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APPLICATION OF MICROENCAPSULATED ESSENTIAL OILS IN COSMETIC AND PERSONAL HEALTH CARE PRODUCTS – A REVIEW

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ABSTRACT

Nowadays, the consumers around the world are increasingly focused on health and beauty. The renewed consumer interest in natural cosmetic products create the demand for new products and reformulated others with botanical and functional ingredients. In cosmetic products, essential oils play a major role as fragrance ingredients. They can optimize its proprieties and preservation, as well as the marketing image of the final product. Microencapsulation of essential oils can protect and prevent the loss of volatile aromatic ingredients, improve the controlled release and stability of this core materials.

The importance of essential oils for cosmetic industry and its microencapsulation was reviewed in this paper. Also a briefly introduction about the preparation of microparticles was presented. Some of the most important and usual microencapsulation techniques of essential oils, as well as the conventional encapsulating agents were discussed.

Despite the fact that microencapsulation of essential oils is a very promising and extremely attractive application area for cosmetic industry, further basic research needs to be carried out; for a better understanding the biofunctional activities of microencapsulated essential oils and its release modulation, as well as the effects of others cosmetic ingredients and the storage time in the microparticles properties.

Keywords: essential oils, microencapsulation, polymers, delivery, stability, cosmetic industry.

INTRODUCTION

The use of natural ingredients in consumer products has a very long history. Apart from being a source of food, many plant species biosynthesize and accumulate extractable substances with economic and health importance. Industrial oils, flavor and fragrances, resins, gums, natural rubber, waxes, surfactants, dyes, pharmaceuticals, pesticides and many specialty products are raw materials that have been used in several consumer products, such as cosmetics, herbal medicines, pharmaceuticals [1], [2]. Furthermore, the consumer demand for nutritional, medicinal and cosmetic products derived from natural sources has been increasing in last decade. Accordingly, the industry of natural products has consecutively been growing. Back the middle 1970s, natural products industry represented an estimated US $2.4 billion/year. In 2011, it was value at US $91 billion/year with a growth rate of 7.4% from the previous year in the global sales [3], [4]. Particularly, natural cosmetic products has an annual growing of 9-10% across Europe, North America and Asia Pacific regions with US $8.2 billion in sale in 2013 [5], [6].

The renewed consumer interest in natural cosmetic products has also sparked the increase of research in field of medicinal, aromatic and cosmetic (MAC) plants extracts to use and/or take advantages from them in health and cosmetic care products [1]. The discovery of the biological properties of natural sources and derivatives allows the formulation of new bioactive products that contribute to health, beauty and wellness of humans, and add value to products marketed [7]–[9].

The European Union (EU) Cosmetics Regulation defines cosmetic product as any substance or mixture used for external parts of the human body (epidermis, hair system, nails, lips and external genital organs), teeth and mucous membranes of the oral cavity in order to cleaning them, perfuming them, changing their appearance and/or correcting

body odors and/or protecting them or keeping them in good condition [10]. Opposing to the European legislation, Food and Drug Administration (FDA) considers that sunbath products, moisturizers and makeup marketed with sun-protection claims, skin-whitening products, anti-wrinkle products, antidandruff shampoos, toothpastes that contain fluoride, deodorants that are also antiperspirants, and cosmetic textiles are drugs, since these products include one or more compounds with biological activity and/or affect the body's structure or functions [11], [12].

Cosmetics can be grouped in 7 categories: skin care and maintenance; cleansing; odor improvement; hair removal; hair care and maintenance; care and maintenance of mucous membranes; and decorative cosmetics [13]. Though not consensual, textile cosmetics can be a skin care cosmetic [14], [15]. The cosmetic properties of aromatic plants, especially as fragrance, are attributed to essential oils (EOs). Hence, EOs are normally an ingredient present in all categories of cosmetic products [16].

EOs have been used to improve the health and physical appearance of the human exterior, and to protect a body part against damage from the environment since ancient times in human history [17]–[19]. Back to 1600 BC, in in ancient Egypt, women used essential oils extracted from flowers and pine trees with sweet and delicate odor to aesthetically improve their femininity. Cleopatra, queen of Egypt (51 BC), was known to use all kinds of perfumes, especially in romantic occasions [20]. Later, these Egyptian practice were inherited by the Greek and Roman women. In infused baths, they used the jasmine, lavender or ylang-ylang oils to relax physically and mentally [18]. In fact, EOs of MAC plants have recognized characteristics which are valued in perfumery and cosmetic industrial products [1], [7], [17], [21], [22]. A survey conducted in the Europe

Union (EU) indicate that for the period 2002-2009, essential oils market grew at 3%/year [23].

EOs are a complex liquid mixture of volatile, lipophilic and odoriferous compounds bio synthesized by living organisms, predominantly aromatic plants [24]. The major plant families from which EOs are extracted include Asteraceae, Myrtaceae, Lauraceae, Lamiaceae, Myrtaceae, Rutaceae and Zingiberaceae, the dicotyledonous angiosperm plant families. They are secondary metabolites produced in cytoplasm and plastids of plant cells [17] and stored in secretory cells, cavities, canals, epidemic cells or glandular trichomes [22]. Present in different parts of the plants (buds, flowers, leaves, stems, twigs, seeds, fruits, roots, wood, bark, or rhizome), EOs are usually extracted by processes of steam distillation, solid phase extraction, cold pressing, solvent extraction, supercritical fluid extraction, hydrodistillation [8], [18], [22], or simultaneous distillation-extraction [25]. Despite EOs encompass substances with distinct organic functions, such as alcohols, aldehydes, esters, phenols, hydrocarbons, EOs are predominantly monoterpenes, sesquiterpenes and diterpenes [26]. 300 of approximately 3000 EOs produced by using about 2000 plant species are commercially important. Their characteristic flavor and fragrance properties, as well as various biological activities, have been increasingly studied and reported in the scientific literature. In cosmetic products, EOs play a major rule as fragrance ingredients [27]. Nevertheless, other properties of EOs may be very promising and interesting for cosmetics products, for example EOs with antibacterial or antifungal activities allow reducing the use of preservatives components in a product [28].

