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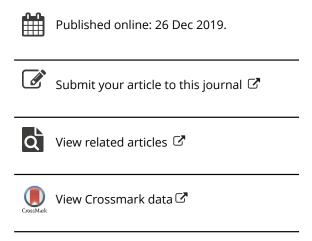
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REVIEW



A review of encapsulation of carotenoids using spray drying and freeze drying

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ABSTRACT

Carotenoids are potent antioxidants, but they are highly unstable and susceptible during processing and storage. Encapsulation technologies protect against degradation and are capable of releasing individual or combination of bioactive substances during processing as well as development of various functional food products. Moreover, encapsulating agents can be used to increase the stability of carotenoids and form a barrier between the core and wall materials. Suitable encapsulating agents, temperature, and drying methods are the most important factors for the encapsulation process. In this report, we reviewed the current status of encapsulation of carotenoids from different fruits, vegetables, spices, seaweeds, microorganisms, and synthetic sources using various types of encapsulating agents through spray drying and freeze drying. We also focused on the degradation kinetics and various factors that affect the stability and bioavailability of encapsulated carotenoids during their processing and storage.

KEYWORDS

Carotenoids; encapsulation; spray drying; freeze drying; fruits; vegetables

Introduction

Carotenoids, the main sources of vitamin A, are useful in preventing degenerative human diseases because of their antioxidative and free radical scavenging properties (Kim et al. 2006; Krishnaiah, Sarbatly, and Nithyanandam 2011). β -carotene, α -carotene, and β -cryptoxanthin lycopene, lutein, and its isomer zeaxanthin are known as carotenoids (McGuire and Beerman 2007). The human body is not capable of synthesizing carotenoids; therefore, carotenoids must be supplied through the diet. Natural antioxidants have attracted considerable attention because of their safety in comparison with artificial antioxidants. Natural antioxidants can be added to different food products in different ways. They can be used to increase stability by preventing lipid peroxidation, thereby increasing the shelf life of food products. Recently, there has been a global trend of using phytochemicals from natural sources, such as vegetables, fruits, oilseeds, and herbs, as antioxidants and functional ingredients (Elliott 1999; Kaur and Kapoor 2001). However, it is very difficult to store fruits and vegetables for a long time because of their perishable nature, even at low temperatures. Elevated temperature, light, oxygen, and pH are parameters that affect the degradation of phytochemicals (Xianquan et al. 2005). Therefore, processing is necessary to prolong the shelf life. Drying is one of the oldest food preservation techniques, and among all drying methods, spray drying, and freeze drying are two of the best methods for preserving bioactive compounds. Spray dryers and freeze dryers are widely used to produce dried fruits and vegetables, and they can preserve heat-sensitive bioactive components, such as phenolic compounds, carotenoids, and anthocyanins, more effectively than other drying methods.

Encapsulation technology is used in the food industry to develop liquid and solid ingredients as effective barriers against environmental parameters, such as oxygen, light, and free radicals (Desai and Park 2005). Bioactive compounds can be improved by using encapsulation techniques, which entrap sensitive ingredients inside a coating material (Saenz et al. 2009). Moreover, encapsulating agents can be used to increase the stability of bioactive compounds. Researchers (Saenz et al. 2009; Ahmed et al. 2010a; Ahmed et al. 2010b; Kha, Nguyen, and Roach 2010) have used various encapsulation materials, such as starch, maltodextrin, corn sirup, inulin, and Arabic gum to improve bioactive compounds during spray drying. Some reviews on encapsulation techniques, such as microencapsulation of oils (Bakry et al. 2016) and microencapsulation of vitamin A (Gonçalves, Estevinho, and Rocha 2016), exist. However, these reviews lack information regarding the selection of encapsulating materials and modeling for encapsulation of carotenoids. Therefore, the objective of this review is to illustrate the impact of encapsulating agents on carotenoids from different sources, as well as the degradation kinetics during processing and storage using spray dryers and freeze dryers.

General characteristics of carotenoids

Carotenoids are isoprenoid compounds. More than 600 different fat-soluble carotenes have been isolated from plants

Figure 1. Structure of β -carotene.

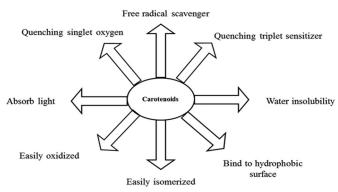


Figure 2. Physical and chemical properties of carotenoids.

(Gul et al. 2016). The chemosynthesis of carotenoids involves tail-to-tail linkage of two C_{20} geranyl-geranyl diphosphate molecules, resulting in a progenitor C₄₀ carbon skeleton from which all individual variations are derived (Figure 1) (Dutta, Raychaudhuri, and Chakarborty 2005). β -carotene, lutein, zeaxanthin, neoxanthin, vioxanthin, and chlorophylls are the most commonly found carotenoids in plants (Gul et al. 2016; Lakshminarayana et al. 2005). β -carotene (chemical formula, $C_{40}H_{56}$; molecular weight, 536.88 g/mol) is widely distributed in plant based foods and microorganisms (Khachik, Beecher, and Smith 1995). Generally, all $trans\beta$ -carotenes are dominant precursors of vitamin A (Krinsky and Johnson 2005). The physicochemical features including color, chemical reactivity, molecular shape, light absorbing intensity, and antioxidant properties of carotenoids depend on the length of the polyene chain (Figure 2) (Britton 1995; Dutta, Raychaudhuri, and Chakarborty 2005). Carotenoids are classified into two categories: (i) alpha-, beta-, gamma-carotene and alpha-, betacryptoxanthin, which can be metabolized by humans into retinol, and (ii) lutein, zeaxanthin, lycopene, which are unrelated to any vitamin A activity in humans (Bohn 2008).

A number of factors are responsible for the degradation of carotenoids. On exposure to heat, light, and oxygen during processing and storage, trans-β-carotene immediately undergoes thermal and chemical oxidation, isomerization, and photosensitization (Figure 3) (Dutta, Raychaudhuri, Chakarborty 2005; Gul et al. 2016). The instability of carotenoids is caused by their structural polyene chain. The oxidation process of carotenoids involves epoxidation, forming apocarotenoids (Marty and Berset 1988), and low molecular weight compounds responsible for the off-flavor in food (Falconer et al. 1964). During digestion, carotenoids also degrade in various ways in the human body (Figure 4). Therefore, retention of carotenoids is a major issue during their processing and storage. Microencapsulation techniques could enhance the retention of carotenoids during processing and storage and protect against degradation from light, heat, and temperature.

General aspects of microencapsulation

The encapsulation technique is widely used in several fields, particularly in the food industry (Higuera-Ciapara et al. 2004; Shen and Tang 2012). The process involves coating or entrapping solid, liquid, or gas particles into thin films using various food-grade encapsulating agents (Gharsallaoui et al. 2007; Gonçalves, Estevinho, and Rocha 2016). During encapsulation, the core materials are surrounded by a wall, which acts as a physical barrier to protect them from external factors. The coating material, encapsulating agents, carrier, shell, capsule, membrane, packaging material, or the external phase, are known as wall materials. Core materials are also called core actives, fills payloads, or the internal phase. The particles obtained are called microcapsules. Most microcapsules are small spheres with diameters ranging between micrometers and millimeters. The sizes and shapes of the microparticles depend on the materials and methods used to prepare them (Gharsallaoui et al. 2007). Some microcapsules may have multiple microencapsulating agents that form different walls with different chemical and physical properties (Botelho et al. 2007). The morphology of microcapsules depends mainly on the core materials and deposition process of the shell. Various microcapsules are shown in Figure 5. The main purposes of the encapsulation process in the food industry are given below:

- i. Reducing the transfer rate of the core materials to the surrounding materials.
- ii. Protecting the core materials from undesirable environmental conditions.
- iii. Preventing incompatibility and reactivity of the compounds.
- iv. Modifying the physical characteristics of the original materials for easy handling.
- v. Masking undesirable taste or unwanted aroma of the core materials.
- vi. Diluting the core materials to decrease quantity of the compound when desirable.
- vii. Controlling the release of core materials.
- viii. Providing better storage conditions by preventing degradative reactions like dehydration and oxidation.

Common microencapsulating agents

Encapsulation efficiency and microcapsule stability depend on the encapsulating agent or wall material.

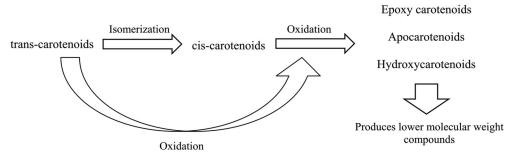


Figure 3. Diametric presentation of carotenoids degradation.

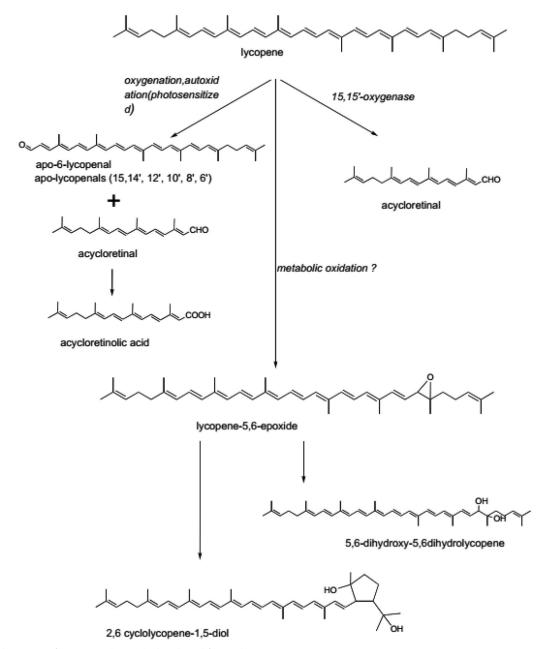


Figure 4. Degradation way of lycopene in human body (adapted from Bohn 2008).

Therefore, selecting appropriate encapsulating agents is necessary to maintain the desirable encapsulation efficiency, microparticle stability, and the required characteristics of the final product (Gonçalves, Estevinho, and Rocha 2016). The wall material can be selected from

a wide variety of natural and synthetic polymers. Different types of encapsulating agents are used as wall materials during spray and freeze drying. In this review, we focus on encapsulating agents that are commonly used during spray drying and freeze drying.

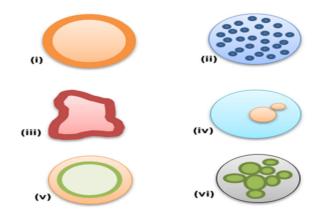


Figure 5. Different types of microcapsules: (i) simple microcapsule, (ii) matrix (microsphere), (iii) irregular microcapsule, (iv) multicore microcapsule, (v) multiwall microcapsule, and (vi) assembly of a microcapsule (adapted from Bakry et al. 2016).

Maltodextrins

Maltodextrins are polysaccharides and water-soluble materials, available as white powders. Maltodextrins are usually classified by their dextrose equivalent value (DE) (Desobry, Netto, and Labuza 1999). Maltodextrins with DE values of 4, 10, 15, 20, 25, 30, and 42 are available in the market. Maltodextrins are commonly used as encapsulating agents for freeze drying, and are also often used in various sugarrich foods such as blackcurrant, raspberry, and apricot juice during spray drying. Addition of maltodextrins during the drying process increases the glass transition temperature and reduces stickiness of the product (Quek, Chok, and Swedlund 2007). Maltodextrins help in retaining certain product properties, such as nutrient content, color, and flavor during drying (Rodriguez-Hernandez et al. 2005).

Starch

Starch is soluble in water and can be separated into its component fractions, amylose and amylopectin, by heating. Due to its qualities, such as abundant availability, low cost, and emulsifying properties during drying starch has been widely used as a wall material. Starch has also been used to enhance storage stability of flavors (Partanen et al. 2002). Different types of starches are used as encapsulating agents during drying: modified tapioca starch, native tapioca starch, and waxy maize starch. However, some studies (Bayram, Bayram, and Tekin 2005; Gharsallaoui et al. 2007) have reported that starch is not a suitable encapsulation agent during spray drying because it caramelizes, attaches to the spray-dryer wall, and clogs the nozzle due to its heterogeneous form during drying.

