FLSEVIER

Review article

Contents lists available at ScienceDirect

Algal Research



journal homepage: www.elsevier.com/locate/algal

Microalgal carotenoids: A promising alternative to synthetic dyes

Fatma Zohra Benbelkhir^{a,*}, Samir Medjekal^b

^a Laboratory of Biology: Application in Health and Environment, Department of Biochemistry and Microbiology, Faculty of Sciences, Med-Boudiaf University of M'sila, Po. Box 166, 28000 M'sila, Algeria

^b Department of Biochemistry and Microbiology, Faculty of Sciences, Med-Boudiaf University of M'sila, Po. Box 166, 28000 M'sila, Algeria

ARTICLE INFO	A B S T R A C T
Keywords: Dyes Pigments Microalgae Carotenoids Production	Natural dyes and pigments (vegetal, animal and microbial) are safer than synthetic dyes which have a polluting and harmful impact on the environment. Among natural microbial sources of pigments, microalgae are widely exploited for the production of phycobiliproteins, chlorophylls but especially carotenoids which have also health benefits. Production process of carotenoids from microalgae includes the steps of: biomass production and harvesting, extraction, saponification, separation and conservation. In this review the whole processes will be reviewed with special interest on different extraction steps and technics aiming to give a summarized overview of how carotenoids are produced from microalgae. Furthermore, improvements in cultivation and extraction sys- tems, as well as carotenoid storage methods, are required for an economical, reproducible and ecofriendly large scale applications.

1. Introduction

Dyes and pigments are color additive substances soluble in the medium where they will fix it, they are used in food, pharmaceutical, cosmetic, textile and paint fields to give or change a color. The major difference between dye and pigment lies in physical and chemical properties of which they influence light-substance interaction that defines the color [1].

Dyes are of two types: synthetic based on petroleum products and natural based on natural products. The first type is known by its toxic and harmful effect on human health and ecosystem equilibrium, while the second type is derived from plants, invertebrates, minerals and microorganisms [2–4]. However, microbial pigments are characterized by their stability, availability and productivity in a short time compared to other natural sources [5,6].

Among microbial pigments, those derived from microalgae specifically carotenoids have been gaining importance in recent years for applications in food and nutrition industry as coloring additives or vitamins, but also in the pharmaceutical and cosmetic industry due to antioxidant, anti-inflammatory and antimicrobial activities [7–11]. These carotenoids are obtained after a multitude of steps passing by a culture of microalgae (open pond systems or photobioreactors), harvesting and extraction by different physical and chemical methods reaching finally the separation and conservation [12–19].

Several publications have appeared in recent years documenting toxicity and health hazards associated with the use of synthetic dyes as well as their polluting environmental impact that requires effluent treatment and bioremediation [4,20–22]. To solve this issue, natural choices are exploited to ensure the safety of used dyes especially in the food sector [23–25]. In this context, most previous works have dealt with plant pigments, while microalgal pigments have been less addressed with a focus on chlorophylls and phycobiliproteins more than carotenoids [26]. That's why this review aims to highlight microalgal carotenoids as an alternative to synthetic dyes, giving an overview of their manufacturing procedure and trends of used technologies.

The review will be divided into three main sections, the first serves as an overview of dyes and pigments from a chemical standpoint, while the second will give a summary of all natural sources of dyes and pigments involving plants, animals, microorganisms (bacteria, fungi and microalgae) which is not provided by other reviews where each type is treated alone or in a brief manner and not together in the same article (see examples of reviews [27–29]). This section will focus on microalgal carotenoids whose view is generalized regarding their use for coloring and not specified to the food field as in most literature. The third section will cover production steps of carotenoids from microalgae (biomass production, harvesting, extraction, saponification, separation, storage and conservation) with details on the extraction step and techniques.

* Corresponding author. *E-mail address:* fatma.benbelkhir@univ-msila.dz (F.Z. Benbelkhir).

https://doi.org/10.1016/j.algal.2022.102823

Received 17 May 2022; Received in revised form 26 July 2022; Accepted 11 August 2022 2211-9264/© 2022 Elsevier B.V. All rights reserved.

2. Overview of dyes and pigments

2.1. Brief background

As a chemical compound used to give or change the color of all sorts of substances, dyes and pigments are widely involved in pharmaceutical, cosmetic, plastic, textile, paint, ink, photography, paper and food industries where pigments are preferred than dyes. They are very diverse in terms of structure, synthesis and applications [1,2].

Internationally, the simplified and most accepted definitions of dyes

and pigments are those given by Towns [30] where dye is a colorant that is in solution during some or all stages of its application to a substrate, while pigment is a colorant that is not in solution at any point during its application to a substrate and whose particle structure remains unaltered throughout. In this definition colorant means a substance used to impart color to another material, while the term substrate refers to the object in which the colorant is incorporated or onto which colorant containing medium is coated [30]. In the same defining context, synthetic and natural dyes are different, synthetic means any kind of product made from chemicals or artificial substances which are in this

Algal Research 66 (2022) 102823



Fig. 1. Classification of dyes and pigments [40].

case petroleum products, while natural dyes are those obtained from natural animal, plant and microbial materials without transformation [2,31].

The history of discovery and use of dyes and pigments is very old, of which researchers think that it was born since Neolithic period 4000 to 9000 years ago. Indeed, techniques and processes used have often remained well-kept secrets [32,33]. In 1856 at the Royal College of Chemistry in London, William Harry Perink could isolated Mallow, the first synthetic dye commercially made and used [34,35]. Successful applications of Perkin and others have directed interest in the production of synthetic dyes which now represents the vast majority of the world's chemical industries [36].

2.2. Difference between dyes and pigments

Although dyes and pigments share the same character of coloration, dyes are soluble in medium and therefore disperse at molecular level during the process of application giving a brighter color by selective absorption of light, while pigments disperse in form of organic or inorganic particles insoluble in medium that modify appearance either by selective absorption and or by scattering of light, they are more stable to heat and resistant to solvents compared to dyes. On the other hand and taking into consideration that it is the result of interaction between light and substance, the color depends strongly on physicochemical properties of this substance; if the latter is a dye, color in this case is defined exclusively by its chemical structure, but if it is a pigment the color depends on the physical characteristics of particles [1,37,38].

2.3. Classification

Mainly, dyes are of two types natural and synthetic. As mentioned before synthetic dyes are based on petroleum products. In contrast, natural dyes are of plant, animal, microbial or mineral origin. They are the most preferred because of their bright nature, soothing and less toxicity [2].

Dyes and pigments can also be classified according to application method, solubility, color, type of fiber (nylon, cotton, polyester...), or according to the electronic origin of color such as acceptor-donor chromogens, cyanic type chromogens and polyene chromogens. However, classification based on chemical structure is the most appropriate because it gives a manageable number of groups and facilitates identification of dyes or pigments belonging to the same group [39,40]. Fig. 1 illustrate the classification of dyes and pigments.

3. Natural sources of dyes and pigments

Synthetic dyes have harmful effects on human health and the environment, especially aquatic environments. Indeed, their toxic, mutagenic and carcinogenic properties cause an imbalance of aquatic ecosystems specifically marine. This imbalance affects diversity, growth and existence of different species which necessitates a treatment of liquid effluents from washing textiles before releasing them to the external environment [3,41,42]. Therefore, the focus of the review will be on dyes of natural origin especially from microalgae which are biodegradable and possess biological activities beneficial for health [43–47].

3.1. Terrestrial plants

Most natural dyes and pigments are of vegetal origin, extracted from different parts of plants (roots, nuts, seeds, flowers, leaves, bark and wood). Red color, for example, can be produced from alkanetes (*Alkanna tinctoria*), bugloss, asafoetida and madder (*Rubia tinctoria*); yellow can also be produced from saffron, pomegranate bark, turmeric, and carthame. The blue color is derived from indigo dye plants mainly *Indigo* genus [48,49]. Other plant species are mentioned in Table 1 and shown

Table 1

Some extracted	dyes from	various	parts of plant	species	[50,51]
----------------	-----------	---------	----------------	---------	---------

Plant species	Part used	Color obtained
Mahonia napaulensis	Stem	Yellow
Salvia splendens	Flower	Red
Canna indica	Flower	Red
Cosmos sulphureus	Flower	Mustard color
Delonix regia	Flower	Olive green
Nymphaea alba	Rhizomes	Blue
Rumex maritimus	Seeds	Brown

in Fig. 2.

3.2. Animals

Although the earliest animal pigment was derived from marine mollusk secretions of *Murex* genus, most animal dyes and pigments are extracted from insects (Fig. 3). The protective resinous secretion of Lac insect gives a purple color, and *Dactylopius coccus* species produces a crimson, scarlet, and pink color. Other dyes are produced such as carmine (*Porphyrophora hamelii*) and cochineal (*Dactylopius coccus, Porphyrophora polonica*), as well as pigments such as chlorocruorin, haemocyanin and melanin. Moreover, there is another green pigment in the hemolymph of *Pieris rapae, Cacoecia australana* and *Amphipyra sanguinpuncta* larvae [48,50,52–56].

3.3. Microorganisms

Microbial origin pigments (fungi, bacteria and microalgae) present some more remarkable advantages than those of animal and plant origin, which are sensitive to light, unavailable and poorly soluble [57–59]. Indeed, microbial pigments are highly stable, available, characterized by a high rate of productivity in a short time with a lower cost. The current literatures aim to study their different synthetic pathways in order to exploit them in various fields. These pigments also have promising antimicrobial, antitumor, antioxidant and anti-inflammatory activities [6,60–62]. In this section the focus will be on microalgal pigments specifically carotenoids because of their wide implication in food, cosmetic and pharmaceutical fields.

3.3.1. Microscopic fungi

Microscopic fungi contain highly light stable pigments, they are known by the production of melanins, anthraquinones, hydroxyanthraquinones, azophilons, carotenoids, axapolyene, quinones and naphtoquinones. Arpink red produced by *Penicillium oxalicum var armenia* CCM8242 was the first fungal pigment produced. The majority of fungal pigments are polyketides or derivatives of polyketides synthesized most often by ascomycetes (genus *Neurospora*) in addition to other pigments of terpenoid and polyphenol classes [6,63,64]. Table 2 shows some fungal pigments.

3.3.2. Bacteria

With their ubiquitous property and high genetic diversity, bacteria and specifically marine bacteria have become an attractive source of new biomolecules including pigments. Marine ecosystems remain unexploited for their microbial diversity which reflects the metabolic diversity, and among the microorganisms inhabiting these ecosystems actinobacteria and myxobacteria are important sources of new compounds. A variety of pigments such as prodigiosin (red), riboflavin (yellow), indigoidin (blue), violacin (purple) and pyocyanin (greenish blue) are of bacterial origin (Table 3), those that are hydrosoluble and others that are liposoluble [62,70–73].

3.3.3. Microalgae

Whether prokaryotic or eukaryotic, microalgae constitute a promising and fascinating alternative source of natural pigments which are



Fig. 2. Some plant species used for dye production, a: Delonix regia; b: Mahonia napaulensis; c: Canna indica; d: Rumex maritimus.



Fig. 3. Insect species used for dye production, a: Dactylopius coccus; b: Pieris rapae; c: Porphyrophora hamelii.

Table 2	
Pigments from microscopic fu	ngal species.

Fungal species	Pigment	Pigment color	Reference
Rhodotorula sp. (yeast)	Torularhodin	Orange-red	[5]
Candida famata (yeast)	Riboflavin	Yellow	[5]
Trypethelium eluteriae	Trypethelon	Violet-red	[65]
Penicillium purpurogenum	N- glutarylmonascorubramine	Purple-red	[66]
Fusarium culmorum	Aurofusarin	Red	[67]
Emericella purpurea	Epurpurin A	Greenish- yellow	[68]
Aspergillus fumigatus	Melanin	Dark-brown	[69]

Table 3

Pigments from bacterial species.

Bacterial species	Pigment	Pigment color	Reference
Zooshikella ganghwensis gen. nov., sp. nov.	Prodigiosin	Red	[74]
Nocardiopsis dassonvillei sp. strain JN1	Melanin	Brown	[75]
Corynebacterium glutamicum sp.	Astaxanthin	Red	[76]
Aquibacter zeaxanthinifaciens gen. nov., sp. nov.	Zeaxanthin	Yellow	[77]
Cyanobacterium synechococcus sp.	Beta carotene	Orange- yellow	[78]
Pseudoalteromonas luteoviolacea sp. Streptomyces sp.	Violacein Melanin	Purple Brown	[79] [72]

essential for their photosynthetic metabolism [80]. This alternative is cheaper and efficient with a high growth rate [5]. Microalgal chlorophylls, phycobiliproteins and carotenoids have recently gained great commercial interest for food and cosmetic applications, as well as pharmaceutical interest due to antioxidant, anticancer, antiinflammatory, antiobesity and neuroprotective activities [9,81–83].