Among cosmetics, the EO are mainly used in perfumes, and skin and hair care products [23]. Skin care remains the most important category in the global beauty market,

accounting for 23% value share of total sales in 2009 [29]. However, EOs have a short shelf life, since they are volatile and reactive in presence of light, heat, moisture, and oxygen. To overcome this challenges, microencapsulation has been considered as one of the most effective techniques [21]. Furthermore, microencapsulation provides the controlled-release delivery and improves the handling of the EOs [30].

This review highlights an overall discussion about the importance of EOs in the cosmetic industry, microencapsulation of EOs and EOs microencapsulated in the cosmetic industry and in the market.

IMPORTANCE OF THE ESSENTIAL OILS IN COSMETICS

Essential oils are complex mixtures containing dozens of substances of varying chemical composition at different concentrations. They are characterized by the compounds present at highest concentration which determine the flavor, fragrance and biological properties of the EOs [26].

The importance of EOs for health, beauty and wellness remote to ancient times. In recent decades the concern about the possible risks of synthetic ingredients for the human health has been increasing. Therefore, the use of natural compounds to enhance health and beauty of human has been showing an increasing trend line. EOs are remarkable used in nowadays cosmetic industry [31].

Cosmetics companies produce diverse kinds of products, such as personal and beauty care, hair care, cleanser, perfume and make-up. The cosmetics industry is continuously innovating and improving products for consumers. As a result the cosmeceuticals products (products that contain one or more bioactive compound and are intended to improve health and beauty) have increasingly become popular [6]. As shown in table I, EOs may be present in the formulations of the various categories cosmetics. An essential oil can be named by the common name and/or specie of the plant from which it was extracted. When only the common name is mentioned, it is understood that the EO can be obtained by the various species related to that plant.

In the past, cosmetic industry used EOs mainly due to their well-known fragrance properties. However, other interesting properties of certain essential oils have been studied, demonstrated and used in cosmetic products [1], [32].

EOs are the ingredients added to natural origin products with fragrance. Once they contain several components with fragrance properties well blended, EOs improve the

odor of a product. Flower EOs, such as rose, tuberose, narcissus, gardenia, jasmine and *Lavandula officinalis*, remain the most popular aroma ingredients in the cosmetic industry [33]. Other EOs commonly used in cosmetics for the same purpose are patchouli (*Pogostemon cablin*), citronella (*Cymbopogon winterianus*), sandalwood (*Santalum álbum*), bergamot (*Citrus* aurantium), rosemary (*Rosmarinus officinalus*), mint (*Mentha piperita*) and vetiver (*Chrysopogon zizanioides*) [1]. Many studies showed that EOs (e.g. *Artemisia afra*, *Pteronia incana* and *Rosmarinus officinalis*) can be used as preservative ingredients in cosmetics, because of their antimicrobial proprieties against a wide range of bacterial strains [8], [22]. Generically, the antimicrobial activity in decreasing order of some common EOs are reportedly: oregano, clove, coriander, cinnamon, thyme, mint, rosemary, mustard and sage [18]. Yorgancioglu *et al*. 2013 [19] studied the effect of some natural essential oils (*Thymus vulgaris*, *Origanum onites*, *Eucalyptus globulus* and *Mentha piperita*) with reported antimicrobial efficacy in cosmetic formulations containing collagen hydrolysate. The antimicrobial effectiveness of cosmetic formulations was performed against *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Enterococcus faecalis*, *Aspergillus fumigatus* and *Candida albicans*. They concluded that formulations containing 2% of *T. vulgaris* or *O. onites* EOs have highest antimicrobial activity and both are effective against *S. aureus*, *E. coli*, *A. fumigatus* and *C. albicans*. The formulation control, as expected, did not show any degrees of antibacterial and antifungal effects. Consequently, it is seen that EOs at reasonably low concentrations prevent the development of pathogenic microorganisms in cosmetic products [19]. In oral care products, EOs also have the same efficacy. Studies showed that EOs mouthwashes have similar efficacy against plaque bacteria as alcohol commercial mouthwashes and they offer additional benefits, such as reduce gingivitis and

oral malodor [34]. This suggests that natural EOs can replace the synthetic chemicals which are harmful for human health and are used in cosmetics with preservative and antimicrobial purposes [19], [34], [35]. Furthermore, cosmetics can contain EOs as cooling agents. Mint and eucalyptus oil give a long-lasting refreshing feeling to the skin and mouth [33], [35].

On the other hand, antioxidants are used in cosmetic preparations to increasing their shelf life [13]. Moreover, they can also be bioactive cosmetic ingredients to protect the skin against free radical responsible for skin aging such as discoloration, loss of elasticity and wrinkles [36]. Various studies reported EOs as an ideal natural source of antioxidants. EOs from *Clausena anisata* and *Eucalyptus camaldulensis* species [37], rosemary [16], coriander, eucalyptus, juniper, cumin, basil, cinnamon, clove, thyme and Egyptian corn silk [18] are examples of sources of highly active antioxidant compounds.

EOs are also used in hair care products in order to provide shine and conditioning effects, and protect and enhance the beauty of the scalp. Chamomile, rosemary, and West Indian bay EOs help to condition and improve healthy hair growth. Bergamot and tea tree EOs can help to control dandruff [33], [37].