Gum Arabic

Gum Arabic, also known as acacia gum, is composed of polysaccharides and glycoproteins. It is often used as an effective encapsulating agent because of its protective colloid functionality (Krishnan, Bhosale, and Singhal 2005). During spray drying, gum Arabic is used as an encapsulating agent to obtain good emulsifying capacity and low viscosity in an aqueous solution. Gum Arabic is 3 to 4 times more stable than maltodextrin in bixin encapsulation (Barbosa, Borsarelli, and Mercadante 2005). However, it not as effective as other wall materials, such as citral, linalool, β -myrcene, limonene, and β -pinene (Bertolini, Siani, and Grosso 2001).

Chitosan

Chitosan is a linear polysaccharide, which is soluble in acidic aqueous media. The application of chitosan as a coating material is increasing because of its biocompatibility, low toxicity, and biodegradability (Grenha et al. 2007). Chitosan alone, rather than a combination of chitosan and maltodextrin, is unable to provide a stable emulsion for fish oil-encapsulated powders after freeze drying (Klaypradit and Huang 2008).

Inulin

Inulin is a polysaccharide that is produced by many types of plants, such as chicory (*Cichorium intybus*) root, dahlia (*Dahlia pinnata* Cav.), and Jerusalem artichoke (*Helianthus tuberosus*). Inulin is an excellent potential encapsulating agent because of its low cost and nutritive properties (Stevens, Meriggi, and Booten 2001). Gandomi et al. (2016) demonstrated that chitosan-coated alginate beads increased bacterial survival in stored apple juices. A mixture of inulin and whey protein isolate was a suitable carrier for the spray drying of rosemary essential oil (Fernandes et al. 2014).

Proteins

Different types of proteins, such as soy protein, whey protein, and gelatin, are used in the food industry as carrier agents. Among them, soy protein is one of the most popular plant protein sources because it is abundant and inexpensive. During spray drying, proteins are used as encapsulating materials because they protect against oxidation (Bylaite et al. 2001) and have high-binding properties (Landy, Druaux, and Voilley 1995). Pea protein could be used as a good carrier agent for the microencapsulation of ascorbic acid (Pierucci et al. 2006). Vega et al. (2005) showed that sodium caseinate showed better encapsulation properties than micellar casein.

Ascorbic acid

Ascorbic acid, known as vitamin C, is a white or light-yellow powder. Many researchers have used ascorbic acid as a protective agent during spray drying (Ahmed et al. 2010a; Desai and Park 2005). Ascorbic acid has the ability to reduce hygroscopicity and dusting, and it provides a high degree of flowability without clumping during the encapsulation process (Shahidi and Han 1993).

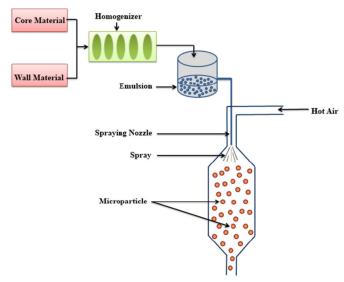


Figure 6. Schematic representation of the microencapsulation process by spray drying (adapted from Bakry et al. 2016).

Other encapsulation agents

The above-mentioned wall materials have been widely used during drying. However, some researchers have also used different wall materials, such as carrageenan, silicon dioxide, sodium caseinate, soy lecithin, and sodium alginate.

Encapsulation techniques

Numerous techniques are used for the encapsulation process in the food industry. Encapsulation techniques can be classified as follows (Munin and Edwards-Lévy 2011): Physical methods: spray drying, fluid bed coating, extrusion-spheronization, centrifugal extrusion, pan coating, drum drying, freeze drying, and processes using supercritical fluids.

Physicochemical methods: spray cooling, hot melt coating, ionic gelation, solvent evaporation extraction, and simple or complex coacervation.

Chemical methods: interfacial polycondensation, in situ polymerization, interfacial polymerization, and interfacial cross-linking.

Spray drying is the simplest and oldest used commercial method for encapsulation (Shahidi and Han 1993). Freeze drying could also be used to obtain bioactive compounds during encapsulation. Therefore, in this review, we focus on the encapsulation of carotenoids from fruits, vegetables, spices, seaweed microorganisms, and synthetic sources using spray and freeze drying.

Spray drying technology

Spray drying has been widely used in the food industry for commercial production of dried fruits and vegetables. Spray drying is highly appropriate for heat-sensitive food ingredients. Various stages are involved in the encapsulation process using spray drying (Figure 6). The encapsulation efficiency depends on a number of factors, such as the feed flow rate, air inlet/outlet temperature, feed temperature, and

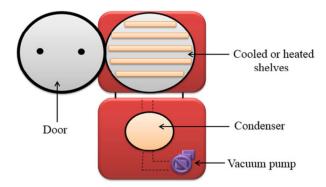


Figure 7. Schematic diagram of a freeze dryer (adapted from Bakry et al. 2016).

wall materials (Bakry et al. 2016). The working principles of spray drying are as follows: first, mixtures are fed through pipes and atomized by a nozzle. Then, water is removed from the solution using hot air, and dried powder is obtained at the bottom of the dryer (Bakry et al. 2016). The advantages of spray drying include good reconstitutional characteristics, low water activity, and suitability for transport and storage. However, scarcity of good wall materials, as well as agglomeration properties of the microcapsule powder, are the limitations of spray drying during the encapsulation process. Carotenoid stability in foods such as carrot, sweet potato, tomato, and melon using different wall materials has been examined during spray drying (Kha, Nguyen, and Roach 2010).

Freeze drying technology

Freeze drying is also called lyophilization, and the process is shown in Figure 7. Sublimation is the main principle of the freeze-drying process. During sublimation, water is directly converted to vapor without passing through the liquid state in vacuum (Bakry et al. 2016). Freeze drying has already been successfully used for encapsulation to maintain nutritional factors and facilitate drying. Velasco, Dobarganes, and Márquez-Ruiz (2003) revealed that encapsulated freeze-dried samples were more resistant to oxidation and protected from heat-sensitive core materials. However, long processing times, high energy, and high production cost are the main drawbacks of freeze drying (Bakry et al. 2016).

Effects of encapsulation agents applied for different carotenoids

Impact of various encapsulating agents on different carotenoids through spray and freeze drying are shown in Tables 1-3.

Encapsulation of carotenoids using maltodextrins and polysaccharides

Table 1 shows the encapsulation of carotenoids using maltodrstring and polysaccharides. Kha, Nguyen, and Roach (2010) and Angkananon and Anantawa (2015) observed that lower concentration of maltrodextrin (10%) retained higher

Table 1. Encapsulation of carotenoids using maltodextrins and others polysaccharides.

Sources of carotenoids	Drying conditions	Carrier agents	Compounds	References
Gac fruit (Momordica cochinchinensis)	Inlet temperature: 120 °C, 140 °C, 160 °C, 180 °C, 200 °C Outlet temperature: 83 °C, 94 °C, 103 °C, 112 °C, 125 °C Air flow rate: 56 ± 2 m³/h Compressor air pressure: 0.06 MPa gauge Feed rate was constant:	12 DE maltodextrin (10%, 20%, and 30% w/v)	Total carotenoid content	Kha, Nguyen, and Roach (2010)
Gac fruit (<i>Momordica</i> cochinchinensis Spreng)	12–14 mL/min Inlet temperature: 120 °C, 150 °C, 170 °C Outlet temperature: 66 °C, 74 °C, 88 °C	Maltodextrin (10%, 20%, and 30% w/v)	eta-carotene and lycopene	Angkananon and Anantawa (2015)
	100% aspirator, 30–40% pump and 30–40 Q-flow			
Pequi (<i>Caryocar</i> brasiliense Camb.)	Inlet temperature: 140 to 200 °C Outlet temperature: 99 to 140 °C Air flow rate: 0.6 m³/h	10 DE maltodextrin (15%, 18%, 22.5%, 27%, and 30% w/v))	Total carotenoids	Santana et al. (2016)
Pink guava (<i>Psidium guajava</i>)	Feed flow rate: 0.2 kg/h Inlet temperature: $150 ^{\circ}\text{C}$, $160 ^{\circ}\text{C}$, $170 ^{\circ}\text{C}$ Outlet temperature: $90 \pm 2 ^{\circ}\text{C}$ Air flow rate: $47 \pm 2 ^{\text{m}3}\text{/h}$ Feed flow rate: $350 \text{ to } 500 \text{mL/h}$ Pressure: $2.1 \pm 1 ^{\text{bar}}$	10 DE maltodextrin (10% and 20% w/v))	Lycopene	Shishir et al. (2016)
Sweet potatoes (Ipomoea batatas)	Inlet temperature: 190 °C Outlet temperature: 100 °C Feed temperature: 60 °C	11 DE maltodextrin (10 g/ 100 g of puree)	β -carotene and all <i>trans</i> forms and <i>cis</i> forms of β -carotene	Grabowski, Truong, and Daubert (2008)
Carrot (Daucus carota L.)	Inlet temperature: 200 ± 5 °C Outlet temperature: 100 ± 5 °C	4, 15, 25, and 36.5 DE maltodextrin	β -carotene and α -carotene	Wagner and Warthesen (1995)
Watermelon (Citrullus lanatus)	•	Maltodextrin (3 and 5% w/v)	eta-carotene and Lycopene	Quek, Chok, and Swedlund (2007)
Dietzia natronolimnaea HS-1	Inlet temperature: 170±2°C Outlet temperature: 90±2°C Air pressure: 0.5 MPa Feed flow rate: 300 mL/min	10% (w/v) soluble soybean polysaccharide suspension in distilled water at 0.25, 0.50, 0.75, and 1.00 ratios.	Canthaxanthin	Hojjati et al. (2011)
Trans- eta -carotene	Freeze drying	6 DE starch, 12 DE starch and native starch	eta-carotene	Spada et al. (2012)
Pequi (<i>Caryocar</i> brasiliense Camb.)	Inlet temperature: 140 to 200 °C Outlet temperature: 82 to 115 °C Air flow rate: 0.6 m³/h Feed flow rate: 0.2 kg/h	Modified starch (15%, 18%, 22.5%, 27%, and 30% w/v)	Total carotenoids	Santana et al. (2014)
Black pepper (Piper nigrum)	Inlet temperature: 178°C Outlet temperature: 110°C Feed flow rate: 300 mL/min	40 g gum Arabic and commercial modified starch	Oleoresin	Shaikh, Bhosale, and Singhal (2006)
Trans-β-carotene Tomato (<i>Lycopersicon</i> <i>esculentum</i> Mill.)	Freeze drying Freeze drying	Almond gum and gum Arabic 1:1 and 1:4 (w/w) of lycopene and β cyclodextrin	eta-carotene Lycopene	Mahfoudhi and Hamdi (2015) Nunes and Mercadante (2007)

amount of total carotenoid content in gac fruit powder than those of higher concentration of maltrodextrin (30%). Pequi was encapsulated with maltodextrin (15% to 30%) by Santana et al. (2016), who reported that a maltodextrin concentration of 18% retained the maximum amount of total carotenoids during spray drying. The results showed that higher concentrations of maltodextrin hindered the formation of emulsion, possibly reducing the protective effect of carotenoids. Shishir et al. (2016) prepared guava powder using 10% and 20% maltodextrin and found that the lycopene content increased with increasing maltodextrin concentrations. Grabowski, Truong, and Daubert (2008) produced flour from yellow-fleshed sweet potatoes by using maltodextrin and spray drying. They revealed that β -carotene contents of maltodextrin-treated powder and untreated

powder were significantly different, and that isomerization and loss of β -carotene were also higher in the maltodextrintreated powder than in the control. Wagner and Warthesen (1995) also used 4, 15, 25, and 36.5 DE maltodextrin to produce spray-dried carrot powder. They concluded that 36.5 DE maltodextrin showed maximum retention of α -carotene and β -carotene, and could, thus, possible provide best protection from oxidation. Carrot juice prepared with maltodextrin had a 70–220 times higher shelf-life than carrot juice produced without maltodextrin (Wagner and Warthesen 1995). The authors hypothesized that the carrier agents might prevent oxidation. Quek, Chok, and Swedlund (2007) also found maltodextrin treated water melon powder had more lycopene and β -carotene contents than raw watermelon juice. Hojjati et al. (2011) revealed that

Table 2. Encapsulation of carotenoids using proteins.