The species *Spirulina* sp. and *Chlorella* sp. are mainly used in food industry as a source of proteins, lipids, vitamins and minerals; but also for production of pigments such as phycobiliproteins and carotenoids (Table 4; Fig. 4). Furthermore, *Dunaliella salina* and *Haematococcus pluvialis* are exploited for the production of β -carotene (precursor of

Table 4	
Microalgae derived pigments and their production status	[60].

Microalgae	Pigment	Pigment color	Status
Haematococcus pluvialis (company AstaReal among many others)	Astaxanthin	Pink-red	Industrial production
Dunaliella salina (company Henkel-cognis Australia)	β-Carotene	Yellow- orange	Industrial production
Many species	Chlorophylls	Green	Development stage
Chlorella and many others	Lutein	Yellow	Industrial production
Arthrospira sp. (formerly Spirulina sp.) and other microalgae and cyanobacteria	Phycocyanin	Blue	Industrial production
Porphyridium and many other cyanobacteria and microalgae	Phycoerythrin	Red	Development stage

Vitamin A) and astaxanthin (powerful antioxidant) [84,85].

Silva et al. [8] summarize the information concerning chlorophylls synthesized by *Chlorella vulgaris*, phycocyanins by *Spirulina platensis*, β -carotene by *Dunaliella salina* and astaxanthin by *Haematococcus pluvialis* [8]. On the other hand, other recent research results show a profile of chlorophylls, violaxanthin, vancheriaxanthin diester and β -carotene pigments in Eustigmatophyceae [44].

3.3.3.1. Microalgal carotenoids. Carotenoids are isoprenoid molecules, light absorbing, liposoluble belonging to tetraterpenes class. Their polyene chain with conjugated double bonds gives them the ability to extinguish excess light and free electrons, thus preventing oxidative damage of photosystems which result from solarization (photo-oxidation). According to the presence or absence of oxygen in aromatic ring attached to chains, carotenoids are classified into two groups: carotenes without oxygen (α -carotene, β -carotene and lycopene) and xanthophylls with oxygen (astaxanthin, zeaxanthin, antheraxanthin, lutein) [7,86]. Biosynthetic pathway of carotenoids in microalgae involves several key enzymes that have a role of transformation of resulting precursors from one form to another giving different subclasses of carotenoids [15]. Chemical structures and biosynthetic pathway of carotenoids are shown in Figs. 5 and 6 respectively.

Several researches are done for studying carotenoid production by microalgae [81,84,87–91]. The species *Synechococcus* sp. PCC7002,



Fig. 4. Some species of pigment producing microalgae, a: Chlorella vulgaris; b: Haematococcus pluvialis; c: Spirulina platensis.



Fig. 5. Chemical structure of different carotenoid subclasses.

Synechocystis sp. PCC6803 and *Rhodosorus* sp. proved the production of zeaxanthin [92]. However, other researchers were able to isolate this pigment from the halophilic species *Dunaliella salina* [87]. Table 5 shows the content and productivity of carotenoids in some microalgae species.

This compounds are not only used for coloring, but they have also an antioxidant, anti-inflammatory, neuroprotective power as well as improvement of cardiac dysfunction and macular degeneration related to age [15,87,92–95].



Fig. 6. Biosynthetic pathway of carotenoids in microalgae, MEP: methylerythritol phosphate; IPP: isopentenyl pyrophosphate; DMAPP: dimethylallyl diphosphate; GPPS: geranyl diphosphate synthase; GGPPS: geranyl diphosphate synthase; GGPPS: geranyl gyrophosphate; PSY: phytoene synthase; *Z*-ISO: ζ-carotene isomerase; ZDS: ζ-carotene desaturase; CrtISO: carotene isomerase; LCYE: lycopene epsilon cyclase; CYP97A: cytochrome P450 beta hydroxylase; CYP97C: cytochrome P450 epsilon hydroxylase; LCYB: lycopene β-cyclase; BKT: β-carotene ketolase; CHYB: β-carotene hydroxylas [15].

Table 5	
Carotenoid content and productivity in certain species of microalgae.	

Microalgal species	Carotenoid	Content in dry weight mg/g	Productivity mg/L/day	Reference
Chromochloris zofingiensis bkt1 (mutant)	Zeaxanthin	7.00	$\begin{array}{c} \textbf{36.79} \pm \\ \textbf{3.23} \end{array}$	[91]
Chromochloris zofingiensis	Astaxanthin	2.88	9.9	[107]
Dunaliella bardawil UTEX 2538 (=Dunaliella salina)	β-Carotene	-	2.2	[108]
Mallomonas sp.	Zeaxanthin	26.6	-	[90]
Chromochloris zofingiensis	Lutein	4.0	-	[109]
^a Dunaliella salina zea1 (mutant)	Zeaxanthin	5.9	-	[110]
^a Tetraselmis sp. CTP4	β-Carotene	4.41	_	[111]
^a Tisochrysis lutea	Fucoxanthin	16.39	9.81	[112]
^a Chlorella ellipsoidea	Zeaxanthin	4.26	-	[113]
^a Phaeodactylum tricornutum	Fucoxanthin	16.33	-	[114]
^a Isochrysis zhanjiangensis	Zeaxanthin	23.29	2.94	[115]
^a Odontella aurita	Zeaxanthin	18.47	7.96	[116]

^a Marin species.

On another side, the comparative study of Lin et al. [96] shows that production rate of microalgae is 3–6 times higher than marigold flowers a common source of lutein. The species of *Chlorella fusca*, *Chlorococcum citroforme*, *Neospondiococcum gelatinosum*, *Tetracystis aplanosporum*, and *Tetracystis tetrasporum* have all a lutein content higher than 4 g/kg biomass [96].

The recovery rate of astaxanthin in Haematococcus pluvialis can reach 70 % and 95.08 \pm 3.02 % as well as its productivity can get to 357 mg/L

after culture in double-layered photobioreactor [97–99]. Another fedbatch strategy also improved astaxanthin productivity to 2.0 mg/L/ d without compromising biomass of *Chromochloris zofingiensis* [100]. Rodrigues et al. [17] valorized agroindustrial waste for *Phormidium autumnale* cultivation, their carotenoid profile results showed a content of β -carotene (70.22 µg/g), zeaxanthin (26.25 µg/g), lutein (21.92 µg/ g), trans-echinenone (19.87 µg/g) and cis-echinenone (15.70 µg/g) [17]. Furthermore, the enhancement of β -carotene productivity by genetic engineering in *Scenedesmus* sp. CPC2 gave a content of 31.8 mg/g [101].

Jeon et al. [102] found that culturing *Chlorella vulgaris* in medium with presence of magnesium sulfate, EDTA-2Na, and trace metal solution increased lutein production from 139.64 \pm 12.88 mg/L to 252.75 \pm 12.92 mg/L [102]. However, the use of light-related strategies improved productivity to 4.08 mg/L/d in *Scenedesmus obliquus* FSP-3 [103]. Another study by Shi et al. [104] shows lutein productivity between 68.42 and 83.81 mg/L under the heterotrophic culture of *Chlorella protothecoides* [104]. Some other microalgae have a fucoxanthin content of 18.23 mg/g which is 15 times higher than that of macroalgae [105,106].

4. How carotenoids are obtained from microalgae?

Production of carotenoids from microalgae requires a series of steps that are carried out by multiple physical and chemical techniques, which will be summarized in this section (see an illustrative diagram in Fig. 7).

4.1. Biomass production

As long as the main goal is increasing carotenoid productivity, both microalgal biomass rate and carotenoid content must be optimized which requires well maintained culture systems. The production of microalgal carotenoids is often carried out in open pond or closed photobioreactor culture systems depending on resistance of microalgal



Fig. 7. Illustration of carotenoid production process from microalgae.

strain to contamination and the purity requirements of the final product; for example, strains of genus *Dunaliella* have the ability to live in a saline environment, so they are grown in open ponds, whereas xanthophyll producing strains are grown in photobioreactors because of their sensitivity [117,118].

Open pond systems such as raceway ponds, circular central-pivot ponds and mixed ponds are the most commonly used because they are cheaper to build and maintain, but they also have a risk of contamination, poor mass transfer and poor resistance to climate change outside of tropical areas. This makes photobioreactors preferred by allowing a better control of physicochemical parameters, optimization of fluid dynamics, mass transfer and minimization of water losses [117,118]. When selecting cultivation systems the following factors should be taken into consideration: investment and operational costs, area available for cultivation, climate, contamination risk, water availability, mixing strategies, level of automation, efficiency and cultivation objective [119].

Furthermore, microalgal culture and biomass production are influenced by three categories of environmental factors, abiotic factors (light, temperature, concentrations of P, N and K, CO₂, O₂, pH, salinity and toxins), biotic factors (bacteria, viruses, fungi and other competitive microalgae) and operational factors (degree of mixing and agitation, addition of bicarbonate, dilution rate, width and depth of containers and frequency of collection) [120,121]. These factors are the variables that researchers act on to improve yield and increase carotenoid content. Some adopted culture strategies are summarized in the following points:

- Strategy of adaptive evolution induced by stress: it consists in induction of an adaptive evolution by stress conditions. For example, high temperature favors growth and accumulation of lutein, high light intensity increases its fraction in cellular pigments, pH influences CO₂ availability by conversions of CO₂, HCO₃⁻ and H₂CO₃, and the addition of oxidizing agents or ferrous salts generates an oxidative stress that increases lutein content. Some of other carotenoids such as astaxanthin can reach their highest contents under extreme stress conditions [117].
- Strategies of reducing nitrogen, phosphorus and introducing salts such as NaCl: they are effective for astaxanthin and β-carotene production especially under high light conditions [117].

- Tow-stages cultivation strategy: it consists of two stages, the first one is under optimal conditions for cell growth and the second one introduces stress conditions for pigmentation [117].
- Hyperaccumulation strategy: it is successful for astaxanthin and β -carotene where it facilitates the recovery of targeted molecules from total biomass and increases yield by creating hyper-accumulation of these carotenoids following nutrient depletion conditions, especially nitrogen [122].
- Metabolic engineering: these are genetic manipulations that affect different enzymes involved in metabolic pathways of carotenogenesis either by mutation induction or by other advanced genomic and proteomic techniques [117].

4.2. Biomass harvesting

The step of removing microalgae from cultivation media called biomass harvesting present a major challenge in the whole process of carotenoid production because even at maximum density, cell fraction constitutes only a small part of media fraction. The difficulty increases as the cell size decreases [18,117].

Physical or chemical harvesting methods vary according to the resources available; they include settling, flocculation, filtration, centrifugation, and combinations of these methods. Other more advanced techniques such as advanced settling tanks, membrane filters, oscillating filters, dissolved air floatation systems, hydrocyclones, electrocoagulation, flow through centrifuges and scalable fractionation are used. Chemical methods are cheaper and consume less energy, but not as fast and efficient as physical methods [117,123]. Advantages and disadvantages of some chemical and physical harvesting methods are presented in Table 6.

4.3. Carotenoid extraction

4.3.1. Pretreatment and cell disruption

Microalgae are characterized by their rigid, complex and dynamic wall that prevents penetration of solvents inside the cell, in addition to the association of carotenoids with fatty acids and or proteins. That's why the pretreatment is required to destroy cell barriers and to facilitate carotenoids extraction afterwards. Physical, chemical and biological methods are used for cell disruption since the choice depends on criteria

Table 6

Advantages and disadvantages of some harvesting methods [117].

Method	Advantages	Disadvantages
Physical methods Centrifugation	 Reliable, fast and efficient Applicable at laboratory and small industrial scale Suitable for most strains of algae 	High capital costRisk of cell damage
Gravity sedimentation	 Inexpensive and suitable for large, dense and non-motile cells Used as a first treatment to reduce energy consumption when combined with other methods 	• Takes a long time if no supplementary flocculent is used
Electromagnetic technics	• More environmental compatible	• Fouling of electro-cathodes can cause problems for large-scale application
Chemical methods Flocculation	• Possibility to treat large scale suspensions with low cost	 Possibility of malfunctioning with marine microalgae High investment cost and operational requirements

of cell wall and matrix [124].

4.3.1.1. Physical methods

4.3.1.1.1. Bead milling. The method consists in the use of small beads made of steel, glass or ceramic which will be agitated in agitators of various designs (concentric or eccentric discs or rings). The increase of the bead diameter has a positive effect when it is lower than 0.5 mm but it has a negative effect when it is higher than 0.5 mm. Thus increase of processing time, stirring speed, number of cycles and bead filling into 85 % of the gridding chamber volume influences positively the cell disruption process. In a highly viscous medium, high density beads such as zirconium are preferred, while for a low viscosity medium less dense beads such as glass are preferred [125–127].

