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Unleashing the potential of castor oil as extraction solvent of carotenoids from tomatoes

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ABSTRACT

Adding carotenoids to cosmetic formulations aligns with the industry's growing ethos of producing safer, more sustainable, and nature-inspired products. While synthetic compounds still have their place in cosmetics, the shift towards natural ingredients such as carotenoids reflects a more significant commitment across the industry to satisfy consumer preferences and contribute to a greener future. Castor oil is a well-known natural oil used in several cosmetic formulations because it reduces moisture loss and enhances skin hydration. However, it's only added to cosmetics simultaneously with all the other components, including natural extracts. Thus, this work goes behind literature and classic downstream approaches. A simplification of cosmetics formulations is intended by using castor oil directly as the extraction solvent of natural bioactive compounds, such as carotenoids from tomatoes. A comparison of its extraction performance with conventional extraction solvents was made, and all the process operating conditions were optimized (SLR = 0.06 $g_{biomass}.mL^{-1}_{solvent}$, percentage of castor oil = 50% (v/v), and time of extraction = 90 min) to achieve a maximum recovery of 3.2 ± 0.2 $mg_{Car}.g^{-1}_{biomass}$. Additionally, its capacity as a preservative of carotenoids degradation was also tested against a conventional solvent to enhance natural pigments' shelf life showcasing increased stability (especially at 75 °C), a current problem of their application in industry. The environmental performance of the process proposed was analyzed based on the carbon footprint, with electricity consumption identified as the most significant contributor. This impact could be greatly reduced by utilizing photovoltaic energy. Lastly, a conceptual process design has been proposed to envision its practical application in an industrial setting.

1. Introduction

The cosmetics industry has a growing demand to replace synthetic compounds with natural alternatives. This shift is being driven by several factors that underscore the industry's commitment to consumer health, environmental sustainability, and a desire for holistic and nature-derived products. The prospective adverse effects of certain synthetic compounds, including skin irritation, allergies, and the presence of reported carcinogenic substances deemed toxic, evoke a sense of alarm among consumers.[1–3] Consequently, cosmetic products incorporating natural compounds provide cosmetic advantages and make meaningful contributions to the overall health and vitality of the skin.[4]

Tomatoes (*Solanum lycopersicum* L.), categorized as a fruit and belonging to the Solanaceae family, have earned global recognition for their culinary versatility, with their production reaching a scale of approximately 164 million tons worldwide.[5] However, this large-scale production also highlights the growing concern of food waste. According to the Food and Agriculture Organization (FAO), food waste is "food appropriate for human consumption being discarded, whether or not after it is kept beyond its expiry date or left to spoil".[6] In the case of tomatoes, this waste can occur during processing, where by-products

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like peels, seeds, and pomace—constituting up to 5% of the total tomato—are often discarded, posing environmental challenges for producers. These residual tomato by-products, though frequently wasted, are rich in valuable compounds, including minerals, vitamins, dietary fibers, proteins, polyphenols, and carotenoids, aligning with the industry's demand for natural ingredients.[7] Notably, carotenoids, for instance, are renowned for their antioxidant properties and potential to promote skin health, making them promising candidates for novel ingredients in the cosmetic industry.[8]

Within the spectrum of carotenoids found in tomatoes, lycopene constitutes roughly 80–90% of the total pigment content in ripe tomatoes, giving rise to the characteristic red coloration of these fruits.[9] Lycopene, characterized by its open-chain structure and 11 *trans*-configurated double bonds, boasts exceptional antioxidant capabilities for neutralizing free radicals and protecting the skin against the harmful effects of light and oxygen. These properties, in turn, lead to reduced roughness, improved hydration, enhanced elasticity, and pigmentation on the skin.[10,11] This carotenoid is currently employed to combat the adverse effects of sun exposure, such as sunburn, and the risk of skin cancer by mitigating the damage provoked by prolonged exposure to sunlight.[12] Consequently, lycopene is a popular choice in cosmetic formulations owing to its remarkable impact on skin rejuvenation, renewal, and thickness enhancement.

While present in smaller amounts, tomato fruits also contain β-carotene.[13] β-carotene is an orange-red C_{40} carotenoid characterized by an extensive chain of conjugated double bonds. Like lycopene, its high antioxidant capacity affords it the capability to regenerate skin against oxidation and adverse effects of UV radiation on observed lesions.[14] Moreover, its tinting ability makes it a valuable ingredient in sun tan creams and lotions, while also promoting healing, scar prevention, and relieving skin irritation and itchiness.[10]

Considering the exceptional attributes of natural pigments and the need to valorize waste resources and add them to circular economy chains, it becomes crucial to possess precise knowledge of straightforward and efficient extraction techniques to achieve a maximum recovery of carotenoids.[15] Additionally, exploring methods to stabilize natural pigments is essential to make them a viable option for industrialization.[16] Conventional solvents such as hexane, chloroform, and acetone have been traditionally employed for lycopene extraction from vegetable matter. However, due to their harmful and toxic nature, the elaboration of multi-step procedures is required to eliminate these solvents from the end product, which still represents a significant process limitation.[17] Also, current industries are starting to recognize their impacts on the environment and strive to adopt more sustainable practices, to fulfil the sustainable development goals.[18] To overcome these drawbacks, new techniques are being developed, and alternative solvents are being employed.[19]

Castor oil, derived from the crushed seeds of the Castor plant, is composed of approximately 90% ricinoleic acid, a hydroxyl-containing fatty acid known for its emollient properties.[20] These fatty acids effectively reduce moisture loss, enhancing skin hydration and making castor oil a standard inclusion in various skincare products such as lotions, creams, and moisturizers, rendering it a valuable asset in skincare routines.[21] Despite its common use in cosmetic products, there is a lack of existing literature exploring the utilization of castor oil as part of the extraction process for the bioactive compounds incorporated in these formulations. In addition to its natural and renewable nature,[22] enhancing sustainability, from an economic perspective, castor oil use could lead to a reduction in production costs by providing an extract that can be directly considered as one of the ingredients to introduce in the formulation. In other words, this eliminates the need for additional solvents in the extraction of bioactive compounds and simplifies the process by skipping the step of adding the oil to the formulation. Another potential, previously unexplored, could be linked to the preservative function of natural oils in cosmetics.[23] Preservatives are primarily used in cosmetics to prevent microbial growth, acting as antimicrobials. However, they can also act as antioxidants to protect against oxygen-induced damage and as photoprotectors against UV light-induced degradation.[24] Hence, castor oil could extend the shelf life of cosmetic products containing natural pigments by protecting them from external damage, heat, and oxygen conditions, leading to color fading over time. Consequently, addressing the stability issue related to these compounds is also crucial.[25]

The main aim of this study is to unleash the potential of castor oil by not only developing a straightforward and cost-effective process for extracting lycopene and β-carotene from tomatoes but also improving their stability. Thus, we hypothesize that castor oil will efficiently support the extraction and stabilization of pigments, offering a sustainable alternative to conventional solvents. With this, tomato waste or ugly tomato fruits could be efficiently exploited, allowing thus cosmetic products to successfully integrate natural pigments into their formulations, representing a significant step towards sustainable and naturally based cosmetics.