Sources of carotenoids	Drying conditions	Carrier agents	Compounds	References
Rosa Mosqueta (Rosa rubiginosa)	For starch Inlet temperatures: 150 ± 5 °C Outlet temperature: 70 ± 5 °C Atomization pressure: 3 kg/cm² For gelatin Inlet temperature: 100 ± 5 °C Outlet temperature: 65 ± 5 °C Atomization pressure: 5 kg/cm²	gelatin and starch	<i>Trans-β-</i> carotene <i>Trans-</i> lycopene <i>Trans-</i> rubixanthin	Robert et al. (2003)
Standard eta -carotene	Inlet temperature: 160 Outlet temperature: 85 °C	soy protein isolate and OSA-modified starch	eta-carotene	Deng et al. (2014)
Phaffia rhodozyma	Freeze drying	soy protein	carotenoid	Nogueira, Prestes, and de Medeiros Burkert (2017)
Paprika (Capsicum annuum)	Inlet temperature: 160 ± 5 °C, 180 ± 5 °C, 200 ± 5 °C Outlet temperature: 110 ± 5 °C	soy protein isolate and gum arabic	Yellow carotenoid Red carotenoid	Rascón et al. (2011)
Lutein	-	whey protein	Lutein	Zhao, Shen, and Guo (2018)

oxidation of canthaxanthin was lower in the microcapsules than that in the non encapsulated control. Trans- β -carotene was prepared with native starch, 6 DE starch, and 12 DE starch by freeze drying (Spada et al. 2012). The results showed that hydrolyzed starch could retain β -carotene better than native starch, due to variation in sizes of particles. Spada et al. (2012) also mentioned that 12 DE starch could retain more β -carotene, as compared to 6 DE starch, as saccharides with long chains are more permeable to oxygen. Microencapsulation of canthaxanthin produced by the bacterium Dietzia natronolimnaea HS-1 using different concentrations of soluble soybean polysaccharides by spray drying (Hojjati et al. 2011) revealed that the degradation of canthaxanthin in the nonencapsulated samples was faster than that in the microencapsulated canthaxanthin samples. Another study performed by Santana et al. (2014) demonstrated that pequi pulp prepared with a modified starch concentration of 22.5% had higher total carotenoids than that prepared with a modified starch concentration of 27% and 30%. Santana et al. (2014) revealed that high concentration of modified starch results in increased porosity, which might influence the oxidative stability of carotenoids. Black pepper oleoresin was microencapsulated using gum Arabic and modified starch by spray drying (Shaikh, Bhosale, and Singhal 2006). According to Shaikh, Bhosale, and Singhal (2006), gum Arabic was more capable of protecting oleoresin than modified starch. Gum Arabic could restrain cracking of the matrix due to good film-forming capability and plasticity (Shaikh, Bhosale, and Singhal 2006). Another study from Mahfoudhi and Hamdi (2015) evaluated that encapsulation with almond gum showed better protection of β -carotene against oxidation than encapsulation with gum Arabic. Therefore, results from many studies summarized that carrier agents are capable of preventing oxidation of carotenoids from oxygen, light, and temperature. However, as every encapsulation material has different characteristics, selecting a suitable material is an essential step for encapsulation of carotenoids.

Encapsulations of carotenoids using protein

Encapsulations of carotenoids using protein are shown in Table 2. High content and lower degradation rate of carotenoids were observed on encapsulation with gelatin, rather than starch because of protective power of gelatin oxidative damage (Robert et Microencapsulation of β -carotene by soy protein isolate could improve the storage stability of β -carotene as compared to the Microencapsulation of β -carotene by modified starch (Deng et al. 2014). Similar results were also observed by Nogueira, Prestes, and de Medeiros Burkert (2017) who mentioned that soy protein might have ability to increase the stability of carotenoids. Rascón et al. (2011) revealed that carotenoid retention was higher in the microcapsules prepared with soya protein than microcapsules prepared with gum Arabic and they also mentioned that the yellow fraction was more stable than the red fraction due to differences in their chemical structures. Zhao, Shen, and Guo (2018) showed whey protein could protect lutein content from oxidation during storage.

Encapsulation of carotenoids using mixtures of various encapsulation agents

Table 3 shows the encapsulation of carotenoids using mixtures of maltodextrin and protein. Different ratios (1:9 to 3:7) of gelatin to sucrose were used to prepare lycopene microcapsules from tomato paste during spray drying. The results showed that a gelatin to sucrose ratio of 3:7 was good for encapsulation, based on the encapsulation yield and encapsulation efficiency (Shu et al. 2006). These researchers also showed that the microencapsulated samples showed higher stability during storage, as compared with the non-microencapsulated control because of oxidative stability. Ranveer et al. (2015) showed that 90% lycopene from tomato waste was retained in the microencapsulated samples using a gelatin to sucrose ratio of 3:7, whereas non encapsulated samples retained less than 5% lycopene during storage. Encapsulation of lycopene with gum Arabic and sucrose showed that gum Arabic treated powder had good encapsulation efficiency during spray drying (Nunes and Mercadante 2007). However, lycopene and β -cyclodextrin (1:4) mixture was more suitable for encapsulation, as compared to lycopene and β -cyclodextrin mixture (1:1), due to complex formation during freeze drying (Nunes and

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Table 3. Encapsulation of carotenoids using mixture of maltodextrins and proteins.

Sources of carotenoids	Drying conditions	Carrier agents	Compounds	References
Tomato paste (<i>Lycopersicon</i> esculentum Mill.)	Inlet temperature: 170–210 °C Outlet temperature: 35–65 °C Air flow rate: 2 m/s Feed flow rate: 100 mL/h	Sucrose and gelatin (1:9, 2:8, 3:7, 4:6, 5:5 w/v)	Lycopene	Shu et al. (2006)
Tomato waste (<i>Lycopersicon</i> esculentum Mill.)	Inlet temperature: 160 °C, 170 °C, 180 °C, Outlet temperature: 35–65 °C Air flow rate: 2 m/s	Sucrose and gelatin (6:4, 7:3, and 8:2 w/v)	Lycopene	Ranveer et al. (2015)
Tomato (Lycopersicon esculentum Mill.)	Feed flow rate: 2 mL/min Inlet temperature: 170 ± 2 °C Outlet temperature: 113 ± 2 °C Air flow rate: 30 mL/min	Gum arabic and sucrose (8:2)	Lycopene	Nunes and Mercadante (2007)
Tomato (Lycopersicon esculentum Mill.)	Air pressure: 5 kgf/cm ² Freeze drying	1:1 and 1:4 (w/w) of lycopene and β cyclodextrin	Lycopene	Nunes and Mercadante (2007)
Carrot pulp waste (Daucus carota L.)	Inlet temperature: 135 °C–145 °C Outlet	35 g sucrose and 25 g gelatin	All $trans$ forms and cis forms of lutein, β -carotene, and α -carotene	Chen and Tang (1998)
Pink-grape fruit (Citrus paradise)	temperature: 90–100°C Freeze drying	Alginate, sugars and galactomannans	Lycopene	Aguirre Calvo, Busch, and Santagapita (2016)
Annatto	Spray drying	Gum Arabic, Maltodextrin and Tween 80	Bixin	Barbosa, Borsarelli, and Mercadante (2005); De Marcoa et al. (2013)
Annatto	Spray drying	Gum Arabic, Maltodextrin and Tween 80	Bixin	Barbosa, Borsarelli, and Mercadante (2005); De Marcoa et al. (2013)
Paprika (<i>Capsicum annuum</i>)	Inlet temperature: 170±5°C Outlet temperature: 95±5°C Atomization pressure: 4.5 bar	Blend of 17% whey protein concentrate, 17% mesquite gum, and 66% (w/w) maltodextrin, or a blend of 66% whey protein concentrate, 17% mesquite gum, and 17% maltodextrin (w/w) with a wall to core material ratio of 2:1 and 4:1, respectively.	Oleoresin	Perez-Alonso et al. (2008)
Red chilies (Capsicum annuum)	Inlet temperature: 170 ± 5 °C Outlet temperature: 80 ± 5 °C Air pressure: 2.8 bar Feed flow rate: 20 mL/min	Gellan gum, 10 DE maltodextrin, mesquite gum	Carotenoid	Rodriguez-Huezo et al. (2004)
Chili pepper (Capsicum annuum)	Inlet temperature: 160 ± 2 °C Outlet temperature: 70 ± 2 °C Air pressure: 0.4 kg/cm ² Feed flow rate: 13.3 mL/min	Gum arabic and maltodextrin	Carotenoids	Guadarrama-Lezama et al. (2012)
Cumin	Inlet temperature: 160 ± 2 °C Out temperature: 120 ± 5 °C Flow rate: 300 g/h.	Gum arabic, maltodextrin, and modified starch	oleoresin	Kanakdande, Bhosale, and Singhal (2007)
Dunaliella salina	Inlet temperature: 200 °C, 265 °C Outlet temperature: 100 °C, 120 °C Air pressure: 0.4 kg/cm ²	12 DE maltodextrin and gum arabic at a ratio of 3.5:1	eta-carotene	Leach, Oliveira, and Morais (1998)
Brown seaweed (Phaeophyceae)	Feed flow rate: 13.3 mL/min Freeze drying at -45° C under high (0.04 mbar)	maltodextrin (70.02 g) and Tween 80 (1.07 g)	Fucoxanthin	Indrawati et al. (2015)
Lutein crystals	vacuum conditions. Inlet air temperature, 185 ± 1 °C; Outlet air	Ratio of maltodextrin-sucrose (3:0, 3:1 and 3:3)	Lutein	Kuang et al. (2015)
Gac fruit (Momordica cochinchinensis)	temperature, 85 ± 1 °C Inlet temperature: 154 °C Outlet temperature: 80 °C Feed flow rate: 970 mL/h, Air flow speed: 4.3 m/s	Whey protein concentrate and gum arabic (7:3 g/g)	eta-carotene and lycopene	Kha et al. (2015)
Neurospora	Pressure: 2 bar Inlet temperature: 170 °C, 180 °C Outlet temperature: 60 °C, 70 °C Feed flow rate: 8 mL/min	Different concentrations (20%, 30%, and 40% w/w) of sodium caseinate, soy protein isolate, and whey protein isolate	Total carotene	Pahlevi, Estiasih, and Saparianti (2008)

Table 3. Continued.