4.3.1.1.2. High pressure homogenization. The principle of cell disruption in this method is based on the high pressure impact of which cell suspension flows radially through a valve, contacts an impact ring, exits the valve and then flows either to a second valve or to discharge. The high pressure of fluid jet accelerated on a stationary surface of the valve induces cell disruption. This latter can also be achieved by hydrodynamic cavitation which is due to shear stress induced by pressure drop. Cavitation is a phenomenon in three steps that occur in short time intervals (μ s or ms) starting with the formation of bubbles followed by their growth and ending with the collapse of microbubbles [126,128].

4.3.1.1.3. High speed homogenization. Characteristic mechanisms of this technique are hydrodynamic cavitation generated by high speed agitation and shear forces at the solid-liquid interphase. Dynamic cavitation occurs when there is a decrease in local pressure almost to liquid vapor pressure which cannot be achieved unless impeller tip speed reaches a critical value of 8500 rpm; as the liquid moves away from the impeller its pressure recovers in proportion to decrease in speed and distance from impeller tip which leads to collapse of cavities. High speed homogenizer is the specialized device for this method, it is a high agitation speed homogenizer consisting of a stator-rotator assembly with a variety of stator-rotator designs [126,129].

4.3.1.1.4. Ultrasonication. The approach uses several ultrasonic systems either for extraction of a compound or production of micro/ nano emulsions or for cell disruption as in this case, where the cells will be destroyed due to high shear forces. Cavitation process is generated by energy of high frequency acoustic waves on one side and on the other side the propagating shock wave forms jet currents in surrounding medium which causes cell disintegration. High power ultrasounds (>20

kHz) can potentially generate strong cavitation effects [126,130].

4.3.1.1.5. *Microwave treatment*. Exposure of cell suspensions to microwaves (generally 250 MHz) generates interactions between them and polar molecules, mainly water, and causes local heating; the water then rapidly reaches boiling point, which leads to an increase in its concentration and internal pressure, as well as to cell expansion. Recovery of intracellular compounds is then facilitated by heat, internal pressure and microwave-induced membrane or wall damage. Treatment efficiency depends on the concentration of free water in the cell [126].

4.3.1.1.6. Pulsed electric field treatment. High Intensity Electric Field Pulsed also called Pulsed Electric Field consists of perforation of the membrane/cell wall by applying an external electric field to induce a critical electric potential through this membrane/wall. Cell disruption is therefore caused by electromechanical compression and electric field induced voltage (electroporation) whose number and size of pores depend on the intensity of applied field [126]. Membrane/wall damage can be reversible or irreversible depending on the ratio between total pore surface and cell membrane surface [131].

4.3.1.2. Chemical and biological methods. Chemical cell disruption is based on effect of different chemical compounds such as antibiotics, chelating agents, chaotropes, detergents, solvents, hypochlorite, acids and bases; each of which has its own mechanism of action. For example, solvents cause perforation or dissolution of membrane or wall, acids also cause pore formation, while bases saponify membrane lipids [126]. Some researchers have studied the action of other surfactants and oxidizing agents on microalgal cells [132–134]. Selection of most effective and appropriate chemical agent depends on the composition of membrane or wall that will be destroyed [126].

Although they consume less energy than physical approaches, chemical approaches present problems of feasibility, efficiency and toxicity which led researchers to turn to a biological enzymatic alternative less harmful on the environment. Glycosidase, glucanase, peptidase and lipase are the most widely used enzymes for cell lysis, they have advantages of specificity of action, operating conditions with low energy requirements [126].

4.3.2. Extraction

After cell lysis, carotenoids must be extracted and released from associated compounds; for this purpose, different methods are developed whose efficiency varies according to the principle of each one as well as chemical properties and sensitivity of targeted carotenoid. In this section several methods will be described along with the advantages and disadvantages of each one (Figs. 8 and 9 respectively).

4.3.2.1. Green solvent extraction. Green solvent extraction has become an alternative of extraction by organic solvents which are powerful environmental pollutants, extremely flammable, volatile and toxic. Deep eutectic solvents, ethanol, surfactants and the new type of ionic liquids (ILs) are green solvents used in this alternative; they are less toxic and more environmentally friendly. For example, ethylammonium caproate can strongly and efficiently dissolve the mannans composing the wall in a very short time (50 s), it has advantages of easy synthesis, low cost and better biocompatibility [124,135,136]. For more information on the applications of green solvents and their results see the studies [98,135,137–140].

4.3.2.2. Soxhlet extraction. To selectively extract compounds, atmospheric-liquid Soxhlet extraction consists in the use of solvents at boiling temperature with low pressure (ambient). This conventional technique allows the highest recovery of carotenoids and is also used to evaluate performance of other methods. Among its disadvantages are time consuming, large amounts of solvents (high cost), in addition to the possibility of degradation and cis-trans isomerization of carotenoids under high temperature [124]. López-Bascón-Bascon and Luque de



Fig. 8. Illustrative diagrams of extraction methods [157-160].

Castro have well described this technique [141].

4.3.2.3. Supercritical and subcritical fluid extraction SFE. Supercritical

consists in using a supercritical fluid extraction solvent which is a fluid

under conditions of temperature and pressure higher than their critical limits. It is therefore a special fluid state which can seep out solid like gas

and dissolve matter like liquid. Generally, carbon dioxide CO2 is the most preferred because it quickly reaches the critical conditions, their

high diffusion coefficient and low viscosity allow a rapid penetration

through pores of complex matrix which improves extraction efficiency

[124,136,142,143].

Extraction steps by supercritical fluid extraction are [142]:

- 1) Absorption of supercritical solvent by solid substrate promoting fluid extraction is an efficient method for extraction of soluble therexpansion of cell structures which facilitates solvent flow; molabile compounds from a solid matrix or insoluble liquid. It is widely studied for extraction of carotenoids from microalgae. The technique 2) Soluble compounds will be dissolved in the solvent simultaneously;
 - 3) Dissolved compounds will be subsequently transferred to a solid
 - surface by diffusion;
 - 4) Transport of compounds by solvent and remove from the extractor.

Extraction temperature (40-60 °C), pressure (300-400 bar), time (30–120 min), CO₂ density (solvent power), CO₂ flow rate (1–5 mL/min) and entertainers concentration (5-25 % ν/ν) are the most critical

9



Pressurized liquid extraction

High temperature and degrade thermolabile

Green solvent extraction

- Environmentally friendly (use of green solvent).

- Selectivity and extraction
- Requires large amounts

due to ageing of ultrasonic probe surface

Supercritical fluid extraction

- Requirement of small particle size to achieve good extraction (_ 50um).
- extraction time that may compounds and cause cistrans isomerization.

Microwave assisted

- Ability to give a purified final product with higher yield.
- Simple, fast and economic which could be used at
- Requires energy and additional separation processes.
- Thermal degradation.

- **Advantages**
- Disadvantages

Fig. 9. Advantages and disadvantages of extraction methods [124,136,142,143,151].

parameters of supercritical carotenoid extraction [144]. However, Ludwig et al. [89] found that this technique allows the recovery rate of β -carotene of >90 % from *Dunaliella salina* at 70 °C and 500 bars with 10 % ethanol as co-solvent [89].

Subcritical fluid extraction is similar to the Supercritical fluid extraction except that temperature and pressure are relatively lower than the critical values (31.06 °C and 73.8 bar) [143]. It has been shown that subcritical CO₂, 1,1,1,2-tetrafluoroethane and diethyl ether have the potential to extract carotenoids from macro and microalgae [16,145,146]. However, the number of studies derived from the subcritical extraction of microalgal carotenoids is limited compared to supercritical extraction [143].

4.3.2.4. Pressurized liquid extraction PLE. This technique is known under different names, Pressurized Liquid Extraction, Pressurized Solvent Extraction (PSE), Accelerated Solvent Extraction (ASE) and Enhanced Solvent Extraction (ESE). Their principle is based on liquid extraction where solvents will be heated to their boiling temperature (20 to 200 °C) under high pressure (34-204 bar) to maintain liquid state. The analyte in this case will go through three main steps: desorption where analyte is removed from its site in matrix, then diffusion where it diffuses through pores of matrix and reaches extraction phase and finally transfer of analyte into bulk solvent and collection. Pressurized liquid extraction can be automated and programmed to analyze several samples in a short time [142,147].

4.3.2.5. Microwave assisted extraction MAE. Microwave assisted extraction is an economical method, fast and requires small amounts of solvents to extract carotenoids, it allows a deeper contact of solvent with sample to improve extraction [124,142]. The principle is an energy transfer (in a form of heat) from microwave radiation to solvents by two mechanisms: dipolar rotation and ionic conduction, which facilitates mass transfer and the dissolution of analytes. Transferred heat causes evaporation of humidity inside the cell inducing a change of pressure, which increases membrane porosity and consequently solvent penetration and release of intracellular compounds. On the other side, heat transfer destroys hydrogen bonds and causes a migration of dissolved ions, which leads to a high solvent penetration [142,143].

Generally, microwave assisted extraction is performed in open or closed reaction vessels, open when extraction is at low temperature and atmospheric pressure and closed when it is at high temperature, this approach can follow several paths using different solvents or without any solvent [142,143]. Recent studies illustrate microwave-assisted extraction of different classes of carotenoids from *Chlorella sor-okiniana*, *Chlorella luteoviridis* and other species [13,148–150].

4.3.2.6. Ultrasound assisted extraction UAE. Ultrasound extraction is based on application of ultrasound waves in a liquid medium, which by acoustic cavitation (formation of small bubbles in a liquid medium) promotes diffusion of intracellular compounds through the plasma membrane and can also destroy the latter, causing release of compounds into the medium [124,143]. Influencing factors of this extraction technique are: power, frequency, intensity, reactor shape and volume, solvents, temperature, presence of dissolved gas and external pressure as well as material parameters [151].

Techniques of ultrasonic extraction are devised in three main types: conventional techniques, hybrid techniques (sono-Soxhlet, sonoclevenger) and combination with other innovative techniques such as the combination with microwave or supercritical fluid extraction or with extrusion extraction [151]. In order to improve extraction of zeaxanthin and β -carotene from marine *Chlorella saccharophila*, Singh et al. [152] tried to optimize the process using ultrasonication, they applied response surface methodology and they optimized the parameters: solvent/CDW ratio, power, pulse length, and extraction time to obtain the highest yield of zeaxanthin (11.2 mg/g) and β -carotene (4.98 mg/g) [152].

4.3.3. Comparison of extraction methods

In this section extraction methods will be compared in terms of difference in yield, ecological impact and extraction efficiency.

For the difference in yield, Soxhlet and green solvent extraction methods show high recovery of carotenoids, Desai et al. [98] had 70 % of astaxanthin from *Haematococcus pluvialis* using ionic liquid ILs as green solvent [98,136]. Supercritical fluid extraction and pressurized liquid extraction have a low yield of carotenoids of which that of PLE (3–39.31 % (*w*/w)) is higher than that of SFE but still remains a low value compared to other methods. Microwave-assisted extraction technique gives high yield whose intermittent irradiation was found to be effective for better recovery [124,142]. On the other hand, an experiment of astaxanthin extraction from *Haematococcus pluvialis* by ultrasound-assisted extraction gave a recovery rate of 95.08 \pm 3.02 % which was the highest until the year 2021 [99,136].

For ecological impact, most of the methods discussed in this review are ecofriendly green techniques except the conventional Soxhlet technique that uses large amounts of organic solvents harmful to the environment [124,143]. SFE uses Super Critical CO₂ SC-CO₂ as a nonflammable, non-toxic and environmentally friendly recyclable solvent, while green solvent extraction uses ecofriendly green solvents produced from renewable biomass resources or non-toxic and biodegradable petroleum products [124]. MAE, UAE and PLE techniques use small amounts of solvent without affecting the yield. PLE reduces waste and allows the replacement of organic solvents by green solvents, as well as UAE reduces their consumption, eliminates post treatment of resulting wastewater and consumes only a fraction of the energy usually used by a conventional extraction method [124,142,151].

For extraction efficiency, SFE presents a significant efficiency due to its use of SC-CO₂ which gives a highly concentrated final product without any trace of toxic organic solvent [124]. MAE gives a purified final product and allows a deep contact with the sample which improves efficiency and time [142]. Similarly, UAE is characterized by high efficiency, reproducibility and purity of the final product [124,151]. Furthermore, Soxhlet method has been shown to be effective for extraction and is sometimes used to evaluate the performance of other methods, whereas PLE is poor in terms of selectivity [124,142]. A comparative study of astaxanthin extraction efficiency between pulsed electromagnetic field, ultrasound, high-pressure micro-fluidization, HCl and ILs showed that ILs, HCl and high-pressure micro-fluidization treatment were the most efficient with >80 % astaxanthin recovery from *Haematococcus pluvialis* [153]. In the same context, Khoo et al. [99] designed an ultrasound-assisted two-phase solution system that gave a very high efficiency of 99.74 \pm 0.05 % not observed previously [99].

