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Review

An updated review on use of tomato pomace and crustacean processing waste to recover commercially vital carotenoids

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ABSTRACT

Globally, the amount of food processing waste has become a major concern for environmental sustainability. The valorization of these waste materials can solve the problems of its disposal. Notably, the tomato pomace and crustacean processing waste presents enormous opportunities for the extraction of commercially vital carotenoids, lycopene, and astaxanthin, which have diverse applications in the food, feed, pharmaceuticals, and cosmetic industries. Moreover, such waste can generate surplus revenue which can significantly improve the economics of food production and processing. Considering these aspects, many reports have been published on the efficient use of tomato and crustacean processing waste to recover lycopene and astaxanthin. The current review provides up-to-date information available on the chemistry of lycopene and astaxanthin, their extraction methods that use environmentally friendly green solvents to minimize the impact of toxic chemical solvents on health and environment. Future research challenges in this context are also identified.

1. Introduction

Food waste throughout the food chain from initial agricultural production to final household consumption has become a concern for global sustainability because of its adverse impacts on food security, natural resources, environment, and human health (Xue et al., 2017). The Food and Agriculture Organization (FAO) of the United Nations estimated that every year, nearly 1.3 billion tons (≈ 30% of total production) of food worth 750 million USD is lost or wasted globally (Gustavsson, Cederberg, Sonesson, van Otterdijk, & Meybeck, 2011). Similarly, a report published by the European Union (EU) in 2010 revealed that 89 million tons (179 kg per capita) of food waste is generated every year in the EU, which is equivalent to 170 Mt. of CO_2. Households produced the largest fraction of this EU food waste (about 42%) followed by manufacturing food waste (39%), food service and catering waste (14%), and the wholesale/retail sector (5%). The EU has forecast that food waste may rise to about 126 Mt. by 2020. The report also revealed that in food production, up to 70% of waste or by-products are generated. For instance, shrimp processing generates head and carapace residues, which represents from 40 to 50% (w/w) of the integral shrimp (Mezzomo, Maestri, dos Santos, Maraschin, & Ferreira, 2011). The valorization of these waste materials or by-products can solve the problems of its disposal. Additionally, it can generate surplus revenue, which can significantly improve the economics of food production and processing.

Citrus peel was one of the first agriculture by-product utilized for the isolation of essential oils, polyphenols, sugar and pectin (Galanakis & Schieber, 2014). In the last decade, several firms have started to commercialize by-products utilization process to produce valuable compounds, predominantly cheese whey, protein concentrates and various sugar derivatives from animal-derived by-products (Galanakis & Schieber, 2014).

Tomatoes (*Lycopersicon esculentum* L.) are the second most produced and consumed vegetable crop, next to potatoes, with a global annual production of 100 million tons (Kalogeropoulos, Chiou, Pyriochou, Peristeraki, & Karathanos, 2012). Because of the high consumption, fresh tomato fruits and tomato-based commercial products provide > 85% of the total dietary intake of lycopene (Amiri-Rigi & Abbasi, 2016). During the processing of tomato in industries, a significant amount of tomato pomace (5–30% of the main product) is produced as food waste or by-products, primarily used as livestock feed or disposed of in a landfill. The tomato pomace is nearly 33% seed, 27% skin, and 40% pulp, whereas the dried form contains approximately 44% seed and 56% skin and pulp (Poojary & Passamonti, 2015). Tomato pomace, especially the skin, contains high amounts of lycopene. Choudhari and Ananthanarayan (2007) recorded nearly five times more than the pulp

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(on a wet basis) (Papaioannou & Karabelas, 2012). Because of the high content of lycopene in tomato pomace, it has been thoroughly explored for the extraction of lycopene and other carotenoids (Strati & Oreopoulou, 2014). Apart from the carotenoids, tomato pomace is also a rich source of other bioactive compounds, such as tocopherols, polyphenols, terpenes, and sterols (Kalogeropoulos, Chiou, Pyriochou, Peristeraki, & Karathanos, 2012).

Shrimp are the most economically important and internationally traded commodity among crustaceans. Shrimp processing generates 50–60% solid wastes, including the head, tail, and carapace. In recent years, this processing waste has been investigated for recovering economically important biomaterials, such as chitin, chitosan, protein, astaxanthin, flavor compounds, and calcium carbonate (Mao, Guo, Sun, & Xue, 2017). Like the high lycopene content in the tomato pomace, the processing waste of shrimp and other crustaceans is a rich source of another commercially important carotenoid, astaxanthin.

Many recent studies and reviews have focused on the valorization of waste or by-products generated in the food manufacturing/processing industries to produce biofuels, industrial enzymes, bioactive and nutraceuticals, nanoparticles, biodegradable plastics, chitosan, and collagen (Ayala-Zavala et al., 2011; Kim & Mendis, 2006; Martins & Ferreira, 2017; Ravindran & Jaiswal, 2016; Santana-Méridas, González-Coloma, & Sánchez-Vioque, 2012). Kim and Mendis (2006) reviewed the use of marine bioprocessing by-products to recover proteins, lipids, chitin, and minerals. Additionally, the applications of these compounds for human health promotion were discussed. Ayala-Zavala et al. (2011) reviewed the use of exotic fruits by-products, rich in ascorbic acid, polyphenols, carotenoids, and tocopherols, in the food industry as antioxidants, antimicrobials, functional food ingredients, food and beverage coloring and flavoring additives. Similarly, Santana-Méridas, González-Coloma, and Sánchez-Vioque (2012) overviewed the potential of crop-based and processing residues as raw materials for the production of bioactive natural products, especially phenolics acids and flavonoids. Galanakis (2013) has discussed emerging technologies, challenges, and opportunities for producing nutraceuticals from agricultural by-products. In a recent book, advantages and disadvantages of various processing technologies and techniques are discussed (Galanakis, 2015). Appropriate approaches for recovering valuable components, including polyphenols, pectin, dietary fiber, and pigments, antioxidant peptides, protein concentrates, and enzymes from food wastes of plant and animal origin are also discussed (Galanakis, 2015). Recently, Martins and Ferreira (2017) reviewed bio-residues valorization, emphasizing chemical composition, contents, and application of carotenoids.

Considering the many recent reviews available on the general use of food processing waste and by-products to recover bioactive compounds, we have focused on the comprehensive use of tomato pomace and crustacean processing waste for the extraction of lycopene and astaxanthin, respectively. With that focus on these two commercially important carotenoids, we discuss their chemistry, occurrence in food chain waste, extraction methods, and application and marketing potential.

2. Chemistry of astaxanthin and lycopene

Carotenoids comprise the family of isoprenoid pigments, which are synthesized by all photosynthetic organisms, including higher plants, mosses, and algae, some non-photosynthetic bacteria (e.g., *Myxococcus xanthus*), fungi (e.g., *Blakeslea trispora*), and a few species of aphids (Moran & Jarvik, 2010). In photosynthetic organisms, carotenoids are essential components of the photosynthetic apparatus (chlorophyll antenna system) and serve as potent antioxidants and light-harvesting pigments. There are over 600 known carotenoids, which can be classified into two functional groups: (i) Xanthophylls, containing oxygen as a functional group, including neoxanthin, violaxanthin, lutein, zeaxanthin, and astaxanthin, and (ii) carotenes, which contain only a hydrocarbon chain without any functional group, including β-carotene, α-carotene and lycopene. In xanthophylls, the oxygen atom can be present in the form of a hydroxyl (-OH) (e.g., lutein), a keto (=O) (e.g., canthaxanthin), or a combination of hydroxyl and keto groups (e.g., astaxanthin) (Saini & Keum, 2018). Carotenoids can be further classified into provitamin A carotenoids (e.g., α-carotene, β-carotene, β-cryptoxanthin, and mutatochrome) and the non–provitamin A carotenoids, which cannot be converted to retinal (e.g., lycopene, lutein, zeaxanthin, and astaxanthin) because they lack the nonsubstituted β-ionone ring structure. All *E*-β-carotene has 100% vitamin A (retinol and retinal) activity because of the presence of two β-ionone ring structures, which can yield 2 molecules of retinal (vitamin A) by the action of carotene dioxygenase (Saini, Nile, & Park, 2015) whereas α-carotene possesses only 53% vitamin A activity, because it has only one β-ionone ring (Fig. 1). Though neither lycopene nor astaxanthin can yield vitamin A, their exceptional antioxidant, anti-inflammatory, and immunomodulatory activities give them extraordinary potential for protecting humans against a wide range of chronic disorders, including cardiovascular disease (CVD), different types of cancer, and oxidative stress (Park, Chyun, Kim, Line, & Chew, 2010; Thies, Mills, Moir, & Masson, 2017; Viuda-Martos et al., 2014).

The characteristic yellow to red-orange color of carotenoids is attributed to the presence of a polyene chain with several conjugated carbon-carbon double bonds that function as a chromophore (Saini, Nile, & Park, 2015). In addition to the chromophore activity, the polyene chain is mainly responsible for the detoxification of free radicals by providing a resonance-stabilized carbon-centered peroxyl radical (e.g., ROO-lycopene) (Giri, Rawat, Singh, Gautam, & Kaithwas, 2015). The presence of hydroxyl and keto functional groups on each ionone ring increases the antioxidant potential of astaxanthin, without pro-oxidative effects (Ambati, Phang, Ravi, & Aswathanarayana, 2014). Additionally, α-hydroxy ketone groups on each ring of the astaxanthin molecule make it more hydrophilic than other carotenoids; so the anchoring of astaxanthin in the lipid/water interface on both sides of the cell membrane makes it more effective for protection against lipid peroxidation (Fig. 2) (Ambati, Phang, Ravi, & Aswathanarayana, 2014).