Furthermore, currently, essential oils are widely used in cosmetic products with pharmacological properties, the named cosmeceuticals products. Geranium oil, for example, is used in cosmetics as cleansing for over-oily skin, acne and eczema. The anti-inflammatory activity of *Agathosma betulina, Eriocephalus africanu* and *Eriocephalus punctulatus* EOs are reported [37]. Chamomile EOs also have anti-inflammatory effects and are used for treating inflammation of skin and prevention of other skin disorders [33]. Ursolic acid, a compound of rosemary EOs, promotes collagen build-up and elastin synthesis, prevents wrinkles, and increases blood circulation in the skin and scalp [16].

In fact, there are several properties and bioactivities which makes EOs so attractive for cosmetic industry. However, due to its physicochemical nature, the cosmetic benefits of EOs are not entirely availed. In this context, microencapsulation have been reported as an effective process to overcome these limitations [38].

MICROENCAPSULATION OF ESSENTIAL OILS

Microencapsulation is the process that, one material or a mixture of materials is coated with or entrapped within another material or system. The coated material is called active or core material and may be solid, liquid or gas, and the coating material is called shell, wall material, carrier or encapsulating agent. Microparticles consist in a multicomponent structure with a diameter of 1-1000 μm [39]. Commonly, microspheres are described as a matrix system, in which the active ingredient is dispersed/dissolved in the carrier matrix. Microcapsules have at least one discrete domain of active agent and sometimes more (reservoir system) [40]. As a result, the microcapsule consists of a layer of an encapsulating agent that isolates and protects the active substance, avoiding its inadequate exposure. Microcapsules can have regular shape (e.g. spherical, tubular and oval) or irregular shape [41].

Microencapsulation technology was first introduced in the 1930´s with a publication that described gelatin microcapsules obtained by the coacervation technique. However, the first large-scale application of microencapsulation dates 1950's, when the American company National Cash Register (NCR) used complex coacervation for development of carbonless copy paper [42]. Nowadays, microencapsulation has numerous applications in different industrial fields, such as food [43], textile [15], pharmaceutical [44], [45], cosmetic [46], and agrochemical [47] industries. This technique allows the improvement and/or modification of the characteristics and properties of the active material, as well as its protection, stabilization, and slow release.

Microencapsulation can modify the color, shape, volume, apparent density, reactivity, durability, pressure sensitivity, heat sensitivity, and photosensitivity of the encapsulated substance [48]. Additionally, it can protect a core substance from the effects

of UV rays, moisture, and oxygen; increase the storage life of a volatile compound; decrease the rate of evaporation or transfer of the active material from the core to the medium; prevent chemical reaction; reduce agglomeration problems of finely divided powders; improve the handling properties of sticky materials; control release of substances; lower local concentrations; and reduce toxicity or irritancy [49].

Essential oils are valuable ingredients in cosmetic industries. However, their components are labile and volatile, and the sensory perception can be changed as a consequence of oxidation, heating, volatilization or chemical interactions. These chemical and physical effects, which can alter the quality of products, can be effectively minimize by microencapsulation. Accordingly, this technique acts as a physical barrier between the core and the wall materials to protect EOs from the external medium [50].

The development of a microparticle must take into account the microencapsulation process, active and carrier materials, the mechanism of release, and the ultimate destination [51]. There are a wide range of substances encapsulated, as well as walls materials. The selection of appropriate coating material decides majority the physical and chemical properties of the resultant microparticles. Consequently, it should be taken in consideration several factors: physical and chemical properties of the core and coating materials, the stability and release characteristics of the core material, and the microencapsulation methods [52]. On the other hand, many techniques have been developed to microencapsulate the different active material. The microencapsulation method should generally be simple, reproducible, fast, effective and easy to implement on industrial scale. Their choice depends on aspects such as physicochemical properties of the encapsulated and encapsulating material, the release characteristics of the encapsulated compound, purpose, and cost [53], [54]. In the following sections, methods

and wall materials for microencapsulation, particularly microencapsulation of EOs for cosmetic applications, are discussed and reviewed.

ENCAPSULATION TECHNIQUES

Currently, there are numerous methods of microencapsulation and this number continues to increase as companies market products from their patented and innovative microencapsulation technologies [55]–[58]. Numerous methods allow encapsulating an active material depending on the type the material to be encapsulated, the release characteristics of the encapsulated compound, the application, and regulatory considerations. It may influence the final characteristics and properties of microparticles [54]. Although a range of techniques have been reported for microencapsulation, they can widely be divided into three main categories: (i) chemical processes (e.g. interfacial and *in situ* polymerization methods); (ii) physiochemical processes (e.g. coacervation (phase separation), and emulsification solvent evaporation/extraction); and (iii) physical-mechanical processes (e.g. air-suspension method, pan coating, spray drying, spray chilling, spray cooling, and fluid bed coating) [49]. Some of the most important and usual microencapsulation techniques are discussed below. Table II summarizes the microencapsulation methods discussed, presenting the particle size, advantages and disadvantages of these methods.

Coacervation (phase separation)

Phase separation microencapsulation consists in obtaining two immiscible liquid phases from a solution that contains a dispersed macromolecule. The liquid or solid to be encapsulated is dispersed in a solution of a macromolecule (wall material). Through different methods, the encapsulating polymer is induced to separate as a viscous liquid

phase (coacervate). This separation process is known as coacervation. The macromolecule is present at high and low concentrations in the coacervate phase and in the supernatant phase, respectively. Under certain conditions, coacervate phase form a continuous layer which coats the material to be encapsulated. The formed microparticles can be collected by centrifugation or filtration, and thereafter washed with the appropriate solvent, dried and hardened by thermal, cross-linking, or desolvation techniques [59]. Therefore, coacervation is a three-step process: (1) formation an oil-in-water (o/w) emulsion (active compound is dispersed in the aqueous phase and polymer is dissolved in the organic phase); (2) deposition of the liquid polymer coating upon the core material; and (3) stabilization and hardening the coating material to form a self-sustaining microcapsules (Fig. 1) [60].

