order to avoid crystallization issues [5]. Example: Butachlor 50 EW, Cfluthrin 5 EW, Tricontanol 0.1 EW etc.
3. **Suspoemulsions (SE):** Suspoemulsions are considered to be mixtures of suspension concentrates and oil-in-water emulsions with added surfactants (to prevent flocculation) and thickeners (to prevent separation of the dispersed phases) [45]. Mixed combination formulations are gaining much more popularity nowadays because of their convenience, ensuring supplication of correct amount of each component pesticide by farmer and conquer problems of tank mix incompatibility. The surfactants which are used as dispersing agents for the solid phase are indistinguishable to those

already stated for suspension concentrates. Proper selection of the suitable dispersing and emulsifying agents is requisite to overcome the problem of hetero-flocculation between the solid particles and the oil droplets. Example: Fenpropimorph 24.5 + Epoxiconazole 8.2 SE.

4. **Invert Emulsions:** Invert emulsions consists of a water-soluble pesticide dispersed in an oil based carrier. A special kind of emulsifier is necessitated, that allows the pesticide to be mixed with a large volume of petroleum-based carrier. These are minimum susceptible to drift as oil evaporates slower compared to water. Invert emulsion droplets do not "shrink" rapidly when applied on a hot, dry day weather condition, while a water-based droplet will become smaller as the water portion of the droplet evaporates. This phenomenon leads to less drift and more targeted delivery of pesticide. Additionally, invert emulsions are applied as very large droplets, which again reduces drift. The oil phase of these formulations also serves as a sticker spreader, which improves rain fast properties and provides good surface coverage. It also increases absorption and/or penetration. which, in turn, reduces runoff losses. Invert emulsions are relatively uncommon and are most often used in weed control.
5. **Microemulsions (ME):** These are thermodynamically stable transparent dispersions of two immiscible liquids which are stable over a wide range of temperature, having a very fine droplet size of less than 0.05 microns (50 nanometers) [22]. For microemulsions, the total concentration of surfactants is as high as 10–30% or more, compared to typical o/w emulsion (5%). These have proportionately very little concentrations of active ingredient, but with high surfactant content and solubilisation of the active ingredient, which leads to intensified biological activity. Example: Neemazal 30 MEC, Pyrithiobac Na 5.4 + Quizalofop-P-Ethyl 10.6 MEetc
6. **Nano emulsions:** Nano-emulsions have a particle size of less than 200 nm, which makes the systems inherently transparent/translucent and kinetically stable. Pesticides formulated with nano-emulsions having a lower surfactant concentration than micro-emulsions and surfactants are considerably more environmentally friendly and are cost efficient and economic [27]. Low-energy emulsification methods are applied to produce nano-emulsions, and the energy store could promote smaller-sized nanoparticles of longer life [36, 39, 52].
7. **Oil dispersion formulations:** ODs are one of the newest type of formulations. This technology allows highly efficient and environmentally benign agrochemical formulations. In ODs the active ingredient (solid) is dispersed in the oil phase hence, making it mainly acceptable for water-sensitive or non-soluble active ingredients [30]. When the oil dispersion comes into contact with water the formulation type formed can be either an emulsion or a suspoemulsion. The oil-phase in general can make up different oils such as mineral oils, vegetable oils or esters of vegetable oils.
8. **Aqueous flowables (AF):**Aqueous flowables are generally 40% to 70% w/w suspensions of micronized insoluble active pesticide in water. Aqueous flowables are diluted with water in a spray tank prior to spraying in order to attain the minimum effective pesticide concentration. These must be formulated for low viscosity and good fluidity for easy and complete transfer to the tank. A wetting agent and dispersing agent is needed to make sure the enough dispersion of the pesticide in the water (Castro *et al.,* 1998). Good suspension stability is essential as the active ingredients are insoluble in AFs. If the suspension settles and leaves sediment at the bottom of the container, the application of the pesticide may be too weak to be effective [10]. Smectite clay (bentonite) and xanthan gum in union form works as synergist in order to provide magnificent and long term suspension stability at low viscosity and cost.
9. **Seed treatment formulations:** With the phrase seed treatment, we refer to the application of definite physical, chemical or biological agents to the seed prior sowing with the motive to suppress, control or repulse pathogens, insects and other pests that attack seeds, seedlings or plants. Seed treatment varies from a basic seed dressing to coating and pelleting. Seed coating is the most common. There can be different kinds of seed coating agent can, according to pesticide formulation, such as water flowable seed coating agent (FS), water-emulsion seed coating agent (EWS), suspended emulsion seed coating agent (SES), microcapsule seed coating agent (CS), dry flowable seed coating agent (DFS), water dispersible granule type seed coating agent (WGS) etc. [11]. Introduction and ban of arsenicals is the key milestones in the history of modern seed treatment practices. Physical and biological seed treatments alone substitute to chemicals or in combination with a chemical treatment are being used worldwide because of their environmental safety and socioeconomic aspects. Biological seed treatments are envisioned to be one of the fastest growing seed treatment sectors in the near future. Seed treatments have played and are still playing a crucial role in sustainable crop production which is also indicated from the history of mankind. Seed treatments have helped to surpass the yields of many different crops by providing the protection from pre and post-emergent

