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Formulation of botanicals for the control of plant-pathogens: A review

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ABSTRACT

Essential oils and plant extracts contain a multitude of bioactive substances against fungi, bacteria and nematodes. In plant pathology research, botanicals are commonly used in their raw state. Without any type of formulation, bioactive compounds of plants can be degraded and volatilized rapidly under field conditions. Controlled-release liquid and solid formulations with plant compounds as active ingredients are common in some fields, such as medicine, pharmaceuticals, food technology and cosmetology. However, the use of controlled-release formulations is an under explored approach in plant pathology, although these technologies are interesting options for managing seed, soil-borne and post-harvest pathogens. In this review, we discuss the potential and options of formulations of botanicals against plant pathogens.

1. Introduction

Secondary metabolism of plants is responsible for the synthesis of numerous bioactive substances, which provide protection against insects, pathogens and limit the growth of other plants species. Essential oils and plant extracts contain a multitude of bioactive substances, including alkaloids, cyanogenic glycosides, glucosinolates, lipids, phenolics, terpenes, polyacetylenes and polythienyls. Scientists have been explored the diversity of these molecules and their use in integrated management of pests and pathogens (Isman, 2000; Zaker, 2016). Products based on plant extracts and essential oils are available for use in managing plant diseases in various countries. However, the number of botanical-based products remains restricted, despite the enormous potential for botanicals in the pesticide market, especially if we consider the increasing demand for ecofriendly options to manage agricultural pests.

The most common scenario in plant pathology research is to use extracts and oils in their raw state for managing fungi, bacteria and nematodes. In controlled conditions, extracts and essential oils from diverse plant species have shown efficiency in inhibiting plant pathogens (Isman, 2000; Zaker, 2016). However, the promising results obtained in laboratory or greenhouse are usually not observed in the field, with few exceptions (Jing et al., 2018). Degradation and volatilization of bioactive compounds are the major factors that reduce the efficiency of plant-based products under field conditions. Consequently, the potential suitability of certain plant material for use in agriculture ends up being underestimated due to losses of bioactive substances. One option to avoid these drawbacks is to formulate bioactive plant products using polymers, plasticizers, stabilizers and biodegradable antioxidants.

Polymers, emulsifying agents, surfactants, solvents, stabilizers, defoamers and other components are used to ensure the stability, adherence and controlled release of the bioactive compounds, depending on the type of formulation (Knowles, 2008; Gasic and Tanovic, 2013). Examples of slow release liquid and solid formulations with plant compounds as active ingredients are common in some fields, such as medicine, pharmaceuticals, food technology and cosmetology (Arriola et al., 2016; Mikulcová et al., 2016). In the agricultural sector, the use of controlled release formulations is still in the initial stage, although these technologies are interesting options for managing seed, soil-borne and post-harvest pathogens (Knowles, 2008). In this type of formulation, active ingredients are released into the environment over time and this feature brings benefits such as reducing losses of the active ingredient, a longer period of activity and reduced toxicity to animals and plants (Knowles, 2008).

The formulation process may vary greatly according to the methods and materials used for encapsulation, but it is important that botanicals be formulated for use in experiments, rather than their use in raw state. In this review, we discuss the potential use of formulations of plant-based extracts, essential oils and isolated active compounds against plant pathogens. We present options for preparing formulations that may be used in plant pathology research and related fields.

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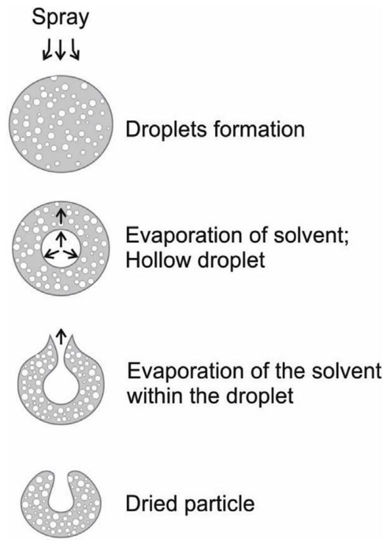

Fig. 1. Formation of particle by spray drying (adapted from Oliveira and Petrovick, 2010).