4.3.4. Mechanisms of extraction

In order to scale up the process and broaden the application range of extraction methods, it is crucial to understand extraction mechanisms. In solvent extraction of microalgal carotenoids, cells will be exposed to a biocompatible solvent where it can be absorbed causing alterations in cell membrane. This contact between solvent molecules and hydrophobic membrane parts can be prevented by the wall and/or hydrophilic parts of external membrane and makes extraction difficult which requires pretreatment and wall destruction. After the solvent is in contact with membrane it dissolves in it and causes changes where some oil globules containing carotenoids will be extracted from the chloroplast to the space between chloroplast and membrane and subsequently to cell exterior. The biocompatibility of solvent, function of compound, localization and the way it accumulates in the cell are the factors that must be taken into consideration during this type of extraction [154].

Electroporation or membrane permeabilization mechanism is not yet fully understood, but it is accepted that it occurs in four steps: 1) Application of an electric field induces an increase in transmembrane potential of cytoplasmic membrane due to its charge. 2) Reaching of a determined threshold potential and induction of the formation of small hydrophilic pores. 3) Evolution of the number and/or size of pores. 4) Entry of extracellular substances and leakage of intracellular compounds during post treatment [155].

Khadraoui et al. [156] studied the mechanisms of metabolites extraction from rosemary leaves by ultrasound assisted extraction. Their observations by different scanning microscopies and cytohistochemistry have shown that there is a chain dexturation mechanism that occurs in a well determined order: local erosion, shear force, sonoporation, fragmentation, capillary effect and dexturation [156].

4.4. Saponification

As mentioned previously, carotenoids are divided into two main classes: carotenes and xanthophylls. Carotenes exist in free form inside cells while xanthophylls exist either in free form or esterified with fatty acids in a more stable form. Saponification is therefore a treatment of these esterified carotenoids (mono or diester) by a base (KOH or NaOH) allowing a removal of esterified xanthophylls but also lipids, chlorophylls and proteins. It is often performed as a separate step after extraction [124,136,161].

During the saponification process, base concentration, temperature and treatment time have a direct influence on carotenoid yield. Inbaraj et al. [162] found that 6 h of incubation with 2 % methanolic KOH (w/v) induced complete saponification of carotenoid esters, while an extension of time to 8 h caused carotenoid degradation. A high temperature (56 °C, 20 min) or low temperature (25 °C, 16 h) is also recommended for extraction of free carotenoids [162]. In addition, some experiments showed that the highest yield, was with 4 % KOH (w/v) in MeOH, while 2 % KOH (w/v) was not sufficient for complete saponification of carotenoids from Scenedesmus almeriensis [163]. Another study elucidates the loss of 20–30 % of β -carotene and 50 % of xanthophylls after treatment with 10 % KOH (w/v) [164]. For Scenedesmus obliquus, treatment with 2.5 % KOH (w/v) for 40 min at 40 °C in a hot water bath increased lutein content by nearly twofold, while the use of 80 % KOH (w/v) and overnight incubation at 4 °C did not significantly affect the lutein content when compared with an unsaponified sample [165].

4.5. Separation, analysis and identification

After extraction and saponification, carotenoids must go through a further separation, analysis and identification processes; for this purpose, their physical and chemical properties must be taken into consideration. Carotenoids are sensitive to temperature, oxygen, acids, alkaline bases, and light whose exposure can cause cis-trans isomerization and induce destruction. In addition to characteristic conjugated double bond system of carotenoids which presents a major problem during its manipulation [12,166].

In general, physicochemical features of compounds are the basis for choice of separation technique, so they are: distillation, crystallization, dialysis, electrophoresis, column and thin layer chromatography [12]. However, chromatographic techniques are the most used for carotenoid separation and are reported in literature for a long time [167–174]. This technique is based on distribution of compounds in a mixture between two phases; one is stationary and the other mobile, which passes through the stationary phase. The latter can be a solid adsorbent, a liquid deposited on the surface of a solid base, an ion exchanger or gel. It is applied in isolation of compounds either by their separation at elution of column (column chromatography), by scraping spots of chromatoplates (thin layer chromatography) or by cutting spots on the paper (paper chromatography). In the case of carotenoids, separation depends on the polarity of functional groups of molecules determining hydrophobic character, there is therefore two methods of separation either by distribution between two immiscible liquid phases or by adsorption of adsorbent [12].

High Performance Liquid Chromatography (HPLC), Thin Layer Chromatography (TLC) and more recently Ultra High Performance Liquid Chromatography (UHPLC) are used not only for separation, but also for analysis (quantitative and qualitative) and identifying where they are coupled with mass spectrometry [175–177].

Quantitative and qualitative analyses of carotenoids are provided by several spectroscopic and mass spectrometric methods. Other techniques such as MALDI-TOF/MS (Matrix Assisted Lazer Desorption Ionization Time Of Flight Mass Spectrometry), ASAP (Atmospheric Solids Analysis Probe) and Raman spectroscopy are used to rapidly profile and qualify carotenoids in several extracts without the need for sample preparation or chromatographic separation [177].

Carotenoid identification can be chemical by characteristic reactions of functional groups, as well as physical which is the most applied way. HPLC and UV visible are the commonly used detectors, but the similarity of UV visible spectrum and carotenoid structures (see Fig. 5) causes coelution, so mass detectors are developed to elucidate structure and facilitate quantification of individual carotenoids that coelute [12,177,178]. Mass spectrometry is based on transformation of carotenoids into ions by electron bombardment and subsequently they will be accelerated, separated and recorded. Many ionization techniques are reported in mass spectrometry analysis of carotenoids: EI Electron Impact, FAR Fast Atom Bombardment, MALDI Matrix Assisted Lazer Desorption Ionization, ESI Electrospray Ionization, APCI Atmospheric Pressure Chemical Ionization, APPI Atmospheric Pressure Photoionization, and ASAP Atmospheric Solids Analysis Probe [12,175,177].

4.6. Storage and conservation

The major problem associated with carotenoids storage is its easy degradation by oxygen, light and temperature; for that researchers tried to find the suitable conditions for their stability during storage. Chan et al. [165] studied storage parameters of lutein extracted from *Scene-desmus obliquus* whose results show that low temperature (4–20 °C) with the addition of antioxidant BHT butylated hydroxytoluene at 0.01 % can maintain lutein stability under light exposure [165]. Another evaluation of freezing and storage temperature effect on carotenoids in food products demonstrates that carotenoid mass fraction is not affected by freezing [179].

More recently, micro and nanotechnological encapsulation have emerged as an effective alternative for improving bioavailability and stability of carotenoids under storage conditions. It is a physicochemical process of entrapment of an active substance in a structurally engineered micro or nanosystem in order to develop an effective thermodynamic and physical barrier against deteriorating environmental conditions [180].

Microencapsulation technologies are: spray drying, freeze drying, coacervation, liposomes, inclusion complexation, and extrusion while nanoencapsulation technologies are: nano liquid-liquid carriers, nanoencapsulation using supercritical fluids, protein self-assembled nanoparticles, solid lipid nanoparticles, nano structured lipid carriers, solvent displacement and emulsification evaporation [14,180–183]. In general, polymeric nanoparticles are the most widely used due to their stability during storage and high release control efficiency of encapsulated carotenoids [183].

5. Conclusion

Compared to synthetic dyes, microalgal carotenoids present a promising alternative with important advantages in terms of safety, beneficial bioactivities, productivity and high yield in a short time. This will help to minimize the time, effort and money losses for the production of safe dyes especially for the food field.

Microalgal carotenoids production consists of biomass production, harvesting, extraction, saponification, separation and finally the storage. During biomass production, successful strategies for increasing productivity and yield are adopted by playing on factors that affect cell growth and carotenogenesis. Biomass harvesting is one of the major challenges in manufacturing processes, because cell fraction represents a small fraction of the total medium fraction. Indeed, several physical and chemical techniques are dedicated to collecting this fraction.

Before extracting carotenoids, a physical or chemical pretreatment is crucial to facilitate the access of solvents to carotenoid compounds by destroying cellular barriers that prevent their penetration. Extraction is performed by different innovative methods whose goal is the recovery of carotenoids localized inside the cells. Indeed, understanding extraction mechanisms allows to scale up the process and to widen the range of application of these techniques. Saponification is often the next step to recover esterified xanthophylls.

After extraction and saponification, carotenoids have to go through further separation and identification processes where their physicochemical properties have to be taken into consideration. The last step of storage and conservation is the other major challenge because carotenoids are sensitive to storage conditions, and for this reason researchers are still working to improve them. In addition, emerging micro and nanoencapsulation technologies have proven their effectiveness in improving bioavailability and storage of carotenoids under storage conditions.

Technological advancements are required to solve some of the issues related to production, extraction, storability and yield, of which cost reduction, environmental safety, efficiency and reproducibility are the points to be considered for a successful large scale application.

CRediT authorship contribution statement

The work described has not been published previously and it is not under consideration for publication elsewhere. Its publication is approved by all authors.

Conception and design: F.Z. Benbelkhir

Drafting of the article: F.Z. Benbelkhir

Critical revision of the article for important intellectual content: S. Medjekal

Final approval of the article: F.Z. Benbelkhir

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgement

We would like to thank all those who helped in this work, especially Mr. Djilali Ghobrini researcher in Applied Research Unit for Renewable Energies (URAER) for his ideas and opinions.

Formatting of funding sources

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

- A. Gürses, M. Açıkyıldız, K. Güneş, M.S. Gürses, Dyes and pigments: their structure and properties, in: Dye. Pigment. Springer Briefs Mol. Sci, Springer, Cham, 2016, pp. 13–29, https://doi.org/10.1007/978-3-319-33892-7_2.
- [2] H.B. Singh, K.A. Bharati, Handbook of Natural Dyes and Pigments, Elsevier, 2015, https://doi.org/10.1016/C2014-0-02803-1.
- [3] A. Tkaczyk, K. Mitrowska, A. Posyniak, Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: a review, Sci. Total Environ. 717 (2020), 137222, https://doi.org/10.1016/j. scitotenv.2020.137222.
- [4] I.S. Khan, S. Ali, K.B. Dar, M. Murtaza, M.N. Ali, S.A. Ganie, S.A. Dar, Toxicological analysis of synthetic dye orange red on expression of NFκBmediated inflammatory markers in wistar rats, Drug Chem. Toxicol. (2021) 1–11, https://doi.org/10.1080/01480545.2021.1979579.
- [5] A.M. Grumezescu, A.M. Holban, Natural and Artificial Flavoring Agents and Food Dyes, Elsevier, 2018, https://doi.org/10.1016/C2016-0-00380-7.
- [6] R. Kalra, X.A. Conlan, M. Goel, Fungi as a potential source of pigments: harnessing filamentous fungi, Front. Chem. 8 (2020) 369, https://doi.org/ 10.3389/FCHEM.2020.00369/BIBTEX.
- [7] E. Christaki, E. Bonos, P. Florou-Paneri, Innovative microalgae pigments as functional ingredients in nutrition, in: K. Se-Kwon (Ed.), Handb. Mar. Microalgae Biotechnol. Adv, Elsevier, 2015, pp. 223–243, https://doi.org/10.1016/B978-0-12-800776-1.00014-5.
- [8] S.C. Silva, I.C.F.R. Ferreira, M.M. Dias, M.F. Barreiro, Microalgae-derived pigments: a 10-year bibliometric review and industry and market trend analysis, Molecules 25 (2020) 3406, https://doi.org/10.3390/molecules25153406.
- [9] A.L. Morocho-Jácome, N. Ruscinc, R.M. Martinez, J.C.M. de Carvalho, T. Santos de Almeida, C. Rosado, J.G. Costa, M.V.R. Velasco, A.R. Baby, (Bio)Technological aspects of microalgae pigments for cosmetics, Appl. Microbiol. Biotechnol. 104 (2020) 9513–9522, https://doi.org/10.1007/S00253-020-10936-X.
- [10] E.G. Nwoba, C.N. Ogbonna, T. Ishika, A. Vadiveloo, Microalgal pigments: a source of natural food colors, in: M.A. Alam, J.-L. Xu, Z. Wang (Eds.), Microalgae Biotechnol. Food, Heal. High Value Prod, Springer Singapore, Singapore, 2020, pp. 81–123, https://doi.org/10.1007/978-981-15-0169-2_3.
- [11] M.A. Alam, J.L. Xu, Z. Wang, Microalgae Biotechnology for Food, Health and High Value Products, Springer Singapore, Singapore, 2020, https://doi.org/ 10.1007/978-981-15-0169-2.
- [12] M. Butnariu, Methods of analysis (Extraction, separation, identification and quantification) of carotenoids from natural products, J. Ecosyst. Ecography 6 (2016), https://doi.org/10.4172/2157-7625.1000193.
- [13] M.K. Sarma, K. Saha, R. Choudhury, S. Pabbi, D. Madamwar, S. Subudhi, Development of a microwave-assisted solvent extraction process for the extraction of high-value carotenoids from Chlorella biomass, Biofuels, Bioprod. Biorefining (2021), https://doi.org/10.1002/BBB.2298.
- [14] J.B. Eun, A. Maruf, P.R. Das, S.H. Nam, A review of encapsulation of carotenoids using spray drying and freeze drying, Crit. Rev. Food Sci. Nutr. 60 (2020) 3547–3572, https://doi.org/10.1080/10408398.2019.1698511.
- [15] Y. Ren, H. Sun, J. Deng, J. Huang, F. Chen, Carotenoid production from microalgae: biosynthesis, salinity responses and novel biotechnologies, Mar. Drugs 19 (2021) 713, https://doi.org/10.3390/MD19120713.
- [16] M. Goto, H. Kanda, Wahyudiono, S. Machmudah, Extraction of carotenoids and lipids from algae by supercritical CO2 and subcritical dimethyl ether, J. Supercrit. Fluids 96 (2015) 245–251, https://doi.org/10.1016/j.supflu.2014.10.003.
- [17] D.B. Rodrigues, É.M.M. Flores, J.S. Barin, A.Z. Mercadante, E. Jacob-Lopes, L. Q. Zepka, Production of carotenoids from microalgae cultivated using agroindustrial wastes, Food Res. Int. 65 (2014) 144–148, https://doi.org/10.1016/j.foodres.2014.06.037.
- [18] L. Novoveská, M.E. Ross, M.S. Stanley, R. Pradelles, V. Wasiolek, J.-F. Sassi, Microalgal carotenoids: a review of production, current markets, regulations, and future direction, Mar. Drugs 17 (2019) 1–21, https://doi.org/10.3390/ md17110640.