Lycopene (ψ,ψ-carotene), a symmetric tetraterpene (eight isoprene units) is a crucial intermediate in the biosynthesis of many important carotenoids. With 11 conjugated and 2 unconjugated double bonds, lycopene possess the highest degree of unsaturation among all carotenoids, responsible for the characteristic profound red color of ripened tomatoes and tomato products (Kehili et al., 2017). The cyclization of the ends of the lycopene chain (Linear ψ end group) into alpha (α), beta (β), or epsilon (ε) rings, by the action of lycopene-α-, β-, or ε-cyclases, gives rise to the α-, β-, and δ-carotene, respectively, which is the first branch point in the carotenoid biosynthetic pathway, results in the production of other carotenoids, including astaxanthin (Fig. 1) (Ruiz-Sola & Rodríguez-Concepción, 2012). The enzymatic activity of β-carotene ketolase and β-carotene hydrolase add the keto and hydroxyl groups to the β and β' rings of β-carotene to raise the astaxanthin (Fig. 1). The carotenoids with α and β rings are common in the plant kingdom, whereas carotenoids with ε rings, such as the lactucaxanthin found in lettuce, are rare (Kim, Shang, Assefa, Keum, & Saini, 2018).

The gac (*Momordica cochinchinensis*), tomato, watermelon, and pink grapefruit are the primary source of natural lycopene. The mature green tomato contains chloroplasts with carotenoids composition remarkably similar to that of leaves and other leafy herbs. However, during the process of the tomato ripening, chloroplasts are differentiated into chromoplasts. In this process, chlorophylls are degraded, and a substantial accumulation of carotenoids, particularly lycopene, takes place, changing the fruit color from green to red.

Astaxanthin (3,3′-dihydroxy-β,β'-carotene-4,4′-dione) can be biosynthesized by some plants (*Adonis aestivalis*), the microalgae (*Haematococcus pluvialis*), red yeast (*Phaffia rhodozyma*), and the marine bacterium (*Agrobacterium aurantiacum*). Among them, the green microalga *H. pluvialis* is the richest and commercially most viable source of

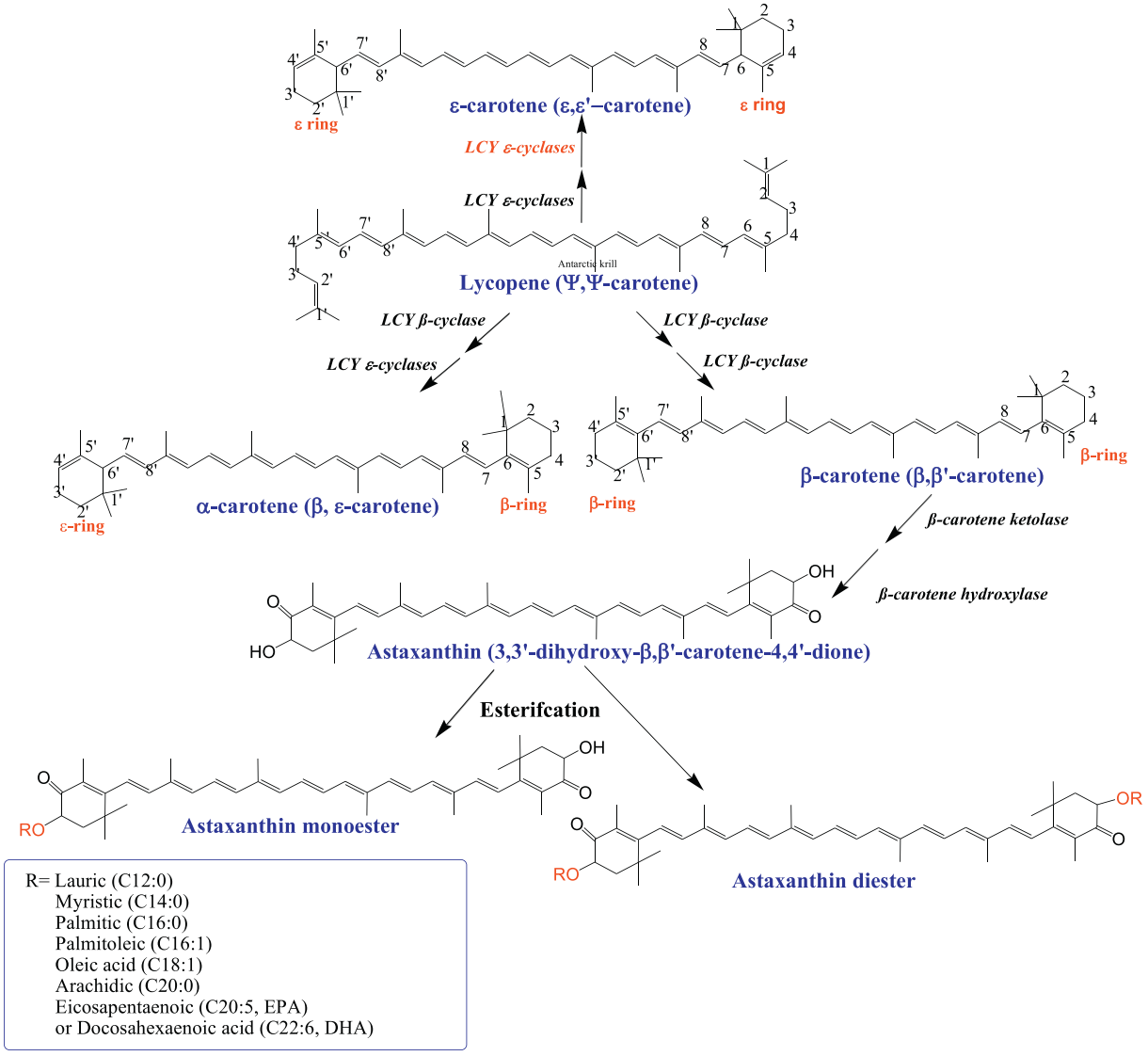

Fig. 1. Systematic representation of cyclization of the ends of the lycopene chain (Linear ψ end group) into alpha (α), beta (β), or epsilon (ε) rings, by the action of lycopene-α-, β-, or ε-cyclases that give rise to the α-, β-, and ε-carotene, respectively. The biosynthesis of all-E-astaxanthin is also summarized. Addtionally, the chemical structure of all-E-astaxanthin monoester and all-E-astaxanthin diester are shown.

natural astaxanthin (80–99% of total carotenoids); it can accumulate astaxanthin up to 3–5% of dry cell weight (Ambati et al., 2014; Saini & Keum, 2017). In the marine environment, microalgae are the primary producer of astaxanthin, and its ingestion by fish accrues astaxanthin in the food chain (Yuan, Peng, Yin, & Wang, 2011). Astaxanthin is responsible for the natural red, orange, and yellow colors of organisms, because if its absorption maxima in the range of 475–500 nm. Carotenoproteins, formed by imine bonding between protein–carotenoid complexes in the carapace of marine crustaceans, are responsible for natural green, blue, and purple colors (Armenta & Guerrero-Legarreta, 2009). In lobster (*Homarus gammarus*) shell, these carotenoproteins occur as either β-crustacyanin (dimers of apoprotein-astaxanthin) or α-crustacyanin (octamer of β-crustacyanins). The formation of carotenoproteins provides the blue coloration of the shell of the lobster, with the absorption maximum around 630 nm in α-crustacyanin and 580–590 nm in β-crustacyanin (Durbeej & Eriksson, 2006). This protein-induced bathochromic shift in the absorption of α-crustacyanin has intrigued scientists from many years, as it's the most significant protein-induced spectral shift known (Durbeej & Eriksson, 2006). Natural astaxanthin is found in the racemic mixture of three stereoisomers: two enantiomers (3R, 3′R, and 3S, 3′S) and a *meso* form (3R, 3′S), formed because of the presence of two chiral centers in the C-3 and C-3′ positions (Higuera-Ciapara, Félix-Valenzuela, & Goycoolea, 2006). In crustaceans, large fractions of astaxanthin are found esterified with one or both hydroxyl groups to form mono- or di-esters, respectively (Ambati et al., 2014). In Antarctic krill (*Euphausia superba*), most astaxanthin is found in the form of diesters (46%), followed by astaxanthin monoesters (34%) and free astaxanthin (20%). Lauric (C12:0), myristic (C14:0), palmitic (C16:0), palmitoleic (C16:1), or oleic acid (C18:1) are commonly found in these esterified forms (Takaichi, Matsui, Nakamura, Muramatsu, & Hanada, 2003). In contrast, in astaxanthin monoesters and dieters of spear shrimp shells (*Parapenaeopsis hardwickii*), arachidic (C20:0), eicosapentaenoic (C20:5, EPA), and docosahexaenoic acid (C22:6, DHA) were also found in significant amounts, with C12:0, C14:0, C16:0, C16:1, and C18:1 fatty acids (Lin, Chien, & Chen, 2005).

3. Occurrence of astaxanthin and lycopene in food chain waste

Food waste is composed of raw or cooked food materials and includes food lost in the household or discarded in the process of manufacturing, distribution, retail, and food service (Monier et al., 2010).