2. Principal methods of encapsulation

2.1. Atomization (spray drying)

This process consists of three steps: first, the product (e.g., extract and essential oil) is dispersed as droplets, which increases its surface area. Second, dispersed droplets came into contact with a heated air stream and in the third, the solvent is evaporated, resulting in the formation of the solid particle (Fig. 1) (Oliveira and Petrovick, 2010). This a low-cost process at industrial scale, especially for the micro-encapsulation of essential oils (Fernandes et al., 2014; Bakry et al., 2016).

Spray-drying formulations have not been extensively explored for the control of plant pathogens (Corrêa et al., 2016; Cortesi et al., 2017). In a few examples, formulations of coffee leaf extracts or gallic acid were used as plant resistance inducers (Corrêa et al., 2016) or in the management of *Pseudomonas syringae* pv. *tomato* (Cortesi et al., 2017).

2.2. Lyophilization (freeze-drying)

In the freeze-drying process, the product (extract or oil) is rapidly frozen, thus preserving its chemical characteristics. In the following step, the frozen material is subjected to a partial vacuum. Then, the ice or other frozen solvents are removed from the material through sublimation and the product is dried to approximately 2% wet basis. The dehydrated solid material is milled until reaching the desired particle size.

Freeze-dried extracts of some plants have fungicidal activity. Freeze-dried extracts of *Ruta graveolens* reduces the mycelial growth of the phytopathogenic fungi *Fusarium solani, Pyrenochaeta lycopersici, Thielaviopsis basicola, Verticillium dahliae* and *Penicilum* sp. (Oliva et al., 1999), while those from *Pelargonium* sp., *Salvia officinalis*, *Lavandula officinalis*, *Mentha pulegium* and *Mentha arvensis* reduces up to 85% the germination of *Phakopsora pachyrhizi* spores (Borges et al., 2013).

2.3. Liposome inclusion (emulsions)

2.3.1. Emulsions

An emulsion is defined as a thermodynamically unstable system containing at least two non-miscible liquid phases, where one phase contains colloidal particles dispersed in the other phase. Nanoemulsions are the most studied form of emulsions. They are colorless emulsions with droplet sizes ranging from 50 to 200 nm, while conventional emulsions appear as blue droplets with size between 1 and 100 μm. In comparison to conventional emulsions, nanoemulsions have higher kinetic and thermodynamic stability, greater ease of diffusion and nanoparticle transport, enhanced incorporation and protection of both hydrophilic or lipophilic molecules in their dispersed phases. The transport of phytochemicals across cellular membranes, for example, is facilitated when the products are encapsulated in nanoemulsions (Huang et al., 2010).

Emulsions of essential oils and plant extracts are valuable options for controlling plant diseases (Lu et al., 2013; Elshafie et al., 2015; El Ouadi et al., 2017; Jing et al., 2018). For example, nanoencapsulated essential oils of cinnamon, lemon and bergamot have antifungal activity toward *Aspergillus niger* (Ribes et al., 2016). Other notable examples are the suppression of *Xanthomonas fragariae* by palmarosa oil nanoemulsion (Luiz et al., 2017) and the inhibition of *Rhizoctonia solani* and *Sclerotium rolfsii* by nanoemulsions of oils of *Azadirachta indica* A. Juss and *Cymbopogon nardus* (L) Rendle (Ali et al., 2017).

2.4. Extrusion – casting

In this method, an emulsion/extract core and coating material (alginate, acetate, starch, etc.) is applied through pipette or nozzle at high pressure into an ionic solution under agitation, such as calcium chloride. Gel beads are collected after 20 min and dried. The resistance of the bead wall depends on the components of the formulation and the contact time between particles and the ionic solution. Care must be taken to minimize or avoid losing active compounds during the encapsulation processes and storage (Arriola et al., 2016; Pasukamonset et al., 2016).

