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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