Coacervation in aqueous phase can be divided into simple or complex. Simple coacervation is induced by a change in conditions that cause the desolvation of the wall material [61]. The complex coacervation is induced by creating electrostatic forces between the macromolecules of shell materials. Complex coacervation is a result of mutual neutralization of two oppositely charged polymers [62]. Among factors that affect the size of the microcapsules are stirring speed, viscosity of both aqueous and organic phases, concentration and type of surfactant (if added), configuration of the vessel and agitator, and the temperature profile during production [63], [64]. Sutaphanit *el al.* 2014 [21] microencapsulated holy basil essential oil into the gelatin matrix by simple coacervation via glutaraldehyde crosslinking. The microencapsulation yield and efficiency obtained for the optimal tested operational conditions was about 99% and 95%, respectively. Lv *at al.* 2012 [65] microencapsulated jasmine oil by complex coacervation

with soybean protein gelatin/gum arabic. The microencapsulation efficiency achieved varied from 76% to 81% [65].

This technique allows high encapsulation efficiency and efficient control of particle size. Additionally, it can provide protection against degradative reactions, prevent the loss of volatile aromatic ingredients, control release and improve the stability of the flavor and EOs core materials [66]. However, the most common problem is agglomeration of microcapsules [67]. It is also operationally complex, requiring careful control of experimental conditions, and expensive [68]. In some cases, the stabilization of the microcapsules using high temperature, extreme pH values or crosslinking agents is required, which limits the encapsulation chemically and thermo-labile materials such as proteins and polypeptides. Other limitations are evaporation of volatiles (e.g. flavors and EOs) during processing, dissolution of active compound into the processing solvent and oxidation of product. [61].

Spray drying, spray chilling and spray cooling

Spray drying is a physical-mechanical microencapsulation method developed in the 1930s [69]. In spray drying technique, the active compound dispersed or dissolved in an aqueous or organic solution of the polymer is atomized into the heated compartment of a spray dryer. After evaporation of the solvent, the dried microparticles are recovered (Fig. 2) [70].

The first step is solubilize or disperse the core material (usually a water immiscible oil) in a concentrated solution of the coating material, often an aqueous solution. The resulting solution or dispersion is then sprayed into droplets in the spray dryer chamber where a hot gas circulates. As a result, the droplets quickly dry and can be continuously collected from the spray drying chamber [71]. The encapsulation efficiency is influenced

by various process parameters, including type of wall material, properties of the core materials, characteristics of the infeed emulsion, and conditions of the spray-drying process (atomization type, inlet air temperature, air flow, and humidity levels) [50]. Additionally, wall composition and properties, core material-to-wall ratio, atomization and drying parameters, dispersion of feed material viscosity, and storage condition affect microstructures of spray-dried capsules [52], [54]. Spray drying is the most widely used technique to encapsulate fragrances, oils and flavors. The aroma retention is dependent on the moisture content of the final microparticles and on the humidity of the exhaust air [72]. Arana-Sánchez *et al.* 2010 [73] microencapsulated oregano (*Lippia graveolens*) EOs by spray drying with β-cyclodextrin to analyze how this technique affect antimicrobial and antioxidant activities of EOs. The average encapsulation efficiency was 81%. In this study, it was shown that microencapsulation of oregano EOs in β-cyclodextrin by spray drying preserves the antimicrobial activity and improves the antioxidant activity of active compound.

Spray drying microencapsulation is a simple, flexible, rapid, low process cost and easy scaling-up technique [74]. It allows a large-scale production in continuous mode, high encapsulation efficiency, good stability of the finished product, and good retention of volatiles. Spray drying can be used for many heat-labile (low-boiling point) materials, due to its short contact time in the drier [53], [75].

However, the microparticles obtained by spray drying are usually no uniform [67], some low-boiling point aromatics can be lost during the process, and the wall material should have low viscosity at relatively high concentrations. Furthermore, it produces a very fine powder which needs further processing, such as agglomeration. To overcome

this last disadvantages, spray-drying powders can be agglomerated by using the fluidized bed coating process [76].

Spray chilling and spray cooling techniques are similar to the spray drying technique. The active compound dissolved or dispersed in a solution of the coating material is atomized through a pneumatic nozzle into a reactor. Though, the vessel contains the cold medium. Consequently, the wall material solidifies, forming a coat film. As spray drying, this techniques are rapid and takes place in one step [48]. The normal meting point of encapsulating material is in the range of 32–42 ºC for spray chilling and 45–122 ºC for spray cooling. These processes are suitable for encapsulate water-soluble materials which can be volatilized during thermal processing. They are also very used for encapsulation of aroma compounds to improve heat stability and control release. The major limitations are the high process costs, and the special handling and storage conditions that they require [61].

Fluid bed spray coating

Fluid bed coating is a three steps physical-mechanical encapsulation method to encapsulate solid core materials, including liquids absorbed into porous solids. Solid particles to be encapsulated are fluidized on a jet of hot air into the coating chamber, and then covered by a spray of liquid coating material. Finally, the capsules are successively wetted and dried by cooling or solvent vaporization until the walls have the desired thickness. The fluid bed process is widely use in cosmetic industry, particularly for encapsulating spray-dried flavors [77]. The particles obtained by this technique are uniform and their range size is between 0.3 to 10 mm. It is a low operational cost and high thermal efficiency process, and allows total temperature control. However, it may take long time [67].