Table of Continued				
Sources of carotenoids	Drying conditions	Carrier agents	Compounds	References
Gac fruit (Momordica cochinchinensis Spreng)	-	Ratio of maltodextrin-gelatin (10%, 20%, 30%, 40%, and 50% w/v)	Total carotenoid content	Lam Dien, Minh, and Anh Dao (2013)
Neurospora intermedia N-1	Inlet temperature: 160°C Outlet temperature: 70°C Air pressure: 1 bar Feed flow rate: 8 mL/min	13–17 DE maltodextrin and gelatin at a ratio of 4:1	Carotenoids	Gusdinar et al. (2011)

Mercadante 2007). Carotenoid powder from carrot pulp waste was processed with sucrose and gelatin by spray drying (Chen and Tang 1998). The study reported that the degradation of all-trans-lutein was lower than those of α -carotene and β -carotene, due to the formation of luteingelatin complexes during spray drying. Lycopene was encapsulated with alginate along with sugars and galactomannans from pink-grape fruit by freeze drying (Aguirre Calvo, Busch, and Santagapita 2016). Aguirre Calvo, Busch, and Santagapita (2016) showed that among different encapsulating agents, alginate with trehalose and vinal gum could preserve more lycopene content due to minimized isomerization and structural changes. Bixin was encapsulated using gum Arabic and maltodextrin with sucrose and Tween 80 from annatto seeds by spray drying (Barbosa, Borsarelli, and Mercadante 2005; De Marcoa et al. 2013). The authors observed that bixin encapsulated with gum Arabic, rather than maltodextrin, provided better protection against oxidation and photochemical degradation. Red chili oleoresin was microencapsulated with a blend of 17% whey protein concentrate, 17% mesquite gum, and 66% (w/w) maltodextrin, or a blend of 66% whey protein concentrate, 17% mesquite gum, and 17% maltodextrin (w/w) with a wall to core material ratio of 2:1 and 4:1, respectively (Perez-Alonso et al. 2008). The results from this study showed that the higher wall-to-core ratio (4:1) provided maximum protection against oxidation. Rodriguez-Huezo et al. (2004) observed that a higher wall-to-core material ratio could help in retaining higher amounts of carotenoids in red chili. Guadarrama-Lezamaetet al. (2012) microencapsulated carotenoids from non-aqueous extracts of chili pepper by using three different oils (corn, sunflower, and safflower), as well as gum Arabic and maltodextrin in a ratio of 4:1 (w/w), as wall materials. They found that carotenoid degradation was lower in the microencapsulated samples than in the non microencapsulated samples because microencapsulation protects against both oxidation and degradation (Guadarrama-Lezamaetet al., 2012). Cumin oleoresin microencapsulation was performed using a combination of gum Arabic, maltodextrin, and modified starch (Kanakdande, Bhosale, and Singhal 2007). The results showed that gum Arabic blended with maltodextrin and modified starch at a ratio of 4/6, 1/6, and 1/6 could better prevent oxidation of oleoresin, as compared to other encapsulating agents. Encapsulated powders of Dunaliella salina were prepared using maltodextrin and gum Arabic by spray drying. The β -carotene in powders treated with maltodextrin and gum Arabic was more stable, as compared to the control. The storage stability of the encapsulated powders also increased significantly (Leach, Oliveira, and Morais 1998). The carrier agents could possibly retard the

oxygen diffusion, thus contributing to the stabilization of β -carotene in encapsulated powders. The encapsulated pigment prepared from brown seaweed (Sargassum spp.) using freeze drying with maltodextrin and Tween-80 as encapsulating agents showed that carotenoids from the brown seaweed could be extracted using encapsulating agents (Indrawati et al. 2015) and that carrier agents could act as barriers of auto-oxidation. Lutein crystal was microcapsulated with maltodextrins and sucrose by spray drying (Kuang et al. 2015), showed oxidation resistance due to the carrier agents. Kha et al. (2015) also found whey protein and gum Arabic could be retained more β -carotene due to protective effect of carotenoid from oxidation during spray drying. Pahlevi, Estiasih, and Saparianti (2008) extracted carotene from Neurospora using different concentrations (20%, 30%, and 40% w/w) of sodium caseinate, soy protein isolate, and whey protein isolate through spray drying. The results showed that encapsulation with 30% sodium caseinate resulted in maximum total carotenoid content. Pahlevi, Estiasih, and Saparianti (2008) demonstrated that sodium caseinate could form a double layer, thus resulting in better resistance to oxidation, as compared to the protein isolate. Lam Dien, Minh, and Anh Dao (2013) showed that carotene loss in gac fruit could be prevented using maltodextrin and gelatin. Neurospora intermedia N-1 was used to extract carotenoids with gelatin-maltodextrins using spray drying (Gusdinar et al. 2011). The results showed that the encapsulated powders were more stable than the non-encapsulated powder.

Factors affecting stability of encapsulated carotenoids

Various conditions, such as relative humidity (RH), temperature, light, and heat play significant roles in retention of carotenoids during storage. Mahfoudhi and Hamdi (2015) reported that lower RH (10%) during storage showed lower degradation rate of encapsulated trans β -carotene with gum Arabic and almond gum, as compared to higher RH (45 and 80%). Similar trends were shown by Sutter, Buera, and Elizalde (2007), who encapsulated trans β -carotene using mannitol by freeze drying and Deng et al. (2014) encapsulated β -carotene using soy protein isolate and octenylsuccinic anhydride-modified starch by spray drying. Most studies reported that initially, the content of encapsulated carotenoids decreased very fast, followed by slower decrease at lower RH (up to 75%) during storage. However, Sutter, Buera, and Elizalde (2007) showed that encapsulated β -carotene content sharply reduced in the first stage, then decreased constantly, and finally showed a sudden decrease. Different RH values showed different retention values of β -carotene due to oxidative stability. However, storage at

higher RH (75% or above) revealed greater reduction in β -carotene content, possibly related to structure collapse. Collapse of structure is related to oxygen diffusion from surface to matrix, and thus to the decrease in the retention of β -carotene. Particle size and surface carotene could influence the retention of β -carotene (Sutter, Buera, and Elizalde 2007). Kha et al. (2015) encapsulated gac oil powder with whey protein concentrate and gum Arabic. Their results revealed that encapsulated powder of β -carotene and lycopene should not be kept at higher equilibrium relative humidity (75%), as the higher moisture content results in more chemical, biological, and microbial degradation during the storage period. Moreover, Desobry, Netto, and Labuza (1999) did not find any significant differences between 11% and 33% RH for β-carotene encapsulated with two maltodextrins, 15 DE and 4 DE. Similar results were shown by Desobry, Netto, and Labuza (1997) for pure β -carotene using maltodextrin DE 25 by spray and freeze drying. However, Qv, Zeng, and Jiang (2011) demonstrated that lower relative humidity (33%) showed higher retention (90.16%) of lutein microcapsule with gelatin and gum Arabic, whereas 68.18% and 30.15% retention was observed for lutein at higher relative humidity (80%) and non-encapsulated lutein, respectively.

Conditions of higher temperature and light exposure during storage were more destructive than lower temperature and dark conditions for encapsulated all trans β -carotene, all trans α-carotene, and all trans-lutein of carotenoid powders from carrot pulp using sucrose and gelatin though spray drying, due to increased occurrence of isomerization (Chen and Tang 1998). The results also showed that all trans β -carotene was more susceptible to degradation than all trans α -carotene and all trans-lutein during various storage conditions. Similar phenomena were observed by Chiu et al. (2007) for the encapsulation of cis-trans-and total lycopene from tomato pulp waste using gelatin and polyglutamic acid by freeze drying. However, light did not accelerate the degradation rates of encapsulated β - carotene and α-carotene using various carrier agents from carrot (Wagner and Warthesen 1995). However, light and higher temperature also reduced the retention of lutein in microencapsulated with gelatin and gum Arabic due to loss of glass state, as well as increase in the molecular chain (Qv, Zeng, and Jiang 2011). Rascón et al. (2011) observed increase in carotenoids with increasing inlet air temperature in encapsulated using gum Arabic and soy protein isolate from paprika oleoresin, due to higher yield and retention of volatile compounds. Encapsulated bixin using gum Arabic or maltodextrin was more stable than non-encapsulated bixin, and also showed greater stability in dark conditions than in light condition throughout storage (Barbosa, Borsarelli, and Mercadante 2005). The authors reported protection against photodegradation, as well as occurrence of isomers, under light conditions, thus influencing the retention of bixin. Encapsulated curcumin with maltodextrin, modified starch, and gum Arabic showed higher retention, followed by encapsulation with gum Arabic and combination of maltodextrin and modified starch for spray drying during storage under light (Cano-Higuita, Malacrida, and Telis 2015). Combination of maltodextrin,

modified starch, and gum Arabic could prevent curcumin loss due to oxidation. However, using freeze drying, encapsulated curcumin from turmeric with gum Arabic retained higher levels of curcumin, as compared to curcumin encapsulated with ternary mixture (maltodextrin, modified starch, and gum Arabic) and binary mixture (maltodextrin and starch) during storage under light (Cano-Higuita, Malacrida, and Telis 2015). Encapsulated canthaxanthin showed greater stability in dark conditions than exposed to light (Hojjati et al. 2011). Similar behavior was found by Ranveer et al. (2015), who also reported that encapsulation of lycopene with sucrose and gelatin in refrigerated temperature and absence of light showed higher retention of lycopene than that at room temperature and in the presence of light. Therefore, lower storage temperature, relative humidity below 75%, and dark conditions would be the ideal conditions for maximum retention of carotenoids during storage.

Relationship between coating materials and microstructure on encapsulated carotenoids

Retention of carotenoids is influenced by the microstructure of the encapsulating material. Morphological structures of microcapsules are also affected by different wall materials. Microstructure of cumin oleoresin microencapsulated with gum Arabic was smooth and irregular, as well as shrinkage of the particle and cavity form, which could result in more protection of cumin than microencapsulation with maltodextrin and modified starch (Kanakdande, Bhosale, and Singhal 2007) (Figure 8). Similar structure was also observed for bixin encapsulated with gum Arabic and sucrose, while that of bixin encapsulated with maltodextrin and sucrose or maltodextrin and Tween was different (Barbosa, Borsarelli, and Mercadante (2005) (Figure 9). Microencapsulation with gum Arabic, maltodextrin, and modified starch showed higher retention of cumin oleoresin due to more uniform and less cracked structure, as compared to the microencapsulation with maltodextrin, modified starch, and gum Arabic (Kanakdande, Bhosale, and Singhal 2007) (Figure 8). Microencapsulated lycopene with gelatin and sucrose showed a bee-hive like structure, whereas non-encapsulated lycopene showed saw dust like structure. Bee -hive resembling structure might be related to the evaporation rate of water from core of microencapsulation that could influence the retention of lycopene during storage (Figure 10). The aforementioned discussion indicates that the carotenoids content depends on microstructure, as well as carrier agents.

Effects of glass transition temperature (T_a) on encapsulated carotenoids

Usually structure collapse, shrinkage, and caking occur above the glass transition temperature (Tg) (Coronel-Aguilera and Martin-Gonzalez 2015). Tg also is related to oxygen transfer (Desobry, Netto, and Labuza 1999). Some studies found higher β -carotene losses in the glassy state (below T_g) (Prado, Buera, and Elizalde 2006). Encapsulated of β -carotene with maltodextrin showed lower rate of β -carotene loss than that encapsulated with a mixture of maltodextrin and gum Arabic

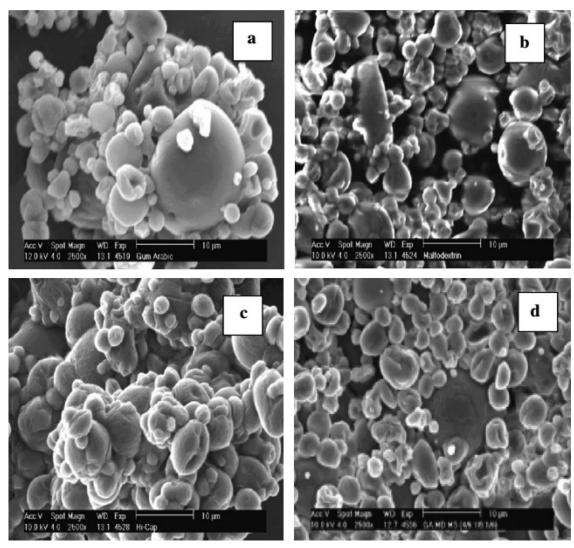


Figure 8. Microcapsules prepared from gum arabic (a), maltodextrin (b), modified starch (c), d) gum arabic/maltodextrin/modified starch(4/6:1/6:1/6) (adapted from Kanakdande, Bhosale, and Singhal 2007).

and with a mixture of maltodextrin and gelatin, due to higher glassy state (Ramoneda et al. 2011). These studies also revealed that the maximum β -carotene degradation was observed when the T_g value was lower than the storage temperature. However, Desobry, Netto, and Labuza (1999) did not observe these phenomena on encapsulation of trans β -carotene with glucose, galactose, and lactose, along with two maltodextrins: 15 DE and 4 DE. Their results showed the glassy state of encapsulated trans β -carotene on storage at a temperature below T_g , but it was not correlated with β -carotene retention. Therefore, the relation between glass transition temperature and encapsulated carotenoids remains unclear.