2. Experimental section

2.1. Biomass

Fresh tomatoes (*Solanum lycopersicum*), precisely the type commonly referred to in Portugal as "Tomate Rama", were purchased from the supermarket Auchan Aveiro (Portugal) in May 2021. A single purchase of a sufficient quantity of tomatoes was made for the entire work, aiming to minimize the variability in the pigments' composition within the fruit. The skins and seeds of the tomatoes were manually removed, and all the pulp was then blended using a hand immersion blender (Silvercrest SSMS 600 A1). Subsequently, the blended pulp was divided into multiple 2 mL Eppendorf tubes and frozen at −80 °C until required.

2.2. Chemicals

Organic solvents tested in the extraction of β-carotene and lycopene as ethanol (HPLC grade, CAS 64–17-5) and acetone (100 wt%, CAS 67–64-1) were acquired from Fisher Scientific, while ethyl acetate (≥99.5 wt%, CAS 141–78-6) was purchased to Sigma Aldrich. Cationic compounds based on the ammonium family, namely dodecyltrimethylammonium bromide ($[N_{1,1,1,12}]Br$, 99 wt%, CAS 1119–94-4) and tetradecyltrimethylammonium bromide ($[N_{1,1,1,14}]Br$, 98 wt%, CAS 1119–97-7), were supplied by Alfa Aesar, while decyltrimethylammonium bromide ($N_{1,1,1,10}]Br$, 99 wt%, CAS 2082–84-0) was acquired from Tokyo Chemical Industry. Tributyltetradecylphosphonium chloride ($[P_{4,4,4,14}]Cl$, 95 wt%, CAS 81741–28-8) and 1-dodecyl-3-methylimidazolium chloride ($[C_{12}C_1im]Cl$, >98 wt%, CAS 114569–84-5) were purchased to IoLiTec. Non-ionic polyethylene glycol sorbitan monolaurate (Tween® 20, CAS 9005–64-5), and anionic sodium dodecylsulfate (SDS, pharma grade, CAS 151–21-3) were supplied by Acros Organics and Panreac, respectively. Castor Oil (Pure, CAS 8001–79-4) was obtained at Soft&Co. Standard β-carotene (≥97 wt%, CAS 7235–40-7) was acquired from Fluka™. The molecular structures of the IL/Surfactants screened in this work are depicted in Figure S1 in ESI.

2.3. Solid-liquid extraction

Several organic and aqueous cationic, non-ionic, and anionic (250 mM) solvents were initially tested to evaluate their pigments' extraction capacity (β-carotene and lycopene) from tomato pulp (previously prepared) and compared with distilled water. Their choice was based on several articles stating their high performance when discussing hydrophobic pigment extraction.[26–31] Concentrations above the critical micellar concentration (CMC) were always used for the aqueous solutions of surface-active compounds (CMC values available at Table S1 in ESI). Furthermore, based on the work developed by Martins *et al.* (2021)

various systems were tested, in this case using castor oil (Oil_C), which was also tested individually, such as $Oil_C + H_2O$, Oil_C + IL in H_2O, Oil_C + Ethanol, Oil_C + IL in Ethanol. Extraction conditions were a solid–liquid ratio (SLR) of 0.1 $g_{biomass}.mL^{-1}_{solvent}$, extraction time of 30 min, all at room temperature (20 − 25 °C) under a constant vertical rotation of 80 rpm in an IKA shaker digital TRAYSTER. For the systems, a ratio of 84% (v/v) of an aqueous/organic solution of $[P_{4,4,4,14}]Cl$ at 250 mM or only water/ethanol + 16% (v/v) of Oil_C was used. Finally, a centrifugation step was performed to separate the cell debris and recover the supernatant for 15 min at 10 °C and 4700 *g* using a Thermo Scientific Heraeus Megafuge 16R centrifuge. All extractions were carried out in triplicate, and the outcomes were reported as the mean ± standard deviations.

The absorption spectra of all samples were measured using a UV–Vis microplate reader (Synergy HT-BioTek microplate reader) within a range spanning from 350 to 550 nm. The quantification of total carotenoids (β-carotene + lycopene) was carried out using β-carotene as standard with calibration curves established at 450 nm for organic/aqueous solutions (r^2 = 0.9926), and at 458 nm for oil systems (r^2 = 0.9994). The carotenoid extraction yield was calculated using Equation (1).

$$\text{Yield of extraction}\left(mg_{Car}.g_{biomass}^{-1}\right) = \frac{\text{Carotenoids concentration}\left(mg.mL^{-1}\right) \times \text{Solvent volume}\,(mL)}{\text{Weight of biomass}\,(g)} \quad (1)$$

2.4. COSMO-RS model

Water, ethanol, $[P_{4,4,4,14}]Cl$, and castor oil molecules were optimized using density functional theory (DFT) calculations with the TURBOMOLE V4.5.2 package.[32] All Conductor-like Screening Model for Real Solvents (COSMO-RS) calculations were performed utilizing the COSMOthermX software package (Version 21.0, COSMOlogic GmbH) at the BP86/TZVP level with the BP_TZVP_21.ctd parameterization.[33,34] COSMO-RS was employed to determine the σ-potentials and σ-profiles of β-carotene, lycopene, and the solvents. Additionally, the activity coefficient at infinite dilution was estimated, and intermolecular interactions (van der Waals and misfit) were also evaluated.