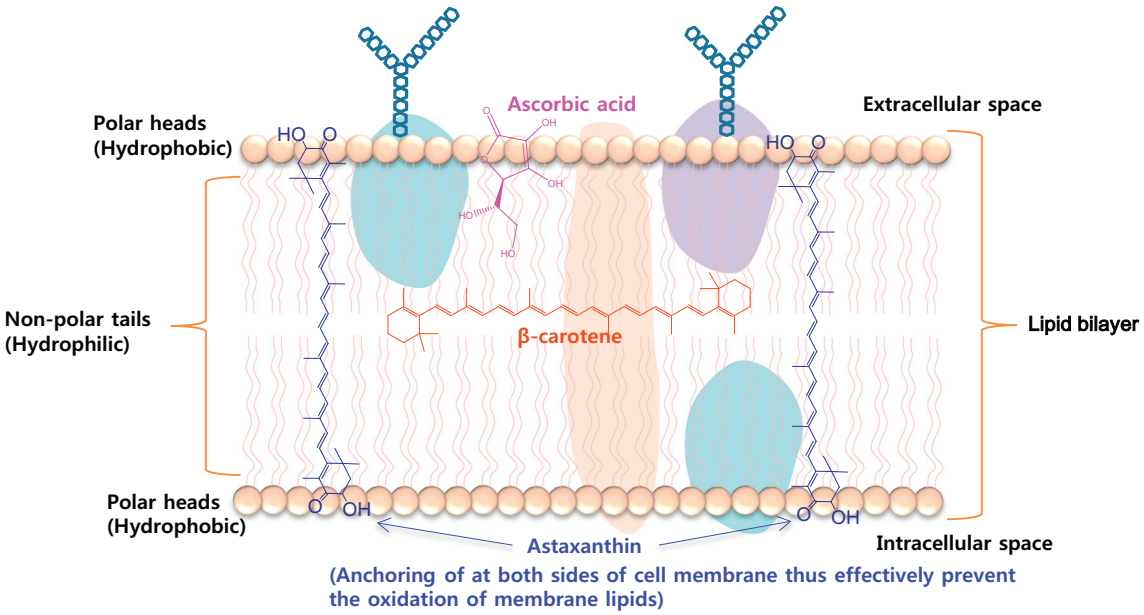

Fig. 2. The anchoring of astaxanthin in the lipid/water interface on both sides of the cell membrane makes it more effective for protection against lipid peroxidation.

According to their biochemical characteristics, food supply-chain waste can broadly be classified as plant-derived or animal-derived (Ravindran & Jaiswal, 2016). Annually, much fruit pomace from olives, tomatoes, grapes, and apples is produced as food waste or by-products by food processing industries. Similarly, fish, shrimp, and crab-shell processing generates much animal-derived food waste. In the United States and many Western countries, the tomato is the primary dietary source of vitamin A and phenolic compounds because of its high per-capita consumption (≈ 6.2 kg per year) (Klee & Giovannoni, 2011). In red ripe tomatoes, lycopene represents 70–80% of total carotenoids. Also, tomato peel contains nearly five times more lycopene than tomato pulp (Saini, Zamany, & Keum, 2017). Thus, the tomato pomace and tomato skin produced as by-products from the fruit-processing industries can be a rich source of lycopene and other carotenoids.

Crustaceans form an abundant, diverse arthropod taxon which includes such familiar animals as crabs, lobsters, crayfish, prawns, shrimp, and krill. According to the FAO statistics (FAO, 2016), 6.9 million tonnes tons of crustaceans, worth US$36.2 billion, were produced in 2014, with a total global aquaculture share of 21.7% in value, and 8.2% in live weight. Shrimp and prawns contributed the vast majority of crustacean production (73%), and nearly 89% is produced in Asia, with China alone producing almost 57% of the world's total. Global catches of shrimp were 3.5 million tonnes, with the highest capture (556 thousand tonnes) of Akiami paste shrimp (*Acetes japonicas*). In Korea, 4.5 thousand tons of farmed crustaceans were produced in the year 2014, with a total aquaculture production of 1567.4 thousand tons (FAO, 2016). Processing of crustaceans generates 50–60% of waste. Thus, their efficient use is crucial. The slow natural degradation rate of shells is also a major problem in their safe disposal. However, this waste material can be used as a natural, cheap source of several commercially vital nutraceuticals, including astaxanthin (Mao, Guo, Sun, & Xue, 2017; Martins & Ferreira, 2017). Shrimp contain a large amount of astaxanthin, between 3.1 (in Northern shrimp; *Pandalus borealis*) to 8.4 mg/100 g (in Kiddi shrimp; *Parapenaeopsis stylifera*) on the fresh wet basis (Razi Parjikolaei et al., 2017). Thus, extraction of nutraceuticals from these waste materials is an important step for its economically feasible use. Recently, Prameela et al. (2017) reviewed the chemistry and role of astaxanthin in the pigmentation of shrimp. They also discussed current progress in applications of astaxanthin and methods for extracting it. In the following sections, we describe the methods used to extract astaxanthin and lycopene from crustacean waste and tomato pomace, respectively.

4. The process of astaxanthin and lycopene recovery

Several investigations have been focused on developing a protocol for extraction and purification of bioactive compounds from food wastes (Tables 1 and 2). Regardless of properties of food waste or physical/chemical characteristics of target compound, Galanakis (2012) has suggested the following five universal stages of the recovery process: i) macroscopic pretreatment; ii) macro- and micromolecules separation; iii) extraction; iv) isolation and purification; and v) product development. Similarly, modification or development of new recovery process should consider the follwoing: a) the highest recovery (yield optimization) of the target compound; b) the process should match demands of large-scale industrial processing; c) the highest purity of added-value ingredients from toxic compounds; (d) avoiding degradation and loss of biological activity during the process; and (e) safeguarding food grade properties of the final product (Galanakis, 2012). More specifically, many conventional and nonconventional methods have been proposed to improve the extraction of carotenoids from crustaceans and tomato processing waste, employing different modes of cell disintegration (chemical, physical or enzymatic), and various degrees of applied temperature and pressure. These methods include, (I) atmospheric liquid extraction of carotenoids with Soxhlet, maceration, or ultrasound (UAE: ultrasound-assisted extraction); (II) supercritical fluid extraction (SFE), which often uses supercritical (SC)-CO_2 as a solvent, with minimal use of organic co-solvents (called entrainers) such as ethanol; and (III) enzyme-assisted extraction (EAE) (Saini & Keum, 2018). The different steps of lycopene and astaxanthin recovery of processing waste are depicted in Fig. 3. To obtain the highest yield with appropriate purity and economic feasibility, various extraction methods need to be optimized in terms of pretreatments, the minimum possible volume of extraction solvents, and extraction temperature, pressure, and time (Tables 1 and 2). These factors fundamentally depend on the complexity, particle size, moisture contents of the sample, and the nature (polarity) of existing carotenoids. Astaxanthin and lycopene are sensitive to heat and light-mediated deterioration during processing and storage. Thus, a short extraction time, extraction in an inert environment with appropriate temperature control, and

Table 1
Methods of lycopene extraction from tomato processing by-products.

Extraction sample	Methodology	Major research output	Reference
Whole tomato, peel, fruit pulper waste and industrial waste	Enzyme-assisted extraction (EAE) using cellulase (3% w/w) and pectinase (2% w/w) enzymes	Cellulase enzyme is more efficient than pectinase for total lycopene extraction from tomato industrial waste	(Choudhari & Ananthanarayan, 2007)
Dehydrated tomato waste	Comparative efficiency of ethanol, hexane, ethyl acetate, and acetone, and solvent mixtures	The highest yield of total carotenoids (36.5 mg kg^{-1}) was obtained with a combination of ethyl acetate and hexane (1:1).	(Irini F. Strati & Oreopoulou, 2011)
Peel of tomato processing waste	Pectinolytic (Peclyve PR) and cellulolytic (Cellulyve 50LC) enzyme-assisted extraction	The optimized conditions of 30 °C extraction temperature, extraction time of 3.18 h, and enzyme load of 1.6% (w/w) resulted in 8- to 18-fold higher lycopene recovery	(Zuorro, Fidaleo, & Lavecchia, 2011)
Dried tomato peel by-products (mixture of peel and seed 37:63 w/w)	Supercritical carbon dioxide (SC-CO_2) extraction in the presence of tomato seed oil	The highest 56% recovery of lycopene was obtained at 90 °C temperature, 40 MPa pressure, and particle size of 1.05 mm. The presence of tomato seed oil was found to improve the lycopene yield.	(Machmudah et al., 2012)
Tomato peel residues	Pectinolytic enzyme pretreatment followed by surfactants assisted extraction	Span 20 at the optimum ratio of 6–7 surfactant molecules per lycopene molecule provided the highest recovery of 23–25%.	(Papaioannou & Karabelas, 2012)
Tomato pomace powder	SC-CO_2 extraction	The highest lycopene content obtained in residual fraction, under the optimized pressure of 30 MPa and CO_2 flow rate of 15 kg h^{-1}	(Perretti et al., 2013)
Tomato processing waste	EAE	Tri-mixture of acetone, ethanol, and hexane (2:1:1) produced the highest recovery. Pectinase treatment (2%) is more effective then cellulase	(Ranveer et al., 2013)
Dry tomato pomace	Ultrasound-assisted extraction (UAE)	The highest yield of carotenoids was obtained by application of vibration amplitude of 94 μm and an external pressure of 50 kPa	(Luengo et al., 2014)
Tomato waste	Enzyme and high pressure (HP) assisted extraction	6- and 10-fold higher yield of total carotenoid and lycopene, respectively in enzyme treated samples, extracted with ethyl lactate.	(Irini F. Strati et al., 2015)
Tomato processing waste (devoid of seeds)	Solvent extraction different ratios (1:3, 2:2 and 3:1, v/v) of acetone and n-hexane at temperatures range of 30–50 °C	The highest yield of lycopene (3.47–4.03 mg/100 g), which corresponds to a percentage recovery of 65.22–75.75%, was obtained with 1:3 acetone and n-hexane at 30 °C	(Poojary & Passamonti, 2015)
Tomato pomace	Surfactants, co-surfactants, ultrasound, and EAE	Combined use of ultrasound, pectinolytic and cellulolytic enzymes pretreatments, saponin as a natural surfactant, and glycerol as a co-surfactant provided the six times higher yield of lycopene (409.68 ± 0.68 μg/g)	(Amiri-Rigi & Abbasi, 2016)
Tomato industrial waste	Surfactants, co-surfactants, ultrasound, and EAE	Surfactant (saponin): lycopene ratio of 20:1, surfactant: co-surfactant (glycerol) ratio of 1:1 and particle size of 400–595 μm was optimized for the highest recovery of lycopene	(Amiri-Rigi et al., 2016)
Tomato peels by-product	SC-CO_2 extraction	Lycopene yield was positively correlated with temperature, pressure and CO_2 flow rate with the highest recovery of 60.85% at 80 °C temperature, 400 bar pressure and 4 g/min flow rate	(Kehili et al., 2017)
Commercial tomato waste stream	Studied the effects on solvent type and order on lycopene extraction efficiency	Use of acetone and/or ethanol to disrupt cellular structure (step 1), followed by addition of hexane with acetone or hexane with ethanol (step 2) produced the highest the extraction yield of lycopene	(Phinney, Frelka, Cooperstone, Schwartz, & Heldman, 2017)

Table 2
Methods of astaxanthin extraction from crustacean-processing by-products.