Degradation kinetics for encapsulated carotenoids

Modeling is used as powerful tool to predict the optimum storage conditions for encapsulated carotenoids. Most of the encapsulated carotenoids models were described by firstorder reaction, but some studies also dealt with zero-order reactions throughout the storage period. Tables 4 and 5 show the modeling of encapsulated carotenoids using spray and freeze drying, respectively, during storage. Degradation

kinetics, such as degradation reaction rate, reaction order, rate constant, half-life, and activation energy are crucial parameters to know the storage conditions for shelf life of encapsulated carotenoids. In this section, we elaborate the degradation kinetics for encapsulated carotenoids using two ways: spray drying and freeze drying.

Modeling during spray drying

Most of authors used the Arrhenius model, but other models such as the Weibull model, Kohlrausch-Williams-Watts model, and Regression model were also used by few authors. Reaction rate constant, half-life, and activation energy depend on the sources of carotenoids, carrier agents, storage temperature, and storage conditions (Table 4). Higher degradation rate and lower half-life were found with increasing storage temperature for all encapsulated carotenoids. Encapsulated lycopene showed a higher degradation rate than encapsulated β -carotene (Kha et al. 2015). These authors also reported that encapsulated carotenoids with gelatin showed higher activation energies, as compared with those encapsulated with starch. Degradation rate and

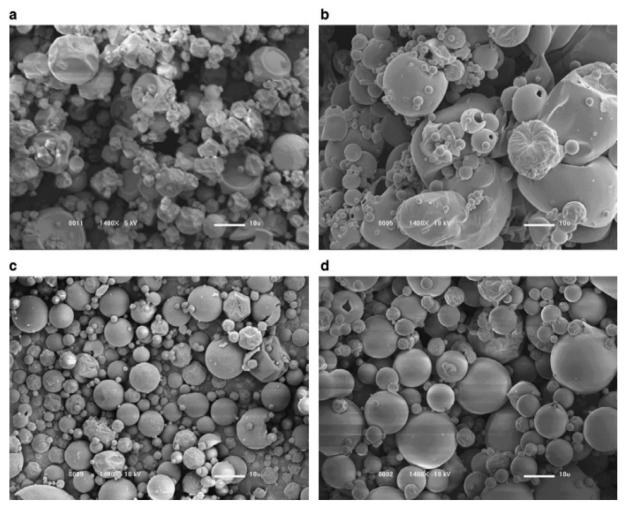


Figure 9. SEM micrographs of spray-dried microencapsulated bixin with (a) GA/sucrose (95:5), (b) MD 20 DE/sucrose (80:20), (c) 100% MD 20 DE (d) MD 20 DE/Tween 80 (99.8:0.2). The magnification of all micrographs was 1400 (adapted from Barbosa, Borsarelli, and Mercadante 2005).

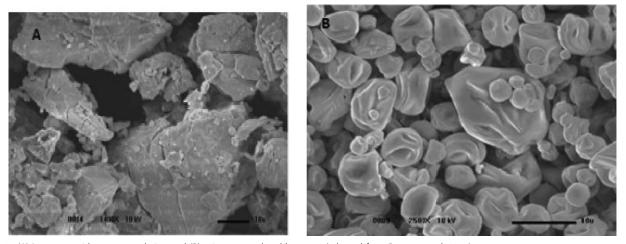


Figure 10. (A) Lycopene without encapsulation and (B) microencapsulated lycopene (adapted from Ranveer et al. 2015).

activation energy might be related to the various complex structures and reactivities of carotenoids connecting with the matrix of encapsulating materials during storage. Carotenoids and surrounding matrix interactions could also influence the degradation rate and activation energy (Kha et al. 2015). Most of the encapsulated carotenoid models were described by first-order reactions, but some studies also dealt with other reaction models throughout the storage

period. Non-encapsulated bixin showed a single first-order decay, whereas encapsulated bixin showed two sequential first-order decays under dark condition because more oxidative and photochemical degradation occurred in the non-encapsulated sample (Barbosa, Borsarelli, and Mercadante 2005). However, Kuang et al. (2015) found that the Kohlrausch–Williams–Watts model was a good fit for encapsulated lutein. Thus, various models might be used to

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References	Robert et al. (2003)	Wagner and Warthesen (1995)	(continued)
Kinetic parameters	For Starch trans- β -Carotene $K_{25^{\circ}C} = 6.7 \times 10^{-3} \pm 5 \times 10^{-4} (h^{-1})$ $K_{40^{\circ}C} = 2.5 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{40^{\circ}C} = 2.5 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 5.1 \times 10^{-2} \pm 5 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 5.1 \times 10^{-2} \pm 5 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 5.2 \times 10^{-2} \pm 8 \times 10^{-4} (h^{-1})$ $K_{56^{\circ}C} = 2.5 \times 10^{-2} \pm 8 \times 10^{-4} (h^{-1})$ $K_{56^{\circ}C} = 4.0 \times 10^{-2} \pm 6 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 4.0 \times 10^{-2} \pm 6 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 4.0 \times 10^{-2} \pm 4 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 8.0 \times 10^{-2} \pm 4 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 6.4 \times 10^{-2} \pm 1 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 6.4 \times 10^{-2} \pm 1 \times 10^{-3} (h^{-1})$ $K_{40^{\circ}C} = 2.9 \times 10^{-3} \pm 1 \times 10^{-3} (h^{-1})$ $K_{40^{\circ}C} = 9.5 \times 10^{-3} \pm 1 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.7 \times 10^{-2} \pm 4 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.7 \times 10^{-2} \pm 4 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.7 \times 10^{-2} \pm 4 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.7 \times 10^{-2} \pm 1 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.7 \times 10^{-2} \pm 1 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 4.1 \times 10^{-2} \pm 1 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 4.1 \times 10^{-2} \pm 1 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.7 \times 10^{-2} \pm 1 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.7 \times 10^{-2} \pm 1 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-3} \pm 3 \times 10^{-4} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 3 \times 10^{-3} (h^{-1})$ $K_{55^{\circ}C} = 3.2 \times 10^{-2} \pm 11$ $(4ays) Ea = 15.4 \pm 3.5$ $(Kca Vmo V)$	For major carotenes α -Carotenes α -Carotene α -Carotene α -Carotene α -Carotene α -	
Mathematical model	Arhenius model k = Ae - (Ea/RV)T	Arrhenius model $k=K_0e^{-(E_0/R)/T}$	
spray drying. Kinetic order	First-order kinetic model. InC = InCo-k(t)	First-order kinetic model. $t_{1/2}=0.693/k \label{eq:t_1/2}$	
Table 4. Degradation kinetics modeling of encapsulated carotenoids during spray Sources of carotenoids Storage conditions	Starch and gelatin	Dry hydrolyzed starch (4DE,' 15DE, 25DE or 36.5DE)	
netics modeling of enc Storage conditions	Storage at (55, 40, 9 and 25°C)	Storage at (21°C) [
Table 4. Degradation kir Sources of carotenoids	Rosa Mosqueta (Rosa rubiginosa)	Carrot	

Sources of carotenoids	Storage conditions	Carrier agents	Kinetic order	Mathematical model	Kinetic parameters	References
Dunaliella salina	Storage at (room temperature)	12 DE maltodextrin and gum arabic at a ratio of 3.5:1	First-order kinetic model.		15% $K_{150E} = 1.65 \pm 0.219 \times 10^{-2} (day^{-1})$ 20% $K_{150E} = 0.908 \pm 0.153 \times 10^{-2} (day^{-1})$ 25% $K_{150E} = 0.493 \pm 0.129 \times 10^{-2} (day^{-1})$ β -Carotene Inlet temperature for 200° C $K = 0.66 (day^{-1})$	Leach, Oliveira, and Morais (1998)
Gac (Momordica cochinchinensis)	Storage at (-20°C, 10°C and room temperature	whey protein concentrate and gum Arabic	First-order kinetic model. In $C = In CO - kt$ $t_{1/2} = In 2/k$.	Arrhenius model $k = Ae^{-Ea/RT}$	In let temperature for 265° C K = 0.10 (day ⁻¹) β -Carotene K ₁₀₂ -20°C = 0.0002 (day ⁻¹); $t_{1/2}$ = 3466 (days) K _{NON-vacuum} + dark = -20° C = 0.0003 (day ⁻¹); $t_{1/2}$ = 2310 (days)	Kha et al. (2015)
	(25–30°C) for 360 days, at 40°C for 120 days and at 63°C for 28 days.				$k_{\text{vacuum}} + \text{dark}$ at $10^{\circ}\text{C} = 0.0004$ (day $^{-1}$); $t_{1/2} = 1733$ (days) $K_{\text{Non-vacuum}} + \text{dark}$ at $10^{\circ}\text{C} = 0.0009$ (day $^{-1}$); $t_{1/2} = 770$ (days) $K_{\text{vacuum}} + \text{dark}$ at $R = 0.0005$ (day $^{-1}$); $t_{1/2} = 1386$ (days) $K_{\text{Non-vacuum}} + \text{dark}$ at $R = 0.0013$ (day $^{-1}$); $t_{1/2} = 533$ (days) $K_{\text{Non-vacuum}} + \text{light}$ at $R = 0.0009$ (day $^{-1}$); $t_{1/2} = 770$ (days) $K_{\text{Non-vacuum}} + \text{dark}$ at $40^{\circ}\text{C} = 0.0015$ (day $^{-1}$); $t_{1/2} = 182$ (days) $K_{\text{Non-vacuum}} + \text{dark}$ at $40^{\circ}\text{C} = 0.0063$ (day $^{-1}$); $t_{1/2} = 19$ (days) $K_{\text{Non-vacuum}} + \text{dark}$ at $63^{\circ}\text{C} = 0.0063$ (day $^{-1}$); $t_{1/2} = 10$ (days) $K_{\text{Non-vacuum}} + \text{dark}$ at $63^{\circ}\text{C} = 0.0063$ (day $^{-1}$); $t_{1/2} = 10$ (days) $K_{\text{Non-vacuum}} + \text{dark}$ at $63^{\circ}\text{C} = 0.01018$ (day $^{-1}$); $t_{1/2} = 7$ (days)	
					$K_{\text{vacuum}} + \text{dark at } -20^{\circ}\text{C} = 0.0004 \; (\text{day}^{-1}); \; t_{1/2} = 1733 \; (\text{days})$ $K_{\text{Non-vacuum}} + \text{dark } -20^{\circ}\text{C} = 0.0004 \; (\text{day}^{-1}); \; t_{1/2} = 1733 \; (\text{days})$ $K_{\text{Non-vacuum}} + \text{dark at } 10^{\circ}\text{C} = 0.0004 \; (\text{day}^{-1}); \; t_{1/2} = 1733 \; (\text{days})$ $K_{\text{Nacuum}} + \text{dark at } 10^{\circ}\text{C} = 0.0004 \; (\text{day}^{-1}); \; t_{1/2} = 1155 \; (\text{days})$ $K_{\text{Nacuum}} + \text{dark at } \text{RT} = 0.0011 \; (\text{day}^{-1}); \; t_{1/2} = 347 \; (\text{days})$ $K_{\text{Non-vacuum}} + \text{dark at } \text{RT} = 0.0020 \; (\text{day}^{-1}); \; t_{1/2} = 347 \; (\text{days})$ $K_{\text{Non-vacuum}} + \text{light at } \text{RT} = 0.0022 \; (\text{day}^{-1}); \; t_{1/2} = 347 \; (\text{days})$ $K_{\text{Non-vacuum}} + \text{light at } \text{RT} = 0.0022 \; (\text{day}^{-1}); \; t_{1/2} = 347 \; (\text{days})$ $K_{\text{Non-vacuum}} + \text{light at } \text{RT} = 0.0022 \; (\text{day}^{-1}); \; t_{1/2} = 315 \; (\text{days})$ $K_{\text{Non-vacuum}} + \text{dark at } 40^{\circ}\text{C} = 0.0048 \; (\text{day}^{-1}); \; t_{1/2} = 90 \; (\text{days})$ $K_{\text{Nacuum}} + \text{dark at } 40^{\circ}\text{C} = 0.0078 \; (\text{day}^{-1}); \; t_{1/2} = 90 \; (\text{days})$ $K_{\text{Nacuum}} + \text{dark at } 40^{\circ}\text{C} = 0.0078 \; (\text{day}^{-1}); \; t_{1/2} = 90 \; (\text{days})$ $K_{\text{Nacuum}} + \text{dark at } 40^{\circ}\text{C} = 0.0078 \; (\text{day}^{-1}); \; t_{1/2} = 90 \; (\text{days})$	
Black pepper	Storage at 31°C for 6 weeks.	Gum arabic and modified starch	First-order kinetic model. $t_{1/2} = 0.693/k \label{eq:t_1/2}$		Non-actual Hain at 63 C (2017) (1) (2) (2017) (1) (2) (2017) (2) (2) (2) (2) (2) (2) (2) (2) (2) (2	Shaikh, Bhosale, and Singhal (2006)
					f(1/2) gum Anabic = 121.57 (weeks) f(1/2) modified starch = 128.33 (weeks) For total volatiles f(1/2) gum Anabic = 25.76 (weeks) f(1/2) modified starch = 26.34 (weeks) For non-volatiles f(1/2) gum Anabic = 77.86 (weeks)	
Red chilies	Storage at 31°C for 35 days	Storage at 31°C for Gellan gum, 10 DE 35 days maltodextrin, mesquite gum	zero-order degradation reaction $t_{(1/2)}=0.5/\mathrm{K}$		The modified satch are considered from the constraints of the constra	Rodriguez-Huezo et al. (2004)

Table 4. Continued.