- [19] J. Hu, D. Nagarajan, Q. Zhang, J.-S. Chang, D.-J. Lee, Heterotrophic cultivation of microalgae for pigment production: a review, Biotechnol. Adv. 36 (2018) 54–67, https://doi.org/10.1016/j.biotechadv.2017.09.009.
- [20] L.D. Ardila-Leal, R.A. Poutou-Piñales, A.M. Pedroza-Rodríguez, B.E. Quevedo-Hidalgo, A brief history of colour, the environmental impact of synthetic dyes and removal by using laccases, Molecules 26 (2021) 3813, https://doi.org/10.3390/ MOLECULES26133813.
- [21] I.G.C. Mota, R.A.M. Das Neves, S.S.D.C. Nascimento, B.L.L. Maciel, A.H.D. A. Morais, T.S. Passos, Artificial dyes: health risks and the need for revision of international regulations, Food Rev. Int. (2021), https://doi.org/10.1080/ 87559129.2021.1934694.
- [22] M. Danouche, H. El Arroussi, W. Bahafid, N. El Ghachtouli, An overview of the biosorption mechanism for the bioremediation of synthetic dyes using yeast cells, Environ. Technol. Rev. 10 (2021) 58–76, https://doi.org/10.1080/ 21622515.2020.1869839.
- [23] I. Luzardo-Ocampo, A.K. Ramírez-Jiménez, J. Yañez, L. Mojica, D.A. Luna-Vital, Technological applications of natural colorants in food systems: a review, Foods 10 (2021) 634, https://doi.org/10.3390/FOODS10030634.
- [24] M.I. Landim Neves, E.K. Silva, M.A.A. Meireles, Natural blue food colorants: consumer acceptance, current alternatives, trends, challenges, and future strategies, Trends Food Sci. Technol. 112 (2021) 163–173, https://doi.org/ 10.1016/j.tifs.2021.03.023.
- [25] S. Ghosh, T. Sarkar, A. Das, R. Chakraborty, Natural colorants from plant pigments and their encapsulation: an emerging window for the food industry, LWT 153 (2022), 112527, https://doi.org/10.1016/j.lwt.2021.112527.
- [26] H. Begum, F.M.D. Yusoff, S. Banerjee, H. Khatoon, M. Shariff, Availability and utilization of pigments from microalgae, Crit. Rev. Food Sci. Nutr. 56 (2016) 2209–2222, https://doi.org/10.1080/10408398.2013.764841.
- [27] A. Aberoumand, A review article on edible pigments properties and sources as natural biocolorants in foodstuff and food industry, World J. Dairy Food Sci. 6 (2011) 71–78. http://www.idosi.org/.../11.pdf.
- [28] K. Malik, J. Tokkas, S. Goyal, Microbial pigments : a review, Int. J. Microb. Resour. Technol. 1 (2012) 361–365. http://ijmrt.inpressco.com/microbial-pigm ents-a-review/.
- [29] H.B. Sowbhagya, S.R. Sampathu, N. Krishnamurthy, Natural colorant from Marigold-chemistry and technology, Food Rev. Int. 20 (2004) 33–50, https://doi. org/10.1081/FRI-120028829.
- [30] A. Towns, Colorants: general survey, Phys. Sci. Rev. 4 (2019) 1–18, https://doi. org/10.1515/psr-2019-0008.
- [31] B.H. Patel, Natural dyes, in: M. Clark (Ed.), Handb. Text. Ind. Dye, Elsevier, 2011, pp. 395–424, https://doi.org/10.1533/9780857093974.2.395.
- [32] F. Brunello, The Art of Dyeing in the History of Mankind, N. Pozza, Vicenza, 1973.
- [33] S.M. Burkinshaw, Application of dyes, in: D.R. Waring, G. Hallas (Eds.), Chem. Appl. Dye, Springer, Boston, MA, 1990, pp. 237–379, https://doi.org/10.1007/ 978-1-4684-7715-3_7.
- [34] F.M. Rows, The life and work of sir William Henry Perkin, J. Soc. Dye. Colour. 54 (1938) 551–562, https://doi.org/10.1111/j.1478-4408.1938.tb01996.x.
- [35] I. Holme, Sir William Henry Perkin: a review of his life, work and legacy, Color. Technol. 122 (2006) 235–251, https://doi.org/10.1111/j.1478-4408.2006.00041.x.
- [36] M. Fox, Dye-makers of Great Britain, 1856-1976 : A History of Chemists, Companies, Products and Changes, Imperial Chemical Industries, Manchester, 1987.
- [37] R. Rothon, Pigment and Nanopigment Dispersion Technologies, Rav Lally, USA, 2012.
- [38] R.E. Kirk, D.F. Othmer, M. Grayson, D. Eckroth, Kirk-Othmer Encyclopedia of Chemical Technology, 4 th, J Wiley, 2004.
- [39] P. Gregory, Classification of dyes by chemical structure, in: D.R. Waring, G. Hallas (Eds.), Chem. Appl. Dye, Springer, Boston, MA, 1990, pp. 17–47, https://doi.org/ 10.1007/978-1-4684-7715-3_2.
- [40] A. Gürses, M. Açıkyıldız, K. Güneş, M.S. Gürses, Classification of dye and pigments, in: Dye. Pigment. Springer Briefs Mol. Sci, Springer, Cham, 2016, pp. 31–45, https://doi.org/10.1007/978-3-319-33892-7_3.
- [41] F.R. Abe, J.N. Mendonça, L.A.B. Moraes, G.A.R. de Oliveira, C. Gravato, A.M.V. M. Soares, D.P. de Oliveira, Toxicological and behavioral responses as a tool to assess the effects of natural and synthetic dyes on zebrafish early life, Chemosphere 178 (2017) 282–290, https://doi.org/10.1016/j. chemosphere.2017.03.030.
- [42] S. Benkhaya, S. M'rabet, H. Lgaz, A.El Bachiri, A.El Harfi, Dyes: classification, pollution, and environmental effects, in: S.S. Muthu, A. Khadir (Eds.), Dye Biodegrad. Mech. Tech, Springer, Singapore, 2022, pp. 1–50, https://doi.org/ 10.1007/978-981-16-5932-4_1.
- [43] S. Adeel, M. Salman, A.F. Zahoor, M. Usama, N. Amin, An insight into herbalbased natural dyes, Recycl. Waste Fash. Text. (2020) 423–456, https://doi.org/ 10.1002/9781119620532.CH19.
- [44] R. Amaral, J.S.S. de Melo, L.M.A. dos Santos, Pigments from eustigmatophyceae: an interesting class of microalgae for carotenoid production, J. Appl. Phycol. 33 (2021) 371–384, https://doi.org/10.1007/S10811-020-02312-Z.
- [45] B. Behan, Botanical Inks: Plant-to-Print Dyes, Techniques and Projects, Quadrille Publishing, London, 2018.
- [46] A. Kamboj, S. Jose, A. Singh, Antimicrobial activity of natural dyes a comprehensive review, J. Nat. Fibers (2021), https://doi.org/10.1080/ 15440478.2021.1875378.
- [47] W. Handayani, A.I. Kristijanto, A.I.R. Hunga, Are natural dyes eco-friendly? A case study on water usage and wastewater characteristics of batik production by

natural dyes application, Sustain. Water Resour. Manag. 4 (2018) 1011–1021, https://doi.org/10.1007/S40899-018-0217-9.

- [48] V.K. Gupta, Fundamentals of natural dyes and its application on textile substrates, in: A.K. Samanta, N. Awwad, H.M. Algarni (Eds.), Chem. Technol. Nat. Synth. Dye. Pigment, Intech Open, 2019, pp. 1–32, https://doi.org/10.5772/ INTECHOPEN.89964.
- [49] T.I. Kakhia, Dyes, Colors & Pigments, 2011.
- [50] S. Saxena, A.S.M. Raja, Natural dyes: sources, chemistry, application and sustainability issues, in: S.S. Muthu (Ed.), Roadmap to Sustain. Text. Cloth, Springer, Singapore, Singapore, 2014, pp. 37–80, https://doi.org/10.1007/978-981-287-065-0 2.
- [51] P.S. Vankar, Natural Dyes for Textiles, Elsevier Ltd, 2017, https://doi.org/ 10.1016/C2015-0-01885-8.
- [52] T.N. Bankar, M.A. Dar, R.S. Pandit, Diversity of pigments in insects, their synthesis and economic value for various industries, Res. Ecol. 3 (2021), https:// doi.org/10.30564/RE.V3I2.2899.
- [53] R. Futahashi, M. Osanai-Futahashi, Pigments in insects, in: H. Hashimoto, M. Goda, R. Futahashi, R. Kelsh, T. Akiyama (Eds.), Pigment. Pigment Cells Pigment Patterns, Springer, Singapore, 2021, pp. 3–43, https://doi.org/10.1007/ 978-981-16-1490-3 1.
- [54] R.H. Hackman, Green pigments of the hemolymph of insects, Arch. Biochem. Biophys. 41 (1952) 166–174, https://doi.org/10.1016/0003-9861(52)90517-1.
- [55] R.I.T. Cromartie, Insect pigments, Annu. Rev. Entomol. 4 (1959) 59–76, https:// doi.org/10.1146/annurev.en.04.010159.000423.
- [56] G. Shamim, S.K. Ranjan, D.M. Pandey, R. Ramani, Biochemistry and biosynthesis of insect pigments, Eur. J. Entomol. 111 (2014) 149–164, https://doi.org/ 10.14411/eie.2014.021.
- [57] T.R. Silva, N.S.N. Tavares, R. Canela-Garayoa, J. Eras, M.V.N. Rodrigues, I. A. Neri-Numa, G.M. Pastore, L.H. Rosa, J.A.A. Schultz, H.M. Debonsi, L.R. G. Cordeiro, V.M. Oliveira, Chemical characterization and biotechnological applicability of pigments isolated from Antarctic bacteria, Mar. Biotechnol. 21 (2019) 416–429, https://doi.org/10.1007/s10126-019-09892-z.
- [58] C.K. Venil, L. Dufossé, P. Renuka Devi, Bacterial pigments: sustainable compounds with market potential for pharma and food industry, Front. Sustain. Food Syst. 4 (2020) 100, https://doi.org/10.3389/fsufs.2020.00100.
- [59] M.E. Pailliè-Jiménez, P. Stincone, A. Brandelli, Natural pigments of microbial origin, Front. Sustain. Food Syst. 4 (2020) 160, https://doi.org/10.3389/ fsufs.2020.590439.
- [60] C.A. Aruldass, L. Dufossé, W.A. Ahmad, Current perspective of yellowish-orange pigments from microorganisms- a review, J. Clean. Prod. 180 (2018) 168–182, https://doi.org/10.1016/j.jclepro.2018.01.093.
- [61] L. Dufossé, Current and potential natural pigments from microorganisms (bacteria, yeasts, fungi, microalgae), in: R. Carle, R.M. Schweiggert (Eds.), Handb. Nat. Pigment. Food Beverages Ind. Appl. Improv. Food Color, Elsevier, 2016, pp. 337–354, https://doi.org/10.1016/B978-0-08-100371-8.00016-6.
- [62] A. Nawaz, R. Chaudhary, Z. Shah, L. Dufossé, M. Fouillaud, H. Mukhtar, I. ul Haq, An overview on industrial and medical applications of bio-pigments synthesized by marine bacteria, Microorganisms 9 (2020) 11, https://doi.org/10.3390/ microorganisms9010011.
- [63] A. Budakoti, R. Kumar, A. Pandey, Exploring ascomycetes fungus Hypoxylon fendleri as a source for natural textile dye, Indian For. 146 (2020) 365–366, https://doi.org/10.36808/if/2020/v146i4/152438.
- [64] Y. Caro, L. Anamale, M. Fouillaud, P. Laurent, T. Petit, L. Dufosse, Natural hydroxyanthraquinoid pigments as potent food grade colorants: an overview, Nat. Products Bioprospect. 2 (2012) 174–193, https://doi.org/10.1007/s13659-012-0086-0.
- [65] B.B. Basnet, L. Liu, W. Zhao, R. Liu, K. Ma, L. Bao, J. Ren, X. Wei, H. Yu, J. Wei, H. Liu, New 1, 2-naphthoquinone-derived pigments from the mycobiont of lichen trypethelium eluteriae sprengel, Nat. Prod. Res. 33 (2019) 2044–2050, https:// doi.org/10.1080/14786419.2018.1484458.
- [66] S.A.S. Mapari, M.E. Hansen, A.S. Meyer, U. Thrane, Computerized screening for novel producers of monascus-like food pigments in penicillium species, J. Agric. Food Chem. 56 (2008) 9981–9989, https://doi.org/10.1021/jf801817q.
- [67] A.G. Medentsev, A.Y. Arinbasarova, V.K. Akimenko, Biosynthesis of naphthoquinone pigments by fungi of the genus fusarium, Appl. Biochem. Microbiol. 41 (2005) 503–507, https://doi.org/10.1007/s10438-005-0091-8.
- [68] H. Takahashi, K. Nozawa, K.I. Kawai, Isolation and structures of dicyanide derivatives, epurpurins a to C, from emericella purpurea, Chem. Pharm. Bull. 44 (1996) 2227–2230, https://doi.org/10.1248/cpb.44.2227.
- [69] R.C.R. Gonçalves, H.C.F. Lisboa, S.R. Pombeiro-Sponchiado, Characterization of melanin pigment produced by aspergillus nidulans, World J. Microbiol. Biotechnol. 28 (2012) 1467–1474, https://doi.org/10.1007/s11274-011-0948-3.
- [70] R. Garcia, J. La Clair, R. Müller, Future directions of marine myxobacterial natural product discovery inferred from metagenomics, Mar. Drugs 16 (2018) 303, https://doi.org/10.3390/md16090303.
- [71] W. Sajjad, G. Din, M. Rafiq, A. Iqbal, S. Khan, S. Zada, B. Ali, S. Kang, Pigment production by cold-adapted bacteria and fungi: colorful tale of cryosphere with wide range applications, Extremophiles 24 (2020) 447–473, https://doi.org/ 10.1007/s00792-020-01180-2.
- [72] V. Vasanthabharathi, R. Lakshminarayanan, S. Jayalakshmi, Melanin production from marine Streptomyces, Afr. J. Biotechnol. 10 (2011) 11224–11234, https:// doi.org/10.5897/ajb11.296.
- [73] B.S. Priya, K. Chitra, T. Stalin, Bioprospecting ecofriendly natural dyes using novel marine bacteria as an efficient alternative to toxic synthetic dyes, in: P. Ponmurugan, J.S. Kumar (Eds.), Microb. Biodivers, Cambridge Scholars Publishing, UK, 2020, pp. 1–13.