Emulsification solvent evaporation/extraction

The emulsification solvent evaporation technique has often been used for preparation of microparticles, especially for controlled release of active compounds. Generally, this technique consists in forming an emulsion of polymer solution in a volatile organic solvent, followed by internal phase solvent evaporation or extraction [78]. A solution or dispersion of the polymer and the active material is emulsified in an external aqueous phase, in which the polymer is insoluble. Core material is usually stabilized with a suspending agent to retain the individuality of the droplets. Whereas solvent evaporation regularly takes place at atmospheric pressure (or under reduced pressure) to promote evaporation of the volatile solvent, the solvent extraction involves a third liquid. This is a precipitant for the polymer and miscible with both water and solvent, in order to solvent diffuses through oil droplets [38]. The single emulsion technique is normally used to microencapsulating hydrophobic core materials, and the double emulsion process or water-in-oil-in-water (w/o/w) method is generally employed to microencapsulating hydrophilic core materials [79].

Teeka *et al.* 2014 [80] microencapsulated jasmine EOs with polymethyl methacrylate (PMMA) by solvent evaporation method in oil in water (o/w) emulsion system with an encapsulation efficiency of 72%.

Emulsification solvent evaporation/extraction is a straightforward method to obtain small droplets with relatively narrow size distribution, widely used for the preparation of biodegradable and non-biodegradable polymeric microparticles and microencapsulation of a wide variety of liquid and solid core materials [81]. Nevertheless, it provides low encapsulation efficiency, leads to amounts of residual solvent, and is expensive [82].

Interfacial and *in situ* polymerization

There are different polymerization techniques for microencapsulation of active compounds. Reactions between oil-soluble and water-soluble monomers can result in interfacial polymerization to form polymeric microparticles, whose size is determined by the droplet size of the emulsion [38]. Alternatively, interfacial polymerization can result in reaction of two reactive monomers dispersed in one phase, induced to polymerize at the interface or in the dispersed phase and precipitate at the interface. Under this conditions, the surface of the core material is coat by a polymer. In this technique are used polymers formed by monomers that have preferential solubility for one of the phases, such that polymerization only happens at the interface [49]. Typically the interfacial polymerization involves the reaction between a diacyl chloride and an amine or alcohol, resulting polyester, polyurea, polyurethane, or polycarbonate polymers [48]. Scarfato *et al.* 2007 [83] produced polyurea microcapsules by interfacial polymerization in o/w emulsion, coating lemon balm (*Melissa officinalis* L.), lavender (*Lavandula angustifolia* Miller), sage (*Salvia officinalis* L.), and thyme (*Thymus vulgaris* L.) EOs. The essential oil loadings was in the range of 25–50wt%.

In situ polymerization is a chemical microencapsulation technique similar to interfacial polymerization. However, *in situ* polymerization no reactants are included in the core material. The polymerization of a single monomer directly occurs on the particle surface [84]. Chung *et al.* 2013 [85] prepared microcapsules containing thyme oil by *in situ* polymerization, using melamine–formaldehyde prepolymer as a wall material and achieve 78% of loading efficiency of thyme oil in microcapsules using 2% sodium laurylsulfate (SLS) as emulsifier.

Polymerization technique is generically a fast and easily scale-up method [84], and provides high encapsulation efficiency. However, polymerization reaction is difficult to

control [67], requires large quantities of organic solvents and monomers may be non-biodegradable and/or non-biocompatible [41].

Microencapsulation techniques discussion

Different techniques have been successfully used for preparing EOs microparticles. Microencapsulation by spray-drying is one of the most common and cheapest techniques for producing microparticles. This technique offers a high relation production rate/operating costs, and resulting microparticles/powders are stable. Although its disadvantages, such as complexity of equipment and difficulty of control particle size, spray drying has been successful applied to prepare encapsulated flavors since 1930s [69]. Coacervation is other effective technique to produce EOs microparticles [59]. This technology avoids the use of high temperature processes to dry solvent, which is an advantage for heat-labile active ingredients [86]. However, due to the high processing cost and complexity of procedure, coacervations is no very used in industrial scale. Jun-xia *et al*. 2009 [87] produced microparticles of sweet orange oil by complex coacervation with soybean protein isolate/gum arabic. The microencapsulation efficiency and microencapsulation yield obtained was respectively 85% and 68% for 20% core material load. Comparatively, Yang *et al.* 2009 [88] achieved 82% of microencapsulation yield for the same flavor as core material for 20% load in the spray-drying method.

Fluidized bed is associated with the spray dryer for further agglomeration of particles, since spray-dried powders usually have a small particle size with poor handling properties. This technique create an additionally layer of molecules, giving a second coating to spray-dried products or products with a sensitive core, such as essential oils [89].

Solvent evaporation microencapsulation technology is widely applied industries for controlled release of active substances, such as pharmaceutical industry. For EOs, insoluble compounds, the simplest oil-in-water (o/w) method is frequently used in microencapsulation by solvent evaporation technique [81]. In contrast to spray-drying and coacervation techniques, in emulsification/solvent evaporation neither requires elevated temperatures nor phase separation-inducing agents, respectively. However, careful selection of encapsulation conditions and materials is needed to yield high encapsulation efficiencies and a low residual solvent content [78]. There are additional problems related to the safety of the operation and environment [90].

Nowadays, *in situ* and interfacial polymerization is used to microencapsulate a wide range of active agents within various polymeric shells [83] [91]. Nevertheless, this technique always involves using many organic solvents and non-biocompatible wall materials [41]. An well-known problem is residual formaldehyde in microparticle suspension after the polymerization [92]. The selection of a suitable wall material is critical for microencapsulation process, affecting the success of the technique as well as the proprieties of final microparticles and its safe applications.