insects and diseases and insurance of a uniform stand across a wide variety of soil types, cultural practices and environmental conditions. Seed treatments furnish an economical crop input that is applied straight on the seed using highly effective technology [9]. Moreover, other crop protection techniques are now being replaced with seed treatments by virtue of their residual systemic efficacy [40] i.e. dressing to coating and pelleting [1, 26].

10. **Combined/mixed formulation technology:** Many pesticide formulations are used in combination to attain different needs. A union of capsule suspension of lambda cyhalothrin insecticide and concentrated emulsion of chlorpyriphos insecticide is observed. [21]. In this unique formulation, two different active ingredients are used in such a way that one active ingredient i.e. chlorpyriphos will be rapidly effective just after application on target pests for quick knock-down effect while, the other pesticide i.e. lambda cyhalothrin will be beneficial slowly in a controlled manner for extended target pest management [46]. As it is micro encapsulated in a polymer membrane, applicator can apply two pesticides concurrently in a single application. The combination will have broad spectrum insecticidal activities and may be used for controlling insects on large number of crops.

NEW DRY FORMULATIONS

1. **Water dispersible granules (WG):** Water dispersible granules famed as dry flowables, are comparatively new type of formulation and are being developed as safer and more commercially pleasing substitute to wettable powders and suspension concentrates [24]. They are manufactured in similar way as wettable powders (diluted with water and applied in a spray) except that the powder is lumped into granular particles. Dry flowables form a suspension in the spray tank and during the mixing process, pour more easily from the container and, also inhalation hazard to the applicator are diminishedbecause of their larger particle size. They are gaining extreme prevalence because of their ease in packaging and use, being non-dusty, free-flowing granules which should disperse quickly when added to water in the spray tank [32]. Therefore, these represent a technological improvement over wettable powders and imitate liquids in their handling characteristics.
   Example: Mancozeb 75 WG, Endosulfan 50 WG, Captan 83 WG, Cypermethrin 40 WG, Thiomethaxam 25 WG, Deltamethrin 25 WG and so on.
2. **Dispersion concentrates (DC):** These formulations is made up of active ingredient dissolved in a water-miscible and polar solvent. Additionally, a dispersing or emulsifying agent, is also used which is intend to dilute in water giving stable, fine particle size dispersions [35]. These serve as prominent replacements to different formulations like SL, SC, EC and ME etc, being appropriate for active ingredients whose physical, chemical or biological properties preclude the use of these more conventional formulations. Generally, the choice of dispersing agent is ultra-critical for good dilution properties in water. Fine particle size dispersion, stable for preferably at least 24 hours as a dilution, is key to prevent plausible spray equipment blockages and reduced bio-efficacy.
   Advantages: Simple process equipment, easy to use and clean down, stable, solution-type formulation, good bio-efficacy.
3. **Microencapsulation/capsule suspensions (CS)/controlled release formulation (CRF):** Encapsulation is a leading technique, gaining enormous popularity in the modern formulation technology. Encapsulation enhances applicator safety while providing timed release of the active ingredient. Microencapsulates comprises of a solid or liquid inert (containing an active ingredient) enclosed by a plastic or starch coating. The polymer membrane, or microencapsulation technique, has become popular in recent years [2]. This well-known method of microencapsulation is based upon the principle of interfacial polymerization. The resulting capsules can be used as dispersible granules (dry flowables), or as a liquid formulation. The desired rate of active ingredient release can be controlled by adjusting the droplet size, and is also determined by the thickness of the polymer membrane as well as the degree of cross-linking or porosity of the polymer. Therefore, we can infer that the rate of release of the pesticide is a diffusion controlled process. Advanced innovations are expected in microencapsulation technology over the next few years which may bring about safer pesticide use [14]. Intelligent release in response to environmental agents has a promising future for transfiguring agricultural production. Results depicted that microencapsulation reduces the pesticide's photolytic rate in aquatic environments. Controlled release formulations are put in the vicinity of the problematic domain and release the active (s) there from, reaching the focused target more effectively in a minimum time interval. The active release rates in such products are modulated and standardized with reasonable precision, allowing combat of the target over time with the needed dose, thus causing minimum damage to non-target organisms and the environment. Example: Lambda Cyhalothrin 10 CS, Lambda Cyhalothrin 25 CS etc.