- [74] H. Yi, Y.H. Chang, H.W. Oh, K.S. Bae, J. Chun, Zooshikella ganghwensis gen. Nov., sp. Nov., isolated from tidal flat sediments, Int. J. Syst. Evol. Microbiol. 53 (2003) 1013–1018, https://doi.org/10.1099/ijs.0.02521-0.
- [75] N. Kamarudheen, T. Naushad, K.V.B. Rao, Biosynthesis, characterization and antagonistic applications of extracellular melanin pigment from marine Nocardiopsis Sps, Indian J. Pharm. Educ. Res. 53 (2019) s112–s120, https://doi. org/10.5530/ijper.53.2s.55.
- [76] N.A. Henke, S.A.E. Heider, P. Peters-Wendisch, V.F. Wendisch, Production of the marine carotenoid astaxanthin by metabolically engineered corynebacterium glutamicum, Mar. Drugs 14 (2016) 124, https://doi.org/10.3390/md14070124.
- [77] B. Bin Xie, Y.L.S. Qin, J.C. Rong, X.Y. Zhang, X.L. Chen, B.C. Zhou, Y.Z. Zhang, Genome sequence of the cycloprodigiosin-producing bacterial strain pseudoalteromonas rubra ATCC 29570 T, J. Bacteriol. 194 (2012) 1637–1638, https://doi.org/10.1128/JB.06822-11.
- [78] O. Montero, M.D. Macìas-Sánchez, C.M. Lama, L.M. Lubián, C. Mantell, M. Rodríguez, E.M. De La Ossa, Supercritical CO2 extraction of β-carotene from a marine strain of the cyanobacterium synechococcus species, J. Agric. Food Chem. 53 (2005) 9701–9707, https://doi.org/10.1021/jf051283n.
- [79] Y.H. Wu, H. Cheng, L. Xu, X. Bin Jin, C.S. Wang, X.W. Xu, Physiological and genomic features of a novel violacein-producing bacterium isolated from surface seawater, PLoS One 12 (2017), e0179997, https://doi.org/10.1371/journal. pone.0179997.
- [80] M.P. de Souza, M. Hoeltz, P.D. Gressler, L.B. Benitez, R.C.S. Schneider, Potential of microalgal bioproducts: general perspectives and main challenges, Waste Biomass Valorization 10 (2019) 2139–2156, https://doi.org/10.1007/s12649-018-0253-6.
- [81] R.R. Ambati, D. Gogisetty, R.G. Aswathanarayana, S. Ravi, P.N. Bikkina, L. Bo, S. Yuepeng, Industrial potential of carotenoid pigments from microalgae: current trends and future prospects, Crit. Rev. Food Sci. Nutr. 59 (2019) 1880–1902, https://doi.org/10.1080/10408398.2018.1432561.
- [82] K.W. Chew, J.Y. Yap, P.L. Show, N.H. Suan, J.C. Juan, T.C. Ling, D.-J. Lee, J.-S. Chang, Microalgae biorefinery: high value products perspectives, Bioresour. Technol. 229 (2017) 53–62, https://doi.org/10.1016/j.biortech.2017.01.006.
- [83] E.B. D'Alessandro, N.R. Antoniosi Filho, Concepts and studies on lipid and pigments of microalgae: a review, Renew. Sust. Energ. Rev. 58 (2016) 832–841, https://doi.org/10.1016/j.rser.2015.12.162.
- [84] G. Di Lena, I. Casini, M. Lucarini, G. Lombardi-Boccia, Carotenoid profiling of five microalgae species from large-scale production, Food Res. Int. 120 (2019) 810–818, https://doi.org/10.1016/j.foodres.2018.11.043.
- [85] B. da S. Vaz, J.B. Moreira, M.G. de Morais, J.A.V. Costa, Microalgae as a new source of bioactive compounds in food supplements, Curr. Opin. Food Sci. 7 (2016) 73–77, https://doi.org/10.1016/j.cofs.2015.12.006.
- [86] S.R. Khadim, A. Mohanta, P. Maurya, P. Singh, R.K. Asthana, Strategies for increased production of lipids and fine chemicals from commercially important microalgae, in: R.P. Sinha, D.-P. Häder (Eds.), Nat. Bioact. Compd, Elsevier Inc, 2021, pp. 165–186, https://doi.org/10.1016/b978-0-12-820655-3.00008-2.
- [87] F.K. El-Baz, R.A. Hussein, D.O. Saleh, G.A.R.A.J. Jaleel, Zeaxanthin isolated from dunaliella Salina microalgae ameliorates age associated cardiac dysfunction in rats through stimulation of retinoid receptors, Mar. Drugs 17 (2019) 290, https:// doi.org/10.3390/md17050290.
- [88] J. Fabrowska, B. Messyasz, J. Szyling, J. Walkowiak, B. Łęska, Isolation of chlorophylls and carotenoids from freshwater algae using different extraction methods. Phycol. Res. 66 (2018) 52–57. https://doi.org/10.1111/pre.12191.
- [89] K. Ludwig, L. Rihko-Struckmann, G. Brinitzer, G. Unkelbach, K. Sundmacher, β-carotene extraction from Dunaliella Salina by supercritical CO2, J. Appl. Phycol. 33 (2021) 1435–1445, https://doi.org/10.1007/s10811-021-02399-y.
- [90] M. Petrushkina, E. Gusev, B. Sorokin, N. Zotko, A. Mamaeva, A. Filimonova, M. Kulikovskiy, Y. Maltsev, I. Yampolsky, E. Guglya, V. Vinokurov, Z. Namsaraev, D. Kuzmin, Fucoxanthin production by heterokont microalgae, Algal Res. 24 (2017) 387–393, https://doi.org/10.1016/j.algal.2017.03.016.
- [91] W. Huang, Y. Lin, M. He, Y. Gong, J. Huang, Induced high-yield production of zeaxanthin, lutein, and β-carotene by a mutant of chlorella zofingiensis, J. Agric. Food Chem. 66 (2018) 891–897, https://doi.org/10.1021/acs.jafc.7b05400.
- [92] L. Bourdon, A.A. Jensen, J.M. Kavanagh, D.D. McClure, Microalgal production of zeaxanthin, Algal Res. 55 (2021), 102266, https://doi.org/10.1016/j. algal.2021.102266.
- [93] A. Bouyahya, N. El Omari, M. Hakkur, N. El Hachlafi, S. Charfi, A. Balahbib, F. E. Guaouguaou, M. Rebezov, N. Maksimiuk, M.A. Shariati, G. Zengin, N. El Menyiy, I. Chamkhi, S. Bakrim, Sources, health benefits, and biological properties of zeaxanthin, Trends Food Sci. Technol. 118 (2021) 519–538, https://doi.org/10.1016/j.tifs.2021.10.017.
- [94] P. Srinivasan, K. Ramalingam, M.L.J. Thilakam, Statistical optimization of culture medium composition for enhanced zeaxanthin production by Cyanophycean microalgae Trichodesmium thiebautii (NIOT 152), Indian J. Sci. Technol. 13 (2020) 4307–4318, https://doi.org/10.17485/IJST/v13i41.1291.
- [95] K.M. Sun, C. Gao, J. Zhang, X. Tang, Z. Wang, X. Zhang, Y. Li, Rapid formation of antheraxanthin and zeaxanthin in seconds in microalgae and its relation to nonphotochemical quenching, Photosynth. Res. 144 (2020) 317–326, https://doi. org/10.1007/s11120-020-00739-6.
- [96] J.-H. Lin, D.-J. Lee, J.-S. Chang, Lutein production from biomass: Marigold flowers versus microalgae, Bioresour. Technol. 184 (2015) 421–428, https://doi. org/10.1016/j.biortech.2014.09.099.
- [97] I.S. Suh, H.-N. Joo, C.-G. Lee, A novel double-layered photobioreactor for simultaneous Haematococcus pluvialis cell growth and astaxanthin accumulation, J. Biotechnol. 125 (2006) 540–546, https://doi.org/10.1016/j. jbiotec.2006.03.027.