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References	Rascón et al. (2011)	Cano-Higuita, Malacrida, and Telis (2015)	Kanakdande, Bhosale, and Singhal (2007)	Kanakdande, Bhosale, and Singhal (2007)
Kinetic parameters	Red fraction oleoresin K, (0.108) gum arabic = 33.09 ± 0.93 ×10 ⁻³ (day ⁻¹) K, (0.318) gum arabic = 55.73 ± 0.63 ×10 ⁻³ (day ⁻¹) K, (0.515) gum arabic = 123.89 ± 1.88 ×10 ⁻³ (day ⁻¹) K, (0.108) spi = 197.95 ± 10.94 ×10 ⁻³ (day ⁻¹) K, (0.318) spi = 201.32 ± 2.88 ×10 ⁻³ (day ⁻¹) K, (0.515) spi = 196.45 ± 6.18 ×10 ⁻³ (day ⁻¹) K, (0.515) spi = 196.45 ± 6.18 ×10 ⁻³ (day ⁻¹) K, (0.515) spi = 106.15 ± 1.94 ×10 ⁻³ (day ⁻¹) K, (0.108) gum arabic = 37.33 ± 1.52 ×10 ⁻³ (day ⁻¹) K, (0.318) gum arabic = 55.41 ± 0.75 ×10 ⁻³ (day ⁻¹) K, (0.318) gum arabic = 130.17 ± 3.98 ×10 ⁻³ (day ⁻¹) K, (0.515) gum arabic = 31.60 ± 3.15 ×10 ⁻³ (day ⁻¹) K, (0.515) gum arabic = 21.02 ×10 ⁻³ (day ⁻¹) K, (0.518) gum arabic = 130.17 ± 3.98 ×10 ⁻³ (day ⁻¹) K, (0.518) gum arabic = 31.60 ± 3.15 ×10 ⁻³ (day ⁻¹) K, (0.518) spi = 209.75 ± 2.25 ×10 ⁻³ (day ⁻¹) K, (0.518) spi = 21.78 1 ± 11.64 ×10 ⁻³ (day ⁻¹) K, (0.518) spi = 21.78 1 ± 11.64 ×10 ⁻³ (day ⁻¹)	.h (25%) and modified starch (33%)	weeks) 1 (weeks) (weeks) 2 (weeks) 2 (weeks) weeks) weeks) weeks) weeks) weeks)	rodextrin (1/3,1/3,1/3) = 27.60 (weeks) codextrin (4/6,1/6,1/6) = 55.88 (weeks) codextrin (1/6,4/6,1/6) = 16.11 (weeks) codextrin (1/6,1/6,4/6) = 19.63 (weeks) codextrin (1/3,1/3,1/3) = 9.88 (weeks) codextrin (4/6,1/6,1/6) = 35.53 (weeks) codextrin (1/6,4/6,1/6) = 9.07 (weeks) codextrin (1/6,4/6,1/6) = 9.07 (weeks) codextrin (1/6,4/6,1/6) = 11.12 (weeks)
Mathematical model		Regression model		
Kinetic order	First-order kinetic model.	pseudo-first order kinetics. Regression model	First-order kinetic model. $t_{1/2}=0.693/k$	First-order kinetic model. $t_{1/2}=0.693/\text{k} \label{eq:t1/2}$
Carrier agents	isolate (SPI)	Storage at 25°C for gum arabic maltodextrin 4 weeks modified starch	Gum arabic; Modified starch; Maltodextrin	Different concentration of gum Arabic; modified starch and maltodextrin
Storage conditions	Storage at 31°C gwith different awfor 35 days	Storage at 25°C for g 4 weeks	Storage at 25°C for 6 6 weeks	Storage at 25°C for I 6 weeks
Sources of carotenoids	Paprika	Turmeric	Cumin	Cumin

Table 4. Continued.

	References		De Marcoa et al. (2013)	Barbosa, Borsarelli, and Mercadante (2005).	Desobry, Netto, and Labuza (1997). Kuang et al. (2015)	Liang et al. (2013).	Desobry, Netto, and Labuza (1999). (continued)
	Kinetic parameters	Total p-cymene $t_{(1/2)gum}$ arabic; modified starch; maltodextrin $(1/3,1/3,1/3) = 22.72$ (weeks) $t_{(1/2)gum}$ arabic; modified starch; maltodextrin $(4/6,1/6,1/6) = 60.78$ (weeks) $t_{(1/2)gum}$ arabic; modified starch; maltodextrin $(1/6,1/6,1/6) = 15.82$ (weeks) $t_{(1/2)gum}$ arabic; modified starch; maltodextrin $(1/6,1/6,4/6) = 27.07$ (weeks) Total volatiles $t_{(1/2)gum}$ arabic; modified starch; maltodextrin $(1/3,1/3,1/3) = 28.87$ (weeks) $t_{(1/2)gum}$ arabic; modified starch; maltodextrin $(4/6,1/6,1/6) = 85.55$ (weeks) $t_{(1/2)gum}$ arabic; modified starch; maltodextrin $(1/6,4/6,1/6) = 34.13$ (weeks) $t_{(1/2)gum}$ arabic; modified starch; maltodextrin $(1/6,4/6,1/6) = 25.01$ (weeks)	$K_{(\text{light})} = 15.7 \times 10^3 \text{ (days}^{-1}) t_{f1/2 \text{ /light}} = 44.15 \text{ (days)}$ Dr $K_{(\text{dark})} = 3.0 \times 10^3 \text{ (days}^{-1}) t_{f1/2 \text{ /light}} = 231.05 \text{ (days)}$	To (95% AG+5% SUC) = 3.3 (h), τ_s (95% AG+5% SUC) = 66 (h) to (95% AG+5% SUC) = 74 (h), τ_0 (95% AG+5% SUC) = 12000 (h) to (95% AD+20% SUC) = 3.5 (h), τ_0 (80% AD+20% SUC) = 3.5 (h), τ_0 (80% AD+20% SUC) = 27 (h), τ_0 (80% AD+20% SUC) = 1.7 (h) τ_0 (80% AD+20% SUC) = 1.2 (h), τ_0 (80% AD+0% SUC) = 1.2 (h), τ_0 (100% AD+0% SUC) = 30 (h) to (100% AD+0% SUC) = 27 (h), τ_0 (100% AD+0% SUC) = 27 (h), τ_0 (100% AD+0% SUC) = 2700 (h)			0SAZ $K_{(75\%)} = 44.06 \pm 0.98$ (10 $^{-7}$ (a9), 0SAZ $n_{(75\%)} = 1.222 \pm 0.003$ 0SAZ $K_{(97\%)} = 21.36 \pm 0.71$ (10 $^{-3}$ (a49), OSAZ $n_{(97\%)} = 0.812 \pm 0.031$ 0SA3 $K_{(17\%)} = 33.2 \pm 0.42$ (10 $^{-3}$ (day), OSA3 $n_{(17\%)} = 1.237 \pm 0.036$ 0SA3 $K_{(35\%)} = 35.4 \pm 0.84$ (10 $^{-3}$ (day), OSA3 $n_{(35\%)} = 1.300 \pm 0.065$ 0SA3 $K_{(57\%)} = 41.60 \pm 0.73$ (10 $^{-3}$ (day), OSA3 $n_{(57\%)} = 1.197 \pm 0.047$ 0SA3 $K_{(97\%)} = 19.94 \pm 0.38$ (10 $^{-3}$ (day), OSA3 $n_{(75\%)} = 1.197 \pm 0.047$ 0SA3 $K_{(97\%)} = 19.94 \pm 0.38$ (10 $^{-3}$ (day), OSA3 $n_{(75\%)} = 1.09 \pm 0.022$ β -Carotene K_{25DE} (t < t,b = 0.095, $E_a = 14.187$ (Kcal/mol), $t_{(1/2)} = 7.1 \pm 1.4$ (weeks) K_{15GL} (t < t,c) = 0.126, $E_a = 11.31$ (Kcal/mol), $t_{(1/2)} = 5.5 \pm 0.8$ (weeks)
Mathematical	model		Arrhenius model		Arrhenius model Kohlrausch-Williams-Watts (KWW) model $\phi_{\rm L}=\exp{(-t/\tau)}^{\beta}$ $\phi_{\rm L}=1-\Delta H_{\rm relax}$	$\Delta_{H\infty} = \exp(-t/\tau)^{\beta}$ $\Delta_{H\infty} = \Delta_{Cp}(Tg - Ta)$ $\Delta_{Cp}(Tg - Ta$	Arrhenius model
	Kinetic order		First-order and secondorder kinetic model. $t_{1/2} = \ln 2/k$	Photodegradation kinetics $[Bix]_l = [Bix]_0 \exp{(-t/\tau_l)}$	First-order and second- order kinetic model.	Time-course degradation model	First-order and second- order kinetic model.
	Carrier agents		Storage at 25°C for Arabic gum and maltodextrin 18 days under DE 10. light and days ondition	Arabic gum, maltodextrin DE 20 and sucrose.	Maltodextrin 25 DE Maltodextrin DE 6.1	Storage at 25°C for Various modified starches thirty days under such as (OSA1), (OSA2) and different (OSA 3) relative humidity	Storage at 25°C for Various concentrations of 17 weeks glucose, galactose and lactose with 15 DE and 4
	Storage conditions		Storage at 25°C for 718 days under light and	5	Storage at 25°C for N seventeen weeks Aging under 5, 10 N and 15°C	Storage at 25°C for \text{thirty days under different relative humidity}	Storage at 25°C for \ 17 weeks
Table 4. Continued.	Sources of carotenoids		Bixin from annatto seed	Bixin from annatto seed	Pure trans eta -carotene Lutein crystals	Pure eta -carotene	Pure trans eta -carotene

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= Degradation rate constants, $t_{1/2}$ = half-life, E_a = Activation energy, ϕ_t = enthalpy relaxation during time, $\Delta_{H\infty}$ = total enthalpy, $\Delta_{H_{caba}}$ = enthalpy relaxation during time, $\Delta_{H\infty}$ = total enthalpy, $\Delta_{H_{caba}}$ = enthalpy relaxation during at the constants, t_s = slow decay components, t_s = delay time, t_s = slow decay components, t_s = delay time, $K\!=\!Degradation$ rate constants, $t_{1/2}\!=\!half\text{-life},$ $E_a\!=\!Activation$ energy, au D =life time under dark condition. determine the shelf life of carotenoids encapsulated using spray drying.