Extraction sample	Methodology	Major research output	Reference
Shrimp by-products	Lactic acid fermentation (LAF)	The highest demineralization, Deproteinization, and astaxanthin yield was obtained from LAF carried out at 27–36 °C, 30–40 °C, and 20–30 °C, respectively.	(Pacheco et al., 2009)
Shrimp waste	Ultrasonic-assisted extraction (UAE) utilizing various task-specific imidazolium-based ionic liquids	Ethanol containing 1-butyl-3-methylimidazolium with bromide (Br^-) was found most efficient and economical for the extraction of astaxanthin	(Bi, Tian, Zhou, & Row, 2010)
Pink shrimp (*P. brasiliensis* and *P. paulensis*) residues	Investigated the different pre-treatments, such as cooking, drying, and milling	Extraction using maceration with acetone or hexane with isopropanol provided the highest yield of total carotenoids	(Mezzomo et al., 2011)
Brazilian red spotted shrimp waste (*Farfantepenaeus paulensis*)	SC-CO_2 extraction	Obtained the highest yield of 20.7 μg astaxanthin/g dry waste (39% recovery), using SC-CO_2 extraction at 43 °C temperature and 370 bar pressure	(Sánchez-Camargo, Martinez-Correa, Paviani, & Cabral, 2011)
Pink shrimp (*P. longirostris*) waste	Enzyme (barbel and bovine trypsin) assisted extraction of carotenoprotein	The mixed trypsins mediated hydrolysis (24 h at 30 °C) of carotenoprotein provided the highest yield of astaxanthin (59 μg/g), followed by barbel trypsin (59 μg/g) and bovine trypsin (51 μg/g) alone	(Sila, Nasri, & Bougatef, 2012)
Pink shrimp processing waste	SC-CO_2 extraction	The highest yield of astaxanthin was obtained at 300 bar pressure and 333.15 K temperature.	(Mezzomo et al., 2013)
Shrimp cooking wastewater	Cooking, lyophilization, and enzyme (alcalase) pretreatments	The higher recoveries of astaxanthin were obtained when both lyophilized and enzyme-treated fractions were extracted in the presence of stabilizing agents (butylated hydroxyanisole and ethoxyquin)	(Amado, Vázquez, Murado, & González, 2015)
Shrimp processing waste	Extraction using green solvents, sunflower oil (SF) and methyl ester of sunflower oil (ME-SF)	ME-SF are more efficient then SF for the extraction of astaxanthin (recovery of 80 and 60% of the total astaxanthin, respectively)	(Razi Parjikolaei, Bahij El-Houri, Fretté, & Christensen, 2015)
Shrimp processing waste	Extraction using green solvents (ME-SF and SF), SC-CO_2 with 5% ethanol (w/w), and extraction with Hexane: isopropanol, (6:4 v/v)	The highest yield and purity (100%) of astaxanthin was achieved using hexane: isopropanol, whereas, SC-CO_2 extrication resulted in the lowest extraction yield (51%)	(Razi Parjikolaei et al., 2017)

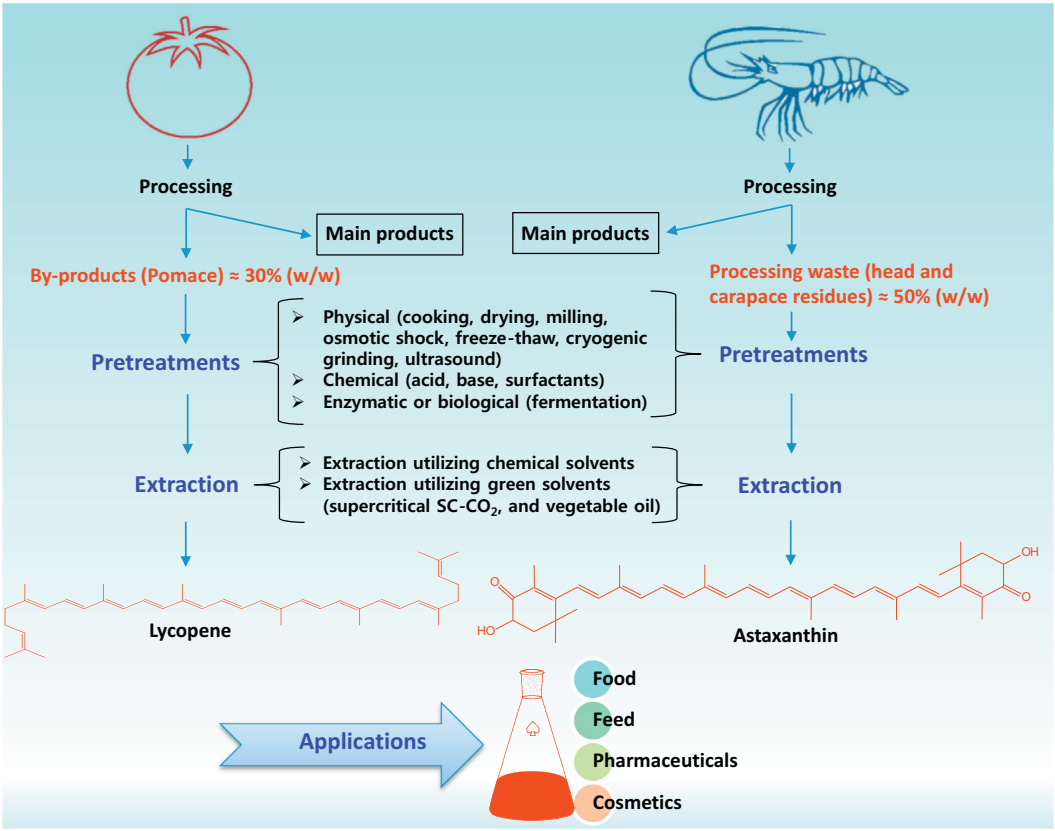

Fig. 3. The different steps involved in the recovery of lycopene and astaxanthin from processing waste.

protection from direct exposure to UV light is recommended to minimize the degradation (Saini & Keum, 2018). In the following sections, we describe the major factors affecting the carotenoid yields and the different methods used for the extraction of lycopene and astaxanthin.

4.1. Factor affecting the recovery of astaxanthin and lycopene

The various factors affecting the yield of carotenoids from plant and animal tissues have been thoroughly investigated. Among them, the choice of suitable solvents or solvent combinations is one of the most critical factors, which basically depends on the solubility, functional group (polarity), and stability of the existing carotenoids (Ranveer, Patil, & Sahoo, 2013). Lycopene is an extremely lipophilic nonpolar carotenoid, because its conjugated hydrocarbon lacks any polar functional groups, and the presence of hydroxy and keto functional groups on both β-rings of astaxanthin at the 3,3′ and 4,4′ positions, respectively, makes carotenoids highly polar. Thus, hexane- and acetone-based solvents are frequently selected for extraction of lycopene and astaxanthin, respectively (Mezzomo, Maestri, dos Santos, Maraschin, & Ferreira, 2011). The combination of acetone, ethanol, and hexane is more beneficial for the highest recovery of lycopene (Ranveer, Patil, & Sahoo, 2013). The water-miscible properties of acetone and ethanol also support efficient extraction of carotenoids from the samples containing a high amount of water. In addition to the extraction efficiency, lycopene extracts obtained with hexane/acetone or hexane/ethanol are much more stable than extracts obtained with other organic solvents (Perretti et al., 2013). Similarly, dichloromethane, chloroform, methanol, and acetonitrile have been reported to promote higher conversion of *trans*-astaxanthin into *cis*-astaxanthin, whereas petroleum ether and acetone prevent the *trans*- to *cis*- isomerization (Armenta & Guerrero-Legarreta, 2009). Moreover, considering the environmental, health, and safety issues, ethanol and acetone are preferred solvents, rather than chloroform, dichloromethane, diethyl ether, and hexane, which are conventionally used for extraction of carotenoids (Alfonsi et al., 2008; Capello, Fischer, & Hungerbühler, 2007). To improve sustainability, environmentally friendly green solvents, such as SC-CO_2, and ionic liquids have also been explored for the efficient extraction of carotenoids from bio-waste, as discussed in the following sections.

Plant and animal tissues contain much moisture, which makes them extremely susceptible to microbial spoilage and unfavorable for efficient extraction of carotenoids. Thus, these samples are generally dehydrated to increase the carotenoid yield (Mezzomo, Martínez, Maraschin, & Ferreira, 2013). For instance, fresh pomace has a high water content (70–80%. and so is often preserved by dehydration, which, however, increases the cost and causes degradation and isomerization of lycopene from *trans* to the less-colored and more-oxidizable *cis* isomer (Allison & Simmons, 2017). Interestingly, Albanese, Adiletta, D'Acunto, Cinquanta, & Di Matteo (2014) observed that the lycopene and β-carotene content in pomace dried by hot air at 50 °C (234 and 28 mg $kg_{,}^{-1}$ respectively) was similar to that obtained by freeze-drying (250 and 43 mg $kg_{,}^{-1}$ respectively), which also has comparatively high process costs. In a stability study, Allison and Simmons (2017) found that light irradiation caused more loss of total carotenoids than heating treatment at 100 °C (30% after 250 min of treatment). In contrast, in comparison with lyophilization, vacuum drying, solar drying, and hot-air drying at 55 °C were significantly detrimental to lycopene recovery from tomato pomace.