Plant extracts and essential oils are encapsulated by extrusion and used in food preservation (Arriola et al., 2016; Pasukamonset et al., 2016), e.g. minimally processed apples and mushrooms (Raybaudi-Massilia et al., 2008). However, this technique still has not been explored in the formulation of botanicals for plant disease management.

2.5. Fluidized bed

The fluidized bed coating consists of spraying an encapsulated agent on a fluidized powder bed (Hemati et al., 2003). The material to be encapsulated is suspended in solid state by a current of gas at a given temperature and sprayed with fine droplets of the encapsulating material liquid, forming a fine liquid film on the particle. Finally, the materials undergo wetting and drying, thus forming a solid homogenous layer (Benelli et al., 2015). The rate of solid circulation, nozzle atomization pressure, humidity and coating temperature may interfere in the efficiency of the coating (Guignon et al., 2002). Fluidized beds are widely used in the pharmaceutical and food industries, as well for synthesizing agrochemicals, dyes and other industrial chemicals.

Granules obtained through this technique have higher bioactive compound retention, better flow properties and higher coating efficiency compared to those obtained by spray drying (Benelli et al., 2015). It is possible to prepare controlled-release formulations using this process (Hemati et al., 2003), which could be used in products for managing soil-borne pathogens. Another advantage of this method is the possibility of large scale applications, by presenting a short circulation time of particles and high heat transport, in addition to being highly controllable and automated (Capece and Dave, 2011). Śmigielski et al. (2011) observed that more than 40% of the essential oils of lavander (*L. angustifolia*) are lost during the drying process. However, if the fresh biomass of a plant is dried by fluidized bed in a system of closed circuit containing a drying agent and a heat exchanger, the generated product will contain more volatile and biologically active substances than other processing methods (Śmigielski et al., 2011).

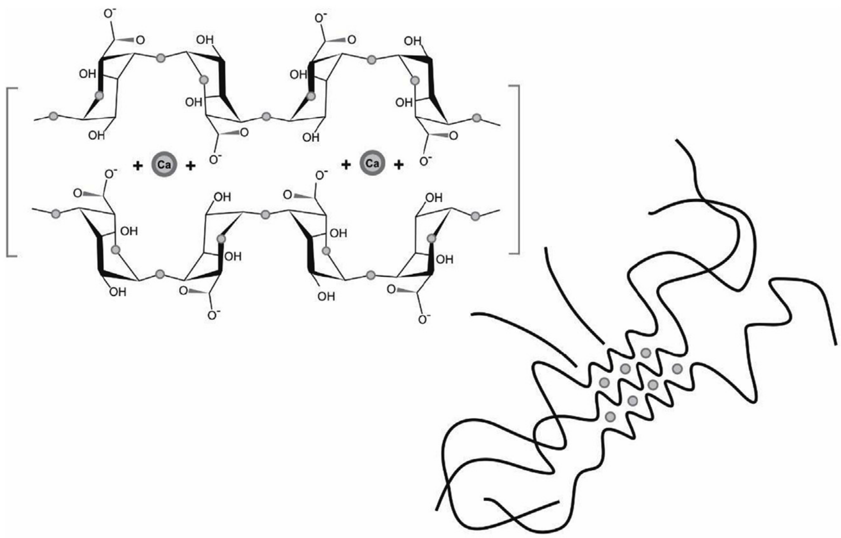

Fig. 2. Tridimensional network of alginate and calcium ("egg-box model"). Adapted from Corona-Hernandez et al. (2013).

2.6. Coacervation

Coacervation is a method of encapsulation done in three steps: preparation of the emulsion, encapsulation and stabilization of the microcapsule (Xiao et al., 2014). Surfactant agents, such as Tween 80, are used during emulsion preparation (Zhang et al., 2011). Tannic acid, glycerol or glutaraldehyde may be used in the hardening process (Xing et al., 2004; Huang et al., 2007; Zhang et al., 2011). Some biopolymers are used as options for encapsulation, protection and release of the lipophilic compounds (García-Saldaña et al., 2016), principally protein of soy/Arabic gum, gelatin/Arabic gum and gelatin/pectin (Jun-Xia et al., 2011; Zhang et al., 2011). Coacervation is a low-cost technique and is the most recommended for microencapsulating oily compounds and essential oils (García-Saldaña et al., 2016).