2.5. Process optimization and kinetics

The chosen system was optimized using a central composite rotatable design (CCRD, 22 plus axial) with a total of 13 assays with 5 central points. As independent variables, the Oil percentage in the chosen system (%Oil_C in %) and the solid–liquid ratio (SLR in $g_{biomass}.mL^{-1}_{solvent}$) were studied according to the carotenoid extraction yield (Yield of extraction in $mg_{Car}.g^{-1}_{biomass}$). Temperature, agitation, and extraction time were maintained at the same levels that were used during the solvent screening phase (room temperature of 20–25 °C, agitation at 80 rpm, and an extraction time of 30 min). The statistical analysis of the results was conducted using Statistica® 7 software at a 95% confidence level, following the methodology outlined by Dean *et al.* [35] and Rodrigues and Lemma.[36] The actual and encoded values can be found in Table S2 in the ESI. Finally, the determined optimal conditions were validated in triplicate using the mean relative deviation (%) values. Following this, a kinetic curve depicting the recovery yield of the pigments over time was developed using first and second-order kinetic models.[37] Here, the previously optimized conditions using CCRD were held constant, with the only variation being the extraction time, ranging from 2 to 240 min. Equation (2) represents the first-order kinetic model in its differential form.

$$\frac{dC_t}{dt} = k_1(C_S - C_t) \quad (2)$$

k_1 (min^{-1}) is the first-order extraction rate constant, t (min) is the extraction time, and C_S and C_t are the carotenoids yield at saturation and for a specific extraction time, respectively. By integrating Equation (2) with the boundary conditions $C_t = 0$ at $t = 0$ and $C_t = C_t$ at $t = t$, Equation (3) is derived.

$$\ln\left(\frac{C_S}{C_S - C_t}\right) = k_1 t \quad (3)$$

k_1 was obtained from the slope of the graph generated by plotting the natural logarithm (ln) values of C_t against t. Equation (4) expresses the second-order kinetic equation for the extraction rate.

$$\frac{dC_t}{dt} = k_2(C_S - C_t)^2 \quad (4)$$

where k_2 ($g_{biomass}.mg^{-1}_{Car}.min^{-1}$) is the second-order extraction rate constant. Upon integrating with the boundary conditions $C_t = 0$ at $t = 0$ and $C_t = C_t$ at $t = t$, and linearization, Equation (5) is derived.

$$\frac{t}{C_t} = \frac{t}{C_S} + \frac{1}{k_2 {C_S}^2} \quad (5)$$

Plotting t/C_t against t, allows the obtention of the C_S and k_2 constants, which correspond to the slope and intercept of the plot, respectively.

2.6. Thermal stability

The thermal stability of the pigments was investigated across four distinct temperatures (20 – 25 °C, 55 °C, 75 °C, and 95 °C) for both acetone and oil + ethanol system (after ethanol removal through rotary evaporation). For 55 °C, 75 °C, and 95 °C, to initiate the experiment, each extract was dispensed into sealed encapsulated vials (1 mL *per* vial) and placed within a heated metal block atop a heating plate, protected from light exposure.[38] The vials were then collected at different times and immediately put in an ice bath to stop the degradation process. For 20 – 25 °C, each vial was kept at room temperature under light exposure and, after collection at the desired time, immediately analyzed. Each sample underwent UV–Vis spectroscopy analysis, from which a range of parameters was calculated. This range includes the degradation rate constant (k_d, in h^{-1} for 1st order and $mL_{solvent}.mg^{-1}_{Car}.h^{-1}$ for 2nd order) and the half-life time ($t_{1/2}$, in h), calculated for both first-order reaction kinetics (Equations (6) and (7) and second-order reaction kinetics (Equations (8) and (9). The thermal activation energy (E_a, in $kJ\cdot mol^{-1}$) was determined using Equation (10).[39–41]

$$\ln\left(\frac{C_t}{C_0}\right) = -k_d t \quad (6)$$

$$t_{1/2} = \frac{\ln(2)}{k_d} \quad (7)$$

$$\frac{1}{C_t} - \frac{1}{C_0} = k_d t \quad (8)$$

$$t_{1/2} = \frac{1}{C_0 k_d} \quad (9)$$

where C_0 and C_t are the initial (t = 0) and the final (t = t) concentration of carotenoids ($mg_{Car}.mL^{-1}_{solvent}$), respectively, t is the time (h).

$$k_d = Ae^{-E_a/RT} \quad (10)$$

where A is the frequency factor (min^{-1}), T is the temperature (K), and R is the gas constant (8.31 $J.K^{-1}.mol^{-1}$).

2.7. Statistical analysis

A one-way ANOVA (Analysis of Variance) analysis was performed followed by the Bonferroni post-hoc test to compare the different outcomes of the various conditions investigated during this work. The results were presented as the mean ± standard error of the mean, and

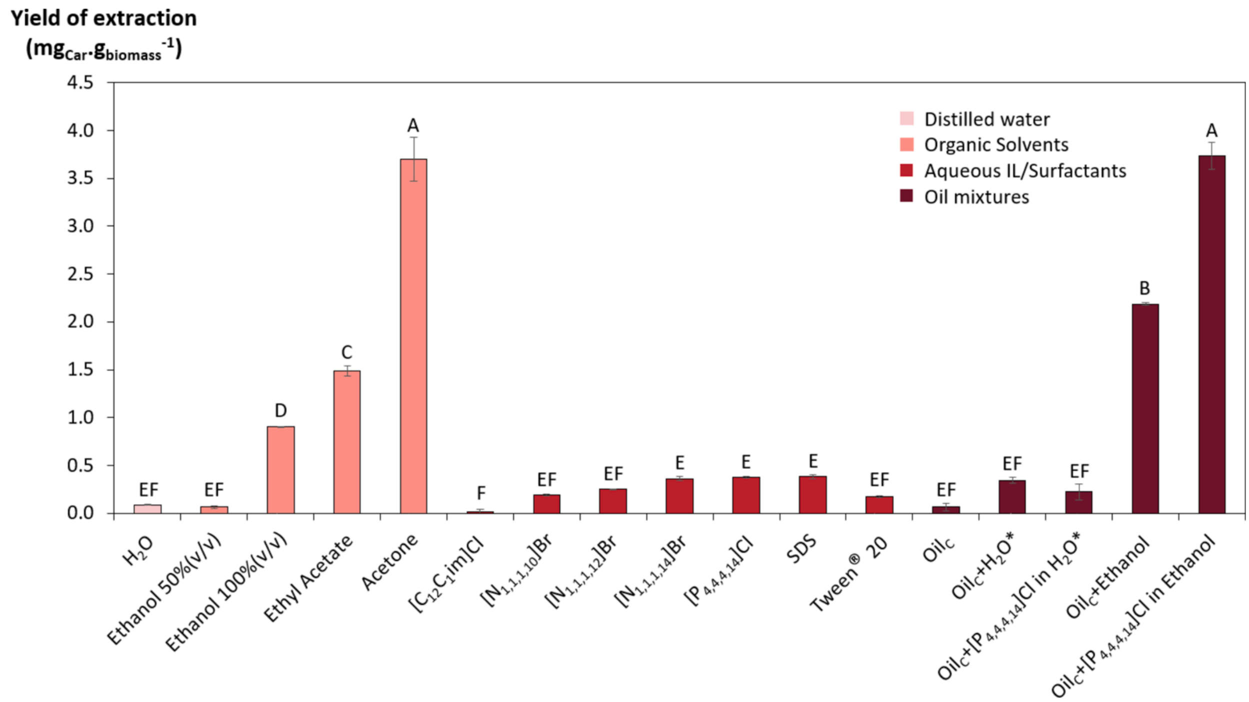

Fig. 1. Yield of extraction of carotenoids, namely β-carotene and lycopene, using distilled water, organic solvents, aqueous solutions of IL/surfactants at 250 mM and castor oil mixtures with 16% (v/v) of Oil_C, at room temperature (20–25 °C), under a constant vertical rotation of 80 rpm, for 30 min, protected from light exposure, and at a fixed SLR of 0.1 $g_{biomass}.mL_{solvent}^{-1}$. Different capital letters represent statistically different values in the conditions under study (*p-value* < 0.05). *Systems with two phases, where these results are related to the bottom phase composed of water.

statistically significant differences were determined with a significance level of 95% (*p-value* < 0.05).