ENCAPSULATED MATERIALS

There are an enormous range of different materials which have been studied and used for their suitability as encapsulating agents and its choice are crucial for properties and characteristics of obtained microparticles. Generically, the encapsulated materials should follow certain criterial: be chemically compatible and non-reactive with the core material; protect the active material of the environment adverse conditions (light, pH, oxygen, heat and other compounds present); have the release desired properties of the

encapsulated ingredient; slow down the diffusion of the active ingredient to the external medium; capable of forming a cohesive film with the core material; and be resistant, flexible, impermeable, stable and easily handled [38], [49], [61], [66], [84], [93].

Encapsulated materials can be natural, semi-synthetic or synthetic polymers [41], [48]. Table III shows a survey of illustrative examples of wall materials used in microencapsulation processes of essential oils with cosmetic importance.

Natural polymers are plant exudates and extracts. Although they are generally nontoxic, biodegradable, and abundant, their composition may vary. Natural shell materials for microencapsulation can be polysaccharides (e.g. carrageenan, gum arabic), proteins/peptides (e.g. collagen, gelatin) and lipids (e.g. lecithin, heparin). The most commonly used natural materials are the polysaccharides alginate and chitosan. Chitosan is a cationic polysaccharide exhibiting β(1→4) linkages, obtained by alkaline deacetylation of chitin. It have many advantages such as availability, low cost, non-toxic, biocompatibility, biodegradability, and versatile. Alginate derives from brown seaweed and is a polyanion copolymer of D-mannuronic and L-guluronic acid linked by β(1→4) linkages. This polymer is applied as encapsulating agents for food and pharmaceutical uses because of its low immunogenicity and biocompatibility, proper to sol–gel transition in the presence of multivalent cations. Additionally, alginate microparticles preparation involves mild reaction conditions [41], [68], [79].

Synthetic polymers have also been used to form microparticles. The modulation and proprieties optimization of synthetic polymers are easily, since they are available in different compositions and molecules. Nevertheless, the wide range of synthetic polymers show lack of biocompatibility [41]. Aliphatic polyesters, such us poly(lactic acid) (PLA) and copolymers of lactic and glycolic acids (e.g. PLGA), have been used in last years as

biodegradable wall synthetic polymers for controlled delivery systems [78]. On the other hand, modified celluloses (e.g. cellulose acetate butyrate, hydroxypropyl cellulose) are the semi-synthetic polymers predominantly used for microencapsulation [41], [48].

ESSENTIAL OILS MICROENCAPSULATED IN THE INDUSTRY AND IN THE MARKET

Cosmetic, perfumery and personal care industry invests in innovative technologies and scientific knowledge to put into the market new or updated products that meet the increasingly demanding expectations of consumers. In this era, consumers are looking for effective, safe and natural products that contribute for their health, wellness and beauty [16], [36]. As a result, consumer creates the need for development of new cosmetic products formulated with natural and nutraceutical ingredients. Nowadays, a significant number cosmetic products that combines natural ingredients and innovative delivery systems have been developed [40]. As natural ingredient, plant EOs for perfumery and cosmetics is a growing market trend, being used in skin creams, balms, shampoos, soaps, and perfumes [7], [94]. On the other hand, cosmetic delivery systems are a millionaire market in expansion and have enormous potential to be the future generation of smarter carrier systems of active substances [40].

Microencapsulation had a global impact in cosmetic market in late 1980s, when Kanebo, Ltd., Japan, developed fragrant fabrics by using microencapsulation technology [95]. Nowadays, microencapsulation techniques are being used to develop and produce a delivery system of active compounds in some cosmetic formulations [40]. The major industrial processes for flavor microencapsulation are spray drying and extrusion. Freeze drying, coacervation and adsorption techniques are also industrially used. In fact, the most important aspect of microencapsulation techniques for the industry is its easy scaling-up. Understanding how process variables and the most important parameters influence a specific microencapsulation technique is crucial to modulate them and to make the transition from laboratory scale to industrial scale production [61]. There are several

studies that report the effect of the different process variables in the final microparticles proprieties produced by spray drying microencapsulation technique. This technology offers the advantage of produce microcapsules in a relatively simple, rapidly and continuous processing operation. Furthermore, it has low processing costs and there are available equipment. Spray drying is suitable for microencapsulate many volatile materials (e.g. like EOs), due to its short contact time in the drier [96]. From these considerations, spray drying has great potential to produce in large scale cosmetic products with microencapsulated EOs.

New microencapsulation technologies continue to emerge and to be patented. Ciba Specialty Chemicals has been conducting researches in the field of microencapsulation of some compounds such as fragrances, colorants, and cosmetically useful oils [97]. Tagra Biotechnologies Ltd., Israel, patented Release on Demand™ (RND™) Microencapsulation Technology and commercializes scale manufacturing Tagrol™ microencapsulated essential oils products produced by that technique. Tagrol™ products are intended to be used in a wide range of cosmetics and personal care products formulations. Tea tree, menthol, borage, evening primerose, chamomile, hippophae, patchouli, eucalyptus citriodora and ginger EOs are the available Tagrol™ products. The EOs are microencapsulated by a four stages process: emulsification, extraction, filtration and freeze drying [98]. Captivates™ encapsulates developed by Ashland Inc., USA, can microencapsulate EOs for customized cosmetic and personal care products. The microparticles can be made up by a complex coacervate based on naturally derived polymers or JetCutter™ processes. By JetCutter technology, the insoluble oil is entrapped in a hydrogel matrix which composition are normally alginate, agar, carrageenan or chitosan [99]. Different microencapsulated EOs are commercial available, since

microencapsulation is a very attractive technology for different industry fields, providing stability and protection to EOs, and its control release. The application of commercial microencapsulated EOs in cosmetics products require a suitable formulation constituted by biodegradable and biocompatible compounds.