The treatment of peanut seeds with microcapsules containing essential oil of *Peumus boldus* Mol., produced by complex coacervation, ensured the best protection against *Penicillium* sp. and *Aspergillus* sp. during 114 days of storage (Girardi et al., 2016). Peng et al. (2014) also encapsulated essential oils of mustard using coacervation and reported high physical-chemical stability of the oils and antimicrobial action.

2.7. Molecular inclusion

Molecular inclusion complexes are generally special compounds, where the molecules of a component, called guest molecules, are totally or partially within the cavity of the other component, the host molecule. Cyclodextrin is the most used host molecule and the formation of these complexes depends on the nature of its cavity (Tan et al., 2012).

Cyclodextrins are cyclic oligosaccharides obtained from the action of the cyclodextrin enzyme glycosyltransferase in starch. External surface of cyclodextrin is hydrophilic, while internal surface is hydrophobic. Therefore, if a molecule guest molecule fits in this cavity, an inclusion complex is formed (Valentini et al., 2015). As a result, organic and inorganic molecules may be encapsulated, and the solubility and stability of the guest molecule are changed (Mura, 2014; Sherje et al., 2017). The main advantage of molecular inclusion with cyclodextrin is to increase the solubility of the compounds in water (Sherje et al., 2017), a desirable characteristic in encapsulating essential oils.

In the last few years, molecular inclusion with cyclodextrin has been used for encapsulating active compounds against plant pathogens, particularly fungi. Eugenol microencapsulated by inclusion within β-cyclodextrin was shown to be effective against *Peronophythora litchi* (Gong et al., 2016). Essential oil of clove and oregano microencapsulated with β-cyclodextrin also inhibited the mycelial growth of *Fusarium oxysporum* (Estrada-Cano et al., 2017). On the other hand, free phenylpropanoids were more efficient in inhibiting the growth of *F. oxysporum* and *Botrytis cinerea* when encapsulated with cyclodextrin (Kfoury et al., 2016). Some hypotheses may explain this result, such as the use of the inclusion complex by the fungus as a carbohydrate source or the encapsulation of substances synthesized by fungi themselves that auto-inhibit mycelial growth (Kfoury et al., 2016).

3. Principal materials used for encapsulation

3.1. Alginate

Alginate is a linear copolymer of mannuronic acid and its C-5 epimer guluronic acid and molecular formula ($C_6H_8O_6$)n. It is found in marine algae and some bacteria. The material varies widely in terms of its proportion between mannuronic waste (M) and guluronic (G), as well as in its sequential structure and degree of polymerization. In this way, the material may present alternate sequences of M-G residues and blocks composed of two or more M-G residues (Skjk-Bræk et al., 1986).

Alginate is a biodegradable polymer that forms a tridimensional gel in the presence of bivalent cations, e.g. Ca^{2+} and Mg^{2+}. Calcium ions bind to guluronic acid blocks of the alginate chains, forming a tridimensional network (Fig. 2) (Corona-Hernandez et al., 2013). This property makes alginate an attractive material for encapsulating bioactive compounds (Corona-Hernandez et al., 2013), including compounds of phytopathological interest.

Sodium alginate may be used, for example, in the formulation of phenolic compounds extracted from plants, ensuring more than 80% efficiency in retaining these substances (Belscak-Cvitanovic et al., 2011; Stojanovic et al., 2012; Deladino et al., 2013). The encapsulation of plant extracts, essential oils and biocontrol agents in Ca-alginate microspheres prolong the viability of active compounds or antagonistic microorganisms (Li et al., 2017; Locatelli et al., 2017).