2.8. Carbon footprint

The carbon footprint of the most promising system at the laboratory scale, using ethanol and castor oil, was calculated based on a life cycle perspective, according to the ISO 14067 standard.[42] The system boundaries include all processes from cradle-to-gate, *i.e.*, from the production of the inputs up to the analyzed process. The functional unit (reference to which the results are related) is 1 kg of tomatoes consumed in the system. The inventory data are provided in Table S3 in ESI, comprising the consumption of tomatoes, ethanol, castor oil and electricity. They also include the production of tomato seeds, peels and used pulp, which were considered by-products that can have additional uses, and, therefore, no impact from those uses was allocated to the system analized. The consumption of electricity was estimated based on the nominal power of the equipment, the duration of the operation, and the percentage of the equipment capacity allocated to each task. Therefore, it represents a worst-case scenario, as the real power may be smaller than the nominal power assumed in the calculations. The carbon footprint from the production of tomatoes, ethanol, and electricity was sourced from the ecoinvent 3.9.1 database,[43] with the carbon footprint of castor oil obtained in literature.[44] The global warming potential of each greenhouse gas applied to convert emissions to a standard unit of mass of carbon dioxide equivalent (CO_2 eq) was sourced from.[45]

3. Results and discussion

3.1. Screening of solvents

The efficiency of carotenoid extraction is significantly influenced by the selection of an appropriate solvent or solvent combination, since factors like the functional group (polarity) and chain length of carotenoids, the composition of the sample matrix and its components, and moisture content, influence the action of the solvent during extraction.[19] Therefore, a comprehensive screening of solvents, spanning from conventional to alternative, was undertaken to assess their effectiveness in recovering β-carotene and lycopene from tomato pulp. Tomato pulp was utilized to demonstrate the proof of concept for the process developed throughout this work. The goal is to transition to utilizing tomato by-products or ugly tomato fruits in the future. Adopting a conventional perspective, some of the least hazard organic solvents with different polarities—such as ethanol, acetone, and ethyl acetate—were tested and compared against distilled water. From an alternative standpoint, the behavior of various aqueous solutions of ILs/surfactants was studied, and their efficiency in extracting carotenoids and other hydrophobic pigments from diverse sources was also reported.[26–31] Lastly, in an exploration beyond existing literature, castor oil and some castor oil mixtures were examined as extraction solvents, to investigate the possibility of their direct incorporation into the final product, particularly in the context of cosmetic formulations. Moreover, a comprehensive list outlining the functions of the tested solvents in cosmetic products can be found in Table S4 in ESI.

Fig. 1 presents the carotenoids yield of extraction ($mg_{Car}.g_{biomass}^{-1}$) from tomato pulp, in terms of the ability of the tested solvents to induce the release of β-carotene and lycopene. UV–Vis spectroscopy results of the obtained extracts can be found in Figure S2 in ESI.

Lycopene and β-carotene are highly lipophilic and non-polar carotenoids due to their conjugated hydrocarbon structure, lacking polar functional groups. Hence, its recovery typically calls for less polar solvents, like acetone and hexane.[19] However, the use of acetone is preferable as it is less toxic. As it can be seen in Fig. 1, from polar to less polar (water < ethanol 50% < ethanol 100% < ethyl acetate < acetone) the yield significantly increases, being proved the expected high performance of acetone (*p-value* < 0.05). Alternatively, the most promising ILs/surfactants were assessed. Here, only tensioactive compounds were tested due to their ability to form micelles above the critical micellar concentration (as it happens at 250 mM for all tested solvents; see

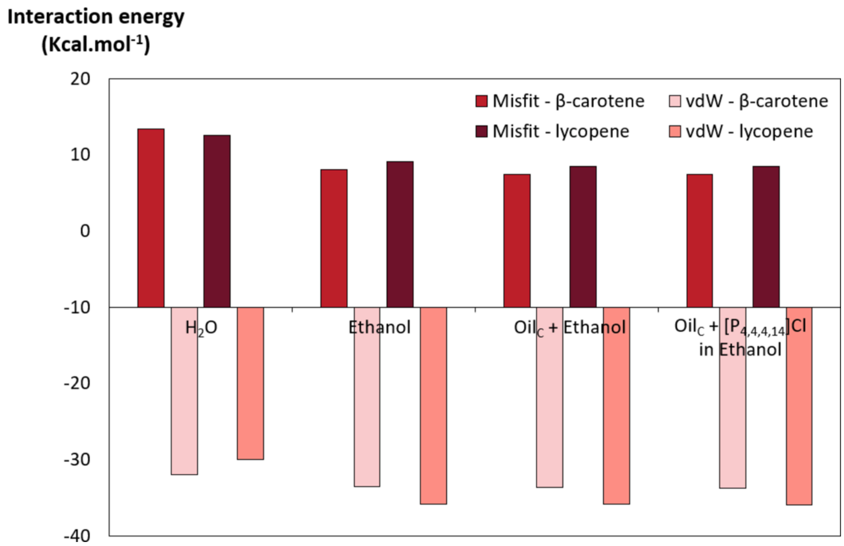

Fig. 2. COSMO-RS calculated interaction energies between β-carotene and lycopene and water, ethanol, Oil_C + Ethanol and Oil_C + $[P_{4,4,4,14}]Cl$ in Ethanol.

Table S1 in ESI), being able to recover more hydrophobic molecules in an aqueous environment. Nevertheless, while they show effective recovery for various carotenoids from diverse biomass sources, its overall performance consistently fell short compared to acetone. $[C_{12}C_1im]Cl$ was found to present the lowest yield of extraction, even lower than water (p-*value* < 0.05). $[N_{1,1,1,10}]Br$, $[N_{1,1,1,12}]Br$ and Tween® 20 present no statistically significant differences compared to water (p-*value* $>$ 0.05). Finally, $[N_{1,1,1,14}]Br$, $[P_{4,4,4,14}]Cl$ and SDS performed a little better than water, however lower than ethanol 100% (p-*value* < 0.05).