CONCLUSION

In this work a briefly review about the use of essential oils and the advantages of its microencapsulation in cosmetic industry was presented. The multimillionaire cosmetic industry continues to invest in research and development of innovative products in order to satisfy the needs of increasingly demanding consumers for products formulated with natural and nutraceutical ingredients, differentiate from competition and add value to the product. The use of essential oils as cosmetic ingredients have several advantages, such as enhancing the cosmetic properties and preservation, and marketing image of the final product. In recent years, a significant effort has been made to microencapsulate cosmetic ingredients, because of its ability to conserve and protect the active compounds from degradation and evaporation, as well as its control release. Consequently, the microencapsulation of essential oils are extremely attractive for formulation cosmetics and personal care products. Although there are many microencapsulation techniques, multidisciplinary cooperation is needed to improve them for its efficient large scale implementation and take full advantage of this technology. Additionally, it is important to develop a better understanding about the biological activities of microencapsulated essential oils for its safety use in cosmetics and the modulation the release of active ingredient.

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FIGURES CAPTURE

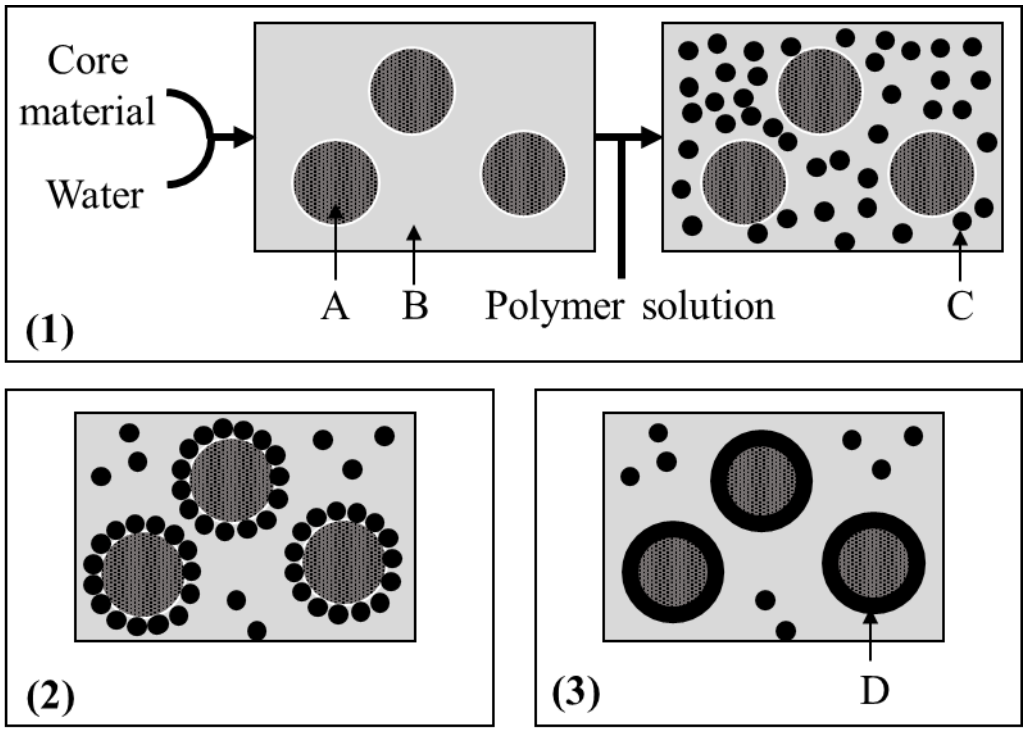

Figure 1. Generic scheme of microencapsulation process by coacervation: (1) formation an oil-in-water (o/w) emulsion (core material (A) is dispersed in water (B), and polymer (C) is dissolved in the organic phase); (2) deposition of the liquid polymer coating upon the core material; and (3) hardening the coating material to form a self-sustaining microcapsules (D). Adapted from Lamprecht *et al.* 2012 [48].

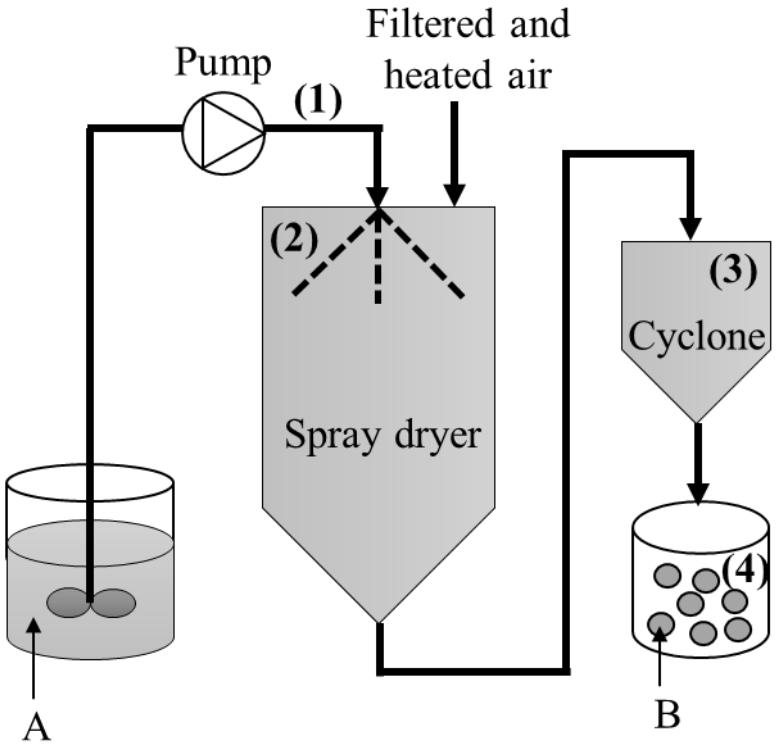

Figure 2. General scheme of microencapsulation process by spray drying technique: (1) pumping the polymer solution containing the core material (A) to a spray dryer; (2) atomization the solution/dispersion into the heated spray dryer; (3) air-particles drying separation into the cyclone; and (4) micro-particles (B) recovery. Adapted from Estevinho *et al.* 2013 [72] and Suri *et al.* 2013[83].