- [98] R.K. Desai, M. Streefland, R.H. Wijffels, M.H.M. Eppink, Novel astaxanthin extraction from Haematococcus pluvialis using cell permeabilising ionic liquids, Green Chem. 18 (2016) 1261–1267, https://doi.org/10.1039/c5gc01301a.
- [99] K.S. Khoo, K.W. Chew, G.Y. Yew, S. Manickam, C.W. Ooi, P.L. Show, Integrated ultrasound-assisted liquid biphasic flotation for efficient extraction of astaxanthin from Haematococcus pluvialis, Ultrason. Sonochem. 67 (2020), 105052, https:// doi.org/10.1016/j.ultsonch.2020.105052.
- [100] H. Sun, Y. Ren, Y. Lao, X. Li, F. Chen, A novel fed-batch strategy enhances lipid and astaxanthin productivity without compromising biomass of chromochloris zofingiensis, Bioresour. Technol. 308 (2020), 123306, https://doi.org/10.1016/j. biortech.2020.123306.
- [101] C.Y. Chen, A.L. Kao, Z.C. Tsai, Y.M. Shen, P.H. Kao, I.S. Ng, J.S. Chang, Expression of synthetic phytoene synthase gene to enhance β-carotene production in scenedesmus sp. CPC2, Biotechnol. J. 12 (2017) 1700204, https://doi.org/ 10.1002/biot.201700204.
- [102] J.Y. Jeon, J.S. Kwon, S.T. Kang, B.R. Kim, Y. Jung, J.G. Han, J.H. Park, J. K. Hwang, Optimization of culture media for large-scale lutein production by heterotrophic Chlorella vulgaris, Biotechnol. Prog. 30 (2014) 736–743, https://doi.org/10.1002/BTPR.1889.
- [103] S.-H. Ho, M.-C. Chan, C.-C. Liu, C.-Y. Chen, W.-L. Lee, D.-J. Lee, J.-S. Chang, Enhancing lutein productivity of an indigenous microalga Scenedesmus obliquus FSP-3 using light-related strategies, Bioresour. Technol. 152 (2014) 275–282, https://doi.org/10.1016/j.biortech.2013.11.031.
- [104] X.-M. Shi, X.-W. Zhang, F. Chen, Heterotrophic production of biomass and lutein by Chlorella protothecoides on various nitrogen sources, Enzym. Microb. Technol. 27 (2000) 312–318, https://doi.org/10.1016/S0141-0229(00)00208-8.
- [105] A. Gómez-Loredo, J. Benavides, M. Rito-Palomares, Growth kinetics and fucoxanthin production of Phaeodactylum tricornutum and Isochrysis galbana cultures at different light and agitation conditions, J. Appl. Phycol. 28 (2016) 849–860, https://doi.org/10.1007/s10811-015-0635-0.
- [106] S.M. Kim, S.W. Kang, O.N. Kwon, D. Chung, C.H. Pan, Fucoxanthin as a major carotenoid in Isochrysis aff. galbana: characterization of extraction for commercial application, J. Korean Soc. Appl. Biol. Chem. 55 (2012) 477–483, https://doi.org/10.1007/s13765-012-2108-3.
- [107] Z. Sun, Y. Zhang, L.P. Sun, J. Liu, Light elicits astaxanthin biosynthesis and accumulation in the fermented ultrahigh-density chlorella zofinginesis, J. Agric. Food Chem. 67 (2019) 5579–5586, https://doi.org/10.1021/acs.jafc.9b01176.
- [108] Y. Xu, I.M. Ibrahim, C.I. Wosu, A. Ben-Amotz, P.J. Harvey, Potential of new isolates of dunaliella Salina for natural β-carotene production, Biology (Basel) 7 (2018) 14, https://doi.org/10.3390/biology7010014.
- [109] J.A. Del Campo, H. Rodríguez, J. Moreno, M.Á. Vargas, J. Rivas, M.G. Guerrero, Accumulation of astaxanthin and lutein in chlorella zofingiensis (Chlorophyta), Appl. Microbiol. Biotechnol. 64 (2004) 848–854, https://doi.org/10.1007/ s00253-003-1510-5.
- [110] E.S. Jin, B. Feth, A. Melis, A mutant of the green alga Dunaliella Salina constitutively accumulates zeaxanthin under all growth conditions, Biotechnol. Bioeng. 81 (2003) 115–124, https://doi.org/10.1002/bit.10459.
- [111] L.M. Schüler, T. Santos, H. Pereira, P. Duarte, N.G. Katkam, C. Florindo, P.S. C. Schulze, L. Barreira, J.C.S. Varela, Improved production of lutein and β-carotene by thermal and light intensity upshifts in the marine microalga Tetraselmis sp. CTP4, Algal Res. 45 (2020), 101732, https://doi.org/10.1016/j. algal.2019.101732.
- [112] F. Gao, I.T.D. Teles (Cabanelas I., R.H. Wijffels, M.J. Barbosa, Process optimization of fucoxanthin production with Tisochrysis lutea, Bioresour. Technol. 315 (2020), 123894, https://doi.org/10.1016/j.biortech.2020.123894
- [113] S.Y. Koo, K.H. Cha, D.G. Song, D. Chung, C.H. Pan, Optimization of pressurized liquid extraction of zeaxanthin from Chlorella ellipsoidea, J. Appl. Phycol. 24 (2012) 725–730, https://doi.org/10.1007/s10811-011-9691-2.
- [114] S.M. Kim, Y.J. Jung, O.N. Kwon, K.H. Cha, B.H. Um, D. Chung, C.H. Pan, A potential commercial source of fucoxanthin extracted from the microalga Phaeodactylum tricornutum, Appl. Biochem. Biotechnol. 166 (2012) 1843–1855, https://doi.org/10.1007/s12010-012-9602-2.
- [115] Y. Li, H. Sun, T. Wu, Y. Fu, Y. He, X. Mao, F. Chen, Storage carbon metabolism of isochrysis zhangjiangensis under different light intensities and its application for co-production of fucoxanthin and stearidonic acid, Bioresour. Technol. 282 (2019) 94–102, https://doi.org/10.1016/j.biortech.2019.02.127.
- [116] X. Xiao, X. Zhang, H. Su, S. Chen, Z. He, C. Zhao, S. Yang, A visible-NIR responsive dye-sensitized solar cell based on diatom frustules and cosensitization of photopigments from diatom and purple bacteria, J. Chem. 2020 (2020) 1–10, https://doi.org/10.1155/2020/1710989.
- [117] M. Gong, A. Bassi, Carotenoids from microalgae: a review of recent developments, Biotechnol. Adv. 34 (2016) 1396–1412, https://doi.org/10.1016/j. biotechadv.2016.10.005.
- [118] T. Naidoo, N. Zulu, D. Maharajh, R. Lalloo, Value-added products from microalgae, in: F. Bux (Ed.), Biotechnol. Appl. Microalgae, 1st ed., CRC Press, 2013, pp. 137–160, https://doi.org/10.1201/b14920-11.
- [119] D. Aitken, B. Antizar-Ladislao, Achieving a green solution: limitations and focus points for sustainable algal fuels, Energies. 5 (2012) 1613–1647, https://doi.org/ 10.3390/en5051613.
- [120] L. Zhu, Microalgal culture strategies for biofuel production: a review, Biofuels Bioprod. Biorefining 9 (2015) 801–814, https://doi.org/10.1002/bbb.1576.
- [121] Y. Maltsev, K. Maltseva, M. Kulikovskiy, S. Maltseva, Influence of light conditions on microalgae growth and content of lipids, carotenoids, and fatty acid composition, Biology (Basel) 10 (2021), https://doi.org/10.3390/ biology10101060.

- https://doi.org/10.1016/j.tibtech.2018.09.006.
 [123] F. Fasaei, J.H. Bitter, P.M. Slegers, A.J.B. van Boxtel, Techno-economic evaluation of microalgae harvesting and dewatering systems, Algal Res. 31 (2018) 347–362, https://doi.org/10.1016/j.algal.2017.11.038.
- [124] R.K. Saini, Y.S. Keum, Carotenoid extraction methods: a review of recent developments, Food Chem. 240 (2018) 90–103, https://doi.org/10.1016/j. foodchem.2017.07.099.
- [125] J. Doucha, K. Lívanský, Influence of processing parameters on disintegration of chlorella cells in various types of homogenizers, Appl. Microbiol. Biotechnol. 81 (2008) 431–440, https://doi.org/10.1007/s00253-008-1660-6.
- [126] E. Günerken, E. D'Hondt, M.H.M. Eppink, L. Garcia-Gonzalez, K. Elst, R. H. Wijffels, Cell disruption for microalgae biorefineries, Biotechnol. Adv. 33 (2015) 243–260, https://doi.org/10.1016/j.biotechadv.2015.01.008.
- [127] G. Hedenskog, L. Enebo, J. Vendlová, B. Prokeš, Investigation of some methods for increasing the digestibility in vitro of microalgae, Biotechnol. Bioeng. 11 (1969) 37–51, https://doi.org/10.1002/BIT.260110104.
- [128] R. Halim, R. Harun, M.K. Danquah, P.A. Webley, Microalgal cell disruption for biofuel development, Appl. Energy 91 (2012) 116–121, https://doi.org/10.1016/ j.apenergy.2011.08.048.
- [129] P.S. Kumar, A.B. Pandit, Modeling hydrodynamic cavitation, Chem. Eng. Technol. 22 (1999) 1017–1027, https://doi.org/10.1002/(SICI)1521-4125(199912)22: 12<1017::AID-CEAT1017>3.0.CO;2-L.
- [130] D.Y. Kim, D. Vijayan, R. Praveenkumar, J.I. Han, K. Lee, J.Y. Park, W.S. Chang, J. S. Lee, Y.K. Oh, Cell-wall disruption and lipid/astaxanthin extraction from microalgae: chlorella and haematococcus, Bioresour. Technol. 199 (2016) 300–310, https://doi.org/10.1016/j.biortech.2015.08.107.
- [131] J.C. Weaver, Y.A. Chizmadzhev, Theory of electroporation: a review, Bioelectrochem. Bioenerg. 41 (1996) 135–160, https://doi.org/10.1016/S0302-4598(96)05062-3.
- [132] V. Ebenezer, Y.V. Nancharaiah, V.P. Venugopalan, Chlorination-induced cellular damage and recovery in marine microalga, Chlorella Salina, Chemosphere 89 (2012) 1042–1047, https://doi.org/10.1016/j.chemosphere.2012.05.067.
- [133] W.-C. Huang, J.-D. Kim, Cationic surfactant-based method for simultaneous harvesting and cell disruption of a microalgal biomass, Bioresour. Technol. 149 (2013) 579–581, https://doi.org/10.1016/j.biortech.2013.09.095.
 [134] G. Ulloa, C. Coutens, M. Sánchez, J. Sineiro, J. Fábregas, F.J. Deive, A. Rodríguez,
- [134] G. Ulloa, C. Coutens, M. Sánchez, J. Sineiro, J. Fábregas, F.J. Deive, A. Rodríguez, M.J. Núňez, On the double role of surfactants as microalga cell lysis agents and antioxidants extractants, Green Chem. 14 (2012) 1044–1051, https://doi.org/ 10.1039/c2gc16262h.
- [135] Y. Fan, Z. Niu, C. Xu, L. Yang, F. Chen, H. Zhang, Biocompatible protic ionic liquids-based microwave-assisted liquid-solid extraction of astaxanthin from Haematococcus pluvialis, Ind. Crop. Prod. 141 (2019), 111809, https://doi.org/ 10.1016/j.indcrop.2019.111809.
- [136] C. Liu, B. Hu, Y. Cheng, Y. Guo, W. Yao, H. Qian, Carotenoids from fungi and microalgae: a review on their recent production, extraction, and developments, Bioresour. Technol. 337 (2021), 125398, https://doi.org/10.1016/j. biortech.2021.125398.
- [137] K.S. Khoo, Y.M. Chong, W.S. Chang, J.M. Yap, S.C. Foo, I. Khoiroh, P.L. Lau, K. W. Chew, C.W. Ooi, P.L. Show, Permeabilization of Chlorella sorokiniana and extraction of lutein by distillable CO2-based alkyl carbamate ionic liquids, Sep. Purif. Technol. 256 (2021), 117471, https://doi.org/10.1016/j. seppur.2020.117471.
- [138] N. Dinheiro, P. Assunção, A. Rodríguez, M.Á. Sanromán, F.J. Deive, Surfactantassisted disruption and extraction for carotenoid production from a novel dunaliella strain, Sep. Purif. Technol. 223 (2019) 243–249, https://doi.org/ 10.1016/j.seppur.2019.04.083.
- [139] W. Routray, D. Dave, S.K. Cheema, V.V. Ramakrishnan, J. Pohling, Biorefinery approach and environment-friendly extraction for sustainable production of astaxanthin from marine wastes, Crit. Rev. Biotechnol. 39 (2019) 469–488, https://doi.org/10.1080/07388551.2019.1573798.
- [140] C.P. Song, Q.Y. Yap, M.Y.A. Chong, R.Ramakrishnan Nagasundara, R. Vijayaraghavan, D.R. Macfarlane, E.S. Chan, C.W. Ooi, Environmentally benign and recyclable aqueous two-phase system composed of distillable CO2based alkyl carbamate ionic liquids, ACS Sustain. Chem. Eng. 6 (2018) 10344–10354, https://doi.org/10.1021/acssuschemeng.8b01685.
- [141] M.A. López-Bascón, M.D.Luque de Castro, Soxhlet extraction, in: C.F. Poole (Ed.), Liq. Extr, Elsevier, 2020, pp. 327–354, https://doi.org/10.1016/B978-0-12-816911-7.00011-6.
- [142] D.A. Esquivel-Hernández, I.P. Ibarra-Garza, J. Rodríguez-Rodríguez, S.P. Cuéllar-Bermúdez, M. de J. Rostro-Alanis, G.S. Alemán-Nava, J.S. García-Pérez, R. Parra-Saldívar, Green extraction technologies for high-value metabolites from algae: a review, Biofuels Bioprod. Biorefining 11 (2017) 215–231, https://doi.org/ 10.1002/bbb.1735.
- [143] M. Poojary, F. Barba, B. Aliakbarian, F. Donsì, G. Pataro, D. Dias, P. Juliano, Innovative alternative technologies to extract carotenoids from microalgae and seaweeds, Mar. Drugs 14 (2016) 214, https://doi.org/10.3390/md14110214.
- [144] K. Zaghdoudi, X. Framboisier, C. Frochot, R. Vanderesse, D. Barth, J. Kalthoum-Cherif, F. Blanchard, Y. Guiavarc'h, Response surface methodology applied to Supercritical Fluid Extraction (SFE) of carotenoids from Persimmon (Diospyros kaki L.), Food Chem. 208 (2016) 209–219, https://doi.org/10.1016/j. foodchem.2016.03.104.
- [145] X.D. Fan, Y. Hou, X.X. Huang, T.Q. Qiu, J.G. Jiang, Ultrasound-enhanced subcritical CO2 extraction of lutein from Chlorella pyrenoidosa, J. Agric. Food Chem. 63 (2015) 4597–4605, https://doi.org/10.1021/acs.jafc.5b00461.