As demonstrated by Martins *et al.* (2021) [46] and observed in Fig. 1, utilizing oil alone as extraction solvent proves to be ineffective in recovering pigments. Its high viscosity impairs mass transfer of the compounds of interest from the biomass to the oil and limits its ability to interact with the cell structure without mechanical assistance. Nevertheless, in the same article, integrating oil into systems with aqueous solutions of ILs showcased remarkable extraction capabilities. Here, considering that a different oil is being used, castor oil, the systems tested with $Oil_C + H_2O$ and Oil_C + IL in H_2O posed some challenges. Two phases were formed; the upper phase, expected to be rich in pigments and composed of oil, presented some difficulties as it could not be analyzed due to turbidity. Contrarily, the aqueous bottom phase, did not exhibit a significant recovery of carotenoids (Fig. 1). On the other hand, replacing water with ethanol in the systems yielded remarkable results, comparable to acetone. In this case only one phase was formed since castor oil and ethanol are completely miscible. Ethanol has indeed several advantages. Its water-miscible properties are beneficial for efficient extractions from biomass with high moisture content,[19] the case of tomatoes. Furthermore, ethanol actively disrupts cell membrane walls, facilitating the release of intracellular compounds and consequently improving the extraction of carotenoids.[27] As previously explained, the polarity of ethanol limits its ability to interact efficiently with lycopene and β-carotene. Nevertheless, when combined with castor oil, it retains its advantages and overcomes the disadvantages associated with oil alone. This combination leads to a decrease in the viscosity of the solution, an effective disruption of the tomato cell membrane, and, consequently, a high recovery of carotenoids. Finally, adding IL to this mixture improved the carotenoid extraction yield even more. The IL chosen here was $[P_{4,4,4,14}]Cl$ since it was one of the tested ones that had the best yield. Furthermore, cationic ILs are able to establish attractive electrostatic interactions between the IL cation and the negatively charged head of the phospholipids present in the cell membrane,[31] probably explaining the increased performance of the mixture, with no statistically significant differences found when compared to acetone (p-*value* > 0.05).

Going beyond, to better understand the intricate mechanisms that govern solvent mixtures in extraction processes, theoretical calculations at the microscopic level were conducted. COSMO-RS was utilized to predict the activity coefficients at infinite dilution ($\ln\gamma^{\infty}$) of β-carotene and lycopene in the tested solvents, along with interaction energy and screen charge distribution. The results of the $\ln\gamma^{\infty}$ calculations for organic solvents and oil mixtures (Figure S3 in ESI) clearly demonstrate a reduction in the $\ln\gamma^{\infty}$ of oil mixtures upon the addition of ethanol and $[P_{4,4,4,14}]Cl$. This indicates an increase in the solubility of these compounds, as a lower value of $\ln\gamma^{\infty}$ signifies a greater solvating capacity of the solvent.[47] Furthermore, increased extraction yield was observed for mixtures with lower $\ln\gamma^{\infty}$ values.

The extraction mechanism of β-carotene and lycopene can also be effectively interpreted by analyzing the intermolecular interactions and σ-profiles determined. The σ-profile graph can be divided into three areas based on the molecule's affinity: the hydrogen bond donor area ($\sigma < -0.0082$ e.Å^{-2}), the non-polar area (-0.0082 e.Å$^{-2} < \sigma < 0.0082$ e.Å^{-2}), and the hydrogen bond acceptor area ($\sigma > +0.0082$ e.Å^{-2}). Concerning the tested solvents, castor oil and $[P_{4,4,4,14}]Cl$ exhibit an intense peak in the non-polar region (Figure S4 in ESI), indicating stronger non-polarity. Therefore, these solvents are expected to have a greater capacity to interact with the target compounds, following the "like dissolves like" rule.[48] Hence, it is understandable that a combination of castor oil, ethanol, and $[P_{4,4,4,14}]Cl$ exhibits better performance than pure castor oil for extracting β-carotene and lycopene in terms of σ-profiles.

From the perspective of intermolecular interactions (Fig. 2), water exhibits a more extensive misfit interaction with β-carotene/lycopene compared to ethanol and oil mixtures (Oil_C + Ethanol and Oil_C + $[P_{4,4,4,14}]Cl$ in Ethanol). In contrast, the van der Waals (vdW) interaction energy tends to be more negative for oil mixtures. A negative van der Waals (vdW) interaction is advantageous, whereas a positive misfit interaction is disadvantageous for the extraction behavior between β-carotene/lycopene and solvents. In this context, it is comprehensive that Oil_C + $[P_{4,4,4,14}]Cl$ in Ethanol exhibits the highest extraction efficiency, presenting the lowest misfit energy value and the most negative van der Waals energy.

Including castor oil in this study presents a novel perspective with no precedent in the scientific literature, potentially contributing to innovative approaches in the formulation of cosmetic products. Considering this, the selected mixture for further processing was Oil_C + Ethanol. Including an IL, besides increasing the cost of the process, would require