The complex and rigid cell wall of plant cells constitutes an obstacle to the entry of solvents. Additionally, the firm association between carotenoids with other macromolecules, such as proteins, and astaxanthin prevents their efficient extraction. Thus, in the first step of extraction, the cell walls are disrupted by physical (cooking, drying, milling, osmotic shock, freeze-thaw, cryogenic grinding) (Mezzomo et al., 2011), chemical (acid, base, surfactants) (Papaioannou & Karabelas, 2012), enzymatic or biological means (e.g., fermentation) to facilitate efficient extraction (Amiri-Rigi & Abbasi, 2016). Lactic-acid fermentation (LAF) has proved useful for the demineralization (DM) and deproteinization (DP) of the solid fraction of animal origin to obtain free astaxanthin and chitin. Also, LAF of shrimp byproducts helps in stabilizing the astaxanthin prior to solvent extraction, thereby increasing extraction yields (Armenta & Guerrero-Legarreta, 2009).

The particle size of the sample is also very critical in the extraction of carotenoids. Usually, reducing particle size to a particular limit increased extraction efficiency, because of the increase in the surface: volume ratio of the sample and better penetration of extraction solvents. However, further reduction in size likely releases more internal contents of the cells into the extraction medium, which can interfere with carotenoid extraction. Moreover, the higher exposure of carotenoids to oxygen and light by the larger surface area of small particles may lead to degradation (Amiri-Rigi, Abbasi, & Scanlon, 2016).

4.2. The process of astaxanthin recovery

For astaxanthin recovery from crustaceans waste, various types of physical, chemical, and biological pretreatment have been investigated for the efficient disintegration of complex animal tissues. Mezzomo et al. (2011) investigated different pretreatments, such as cooking, drying. and milling, of pink shrimp (*P. brasiliensis* and *P. paulensis*) residues, followed by extraction using various solvents and extraction techniques, including (i) maceration with hexane, hexane with isopropanol, acetone, and ethanol; (ii) Soxhlet with hexane, hexane with isopropanol, isopropanol, and acetone; and (iii) ultrasound treatment with ethanol to obtain the carotenoid-rich fraction. The highest yield of extract and total carotenoids was obtained by the combination of cooking, drying, and milling. Also, extraction using maceration with acetone and hexane with isopropanol provided the highest yield of total carotenoids. Interestingly, cooking pretreatment most significantly improved the extraction yield (especially with drying and milling), whereas milling and drying of non-cooked samples were not effective, probably because of the cooking-mediated disintegration of the astaxanthin-protein complexes, thereby increasing the extraction yield. LAF has been used as an efficient way for the DM and DP of shrimp waste to obtain the free astaxanthin and chitin. Pacheco et al. (2009) optimized the temperature in LAF for the highest recoveries of chitin and astaxanthin from shrimp waste. The results of response surface methodology showed that the LAF carried out in the temperature range of 27–36 °C with lactic acid above 0.319 mmol/g give rise to the highest DM. The highest DP (89–91%), which has greater proteolytic activity, was obtained at 30 to 40 °C. The highest content of free astaxanthin was attained at 20 to 30 °C, whereas the higher temperature (> 30 °C) increased the proportion of *cis* isomers.

The proteolytic activity of trypsin, pepsin, or papain has been used as an enzymatic pretreatment for the extraction of carotenoprotein from shrimp waste. Sila, Nasri, & Bougatef (2012) studied the comparative efficiency of barbel (*Barbus callensis*) and bovine trypsin for the recovery of carotenoprotein from pink shrimp (*Parapenaeus longirostris*) waste. They used enzymatic hydrolysis followed by filtration with ultrafiltration membrane with a cut-off of 30 kDa to yield the protein and carotenoid fractions. The yields of protein and carotenoids attained with barbel trypsin were significantly higher than those obtained with bovine trypsin. Also, the mixed trypsin-mediated hydrolysis of carotenoprotein for 24 h at 30 °C provided the highest yield of astaxanthin (59 μg/g), followed by barbel trypsin (59 μg/g) and bovine trypsin (51 μg/g) alone. Amado, Vázquez, Murado, & González (2015) also used the membrane technology (300 kDa ultrafiltration) to recover the concentrated fraction of protein and astaxanthin from shrimp cooking wastewater. They demonstrated that cooking could break the carotenoid-protein complex and facilitate its extraction. Thus a significant amount of astaxanthin can be extracted from the recovered fraction using sunflower oil (3:1 v/v) at a low temperature (< 40 °C). Interestingly, no improvement in astaxanthin yield was observed after hydrolysis with commercial protease (alcalase or subtilisin; 0.01:1 AU/mL) at

45 °C for 30 min. However, the higher recoveries of astaxanthin were obtained when both lyophilized and enzyme-treated fractions were extracted in the presence of stabilizing agents (synthetic antioxidants), such as butylated hydroxyanisole (BHA) and ethoxyquin. Thus, the synthetic antioxidants can be used during extraction steps to prevent the degradation of carotenoids. In general, tert-butlylhydroqinone (TBHQ), BHA, pyrogallol, or ascorbyl palmitate are added to extraction solvents at concentrations of ≈0.1% (w/v) (Saini & Keum, 2018).

Similar to conventional organic solvents, several green solvents including hydrotropes, vegetable oil, and SC-CO_2 have been successfully utilized for efficient extraction of carotenoids and other hydrophobic phytochemicals (Bi, Tian, Zhou, & Row, 2010; Nagarajan et al., 2016). Hydrotropes (or hydrotropic agents) are organic molecules having both hydrophilic and hydrophobic portions in the structure comparable to surfactants. However, contrasting to surfactants, they cannot form micelles. Ionic liquids (ILs) are also a class of catanionic hydrotropes. They are capable of enhancing the solubility of poorly water-soluble or hydrophobic compounds in aqueous solutions. From the shrimp waste, Bi, Tian, Zhou, & Row (2010) investigated the relative efficiency of various task-specific imidazolium-based ILs with combinations of diverse cations and anions for ultrasonic-assisted extraction (UAE) combined with molecularly imprinted solid-phase extraction (MISPE) and non-imprinted SPE (NISPE). It was found that ethanol containing 1-butyl-3-methylimidazolium (0.50 mol L^{-1}) with bromide ($Br-$) provided a more efficient and economic extraction of astaxanthin, than did other cations (1-ethyl-3-methylimidazolium and 1-hexyl-3-methylimidazolium) and anions (chloride, Cl^-; tetrafluoroborate, $BF4^-$; and methylsulfate, MS^-). Also, UAE conditions of 75 W power for 60 min at a solid/liquid ratio of 1:10 (g L^{-1}) was best for moderate astaxanthin contents. In the sorbent study, solid-phase extraction (SPE) using molecularly imprinted polymeric sorbent (MIPs) showed a significantly higher affinity to astaxanthin than did use of the nonimprinted polymeric sorbent (NIPs). The higher efficiency of ILs was probably because of the π- π and η- π hydrophobic and hydrogen bond interactions. Moreover, the strong dissolving power of ILs and their charged environment (reductive amine group) prevent the degradation of astaxanthin.

The use of edible vegetable oil is also an emerging novel way to extract the carotenoids. Razi Parjikolaei, Bahij El-Houri, Fretté, & Christensen (2015) reported that methyl esters of sunflower oil (ME-SF) are more efficient then sunflower oil (SF) for the extraction of astaxanthin (recovery of 80 and 60% of the total astaxanthin, respectively) from shrimp processing waste. For both of the green solvents, the highest astaxanthin content was obtained at a temperature of 70 °C, solvent-to-waste ratio of 9, stirrer speed of 400 rpm, waste particle size of 0.6 mm, and moisture content of 86.8%. Interestingly, freeze-drying or reducing the moister content from shrimp processing waste before extraction did not improve the extraction of astaxanthin, using ME-SF and SF. It was interesting to observe that the structure of non-dried shrimp waste was more porous, thus more accessible to the solvents for the higher mass transfer of astaxanthin during extraction. In further developments, Razi Parjikolaei et al. (2017) recently investigated the comparative efficiency of these green solvents (ME-SF and SF) as alternatives to SC-CO_2 with 5% ethanol (w/w), and extraction with a fossil-based organic solvent mixture (Hexane:isopropanol, 6:4 v/v) for the extraction of astaxanthin from shrimp processing waste. The highest yield and purity (100%) of astaxanthin was achieved using hexane: isopropanol, whereas SC-CO_2 extraction resulted in the lowest extraction yield (51%). The extraction using SF and ME-SF provided 60 and 80% recovery of astaxanthin, respectively. The production cost of astaxanthin was highest using SC-CO_2 (0.8 $/mg), followed by organic solvent mixture (0.6 $/mg), ME-SF (0.16 $/mg), and SF (0.06 $/mg). Despite the significantly higher cost of astaxanthin produced using SC-CO_2, it has wide advantages for food applications, with no risk of residual solvent toxicity. In comparison with solvent and SC-CO_2 extraction, extraction using SF and ME-SF yielded a very low concentration of astaxanthin (155 ppm after concentration). However, the low cost of astaxanthin production using SF and ME-SF may suit it to large-scale industrial production without using toxic solvents. Additionally, astaxanthin in SF and ME-SF can be directly used for food applications. Overall, compared to natural astaxanthin produced using these methods, synthetic astaxanthin is very low cost (≈2.5 $/g). Thus, Razi Parjikolaei et al. (2017) argued that further optimization of these methods is necessary in order to obtain an economically viable production price that is competitive to the price for synthetic astaxanthin.

SC-CO_2 has proved to be an efficient and green extraction method for thermolabile compounds, including carotenoids. The pressure, temperature, CO_2 flow rate, extraction time, and addition of co-solvents (called entrainers), such as ethanol, play a significant role in the extraction of carotenoids using SC-CO_2. In general, an extraction temperature of 40–60 °C, pressure of 300–400 bar, extraction time of 30–120 min, CO_2 flow rate of 1–5 mLmin, and entrainers concentration of 5–25% (v/v) are frequently used for SC-CO_2 extraction of carotenoids (Saini & Keum, 2018). However, these parameters need to be fine-tuned depending on the nature and properties of the extraction material. Sánchez-Camargo, Martinez-Correa, Paviani, & Cabral (2011) showed that in the SC-CO_2 extraction of astaxanthin from Brazilian red-spotted shrimp waste (*Farfantepenaeus paulensis*), the highest yield of astaxanthin could be obtained at the lowest temperatures and highest pressures, which also limit the heat-mediated degradation of carotenoids. The highest yield of 20.7 μg astaxanthin/g dry waste (39% recovery) was obtained using SC-CO_2 extraction at 43 °C and 370 bar pressure. Under these optimized conditions, the concentration of astaxanthin in the extract (1074 μg astaxanthin/g extract) was equal to that obtained in the extraction with common organic solvents, indicating the absolute suitability of the use of SC-CO_2 for the recovery of astaxanthin.