3.2. Chitosan

Chitosan is a cationic amino polysaccharide, derived from the deacetylation process of chitin, which constitutes the highest fraction of insect and crustacean exoskeletons (Dias et al., 2008). Its structure is formed by repeating units of β (1–4) 2-amino-2-deoxy-D-glucose (or D-glucosamine) and its molecular formula is ($C_6H_{11}O_4N$)n. Chitosan may be used as component in various methods of encapsulation, such as coacervation, emulsions and extrusion (Kashyap et al., 2015). Chitosan nanogels are biocompatible and stable when dispersed in water, which facilitates the handling of the nanocapsules (Brunel et al., 2009).

The mixture of powder and cinnamon extract with chitosan showed potential for controlling *Rhizoctonia solani* and *Meloidogyne incognita* in vitro, although studies have not been done in the field (Seo et al., 2014). In the laboratory, chitosan capsules containing essential oils of *Citrus bergamia* and *Citrus aurantium* inhibited the growth of *Aspergillus flavus* (Aloui et al., 2014).

3.3. Cellulose acetate

Cellulose is the most abundant natural polymer on Earth (Huber et al., 2012). Due to its low melting point, cellulose is normally converted into its derivatives to make it more processable. This is the case for some cellulose-derived thermoplastic esters, such as cellulose acetate (CA), cellulose propionate and cellulose butyrate (Huber et al., 2012).

CA is produced by the reaction of wood fiber with acetic anhydride and acetic acid, forming an ester. This reaction occurs in the presence of sulfuric acid. The product is subsequently hydrolyzed to remove the acid, the sulfate groups and the acetate until obtaining the desired properties. CA crude fiber is derived from the physical transformation of CA flakes, where the CA is dissolved in acetone and then dilated in crude fiber (Fischer et al., 2008). CA may be produced with wide range of degrees of substitution (DS). However, the most common is the production of acetates with DS of 2.5, due to the necessity of achieving products with adequate molar mass, melting temperature and adequate solubility. For DS $>$ 2.5, dichloromethane is used as solvent (Fischer et al., 2008).

Cellulose acetate films can contain plant extracts and oils. Depending on the required properties of the film, plasticizers may be added to the CA, such as dioctyl phthalate (DOP), triethyl citrate (TEC) and glycerol (Fridman and Sorokina, 2006). Pola et al. (2016) developed CA films containing essential oil of oregano and montmorillonite clay for the control of the post-harvest pathogens *Alternaria alternata* and *Rhizopus stolonifer*. The films had antifungal effect by direct contact and by the release of active volatile compounds (Pola et al., 2016).

3.4. Starch

Starch is a reserve polysaccharide of plants stored in the form of granules (Mali et al., 2010). It is a low-cost polymer, easily available from diverse sources, such as corn, rice, cassava, wheat, etc. The starch structure consists of anhydroglucose units linked by α-D-(1, 4) glucosidic bonds. It is composed of two fractions of homopolymers: amylose (15–30%) and amylopectin (85-70%) (Mali et al., 2010). In plant pathology research, starch-based films may be used in post-harvest preservation of fruits preservation and may contain extracts of plants, salicylic acid and essential oils (Ghasemlou et al., 2013; Santacruz et al., 2017).

The application of starch in film production is based on chemical, physical and functional properties of the amylose to form gels and on their abilities to form films. Due to their linearity, the amylose molecules in solution tend to be oriented in parallel, thus forming hydrogen bonds between the hydroxyls of adjacent polymeric chains. As a result, the affinity of the polymer to water is reduced, which favors the formation of opaque pastes and resistant films (Mali et al., 2010). The preponderance of amylose in starches results in stronger and more flexible films, since the branched structure of the amylopectin generally takes the form of films with inferior mechanical properties (Huber et al., 2012).