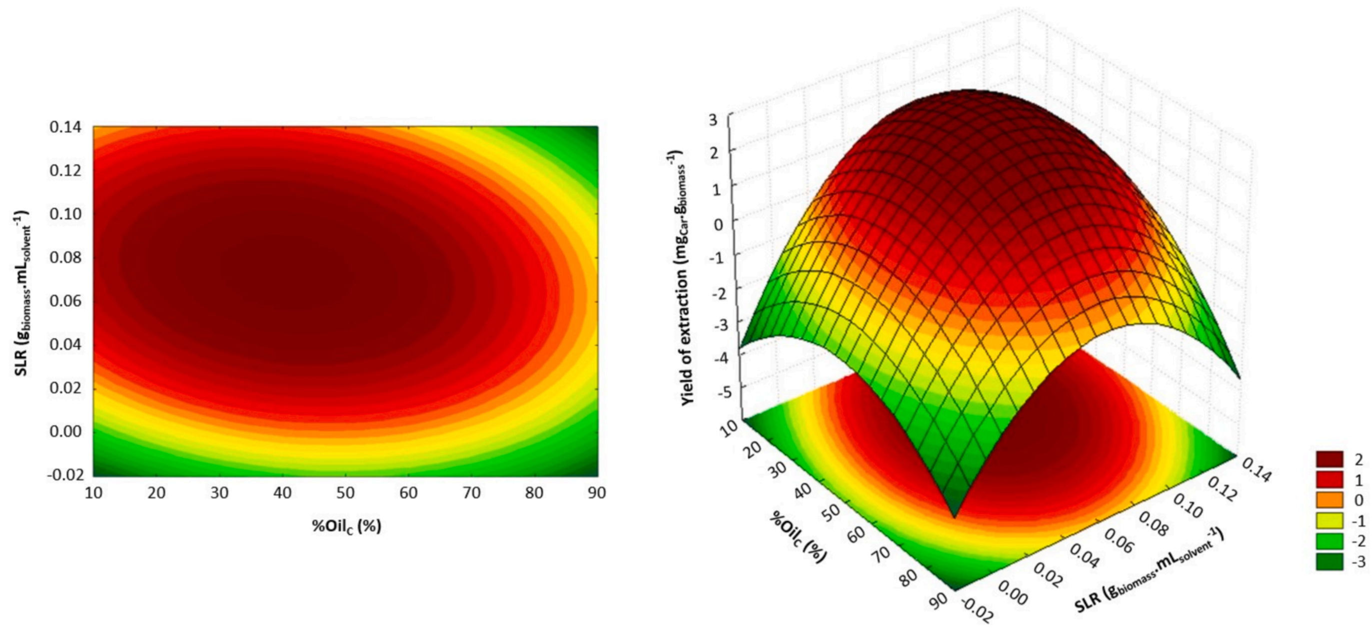

Fig. 3. Response surface plot (right side) and respective contour plot (left side) obtained for the CCRD (2^2) using an Oil_C + Ethanol system regarding SLR ($g_{biomass}$·$mL_{solvent}^{-1}$) and %Oil_C (%) in terms of carotenoids yield of extraction (Yield of extraction, mg_{Car}·$g_{biomass}^{-1}$).

an additional polishing step before its integration into a formulation, introducing complexity to the process. Moreover, in this case, a performance enhancement could be achieved by adjusting the oil-to-ethanol ratio to align more closely with the yield of acetone (check results after optimization step).

3.2. Optimization of the process conditions

To attain the optimal carotenoids extraction yield (response defined as mg_{Car}·$g_{biomass}^{-1}$) through the central composite rotatable design (CCRD), two variables were investigated: castor oil percentage in the Oil_C + Ethanol system (%Oil_C in % as X1), and solid–liquid ratio (SLR in $g_{biomass}$·$mL_{solvent}^{-1}$ as X2). A total of 13 runs were performed with three typical levels (−1, 0, +1), axial (−1.41, and + 1.41 levels), and five central points (level 0). The extraction time was kept constant in all assays, at 30 min (this variable will be optimized later). During this experiment, the observed carotenoid yield of extraction ranged from 0.05 mg_{Car}·$g_{biomass}^{-1}$ in assay 6 to 2.53 mg_{Car}·$g_{biomass}^{-1}$ in assay 12 (see Table S2 in ESI). Using pure error obtained from the Analysis of Variance (ANOVA), the predicted values were fitted into the model described by Equation (11).

$$\text{Yield of extraction}\left(mg_{Car}\cdot g_{biomass}^{-1}\right) = -3.032 + 0.125(XI) - 0.001(X1)^2 + 85.915(X2) - 515.471(X2)^2 - 0.254(X1)(X2) \quad (11)$$

The model demonstrated a high predictability at a confidence level

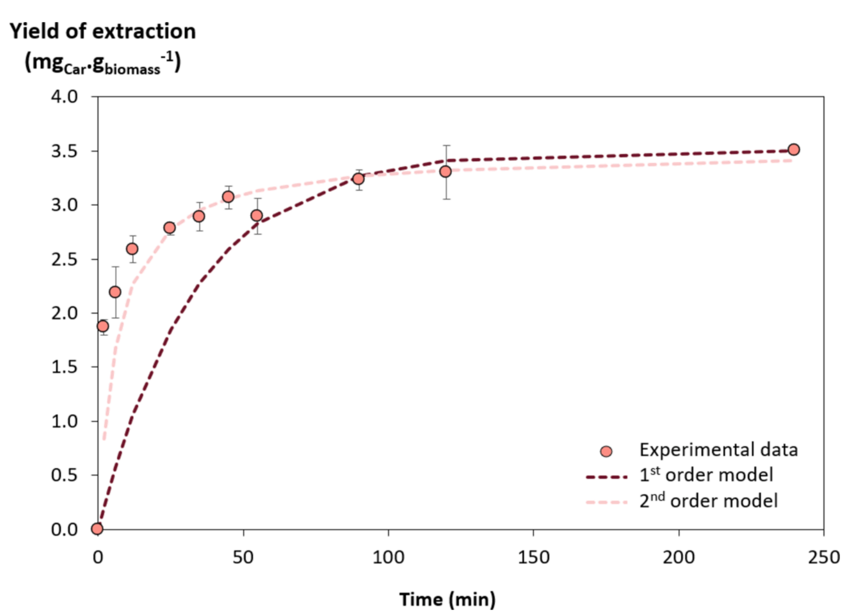

Fig. 4. Kinetic performance of carotenoids extraction, namely β-carotene and lycopene, using Oil_C + Ethanol system optimized by CCRD [operational conditions: SLR = 0.06 $g_{biomass}$·$mL_{solvent}^{-1}$, and %Oil_C = 50% (v/v), at room temperature (20–25 °C)], along with the fitting obtained using the first and second-order kinetic models.

Table 1
Linearization of the first and second-order kinetic models for lycopene and β-carotene extraction for optimum conditions (SLR = 0.06 $g_{biomass}.mL^{-1}_{solvent}$, % Oil_C = 50% (v/v)), at room temperature (20–25 °C).

1st order model		2nd order model	
Slope	0.0299	Slope	0.282
Intercept	0	Intercept	1.83
r^2	0.857	r^2	0.998
C_S ($mg_{Car}.g^{-1}_{biomass}$)	3.51	C_S ($mg_{Car}.g^{-1}_{biomass}$)	3.55
k_1 (min^{-1})	0.0299	k_2 ($g_{biomass}.mg^{-1}_{Car}.min^{-1}$)	0.0435

of 95%, with an r^2 value of 0.94264 and $F_{calculated} > F_{tabulated}$. Additionally, the model adequacy was also confirmed by the predicted *vs.* observed values graph (Figure S5 in ESI) as the predicted values closely align with the observed values. By utilizing the model described in Equation (11), the response surface illustrated in Fig. 3 was drawn.