- [146] H. Kanda, Y. Kamo, S. Machmudah, M.Goto Wahyudiono, Extraction of fucoxanthin from raw macroalgae excluding drying and cell wall disruption by liquefied dimethyl ether, Mar. Drugs 12 (2014) 2383–2396, https://doi.org/ 10.3390/MD12052383.
- [147] A. Mustafa, C. Turner, Pressurized liquid extraction as a green approach in food and herbal plants extraction: a review, Anal. Chim. Acta 703 (2011) 8–18, https://doi.org/10.1016/j.aca.2011.07.018.
- [148] N. Ahmad, J.R. Mounsef, R. Lteif, A simple and fast experimental protocol for the extraction of xanthophylls from microalga Chlorella luteoviridis, Prep. Biochem. Biotechnol. 51 (2021) 1071–1075, https://doi.org/10.1080/ 10826068.2021.1901231.
- [149] J.T. Mary Leema, T. Persia Jothy, G. Dharani, Rapid green microwave assisted extraction of lutein from Chlorella sorokiniana (NIOT-2) – process optimization, Food Chem. 372 (2022), 131151, https://doi.org/10.1016/j. foodchem.2021.131151.
- [150] X. Zhou, W. Ding, W. Jin, Microwave-assisted extraction of lipids, carotenoids, and other compounds from marine resources, in: M. Garcia-Vaquero, G. Rajauria (Eds.), Innov. Emerg. Technol. Bio-Marine Food Sect. Appl. Regul. Prospect, Elsevier, 2022, pp. 375–394, https://doi.org/10.1016/B978-0-12-820096-4.00012-2.
- [151] F. Chemat, N. Rombaut, A.G. Sicaire, A. Meullemiestre, A.S. Fabiano-Tixier, M. Abert-Vian, Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review, Ultrason. Sonochem. 34 (2017) 540–560, https://doi.org/10.1016/j. ultsonch.2016.06.035.
- [152] D. Singh, C.J. Barrow, A.S. Mathur, D.K. Tuli, M. Puri, Optimization of zeaxanthin and β-carotene extraction from Chlorella saccharophila isolated from New Zealand marine waters, Biocatal. Agric. Biotechnol. 4 (2015) 166–173, https:// doi.org/10.1016/j.bcab.2015.02.001.
- [153] Z.W. Liu, X.A. Zeng, J.H. Cheng, D.B. Liu, R.M. Aadil, The efficiency and comparison of novel techniques for cell wall disruption in astaxanthin extraction from Haematococcus pluvialis, Int. J. Food Sci. Technol. 53 (2018) 2212–2219, https://doi.org/10.1111/ijfs.13810.
- [154] M.A. Hejazi, R.H. Wijffels, Milking of microalgae, Trends Biotechnol. 22 (2004) 189–194, https://doi.org/10.1016/j.tibtech.2004.02.009.
- [155] F. Chemat, N. Rombaut, A. Meullemiestre, M. Turk, S. Perino, A.S. Fabiano-Tixier, M. Abert-Vian, Review of green food processing techniques. Preservation, transformation, and extraction, Innov. Food Sci. Emerg. Technol. 41 (2017) 357–377, https://doi.org/10.1016/j.ifset.2017.04.016.
- [156] B. Khadhraoui, M. Turk, A.S. Fabiano-Tixier, E. Petitcolas, P. Robinet, R. Imbert, M. El Maâtaoui, F. Chemat, Histo-cytochemistry and scanning electron microscopy for studying spatial and temporal extraction of metabolites induced by ultrasound. Towards chain detexturation mechanism, Ultrason. Sonochem. 42 (2018) 482–492, https://doi.org/10.1016/j.ultsonch.2017.11.029.
- [157] A.S. Bello, I. Saadaoui, R. Ben-Hamadou, "Beyond the source of bioenergy": microalgae in modern agriculture as a biostimulant, biofertilizer, and anti-abiotic stress, Agronomy 11 (2021) 1610, https://doi.org/10.3390/agronomy11081610.
- [158] N.A.Md Salehan, A.Z. Sulaiman, A. Ajit, Effect of temperature and sonication on the extraction of gallic acid from Labisia Pumila (Kacip Fatimah), ARPN J. Eng. Appl. Sci. 11 (2016) 2193–2198. http://umpir.ump.edu.my/id/eprint/11568.
- [159] S.K. Tulashie, S. Salifu, Potential production of biodiesel from green microalgae, Biofuels 11 (2020) 201–208, https://doi.org/10.1080/17597269.2017.1348188.
- [160] N. Zghaibi, R. Omar, S.M.M. Kamal, D.R. A.B, R. Harun, Microwave-assisted brine extraction for enhancement of the quantity and quality of lipid production from microalgae Nannochloropsis sp, Molecules 24 (2019) 3581, https://doi.org/ 10.3390/molecules24193581.
- [161] P. Mäki-Arvela, I. Hachemi, D.Y. Murzin, Comparative study of the extraction methods for recovery of carotenoids from algae: extraction kinetics and effect of different extraction parameters, J. Chem. Technol. Biotechnol. 89 (2014) 1607–1626, https://doi.org/10.1002/jctb.4461.
- [162] B.S. Inbaraj, H. Lu, C.F. Hung, W.B. Wu, C.L. Lin, B.H. Chen, Determination of carotenoids and their esters in fruits of Lycium barbarum linnaeus by HPLC–DAD–APCI–MS, J. Pharm. Biomed. Anal. 47 (2008) 812–818, https://doi. org/10.1016/j.jpba.2008.04.001.
- [163] M.C. Cerón, I. Campos, J.F. Sánchez, F.G. Acién, E. Molina, J.M. Fernández-Sevilla, Recovery of lutein from microalgae biomass: development of a process for Scenedesmus almeriensis biomass, J. Agric. Food Chem. 56 (2008) 11761–11766, https://doi.org/10.1021/jf8025875.
- [164] P. Divya, B. Puthusseri, B. Neelwarne, Carotenoid content, its stability during drying and the antioxidant activity of commercial coriander (Coriandrum sativum)

L.) varieties, Food Res. Int. 45 (2012) 342–350, https://doi.org/10.1016/j. foodres.2011.09.021.

- [165] M.C. Chan, S.H. Ho, D.J. Lee, C.Y. Chen, C.C. Huang, J.S. Chang, Characterization, extraction and purification of lutein produced by an indigenous microalga Scenedesmus obliquus CNW-N, Biochem. Eng. J. 78 (2013) 24–31, https://doi.org/10.1016/j.bej.2012.11.017.
- [166] J. Oliver, A. Palou, Chromatographic determination of carotenoids in foods, J. Chromatogr. A 881 (2000) 543–555, https://doi.org/10.1016/S0021-9673(00) 00329-0.
- [167] A.Kamaraki Farahani, P. Baghaee, M.B. Rezaee, K. Jaimand, Methodes for the analysis of carotenoides (crocins and crocetin of Saffron) using thin layer chromatography (TLC), Iran. J. Med. Aromat. Plants 20 (2005) 407–416. htt ps://ijmapr.areeo.ac.ir/article_115222.html?lang=en.
- [168] A.J. Melendez-Martinez, C.M. Stinco, C. Liu, X.-D. Wang, A simple HPLC method for the comprehensive analysis of cis/trans (Z/E) geometrical isomers of carotenoids for nutritional studies, Food Chem. 138 (2013) 1341–1350, https:// doi.org/10.1016/j.foodchem.2012.10.067.
- [169] S. Li, X. Tang, Y. Lu, J. Xu, J. Chen, H. Chen, An improved method for the separation of carotenoids and carotenoid isomers by liquid chromatography-mass spectrometry, J. Sep. Sci. 44 (2021) 539–548, https://doi.org/10.1002/ jssc.202000902.
- [170] M.M. Mendes-Pinto, A.C.S. Ferreira, M.B.P.P. Oliveira, P. Guedes de Pinho, Evaluation of some carotenoids in grapes by reversed- and Normal-phase liquid chromatography: a qualitative analysis, J. Agric. Food Chem. 52 (2004) 3182–3188, https://doi.org/10.1021/jf0499469.
- [171] A.Z. Mercadante, D.B. Rodriguez-Amaya, G. Britton, HPLC and mass spectrometric analysis of carotenoids from mango, J. Agric. Food Chem. 45 (1997) 120–123, https://doi.org/10.1021/jf960276j.
- [172] A. Piovesana, E. Rodrigues, C.P.Z. Noreña, Composition analysis of carotenoids and phenolic compounds and antioxidant activity from hibiscus calyces (Hibiscus sabdariffa L.) by HPLC-DAD-MS/MS, Phytochem. Anal. 30 (2019) 208–217, https://doi.org/10.1002/pca.2806.
- [173] M. Zapata, F. Rodríguez, J.L. Garrido, Separation of chlorophylls and carotenoids from marine phytoplankton: a new HPLC method using a reversed phase C8 column and pyridine-containing mobile phases, Mar. Ecol. Prog. Ser. 195 (2000) 29–45, https://doi.org/10.3354/meps195029.
- [174] Y. Soma, T. Imaizumi, K.I. Yagi, S.I. Kasuga, Estimation of algal succession in Lake water using HPLC analysis of pigments, Can. J. Fish. Aquat. Sci. 50 (1993) 1142–1146, https://doi.org/10.1139/F93-130.
- [175] K.T. Amorim-Carrilho, A. Cepeda, C. Fente, P. Regal, Review of methods for analysis of carotenoids, TrAC - Trends Anal. Chem. 56 (2014) 49–73, https://doi. org/10.1016/j.trac.2013.12.011.
- [176] E.I. Finkel'shtein, Modern methods of analysis of carotenoids (review), Pharm. Chem. J. 50 (2016) 96–107, https://doi.org/10.1007/s11094-016-1405-2.
- [177] S.M. Rivera, R. Canela-Garayoa, Analytical tools for the analysis of carotenoids in diverse materials, J. Chromatogr. A 1224 (2012) 1–10, https://doi.org/10.1016/ j.chroma.2011.12.025.
- [178] M. Honda, Carotenoid isomers: a systematic review of the analysis, biological activity, physicochemical property, and methods for isomerization, in: Atta-ur-Rahman (Ed.), Stud. Nat. Prod. Chem, Elsevier, 2021, pp. 173–220, https://doi. org/10.1016/B978-0-12-819485-0.00002-5.
- [179] M.G. Dias, M.F.G.F.C. Camões, L. Oliveira, Carotenoid stability in fruits, vegetables and working standards – effect of storage temperature and time, Food Chem. 156 (2014) 37–41, https://doi.org/10.1016/j.foodchem.2014.01.050.
- [180] C. Soukoulis, T. Bohn, A comprehensive overview on the micro- and nanotechnological encapsulation advances for enhancing the chemical stability and bioavailability of carotenoids, Crit. Rev. Food Sci. Nutr. 58 (2018) 1–36, https:// doi.org/10.1080/10408398.2014.971353.
- [181] O.P. Bamidele, M.N. Emmambux, Encapsulation of bioactive compounds by "extrusion" technologies: a review, Crit. Rev. Food Sci. Nutr. 61 (2021) 3100–3118, https://doi.org/10.1080/10408398.2020.1793724.
- [182] L. Chen, X. Liu, D. Li, W. Chen, K. Zhang, S. Chen, Preparation of stable microcapsules from disrupted cell of Haematococcus pluvialis by spray drying, Int. J. Food Sci. Technol. 51 (2016) 1834–1843, https://doi.org/10.1111/ IJFS.13155.
- [183] P.P. dos Santos, L.de A. Andrade, S.H. Flôres, A. de O. Rios, Nanoencapsulation of carotenoids: a focus on different delivery systems and evaluation parameters, J. Food Sci. Technol. 55 (2018) 3851–3860, https://doi.org/10.1007/s13197-018-3316-6.