Traditionally, starch-based films have been produced by the casting method (Mali et al., 2010), since the starch in its natural form has a melting temperature higher than its degradation temperature. In this method, the starch is solubilized in a solvent and the resulting filmogenic solution is applied on a clean flat surface. The solution is left at 25–30 °C for the solvent to evaporate. Dias et al. (2010) reported a technique to prepare rice starch and rice flour films by casting. Briefly, aqueous solutions with raw starch or flour (5%, m: v) is stirred for 15 min at 4000 rpm. Plasticizer (glycerol or sorbitol) is added to the aqueous solution at concentrations of 0.20 or 0.30 $g\,g^{-1}$ dry raw starch or flour. Then, the mixture is heated to 85 °C under constant stirring for 1 h, and poured homogeneously onto plexiglass plates and dried at 30 °C for 14 h in an oven with circulating air. For preparation of rice flour films, the pH of the aqueous solution is adjusted to 10.0 to promote protein solubilization.

Plasticizers are incorporated into films to increase their flexibility, processability and extensibility (Rabelo and Paoli, 2013). The most commonly used plasticizers are glycerol and sorbitol. Glycerol is a small hydrophilic molecule with hydroxyl groups that easily interacts with the starch chains (Mali et al., 2010). Fatty acids and essential oils also may be used as plasticizers when it is desirable to reduce the hydrophilic character of starch films (Mali et al., 2010).

Starch films biodegrades rapidly in environments with available water (Mali et al., 2010). The incorporation of other more stable components in the blend slows the degradation of starch films. Starch blends can be produced with chitosan, polylactic acid (PLA); poly(butylene adipate-*co*-terephthalate) (PBAT) and poly butylene succinate co-adipate (PBSA) (Mali et al., 2010; Elsabee and Abdou, 2013; Shirai et al., 2013).

3.5. Polycaprolactone and poly (butyl-adipate-co-terephthalate) (PBAT)

Polycaprolactone (PCL) is a biodegradable synthetic polymer with high permeability to active compounds. PCL is a semi-crystalline polymer, with glass transition temperature is −60 °C and melting temperature from 59 to 64 °C (Woodruff and Hutmacher, 2010). PCL ensures formulation stability, increases stress-crack resistance and enhances controlled-release properties. PCL-based nanocapsules containing essential oil of *Lippia sidoides*, a plant species rich in thymol, remained stable for 60 days at 5 °C (Pinto et al., 2016). Cellulose propionate, cellulose acetate butyrate, polylactic acid and polylactic acid-*co*-glycolic acid can be mixed with PCL to improve formulation characteristics (Woodruff and Hutmacher, 2010).

Poly (butyl-adipate-co-terephthalate) (PBAT) is a synthetic copolyester produced from the combination of butane-1,4-diol, adipic acid and terephthalic acid. Although it is derived from petroleum, it may completely biodegrade in a few weeks (BASF, 2003). PBAT films have good processability, elevated flexibility, hydrophobic characteristics and good mechanical and barrier properties. It is more expensive than the other polymers. However, PBAT's mixture with low cost biopolymers may result in the production of cheaper biodegradable films with good mechanical and barrier properties (Brandelero et al., 2012; Shirai et al., 2013; Olivato et al., 2015).

4. Concluding remarks

Plants synthesize a range of compounds that can be used in the management of plant pathogens. Due to the diversity of plant species in many countries, especially those located in tropical and subtropical regions, several substances with inhibitory action against phytopathogens have not been discovered yet. However, the potential of many promising botanicals has been underestimated because of the inefficiency of these materials in experiments under field conditions. We strongly believe that the formulation of plant extracts and essential oils reduces losses of bioactive compounds and many plant-based products can be used as alternatives for controlling plant diseases. In plant pathology research, few studies have focused on the bioactivity of formulated botanicals. As discussed here, some low-cost formulations can be prepared for experimental purposes and the losses of bioactive compounds may be reduced. The development of potential plant-based materials into commercial products depend on various factors, such as operational processes and financial viability. However, nanomaterials and nanotechnologies have led to unprecedented possibilities for the development of novel plant-based products (Khot et al., 2012). Therefore, plant pathologists must be encouraged to formulate botanicals rather than to use them in their raw state, and this approach may increase the number of eco-friendly options for plant disease management.

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