Modeling during freeze drying

Most authors analyzed the stability of encapsulated carotenoids by applying the Arrhenius model during freeze drying. However, Weibull model, Regression model, Higuchi model, Hixson-Crowell cube root law, and Korsmeyer Peppas model were also used to predict the shelf life of carotenoids encapsulated using freeze drying. Kinetics parameters are highly correlated with encapsulating materials, sources of carotenoids, and storage conditions (Table 5). Higher temperatures resulted in a higher degradation rate and higher half-life than lower temperature for all encapsulated carotenoids (Table 5). Tang and Chen (2000; Chen and Tang 1998) encapsulated lutein from carrot using sucrose and gelatin and showed that the degradation rate constant of lutein was lower than those of α -and β -carotene because of the formation of lutein and gelatin complex. Activation energy was related to the amounts of carotenoids and encapsulating materials. First order kinetic reaction for encapsulated carotenoids was described by the most of the authors using the Arrhenius model. However, Weibull model and Regression model were also fitted to measure the kinetic parameters for encapsulated carotenoids. However, Sen Gupta and Ghosh (2015) used Zero order, First order, Higuchi model, Hixson-Crowell cube root law, and Korsmeyer-Peppas model were used for determination of the controlled release kinetics from encapsulated crude palm oil using isabgol fiber. Sen Gupta and Ghosh (2015) also confirmed fitting of five models that followed a non-Fickian diffusion pattern for encapsulated crude palm oil. Moreover, Higuchi model showed the best linearity due to higher R² value. Therefore, different models could be applied to obtain information regarding the degradation of carotenoids encapsulated using freeze drying.

Effects of encapsulated carotenoids on bioavailability

Bioavailability of any bioactive compounds refers to the proportion of a particular nutrient that is digested, absorbed, and metabolized via the normal pathways (Gul et al. 2016). A number of factors are responsible for stimulating or limiting the bioavailability of carotenoids (Ribeiro et al. 2008; Bohn 2008). Carotenoids need to be released mechanically or enzymatically from the food matrix to be bioavailable. Carotenoids have limited water solubility, and they need to be incorporated into lipid droplets. The low bioavailability of carotenoids from natural sources is thought to be either due to their existence as crystals or location within protein complexes that cannot be properly released in the GI tract during digestion (Williams, Boileau, and Erdman 1998). Use of coating material during processing of carotenoids enhances the stability and helps in controlled released of these bioactive compounds in the human body (Gul et al. 2016). A number of studies reported that microencapsulation significantly affects the bioavailability of carotenoids in both



in-vitro and in-vivo studies (Roman, Burri, and Singh 2012; Han et al. 2008; Donhowe and Kong 2014; Aissa et al. 2012). The higher water dispensability of carotenoids results in higher bioavailability (Thurmann et al. Microencapsulation of carotenoids promotes their bioavailability (Soukoulis and Bohn 2015) by a number of ways:

- increasing the stability against isomerization and degradation due to different factors,
- improving solubility resulting in increased bioaccessibility, and
- helping targeted release kinetics.

Effects of encapsulated carotenoids in vitro studies

In vitro intestinal digestion of β -carotene encapsulated by alginate and chitosan was investigated in some studies (Han et al. 2008; Roman, Burri, and Singh 2012), proving that, it is not necessarily correlated with complete transfer of β -carotene into micelle phase during intestinal digestion. The authors found that the total concentration of β -carotene in the micelle cell was negligible. This could be due to inhibition of micelle formation by soluble fiber alginate. These results necessitated further studies of micelle formation to obtain a clear understanding for bioavailability of microencapsulated β -carotene. Encapsulated β -carotene also showed high resistance to gastric pH (Han et al. 2008). This resistance of encapsulated beads during the transit through stomach may be because of the existence of an external layer of chitosan-alginate coacervate. The release behavior of encapsulated β -carotene showed efficient controlled release and maintained maximum release percentage. This may be due to minimal water absorption of the encapsulating polymers, which enhance swelling and result in no hydrophobic interaction between cohesive forces within the polymeric matrix. Microencapsulating agents can protect the micronutrients from enzymatic and acidic environments during the release condition, as well as result in controlled release mechanism of encapsulated micronutrients through gastrointestinal transit (Tiena, Ispas-Szaboa, and Mateescu 2003). Similar results were found in isabgol fiber (Phyllium husk) encapsulated carotenoids from the crude palm oil, showing that fibrous coated carotene regulated effective release (Sen Gupta and Ghosh 2015).

Effects of encapsulated carotenoids in vivo studies

The in vivo studies of gum arabic microencapsulated β -carotene by spray drying and pure β -carotene activity against genotoxicity showed that the microencapsulated β -carotene had higher potential, as compared to pure β -carotene because microencapsulation process induces the bioavailability of carotenoids (Aissa et al. 2012). Thus, the encapsulated β -carotene maintained the anti-oxidative properties. The physicochemical properties and bioavailability of lutein microencapsulation showed that encapsulated lutein showed more bioavailability, compared to the commercial reference sample (Zhang et al. 2015). Matrix of modified food starch was used as wall material for preparing lutein microencapsulated product. The enhanced bioavailability was because the high solubility of wall materials induces the aqueous solubility of lutein. The results under the condition of dissolution test, LM dissolution rate was very high, which may be because bioavailability of LM was not restricted by dissolution behavior. Similar findings reported that encapsulated carotenoids enhance their solubility and release during digestion (Wang and Bohn 2012). Encapsulated carotenoids are more easily delivered into the cellular compartments, resulting in better bioavailability.

Advantages of the encapsulated carotenoids and compared to the non-encapsulated carotenoids in the food system

It is important to determine whether the encapsulated carotenoids are stable or not in the food system. However, there are very few studies of encapsulated carotenoids in the food systems. Synthetic trans β -carotene, encapsulated with almond gum and gum arabic, was used to prepare cake. The results showed that cake made with almond gum had significantly higher a* value than cake made with gum arabic (Mahfoudhi and Hamdi 2015). These results might be due to higher protection of β -carotene on encapsulation with almond, as compared to encapsulation with gum arabic. Another study reported by Kha et al. (2015), who developed yogurt, pasteurized milk, and cake with encapsulated gac oil using whey protein concentrate and gum arabic. The results showed that incorporation with encapsulated gac oil products color was unchanged, as well as β -carotene and lycopene was slightly decreased during storage. The authors reported that auto-oxidation, photo-oxidation, and photoisomerization were responsible for changes in the β -carotene and lycopene through the storage period. Coronel-Aguilera and Martin-Gonzalez (2015) produced β -carotene spray dried powder using maltodextrin and sodium casemate, followed by fluidized bed coater and applied to a yogurt system and also compared with commercial peach yogurt. These studies revealed that the total color value of yogurt made with encapsulated β -carotene was comparable with the standard value and also stable in acidic media for four weeks during storage at 4°C. Food matrix (pudding and yogurt) was manufactured using encapsulated β -carotene with maltodextrin, water-dispersible powder, and chitosanalginate beds (Donhowe et al. 2014). Food matrix significantly affected in terms of release of β -carotene during digestion and incorporation into the micelle phase. Yogurt made with encapsulated β -carotene showed lower release rate of β -carotene and content of β -carotene in the micelle phase than those of pudding made with encapsulated β -carotene. This might be due to the pH of the food matrix and coagulation of the food matrix, as well as protein composition of the food matrix (Donhowe et al. 2014).

Conclusions

In this review, we discussed the encapsulation of carotenoids using various encapsulating agents through spray and freeze

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Sources of carotenoids	Operating conditions	Carrier agents	Kinetic order	Mathematical model	Kinetic parameters	References
Carrot pulp	Storage at (4°C dark, 25°C dark, 45°C dark and 25°C light)	Sucrose and gelatin	First-order kinetic model		Lutein K _{4°C} (dark) = 0.004 (day ⁻¹) K _{5°C} (dark) = 0.004 (day ⁻¹) K _{5°C} (dark) = 0.006 (day ⁻¹) K _{5°C} (light) = 0.013 (day ⁻¹) K _{5°C} (dark) = 0.013 (day ⁻¹) K _{5°C} (dark) = 0.020 (day ⁻¹) K _{5°C} (dark) = 0.032 (day ⁻¹) K _{5°C} (dark) = 0.043 (day ⁻¹) K _{5°C} (dark) = 0.043 (day ⁻¹)	Tang and Chen (2000)
Carrot pulp waste	Storage at (4°C dark, 25°C dark, 45°C dark and 25°C light)	Sucrose and gelatin	First-order kinetic model,		Lutein Lutein $K_{q^{-}c}$ (dark) = 0.005 (day ⁻¹) $K_{25^{-}c}$ (dark) = 0.008 (day ⁻¹) $K_{45^{-}c}$ (dark) = 0.011 (day ⁻¹) $K_{25^{-}c}$ (light) = 0.015 (day ⁻¹) α -Carotene $K_{q^{-}c}$ (dark) = 0.014 (day ⁻¹) $K_{25^{-}c}$ (dark) = 0.026 (day ⁻¹) $K_{25^{-}c}$ (light) = 0.043 (day ⁻¹) $K_{25^{-}c}$ (light) = 0.049(day ⁻¹) $K_{25^{-}c}$ (dark) = 0.018(day ⁻¹) $K_{25^{-}c}$ (dark) = 0.018(day ⁻¹)	Chen and Tang (1998)
:	3		-	-	$K_{45^{\circ}C}$ (dark) = 0.050(day ') $K_{25^{\circ}C}$ (light) = 0.058 (day ⁻¹)	
Sources of carotenoids	Storage conditions	Carrier agents	Kinetic order	Mathematical model	Kinetic parameters	References
Brown seaweed (Phaeophyceae)	Storage at (28, 45 and 65 °C in dark)	Maltodextrin and Tween 80	First-order kinetic model. $InC = InCO - k(t)$	Arrhenius model $k = Ae^{-Ea/R/T}$	Trans-fucoxanthin a* (thermo-labile carotenoids) $K_{38^{\circ}C} = 0.0356 \text{ (day}^{-1})$ $K_{45^{\circ}C} = 0.1454 \text{ (day}^{-1})$ $K_{65^{\circ}C} = 0.6349 \text{ (day}^{-1})$ $t_{1/2} (s_{8^{\circ}C}) = 63 \text{ (days)}$ $t_{1/2} (s_{5^{\circ}C}) = 15 \text{ (days)}$ $t_{1/2} (s_{5^{\circ}C}) = 4 \text{ (days)}$ $E_{1} = 15.73 \text{ (Kcal/mol)}$ $b^* \text{ (pheophytin a and chlorophyll c)}$ $K_{45^{\circ}C} = 0.0659 \text{ (day}^{-1})$ $K_{45^{\circ}C} = 0.059 \text{ (day}^{-1})$ $K_{45^{\circ}C} = 0.3518 \text{ (day}^{-1})$ $K_{45^{\circ}C} = 0.3518 \text{ (day}^{-1})$ $t_{1/2} (s_{8^{\circ}C}) = 88 \text{ (days)}$ $t_{1/2} (s_{8^{\circ}C}) = 16 \text{ (days)}$ $t_{1/2} (s_{8^{\circ}C}) = 3 \text{ (days)}$	Indrawati et al. (2015)
Crude palm oil	Storage at (30 $^{\circ}$ C) for 30 days lsabgol fiber (Psyllium I	s Isabgol fiber (<i>Psyllium husk</i>)	zero order (k_o) , first order (k_t)	Higuchi model (k_H) , Hixson-Crowell cube root law (kHC)	Zeı	Sen Gupta and Ghosh (2015).
						(continued)