The independent variables influence over the predictive model can be further detailed in Table S5 of ESI and Pareto Chart (Figure S6 in ESI). Here, both castor oil percentage in the Oil_C + Ethanol system and solid–liquid ratio variables significantly influence the predictive model response (*p-value* < 0.05). Notably, the solid–liquid ratio (Q) emerges as the variable with the most pronounced effect. The analysis of the response surface depicted in Fig. 3 allows us to pinpoint the optimal recovery condition described by a solid–liquid ratio (SLR) of 0.06 $g_{biomass}.mL^{-1}_{solvent}$, and a 50% (v/v) of castor oil in the system, Oil_C + Ethanol. Three repetitions of the extraction were conducted under the optimized conditions to affirm the model's validity. This yielded an extraction of 3.0 ± 0.3 $mg_{Car}.g^{-1}_{biomass}$, with a relative deviation of 9.48% (refer to Table S6 in ESI). This consistent outcome serves to validate the accuracy and robustness of the model.

Next, a kinetic study was carried out to determine the most effective extraction time that maximizes the extraction yield of lycopene and β-carotene by fitting the first- and second-order kinetic models (described in the Experimental Section through Equations (2) to (5) to the experimental data, as shown in Fig. 4. The optimal operational conditions outlined in the CCRD are used here and are kept constant. All fitting parameters are summarized in Table 1.

The results illustrated in Fig. 4 reveal a significant increase in extraction yield with extended extraction time, plateauing from 90 to 240 min at an extraction yield of approximately 3.2 to 3.5 $mg_{Car}.g^{-1}_{biomass}$. Considering the preference for shorter times due to energy costs and the risk of pigment degradation, a 90-minute extraction time was selected in this process. As can be seen, after optimization of the operating conditions, the extraction yield of carotenoids increased to a value comparable to that of acetone (3.7 ± 0.2 $mg_{Car}.g^{-1}_{biomass}$).

The summarized parameters in Table 1 showcase an improved fitting of the experimental data achieved through the utilization of the second-order model, unveiling an extraction rate constant of $k_2 = 4.35 \times 10^{-2}$ $g_{biomass}.mg^{-1}_{Car}.min^{-1}$.

3.3. Thermal stability

It is recognized that the unsaturated structure gives carotenoids a particular sensitivity to high temperatures, light, and pro-oxidant molecules.[49] This unique structural feature makes carotenoids prone to degradation under environmental stressors, leading to color, flavor, and nutritional content changes in various food and plant-based products.[50] This sensitivity can lead to the isomerization and oxidation of carotenoids, resulting in compounds that manifest less or do not manifest biological activities. For example, carotenoids naturally exist in the all-trans form, however, isomerization of all-trans carotene to cis forms occurs due to heating, with an increase in cis isomers as temperature and processing time increase. From a biological point of view, trans and cis isomers can present distinct biological properties, for example, all-trans β-carotene has superior antioxidant properties than 13-cis β-carotene.[51,52]

Therefore, understanding the factors that influence the stability of carotenoids is crucial for developing effective preservation methods, ensuring the retention of their beneficial properties in their end applications, especially if commercialization is being considered.[53,54] In industries, during the processing and post-processing stages of products, an increase in temperature may occur, resulting in an induced degradation of carotenoids. Therefore, ongoing research in the field of food technology seeks to identify new approaches and ingredients that can improve the stability of carotenoids.[49,53]

In this work, the stabilizing effect of the castor oil (Oil_C) was investigated, and the results were compared with the data obtained for acetone. The extracts obtained from extraction with the Oil_C + Ethanol system (%Oil_C = 50% (v/v)) and acetone, with operational conditions: SLR = 0.06 $g_{biomass}.mL^{-1}_{solvent}$, room temperature (20–25 °C), constant vertical rotation of 80 rpm, and protection from light exposure, were analyzed by monitoring the lycopene and β-carotene concentrations over time under three different temperatures (55 °C, 75 °C and 95 °C). It is essential to highlight that at this stage, the ethanol content in the resulting carotenoid-rich extract underwent removal through the utilization of a rotary evaporator. This process was executed to isolate the extract, leaving behind only the oil component, to be ready for incorporation into a cosmetic product, and proceed with its thermal stability assessment, Table 2.

Upon analyzing Table 2, as expected, and independently of the extraction solvent, the higher temperature leads to a more significant decrease in the carotenoids half-life time. It is also possible to notice that there is a decrease in the half-life of carotenoids in both solvents when comparing the 3 temperatures (55 °C, 75 °C and 95 °C). Notably, the decrease is generally less significant for extracts produced by castor oil, especially at 75 °C, where the use of castor oil more than doubled the half-life of carotenoids from 51.0 h (using acetone) to 115.7 h (using castor oil). Although less pronounced, at 55 °C, castor oil still increased the carotenoids half-life by nearly 12 h, from 362.6 h (using acetone) to 374.5 h (using castor oil). At 95 °C, the results are nearly identical, with only a 36-minute difference, indicating that castor oil is as effective as acetone, making it a preferable substitute. This trend reflects the highest

Table 2
Kinetic parameters obtained using a first-order kinetics model[a] regarding the influence of the extraction solvent (acetone and Oil_C) on lycopene and β-carotene thermal stability (55 °C, 75 °C and 95 °C) under dark conditions.

Extraction solvent	55 °C			75 °C			95 °C			E_a (kJ.mol^{-1})
	k_d (h^{-1})	$t_{1/2}$ (h)	r^2	k_d (h^{-1})	$t_{1/2}$ (h)	r^2	k_d (h^{-1})	$t_{1/2}$ (h)	r^2	
Acetone	0.0019	362.6 (~15 days)	0.988	0.0136	51.0 (~2 days)	0.988	0.0212	32.7 (~1 day)	0.969	61.1
Oil_C[b]	0.0019	374.5 (~16 days)	0.989	0.0060	115.7 (~5 days)	0.966	0.0216	32.1 (~1 day)	0.976	61.6

k_d = thermal degradation constant (h^{-1}); $t_{1/2}$ = half-life time (h); E_a = thermal activation energy (kJ.mol^{-1}).
[a] A first-order kinetics model was assumed since second-order parameters were very similar.
[b] Extract obtained under the optimal operational conditions.

Table 3
Kinetic parameters obtained using a first-order kinetics model[a] regarding the influence of the extraction solvent (acetone and Oil_C) on lycopene and β-carotene thermal stability at room temperature (20 – 25 °C) under light conditions.

Extraction solvent	20 – 25 °C		
	k_d (h^{-1})	$t_{1/2}$ (h)	r^2
Acetone	0.0011	640.5 (~27 days)	0.999
Oil_C[b]	0.0011	648.9 (~27 days)	0.998

k_d = thermal degradation constant (h^{-1}); $t_{1/2}$ = half-life time (h).
[a] A first-order kinetics model was assumed since second-order parameters were very similar.
[b] Extract obtained under the optimal operational conditions.

thermal activation energy obtained for the carotenoids in castor oil (61.6 $kJ.mol^{-1}$).