Regarding physicochemical properties, SC-CO_2 has higher diffusivity, lower viscosity, and lower surface tension than conventional solvents, thus facilitating mass transfer and allowing efficient extraction. Primarily, CO_2 is as a nonpolar lipophilic solvent owing to its zero molecular dipole moment and low dielectric constant. The nonpolar and lipophilic nature of SC-CO_2 is potentially useful for the extraction of nonpolar and moderately polar lipophilic carotenes, such as β-carotene and lycopene. However, the extraction performance is slightly limited for polar carotenoids. However, in the supercritical state, above its critical temperature (31.05 °C or 304.2 K) and critical pressure (7.38 MPa or 73.8 bar), the polarity of CO_2 positively correlates with pressure and temperature. Hence the polarity of SC-CO_2 can be adjusted to match the polarity of the targeted carotenoid, resulting in a higher extraction yield, with high purity, because of the selective extractions. Additionally, an increase in the CO_2 flow rate improves the solvent velocity and accessibility, increasing the concentration gradient between sample and solvent phases, thus gradually promoting the mass transfer of carotenoids following the convection mechanism. To increase the extraction yield of polar carotenoids, small volumes of entrainers (called modifier or co-solvents) such as methanol, ethanol, and hexane are often added.

Mezzomo, Martínez, Maraschin, and Ferreira (2013) evaluated the SC-CO_2 extraction of carotenoids from pink-shrimp processing waste, under various conditions of moisture content, solvent flow rate, operating temperature and pressure, with the addition of various co-solvents, including hexane with isopropanol, and sunflower oil at the concentration of 2% and 5%. Increasing the CO_2 flow rate (8.3 g/min to 13.3 g/min) and pressure and dehydration of the raw material increased the carotenoid yield. The highest yield of astaxanthin was obtained at 300 bar pressure and 333.15 K. The use of co-solvents in order to increase the solubility of the extract in SC-CO_2 did not increase the carotenoids yields. Mezzomo et al. assumed that these observations may have resulted because the high lipid content of the pink shrimp can change the extraction selectivity toward the lipids, thus reducing the carotenoids yields. However, using sunflower oil as a co-solvent may have some other potential advantages, as the final product is food oil

enhanced with carotenoids that can be directly used in food products.

During extraction and storage, carotenoid oxidation is accelerated by heat, and oxidation is triggered by the presence of air (oxygen) and light. Armenta and Guerrero-Legarreta (2009) studied the various factors, including illumination, temperature, and oxygen availability, behind the oxidation of natural (carotenoproteins) and free astaxanthin (Carophyll pink) obtained from lactic-acid-fermented shrimp by-products. Since the natural astaxanthin is protected by the protein fraction of the carotenoprotein complex; natural astaxanthin showed an oxidation pattern relatively similar to that of the synthetic astaxanthin. The combination of high light intensity (600 lx), high temperature (45 °C), and oxygen from air caused the highest oxidation of natural and synthetic astaxanthin. Thus, for minimum oxidation of astaxanthin from shrimp products, darkness and nonoxygen conditions at relatively low temperatures (5 °C) were recommended.

4.3. The process of lycopene recovery

Like the extraction of astaxanthin form crustacean-processing waste, various enzymatic pretreatments are applied to tomato processing waste for the efficient extraction of lycopene and other carotenoids. Especially, in tomato peel, lycopene is deeply embedded within the chromoplast membrane structures of thick tomato-peel tissue, which makes it difficult for a solvent to effectively penetrate and solubilize the pigment, resulted in a low extraction yield of lycopene. Additionally, tomato peel is a highly structured material containing many rigid layers of polysaccharide components, such as cellulose, hemicelluloses, and pectins, which hinder efficient extraction of lycopene (Papaioannou & Karabelas, 2012). Enzymes can help degrade the cell walls, thereby allowing efficient extraction of the bioactive compounds. Especially, in the enzymatic pretreatment, cellulase- and pectinase-based extraction of lycopene from whole tomatoes, peel, fruit pulper waste, and industrial waste has been thoroughly investigated by Choudhari and Ananthanarayan (2007). Their results showed that both cellulase and pectinase were effective in increasing the lycopene yield with the optimized parameters of 3% cellulase (w/w) at pH 4.5 (55 °C for 15 min), and 2% pectinase (w/w) at pH 5.0 (60 °C for 20 min). Under optimized conditions, 132 μg/g and 1104 μg/g of lycopene were recovered from whole tomatoes and tomato peel, respectively. For whole tomatoes, peel, and fruit pulper wastes, pectinase was more effective than cellulase. Interestingly, from industrial wastes, cellulase enzymes were more effective than pectinase. Zuorro, Fidaleo, & Lavecchia (2011) developed a second-degree polynomial equation using a central composite design to optimize the pectinolytic (Peclyve PR) and cellulolytic (Cellulyve 50LC) enzyme-assisted extraction of lycopene from tomato-peel processing waste. They optimized the various extraction parameters, such as temperature (10–50 °C), enzyme pretreatment time (0.5–6.5 h), enzyme-to-waste ratio (10–50 dm^3/kg), extraction time (0.5–4.5 h), and enzyme concentration (0–2%, w/w). The optimized conditions of 30 °C extraction temperature, extraction time of 3.18 h, and enzyme load of 1.6% resulted in a lycopene recovery that was 8- to 18-fold higher than that of the untreated plant material. In another enzyme-assisted pretreatment extraction, Papaioannou and Karabelas (2012) studied sequential pectinolytic enzyme pretreatment followed by surfactants-assisted extraction for better recovery of lycopene from tomato peel residues, and obtained a recovery of lycopene ten times higher than that from untreated peels. Among eight surfactants with a broad range of hydrophilic-lipophilic balance that were used, Span 20, Span 40, and Span 60 at the optimum ratio of 6–7 surfactant molecules per lycopene molecule provided the highest (23–25%) recovery of lycopene. In another study, Ranveer et al. (2013) recorded the highest yield of lycopene in tomato peel (417.97 μg/g), followed by industrial waste (195.74 μg/g), whole tomato (83.85 μg/g), and pulp (47.6 μg/g). A mixture of acetone, ethanol, and hexane (2:1:1) produced the highest recovery of lycopene from industrial waste compared with other individual solvents (hexane, ethyl acetate, and petroleum ether). They also observed that pectinase treatment (2%) is more effective for the higher recovery of lycopene from tomato-based products than cellulase is. A smaller particle size also improved the extraction yield of lycopene, whereas cooking (on a low flame and in the microwave) and prolonged enzymatic pretreatment time (> 4 h) caused significant degradation of lycopene.

In a comparative study of carotenoid extraction efficiency from dehydrated tomato waste using various solvents, including ethanol, hexane, ethyl acetate, acetone, and solvent mixtures, the highest yield of total carotenoids (36.5 mg kg^{-1}), composed of 83% lycopene, 13% β-carotene, and 4% lutein, was obtained with a mixture of ethyl acetate-hexane (1:1) (Strati & Oreopoulou, 2011). Interestingly, acetone alone extracted more total carotenoids (33.4 mg kg^{-1}) than did the 1:1 mixture of acetone and hexane (30.5 mg kg^{-1}), suggesting no synergistic effects of the solvents, probably because of the higher penetration of acetone in the dehydrated matrix, compared to that of the acetone-hexane mixture. Similarly, Poojary and Passamonti (2015) investigated the extraction kinetics of lycopene from tomato-processing waste (devoid of seeds, with 60.5 mm particle size and 35% water content) using different ratios (1:3, 2:2 and 3:1, v/v) of acetone/n-hexane at temperatures from 30 to 50 °C. The highest yield of lycopene (3.47–4.03 mg/100 g), which corresponds to a recovery of 65.22–75.75%, was obtained with 1:3 acetone/n-hexane at 30 °C. In addition to the nature of solvent used, the order of solvent addition affects the extraction yield. Phinney, Frelka, Cooperstone, Schwartz, & Heldman (2017) investigated the effects of the solvent type and order on lycopene extraction from a commercial tomato-waste stream (12.5 pH and 5% solids). A constant volume dilution process using membrane filtration was used to reduce the alkalinity of the caustic tomato slurry. Use of acetone and/or ethanol to disrupt cellular structure (step 1), followed by addition of hexane with acetone or hexane with ethanol (step 2) produced the highest extraction yield of lycopene from the neutralized tomato waste stream. In all the samples, extraction using three different solvents (acetone with ethanol and hexane) provided higher extraction efficiency than did other solvent combinations. The results also showed that use of hexane alone in step 2 significantly reduced the lycopene recovery.