Advantages: It enhances the applicator safety, are easy to mix, handle, and apply. The encapsulation process can provide "timed" slow release of the active ingredient, extending effectiveness. Encapsulation also reduces volatility and odor. Phytotoxicity is also reduced.

Table 2. Main pesticide microcapsule preparation methods

Method	Preparation process	Example
Interfacial polymerization	Two reactive monomers are dissolved in two different solvents. When one solvent is dispersed in another solvent, the two monomers undergo a polycondensation reaction at the phase interface to form microcapsules [18].	Natural pyrethrin nanocapsules [54]
In situ polymerization	Two or more water-soluble monomers are polymerized to form a water-insoluble polymer and are deposited on the surface of the core material for coating [48].	S-ethyl dipropylthiocarbamate,acetochlor, atrazine, methotrexate
**Emulsion polymerization	A solvent-insoluble monomer is dispersed in a solvent to form a uniform emulsion via mechanical agitation, high-speed shearing, and vigorous shaking with a surfactant (an emulsifier). Then, the polymerization reaction is initiated to form the polymer to achieve core material encapsulation [43].	Abamectin nanocapsule suspension [41], natural pyrethrin nanocapsules [50]
Membrane emulsification	The dispersion phase enters the continuous phase through a shirasu porous glass membrane under inert gas pressure, and the continuous phase breaks into droplets on the membrane surface by the shear forces of the SPG membrane and droplets	Chlorantraniliprole nanocapsules [28], avermectin nanocapsules [13]
Solvent evaporation	The wall material and core material are dispersed in the organic phase, added to the solution immiscible with the wall material, and the wall material is precipitated to form the microcapsule by heating and evaporating the solvent [4].	Spinosad nanocapsules [51]
Nano-precipitation	The interfacial interaction between solvent and non-solvent disperses the polymer and drug from the oil phase into the aqueous phase. This material can quickly wrap the drug and obtain nanocapsules through precipitation [48].	Pyrazole azoxystrobin nanocapsules [54], azoxystrobin microcapsules [28]
Double coacervation	Two oppositely charged water-soluble polymers form a wall around the water-insoluble pesticide active ingredient, which is a spontaneous liquid-to-liquid separation caused by electrostatic interactions [48].	Azoxystrobin microcapsules [31]

MISCELLANEOUS

Liquid Formulations: Most of liquid formulations are planned to be used next to mixing with a carrier before application. nevertheless, some products are sold ready-to-use (RTU). These do not entail any further dilution prior to application and consist of a small amount of active ingredient (often 1% or less per unit volume).They contain petroleum-based solvents as well as can be water-based. Typically, the container also serves as the application device.

Low and ultra-low volume (ULV) concentrates used in special situations (e.g., space spraying and fogging) are frequently applied undiluted and consists of almost 100% active ingredient. These are marked purpose formulations, most suitable for outdoor applications, like agricultural, forestry, ornamental, and mosquito control programs. Low and ultra-low volume concentrated formulations make use of special equipment to supply the product in the form of very tiny droplets. ULV formulations are applied as very fine droplets at very low rates per unit area/volume. As a result, while providing excellent coverage, drift potential and inhalation problems during application can be quite high.

CONCLUSION

This article describes well, the major and minor advancements in formulation types employed and the further trends and driving technologies such as water-based dispersion formulation technology for oil-in-water emulsions, suspensions, micro-emulsions etc. as well as other formulation types such as gel and dry product formulations. Pesticide formulation science is a very broad sector as it handouts the development, production and storage methods of formulation as well as the interlinkage of these pesticide formulations with environment (plants, insects, mammals, soil, air and water).There are innumerable factors that sways the choice of formulation specifically physical properties (melting point, solubility, volatility), pesticide chemical properties (hydrolytic stability, thermal stability), soil application vs. foliar application, crop and cultural practice, pesticide biological properties (crop selectivity, transport), and economics. Newer technologies are accepted which have the properties like broader formulation inserts, solvent reduction and safer solvent selection, safer surfactant components with low toxicity, low skin irritation and enhanced biodegradability [12], indelible physical and chemical stability, enhanced bio efficacy by incorporation of adjuvant, controlled and sustained release formulations and compatibility of various formulations in tank mixes. This review paper is a assemblage of papers focusing on pesticide formulations which are currently acquiring the eminent attention and where the greatest advances are being made. In inference, it can be safely said that the advances in pesticide formulation technology which are outlined in this article are playing a vital role in the development of safe, effectual and economically attractive pesticide products. The prime motto for these developments is to give protection to the crops along with safety to the natural enemies of different pests as a whole safety to environment.

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