TABLES CAPTURE

Table I. Example of essential oils present in the different categories of cosmetic products.

Type of cosmetic products	Essential Oils	Reference
Skin care and maintenance		
Softener/smoothing (emollients)	Fenugreek (*Trigonella foenumgraeceum*)	[33]
Moisturizers	Chamomile	[100]
Antiaging	Vanillin Sandalwood Olive	[101]
	Borage Evening primerose Chamomile	[98]
Repairing (antichapping and antiwrinkling agent)	Camellia (*Camellia japonica*)	[102]
	Centella asiatica	[31], [36]
	Hippophae	[98]
Repairing (antiacne agents)	Rosemary (*Rosmarinus officinalis*)	[103]
Sunscreens	Lavender (*Lavandula stoechas*) Oregano (*Origanum majorana*)	
After-sun	Tea tree Menthol Chamomile Patchouli	[98]
Cosmetic textiles	Lavander (*Lavandula hybrida*) Sage (*Salvia officinalis*)	[14]
	Rosemary (*Rosmarinus officinalis*)	[15]
	Aloe Vera (*Aloe vera* L.)	[104]
Cleansing		
Shampoos	Rosemary (*Rosmarinus officinalis*)	[16], [33], [37]
Soaps	Sweet orange (*Citrus sinensis* L.) Lavender (*Lavendula angustifolia, L. latifolia, L. stoechas*)	
Dentifrices and toothpastes	Sage (*Salvia officinalis*) Clove Eucalyptus Peppermint (*Mentha piperita*) Menthol mint (*Mentha arvensis*) Myrrh (*Commiphora myrrha*)	[35]
Odor improvement		
Perfumes, deodorants, and antiperspirants	Lemon (*Citrus limonum* L.) Sweet orange (*Citrus sinensis* L.) Geranium (*Pelargonium graveolens* L.)	[33], [105]
	Clove (*Syzygium aromaticum*)	[100]
Hair removal		
Depilatories	Peppermint	[106]
Hair maintenance		
Conditioning and shine	West Indian bay Chamomile Lavender	[33]
Antidandruff	Thyme (*Thymus vulgaris* L.) Garlic (*Allium sativum* L.) Bergamot Tea tree (*Melaleuca alternifolia*)	
Hair growth stimulants	Sage (*Salvia officinalis* L.)	
Care and maintenance of mucous membranes		
Mouthwashes	Eucalyptol Menthol Thymol	[107]

Table II. Particle size produced by different microencapsulation technologies and their advantages and disadvantages.

Microencapsulation technique	Particle size (μm)	Advantages	Limitations	References
Simple coacervation	20-200	• High encapsulation efficiency • Efficient control of particle size	• Expensive method • Aggregation of particles • Hard scaling-up • Evaporation of volatiles • Possibility of dissolution of active compound into the processing solvent • Oxidation of product	[61], [66]–[68]
Complex coacervation	5-200			
Spray drying	1-50	• Simple • Versatile • Low process cost • Easy scaling-up technique	• Particles no uniform • Low oil loading level • Require further processing • Possibility of lost low-boiling point aromatics	[61], [67], [68], [70], [89]
Spray chilling	20-200	• Suitable for water-soluble materials	• High process costs • Require special handling and storage conditions	[61]
Fluid bed spray coating	>100	• Low operational costs • High thermal efficiency process • Total temperature control	• Long time process	[61], [67]
Emulsification	0.1-100	• Small droplets • Narrow particle size distribution • Suitable for biodegradable and non-biodegradable polymeric micro-particles, and a wide range of liquid and solid core materials	• Low encapsulation efficiency • Production of high quantity residual solvent • Expensive method	[67], [84], [108]
Interfacial polymerization	0.5-1000	• Easy scaling-up technique • Fast • High encapsulation efficiency	• Difficult to control • Production of high quantity residual solvent • Possibility of non-biodegradable and/or non-biocompatible monomers	[41], [67], [84]

Table III. Representative list of shell materials used in microencapsulation of essential oils with cosmetic significance.

Shell material	Core material: Essential oil	Microencapsulation technique	Reference
GA and maltodextrin	*Pterodon emarginatus*	Spray drying	[71]
	Lime	Spray drying	[72]
Alginate	Clove (*Eugenia caryophyllata*) Thyme (*Thymus vulgaris*) Cinnamon (*Cinnamomum zeylanicum*)	Emulsion extrusion	[109]
Chitosan	Citronella	o/w emulsification	[110]
Gelatin	Holy basil	Simple coacervation	[21]
Ethylcellulose	Rosemary	Phase separation	[15]
	Lavender	o/w emulsification solvent diffusion	[95]
Melamine formaldehyde	Rosemary (*Rosmarinus officinalis*) Lavender (*Lavandula hybrida*) Sage (*Salvia officinalis*)	Modified *in situ* polymerization	[14]
PMMA	Jasmine	o/w emulsification solvent evaporation	[80]

GA - gum arabic; PMMA - polymethyl methacrylate; o/w – oil in water.