As with the astaxanthin, SC-CO_2 has been well studied for the extraction of lycopene from tomato-processing waste. Machmudah et al. (2012) studied the effects of temperature (70–90 °C), pressure (20–40 MPa), particle size (1.05 ± 0.10 mm), and CO_2 flow rate (2–4 mL/min) on the recovery of lycopene and β-carotene from dried tomato-peel by-products (mixture of peel and seed 37:63 w/w). With increasing pressure (at a constant temperature of 90 °C), the recovery of lycopene and β-carotene was improved, probably because of the higher solubility of lycopene in supercritical CO_2 at higher solvent density. The highest recovery of lycopene (56%) was obtained at 90 °C, 40 MPa pressure, and particle size of 1.05 mm. The presence of tomato-seed oil improved the mass transfer and solubility of the lycopene and β-carotene from the matrix into SC-CO_2 more than SC-CO_2 alone did. Moreover, during the extraction, the presence of vegetable oil prevented the degradation of lycopene. Perretti et al. (2013) also optimized the different parameters of SC-CO_2 extraction of lycopene tomato pomace powder. After the SC-CO_2 extraction, they quantified the lycopene in separate fractions (SF) and residual fractions (RF) from the bottom of the column. The regression models and response surface models revealed that SC-CO_2 produced the highest lycopene content in the RF, obtained under the optimized pressure of 30 MPa and a CO_2 flow rate of 15 kg h^{-1}. They further stated that operating pressure plays a significant role in the lycopene extraction, as increasing pressure rationally increases the solvent power of SC-CO_2. In a recent study, Kehili et al. (2017) optimized the various SC-CO_2 parameters to obtain the lycopene and β-carotene enriched oleoresin from a Tunisian industrial tomato-peel by-product. The smaller particle size (≈ 300 μm) resulted in better recovery of oleoresin and lycopene from tomato dried peels than did particles of 1000 μm. The lycopene extraction yield

was positively correlated with temperature ($r = 0.411$), pressure ($r = 0.472$) and CO_2 flow rate, with the highest recovery of 60.85% at 80 °C, 400 bar pressure, and 4 g/min flow rate.

Tomato pomace and other tomato-based by-products have been extensively studied for the recovery of lycopene (in some cases, lycopene with β-carotene). However, few reports are available for the recovery of other carotenoids such as lutein, α-carotene, and β-carotene from carrot peel or β-cryptoxanthin and apocarotenoid from citrus feel (de Andrade Lima, Charalampopoulos, & Chatzifragkou, 2018; Ravindran & Jaiswal, 2016). Carrot is rich in α-carotene and β-carotene, representing about 60% and 30% of total carotenoids, respectively, with a minor presence of lycopene and lutein. Interestingly, 60% of these carotenoids are accumulated in the peel, highlighting the potential of peel by-products for the recovery of carotenoids. de Andrade Lima, Charalampopoulos, and Chatzifragkou (2018) have achieved 97% recovery of carrot peel carotenoids employing SC-CO_2 extraction at temperature of 59.0 °C, pressure of 349 bar, 15.5% ethanol, and 30 min of extraction time.

Ultrasound-assisted extraction (UAE) also has been successfully employed for the improved extraction of lycopene from tomato pomace. Effects of high power ultrasound (> 20 kHz) on target compounds are attributed to acoustic cavitation that consists formation (nucleation), rapid growth (expansion), and collapse of micro-bubbles in liquid under high-frequency sound waves (Tzanakis, Lebon, Eskin, & Pericleous, 2017). This collapse is accompanied by localized extreme pressures and temperatures, high shear stress near the bubble wall, and high-speed jets (300–1000 m/s) due to asymmetric collapse of cavitational micro-bubbles and turbulence. These mechanical effects of ultrasound efficiently can disrupt complex plant cellular tissues and enhance penetration of solvent into cellular materials, thus efficiently facilitating the release of target compounds (Luengo, Condón-Abanto, Condón, Álvarez, & Raso, 2014). They obtained the highest yield of carotenoids by applying a vibration amplitude of 94 μm and an external pressure of 50 kPa. The higher vibration amplitudes probably increased the effective size of the zone of the liquid and the range of bubble size undergoing cavitation, thus improving the extraction yield (Luengo, Condón-Abanto, Condón, Álvarez, & Raso, 2014).

Strati, Gogou, & Oreopoulou (2015) studied the extraction assisted by enzyme and high pressure (HP) of carotenoids from tomato waste using various polar and nonpolar solvents, including ethanol, hexane, ethyl acetate, hexane-ethyl acetate, acetone, and ethyl lactate. They obtained a 6-fold and 10-fold higher yield of total carotenoid and lycopene, respectively in enzyme-treated samples (pectinase and cellulase at concentrations of 70 U/g and 122.5 U/g, respectively), extracted with ethyl lactate, over that from nontreated enzyme samples. Also, HP-assisted extraction (700 MPa) led to a 2 to 64% increase in carotenoids yield at a reduced volume of solvent and extraction time. HP processing helps break down the structural integrity of cell walls by cell deformation, cell membrane damage, and disruption of chromoplast, thus increasing the cell permeability, which results in improved extraction of metabolites. Additionally, HP deprotonates (removal of H^+) charged groups and disrupts salt bridges and hydrophobic interactions, which helps diminish the selective permeability of cellular membranes, thereby rendering the secondary metabolites more accessible to extraction (Strati, Gogou, & Oreopoulou, 2015).

Combined and integrated pretreatment have shown a synergetic effect to obtain an improved yield of lycopene. For instance, Amiri-Rigi and Abbasi (2016) obtained a six times higher yield of lycopene (409.68 μg/g) from dehydrated tomato pomace by combined ultrasound, pectinolytic, and cellulolytic enzyme pretreatments, saponin as a natural surfactant, and glycerol as a co-surfactant. They projected that surfactant molecule can lower the surface tension efficiently, converting hydrophobic molecules into polar ones, thus forming the microemulsion and increasing the extraction yield, while the co-surfactants play a vital role in the stabilization of microemulsions by lowering the interfacial tension between immiscible fluids. The presence of more hydroxyl groups (three in the case of glycerol) of the cosurfactants was beneficial for the improved extraction of lycopene, possibly by increasing hydrogen bonding with the aqueous phase. Also, the ultrasonic pretreatment promotes cavitation, which contribute significantly toward the breakdown of plant cell walls, leading to improved mass transfer of lycopene into the microemulsion. They summarized that microemulsion, using low-cost naturally available surfactants, could be promising for a safe and higher recovery of lycopene from tomato pomace.

In the above-discussed study, under optimized conditions, the combined use of surfactants, co-surfactants, enzymatic and ultrasound treatments have improved the yield of lycopene, with a lycopene recovery of 35%, higher than that from hexane:acetone:ethanol (2:1:1 v/v/v) extraction. Thus, although this methodology is novel in terms of green extraction, these methods need to be investigated further to obtain the higher recoveries.

In further experiments, surfactant (saponin):lycopene ratio of 20:1, surfactant:co-surfactant (glycerol) ratio of 1:1, and particle size of 400–595 μm was optimal for the highest recovery of lycopene from tomato industrial waste (Amiri-Rigi, Abbasi, & Scanlon, 2016). Additionally, ultrasound pretreatment (50 W for 30 s) and enzymatic pretreatment with pectinase at 45 °C for 60 min (pH of 4.5) showed the highest (39%) extraction efficiency.

Carotenoids are usually extracted as oleoresin (Kehili et al., 2017). They are directly used in food and other formulations without complete purification. Moreover, carotenoids extracted from dietary sources are devoid of toxic substances. Thus, complete purification steps are unnecessary. Lycopene oleoresin from tomatoes is approved as food coloring agent (E160d) by European Food Safety Authority (EFSA). The Panel of EFSA considers that lycopene oleoresin from tomatoes is safe for consumption (European Food Safety Authority, 2008). Similarly, several commercial products containing 5–10% astaxanthin from various sources are available in the market (Ambati et al., 2014).

5. Microencapsulation of astaxanthin and lycopene

Owing to several conjugated double bonds, carotenoids are highly susceptible to light, heat, oxygen, acid, and transition metals mediated isomerization and oxidation that can lead to significant loss of their biological activity. Among several approaches used to protect carotenoids, encapsulation is one of the prominent methods principally used in food processing industries (Janiszewska-Turak, 2017). Microencapsulation is a process of physically isolating bioactive molecules from environmental conditions using semipermeable membrane wall materials. Among several microencapsulation techniques, spray drying and SC-fluid micronization are widely used for carotenoids (Janiszewska-Turak, 2017). Microencapsulation by spray drying (syn. encapsulation) is the oldest and most widely used method. For spray drying, gum arabic, maltodextrin, gelatin, sucrose, trehalose, and whey protein isolate have been successfully utilized for efficient encapsulation of carotenoids (Janiszewska-Turak, 2017). Rocha, Fávaro-Trindade, & Grosso (2012) have obtained 29% efficiency of lycopene microencapsulation by spray drying using modified starch (Capsul®) as encapsulating agent. Retention rates of free and encapsulated lycopene during 73 days of storage at 10 °C were found to be 63.7 and 82.5%, respectively, presenting excellent storage stability for use in foods.

Bustos-Garza, Yáñez-Fernández, & Barragán-Huerta (2013) have studied thermal and pH stability of astaxanthin oleoresin encapsulated by spray drying using gum arabic and whey protein alone or in combination with maltodextrin or inulin. Their results showed that selection of the carrier material was the most critical task. With the use of 100% whey protein, astaxanthin oleoresin showed the highest color and antioxidant stability. Gomez-Estaca, Comunian, Montero, Ferro-Furtado, & Favaro-Trindade (2016) have utilized cashew gum with gelatin to obtain the high encapsulating efficiency (59.9%), stability, and coloration capacity of astaxanthin oleoresin from shrimp waste. An

accelerated stability study (43 days at 36 °C) revealed significant improvement in astaxanthin stability as a result of encapsulation. Moreover, microcapsules showed significant water solubility of 28.6%, dispersing well in plain yogurt with adequate coloring capacity.

6. Applications and marketing potential of astaxanthin and lycopene

In recent years, the increasing demand for health-promoting nutraceuticals has witnessed an exponential growth, especially for carotenoids such as astaxanthin and lycopene, because of their versatile use in the feed, food, cosmetic, and pharmaceutical industries. In the year 2014, the global carotenoid market was valued at $1.5 billion, which is growing with a compound annual growth rate (CAGR) of 3.9% (BBC Research, 2015). In market value, this market is primarily dominated by astaxanthin (24%), followed by capsaxanthin (21%), lutein (16%), β-carotene (14%), annatto (10%) and lycopene (7%). Nearly 76% of this market is for synthetic carotenoids from the chemical industries. Animal feed was the most prominent sector, accounting for 41% of the overall revenue share, followed by food, dietary supplements, pharmaceuticals, and cosmetics. Synthetic astaxanthin, astaxanthin rich *Phaffia rhodozyma* yeast, and red carotenoid-rich bacterium *Paracoccus carotinifaciens* are predominantly used in the aquaculture feedstuffs, and the astaxanthin derived from *H. pluvialis* microalgae is the key source for applications in dietary supplements, cosmetics, food, and beverages (Industry experts, 2015).