Table 5. Continued. Sources of carotenoids	Operating conditions	Carrier agents	Kinetic order	Mathematical model	Kinetic parameters	References
				and Korsmeyer Peppas model (K _{KP})	$k_1 (h^{-1}) = 0.267$ Higuchi $k_H (h^{-1/2}) = 32.8$ Hixson-Crowell $kHc (h^{-1/2}) = 0.347$ Korsmeyer-Peppas $k_{KP} (h^{-n}) = 3.418$	
Turmeric	Storage at 25 °C for 8 weeks	gum arabic maltodextrin modified starch	gum arabic maltodextrin Pseudo-first order kinetics. modified starch	Regression model (Curcumin Maltodextrin (75%) and modified starch (25%) In(CR) = 4.61–0.088(t) Gum arabic In(CR) = 4.62–0.048(t) gum Arabic (33%), maltodextrin (33%) and modified starch (33%)	Cano-Higuita, Malacrida, and Telis (2015)
Tomato pulp waste	Storage at (4, 25 and 35 °C) for 35 days	gelatin and poly(;)- glutamic acid)	First order kinetics. $L = L0 \times [\exp^{(+k2)}]$	Arrhenius model In(k) = -Ea/R (T/ 1) + In(A)	For total lycopene L($_{4^{\circ}C}$) = 4.32° 0.03 1(0) For tis lycopene ($_{1.5^{\circ}C}$) = 46.13(-exp(0.0062)t], K($_{4^{\circ}C}$) = 6.20 × 10 ⁻³ (days ⁻¹), L($_{5^{\circ}C}$) = 46.13(-exp(0.0133)t], K($_{5^{\circ}C}$) = 1.33 × 10 ⁻³ (days ⁻¹) L($_{5^{\circ}C}$) = 44.07(-exp(0.0199)t], K($_{5^{\circ}C}$) = 1.99 × 10 ⁻³ (days ⁻¹) For trans lycopene L($_{4^{\circ}C}$) = 89.88(-exp(0.0077)t], K($_{4^{\circ}C}$) = 7.70 × 10 ⁻³ (days ⁻¹) L($_{5^{\circ}C}$) = 80.55(-exp(0.0077)t], K($_{5^{\circ}C}$) = 1.81 × 10 ⁻³ (days ⁻¹) L($_{5^{\circ}C}$) = 80.55(-exp(0.0047)t], K($_{5^{\circ}C}$) = L($_{4^{\circ}C}$) = 13.715(-exp(0.0071)t] K($_{4^{\circ}C}$) = 7.17 × 10 ⁻³ (days ⁻¹) L($_{5^{\circ}C}$) = 13.218(-exp(0.0051)t], K($_{5^{\circ}C}$) = 1.63 × 10 ⁻³ (days ⁻¹) L($_{5^{\circ}C}$) = 124.56[-exp(0.0163)t], K($_{5^{\circ}C}$) = 1.63 × 10 ⁻³ (days ⁻¹) L($_{5^{\circ}C}$) = 124.56[-exp(0.0229)t], K($_{5^{\circ}C}$) = 1.63 × 10 ⁻³ (days ⁻¹)	Chiu et al. (2007).
Pure trans eta -carotene	Storage at 25°C for seventeen weeks	Maltodextrin 25 DE	First-order kinetic model	Arrhenius model	$K_{\rm SDE}$ (t < t _r)=0.110 ± 0.008, E _a = 12.64 (Kcal/mol), $t_{\rm 1/12}$) = 6.3 (weeks) $K_{\rm SDE}$ (t > t _r)=0.020 ± 0.004, E _a = 8.74 (Kcal/mol) + 0.004, E _a = 8.74 (Kcal/mol) + 0.004, E _a = 8.75 (Kcal/mol) + 0.004, E _a = 9.004, E _a + 9.004, E _a = 9.004, E _a + 9.004, E _a = 9.004, E _a + 9.004, E _a + 9.004,	Desobry, Netto, and Labuza (1997)
Trans-β-carotene	Storage at 25 °C under different relative humidities	Almond and gum arabic First-order kinetic model	First-order kinetic model	Weibull model In[$(R-R_{\infty})/(R_0-R_{\infty})] = -k_{\rm D}t$	For Almond gum No. (RH 10%) = 0.0178 ± 0.0025; R_{∞} (RH 10%) = 88.4 ± 4 $R_{\rm D}$ (RH 45%) = 8.0025 ± 0.0013 ; R_{∞} (RH 45%) = 6.53 ± 1.2 $R_{\rm D}$ (RH 80%) = matrix collapsed; R_{∞} (RH 80%) = matrix collapsed For Gum arabic $R_{\rm D}$ (RH 10%) = 0.024 ± 0.0015 ; R_{∞} (RH 10%) =	Mahfoudhi and Hamdi (2015)

	Sutter, Buera. and Elizalde (2007)	Spada et al. (2012)	Spada et al. (2012)	(continued)
55.08 ± 3.2 K _D (RH 45%) = 0.0397 ± 0.002; R_{∞} (RH 45%) = 3.99 ± 1.1 K _D (RH 80%) = \cdot ; R_{∞} (RH 80%) = -	$K_{\rm D~(RH~1196)}=0.035\pm0.005; R_{\infty}$ (RH 1196) = 60 ± 3 $K_{\rm D~(RH~4496)}=0.081\pm0.01; R_{\infty}$ (RH 4596) = 2.20 ± 1 $K_{\rm D~(RH~7596)}=$ $K_{\rm D~(RH~7596)}=$ matrix collapsed; R_{∞} (RH 7596) = matrix collapsed	For native starch First-order kinetic model K ₁₀ °C (dark) = 0.048 ± 0.001 (day ⁻¹) K ₂ °C (dark) = 0.076 ± 0.006 (day ⁻¹) K ₂ °C (UV light) = 0.149 ± 0.006 (day ⁻¹) Weibull model b ₁₀ °C (dark) = 0.059 ± 0.015 b ₂ °C (UV light) = 0.246 ± 0.058 n ₁₀ °C (dark) = 0.0246 ± 0.031 n ₂ °C (UV light) = 0.246 ± 0.031 n ₂ °C (UV light) = 0.821 ± 0.070 For 6 DE starch First-order kinetic model K ₁₀ °C (dark) = 0.030 ± 0.002 (day ⁻¹) K ₂ °C (dark) = 0.031 ± 0.001 (day ⁻¹) K ₂ °C (dark) = 0.032 ± 0.003 b ₂ °C (UV light) = 0.088 ± 0.004 (day ⁻¹) K ₂ °C (dark) = 0.050 ± 0.007 b ₂ °C (UV light) = 0.177 ± 0.027 n ₁₀ °C (dark) = 0.695 ± 0.063 n ₂ °C (UV light) = 0.177 ± 0.049 For 1 DE starch First-order kinetic model K ₁₀ °C (dark) = 0.014 ± 0.001 (day ⁻¹) K ₂ °C (UV light) = 0.017 ± 0.0016 b ₁₀ °C (dark) = 0.017 ± 0.001 (day ⁻¹) K ₂ °C (UV light) = 0.017 ± 0.001 b ₂ °C (dark) = 0.017 ± 0.001 b ₂ °C (dark) = 0.017 ± 0.001 b ₂ °C (dark) = 0.014 ± 0.006 n ₁₀ °C (dark) = 0.038 ± 0.003 b ₂ °C (UV light) = 0.014 ± 0.006 n ₁₀ °C (dark) = 0.821 ± 0.108 n ₂ °C (UV light) = 0.38 ± 0.006 n ₂ °C (UV light) = 0.38 ± 0.006 n ₂ °C (UV light) = 0.38 ± 0.006 n ₂ °C (UV light) = 0.38 ± 0.006 n ₂ °C (UV light) = 0.171 ± 0.134	For native starch First-order kinetic model $K_{10^{\circ}C} (dark) = 0.048 \pm 0.001 (day^{-1})$ $K_{25^{\circ}C} (dark) = 0.076 \pm 0.006 (day^{-1})$ $K_{25^{\circ}C} (UV \ light) = 0.149 \pm 0.006 \ (day^{-1})$	
	Weibull model $\ln[(R-R_\infty)/(R_0-R_\infty)]=-k_{ m D}$ t	Weibull model In $(C_t/C_0) = -bt^n$	Weibull model $\text{In } (C_t/C_0) = -bt^n$	
	First-order kinetic model	First-order kinetic model In $(c_{\nu}/C_0)=\pm kt$ $t_{1/2}=0.693/k$	First-order kinetic model In $(C_t/C_0) = \pm kt$ $t_{1/2} = 0.693/k$	
	Mannitol-phosphate matrices (from solutions prepared with phosphate buffer 50 mM pH 7.4)	starch, 12 DE starch	Native starch, 6 DE starch, 12 DE starch	
	Storage at 25°C under different relative humidities	Storage at (10 °C dark, 25 °C dark, and UV light)	Storage at (10 °C dark, 25 °C dark, and UV light)	
	β-carotene	Trans β-carotene	Pure eta -carotene	

Table 5. Continued.						
Sources of carotenoids	Operating conditions	Carrier agents	Kinetic order	Mathematical model	Kinetic parameters	References
Pure eta -carotene	Storage at 25 °C under different relative humidities	Maltodextrin, gelatin, and gum arabic	First-order kinetic equation of fractional retention.	Weibull model $\ln[(R-R_\infty)/(R_0-R_\infty)]=k_{ m D}$ t	Weibull model Weibull model b_10°C (dark) = 0.059 ± 0.015 b_29°C (dark) = 0.010 ± 0.004 b_29°C (dark) = 0.246 ± 0.058 n_10°C (dark) = 0.524 ± 0.081 n_29°C (dark) = 0.521 ± 0.070 For 6 DE starch First-order kinetic model K₁0°C (dark) = 0.030 ± 0.002(day⁻¹) K₂5°C (UV light) = 0.081 ± 0.001(day⁻¹) K₂5°C (UV light) = 0.079 ± 0.013 b_29°C (dark) = 0.079 ± 0.013 b_29°C (dark) = 0.079 ± 0.007 b_29°C (UV light) = 0.177 ± 0.027 n₁0°C (dark) = 0.050 ± 0.007 b_29°C (UV light) = 0.071 ± 0.001(day⁻¹) K₂5°C (UV light) = 0.171 ± 0.014 For 12 DE starch First-order kinetic model K₁0°C (dark) = 0.014 ± 0.001(day⁻¹) K₂5°C (UV light) = 0.014 ± 0.001 b_29°C (UV light) = 0.171 ± 0.014 For 12 DE starch First-order kinetic model K₁0°C (dark) = 0.035 ± 0.003 b_29°C (UV light) = 0.014 ± 0.001 K₂5°C (UV light) = 0.015 ± 0.003 b₂5°C (UV light) = 0.015 ± 0.003 b₂5°C (UV light) = 0.026 ± 0.005 b₂7°C (Gark) = 0.035 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 44%) = 0.97 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 44%) = 0.97 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 44%) = 0.97 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.08 ± 0.02; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.08 ± 0.02; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05; R∞ (RH 11%) = 44 ± 3 K₀ (RH 11%) = 0.09 ± 0.05;	Ramoneda et al. (2011)
		-				

 $K = Degradation \ rate \ constants, \ t_{1/2} = half-life, \ E_a = Activation \ energy, \ CR = curcumin \ retention, \ L = degradation \ rate \ equation \ t = first \ phase, \ t_c = second \ phase, \ b \ and \ n \ are \ dependent \ coefficients, \ R_o = asymptotic \ v_o = rate \ constant, \ R_o \ and \ R = percentage \ of \ \beta$ -carotene retention at zero time and time t.



drying of different food materials. Moreover, we also elucidated the impact of various encapsulating agents on carotenoids from various sources, as well as degradation kinetics of encapsulated carotenoids during processing and storage. Most of the studies performed to produce encapsulated carotenoids using various encapsulating agents through spray and freeze drying. Among these, maltodextrins are commonly used as encapsulating agents and spray drying is most suitable drying methods for encapsulation. However, several studies can be applied in near future:

- How to improve encapsulated carotenoids absorption efficiency.
- Absorption mechanisms of encapsulated carotenoids.
- Which encapsulating agent is more involved in bioavalibility of encapsulated carotenoids during ive process?
- Effects of encapsulated carotenoids on human health especially in the treatment of specific disorder.

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