6.1. Applications in food, cosmetic, and pharmaceutical industries

Reactive oxygen species (ROS), including singlet oxygen ($^1\Delta_g$), superoxide ($^{\bullet}O_2^-$), and hydroxyl radical ($^{\bullet}OH$), play a pivotal role in the development of cardiovascular diseases (CVD). Lycopene and astaxanthin are the most potent ROS scavengers among carotenoids and other well-known dietary antioxidants, including, α-tocopherol and ascorbic acid (Visioli & Artaria, 2017). Astaxanthin and lycopene are potent inhibitors of ROS-induced lipid peroxidation, lipopolysaccharide (LPS)-induced superoxide production, peroxide-induced cytotoxicity, and low-density lipoprotein (LDL) oxidation (Kim et al., 2011; Visioli & Artaria, 2017). Apart from the potent antioxidant activities, the anti-inflammatory and immunomodulatory activities of these carotenoids have received significant attention for their potential role in preventing oxidative stress, cancer, and CVD (Kim et al., 2011).

The results of in vivo clinical trials have shown that lycopene can potentially inhibit tumor metastasis by promoting E-cadherin and β-catenin immune expression, decreasing the proliferating cell nuclear antigen (PCNA), matrix metalloproteinase (MMP), and insulin-like growth factor-1 (IGF−I), thereby slowing down cell-cycle progression (Viuda-Martos et al., 2014). Also, lycopene can potentially inhibit the proliferation of diverse cancer cell lines originating from the human colon, lymphocyte, breast, prostate, and hepatoma (Viuda-Martos et al., 2014). The consumption of 15 mg of lycopene/day for 8 weeks is potentially beneficial for reducing oxidative stress by improving endothelial function, thereby preventing early atherosclerosis, increased LDL particle size, decreased blood pressure, and lipid peroxidation (Kim et al., 2011). Lycopene consumption has also shown beneficial effects in preventing the oxidative DNA damage of leukocyte and prostate tissue, modulation of cardiorenal and inflammatory markers, increased gap junctional intercellular communication (upregulating gap junction protein, connexin 43), protecting from Type 2 diabetes by improving the glucose metabolism, and improving bone health by reducing bone resorption (Thies, Mills, Moir, & Masson, 2017; Viuda-Martos et al., 2014).

As with lycopene, astaxanthin also modulates the immune response, inhibits cancer proliferation, and decreases oxidative DNA damage (Park, Chyun, Kim, Line, & Chew, 2010). Apart from that, treatment with topical or oral administration of astaxanthin can prevent UVA-associated photoaging, such as skin sagging or wrinkling, by down-regulating MMP-1, which is responsible for the degradation of dermal components, elastin, and collagen, thus causing wrinkling and sagging (Suganuma, Nakajima, Ohtsuki, & Imokawa, 2010). Thus, because of its strong antioxidant and anti-aging functions, astaxanthin can be used as a functional ingredient in cosmetics.

Considering the potent health benefits of astaxanthin, various astaxanthin-based commercial products for improved antioxidant activity, vision, cardiovascular, gastrointestinal, bone health, skin health (anti-aging), and stamina (sports nutrition) are available in the market (Ambati et al., 2014). Similarly, various astaxanthin-based formulations, useful for protection against vascular failure, cancer, and CVD, inhibiting lipid peroxidation, cell damage, body fat, joint pain, and osteoporosis, and improving neuroprotection, brain function, and skin thickness, have been patented (Ambati et al., 2014). In the food industry, lycopene is widely used as natural food colorants; moreover, their nutritional and health benefits make them very appropriate for applications in functional foods (Viuda-Martos et al., 2014).

In addition to carotenoids, several other nutritionally and commercially important phytochemicals such as polyphenols, pectin, and dietary fiber can be simultaneously or sequentially extracted from agro-food by-products. Polyphenols extracted from olive mill wastewater have shown potent antioxidant activities (Galanakis, Tsatalas, Charalambous, & Galanakis, 2018b), antimicrobial activities (Galanakis, Tsatalas, Charalambous, & Galanakis, 2018a), and UV-protection (UV filters) abilities (Galanakis, Tsatalas, & Galanakis, 2018a, 2018b). Thus, integrated approach targeting several compounds during valorization can effectively utilize resources with significantly lower cost of production.

6.2. Applications in aquaculture feedstuffs

In recent years, keeping marine and freshwater crustaceans and fishes in aquaria has become a popular and growing trend. Striking red-orange coloration is the key marketing factor for many of these ornamental animals. In nature, fish and crustaceans accumulate the necessary carotenoids, including astaxanthin, via the food chain (microalgae). However, this is not possible for captive animals, and a deficiency of carotenoids in the body can lead to skin discoloration. Thus, carotenoids are supplied as dietary supplements to restore the coloration of various commercially important crustaceans and fish. The red pigmentation to the flesh (e.g., salmon), skin (e.g., sea bass), or exoskeleton (e.g., crustaceans) also acts as a quality and nutritional attribute (Auerswald & Gäde, 2008). The Council Directive of the EU has allowed the used of purified astaxanthin (EC No. E 161j) and astaxanthin-rich Phaffia rhodozyma (ATCC 74219) as an additive for the feed of salmon and trout (Directive, 2004). However, use is permitted only from the age of six months onwards, with the maximum total concentration of the astaxanthin not exceeding 100 mg kg^{-1} in the feed. Gouveia and Rema (2005) found that the source and concentration of carotenoids play a significant role in skin pigmentation and carotenoids accumulation in goldfish (*Carassius auratus*). Their results showed that natural astaxanthin from microalgae, *Chlorella vulgaris,* were more beneficial for improved skin pigmentation and carotenoids accumulation than was synthetic astaxanthin. Interestingly, differences in use of alternative forms of astaxanthin (such as esterified and non-esterified) in various species have also been studied. Yi et al. (2015) found that esterified astaxanthin is more efficient than the nonesterified synthetic astaxanthin for the skin pigmentation of the large yellow croaker (*Larimichthys croceus*) and sea bream (*Pagrus major*) fish. However, for rainbow trout and Atlantic salmon, esterified astaxanthin was less efficient than free astaxanthin for flesh pigmentation. It was fascinating to notice that in salmon, carotenoids are found in the non-esterified forms, whereas the carotenoids in fish skin, such as sea bream, are found in the esterified form. They assumed that these observations probably arose because of the species-specific differences in

the carotenoid metabolism and enzyme selectivity toward esterified and nonesterified forms. In addition to the skin pigmentation, astaxanthin is potentially beneficial for the health and reproduction of aquatic animals, including potent antioxidant activity and formation of in-chain epoxides that act as oxygen reserves under anoxic condition; it also induces provitamin A activity, improves immune response, embryonic and larval development, maturation, and photoprotection (Auerswald & Gäde, 2008; Yi et al., 2015). Considering the wide functional role and applications of astaxanthin, aquatic feed is the most prominent sector that accounts for the major revenue generated by astaxanthin. The market for astaxanthin and other carotenoids is growing; thus, in the future, research on carotenoid sources and extraction will most likely expand into other dimensions.

7. Future challenges and conclusion

We conclude that tomato pomace and crustacean processing waste present unlimited opportunities for the extraction of commercially vital carotenoids, which have diverse application in the food, feed, pharmaceuticals and cosmetic industries. Most methods for the extraction of carotenoids use solvents that are hazardous for the environment and human health. In recent years, several green extraction methods, using SC-CO_2, ethanol, ionic liquids, vegetable oil, and surfactants, have been investigated for the efficient extraction of carotenoids. The use of these green retraction solvents with effective pretreatments, such as drying, cooking, milling, and ultrasound presentments, has proven to provide cost-effective ways to further improve the extraction yield. Moreover, carotenoids extracted with vegetable oil can be used directly in food products. SC-CO_2 extraction, on the other hand, has several advantages over the conventional techniques, in relation to extract quality (organic production), high purity and yield, and low use of toxic solvents, and could be used instead of organic solvent-based methods. Kinetic studies have established optimal values of pressure, temperature, CO_2 flow rate, extraction time, and moisture content of raw materials, and the addition of co-solvents plays a significant role in the extraction of carotenoids using SC-CO_2. Thus, to obtain the highest yields of carotenoids, these process parameters needed to be thoroughly investigated with a diverse range of samples.

To date, there is no extraction method that is more economically viable than the synthetic production of lycopene and astaxanthin. Thus, natural astaxanthin cannot compete with synthetic ones, at least as a fish-feed additive for pigmentation. Considering the health issues associated with synthetic carotenoids, natural carotenoids are attractive for commercial applications in food and pharmaceuticals. In the future, efforts can be made to reduce the cost of producing carotenoids to improve the economic feasibility for commercial large-scale production process.

The esterified astaxanthin is more efficient than the nonesterified synthetic astaxanthin for the skin pigmentation of ornamental fish, probably because of the higher bioavailability, bioaccessibility, and stability of esterified forms. However, only a few studies are available in this regard. Also, the comparative efficiency of mono- or di-esters of astaxanthin bound with different fatty acids is not well known. Thus, the biological activities of natural mono- and di-esters of astaxanthin can be studied in detail, with the help of in vitro and in vivo models.

Animal feed is the most prominent sector of the applications of astaxanthin; however, its potential application in the food, dietary supplements, pharmaceuticals, and cosmetics sectors is still not achieved. Especially, lycopene use as a food colorant can be explored to replace the synthetic chemicals. Additionally, its applications in food products can significantly improve their shelf life and nutritional and functional properties.

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Conflict of interest

The authors have declared that there is no conflict of interest.

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