Next, a real-case scenario was assessed where both extracts were subjected to room temperature (20 – 25 °C) under light exposure. This was done to mimic the typical conditions that cosmetic products encounter, both in stores and during regular use, Table 3.

The results in Table 3 highlight again the protective role of castor oil during thermal degradation of carotenoids, in this case β-carotene and lycopene. Under light conditions at room temperature (20–25 °C), an 8-hour longer half-life is observed with castor oil compared to acetone. These findings underscore the novel perspective examined in this study regarding the use of castor oil for the recovery of carotenoids, presenting an additional advantage compared to acetone. The protective role of oil in the thermal degradation process suggests its potential as a safer and more environmentally friendly alternative to traditional organic solvents. This not only enhances the sustainability of carotenoid recovery processes but opens also new possibilities for their application in the cosmetics industry.

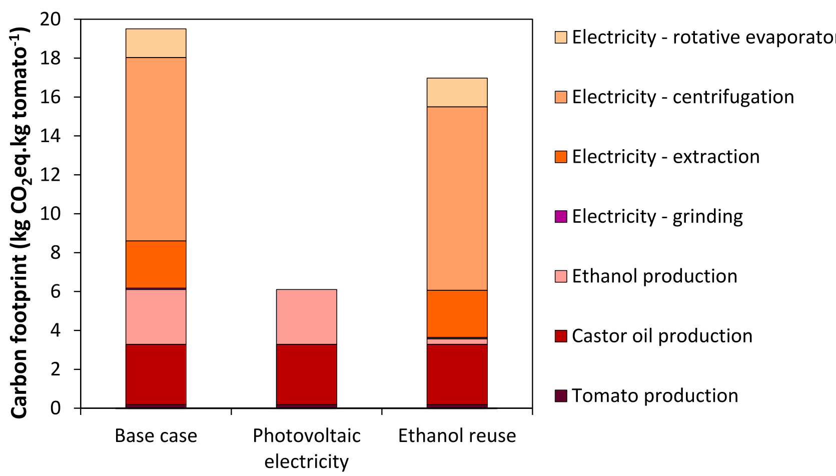

Fig. 5. Carbon footprint results. “Base case”: electricity consumed from the national grid and ethanol is not reused; “Photovoltaic electricity”: electricity consumed of photovoltaic origin and ethanol is not reused; “Ethanol use”: electricity consumed from the national grid and 90% of the ethanol is reused in the process.

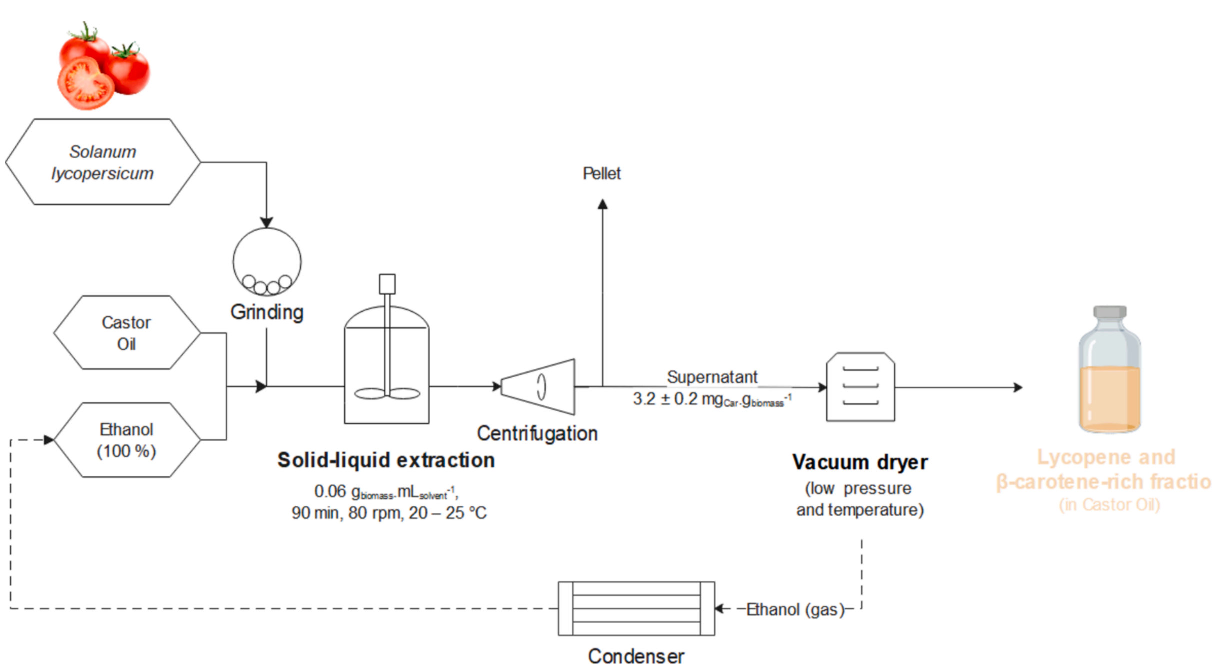

Fig. 6. Schematic diagram of the downstream process developed in this work, consisting of (i) solid–liquid extraction of lycopene and β-carotene using an Oil_C + Ethanol system, and (ii) ethanol removal, for future implementation into cosmetic formulations. Dashed lines indicate a proposed industrial implementation of the process and have not been experimentally executed in this work.

3.4. Carbon footprint

Fig. 5 presents the carbon footprint results of the most promising system (Castor oil + ethanol) for three scenarios. The first is the base case, where the carbon footprint of the electricity is representative of the average Portuguese electricity mix, and there is no ethanol reuse. The second case ("Photovoltaic electricity") differs from the base case in the source of electricity, which is of photovoltaic origin. The third case ("Ethanol reuse") differs from the base case in the fact that 90% of the recovered ethanol is used in the process replacing "new" ethanol.

The total carbon footprint of the base case is 19.5 kg CO_2 eq *per* 1 kg of tomatoes used. About 69% of this carbon footprint is due to electricity consumption in the process, mainly during centrifugation. Castor oil and ethanol production contribute 16% and 14% of this carbon footprint, respectively, while tomato production is irrelevant. However, it should be noted that the carbon footprint at the laboratory scale is overestimated and the upscaling of this process is expected to result in a much lower contribution from electricity production.

Despite this overestimation, the carbon footprint at the laboratory scale can be significantly reduced if photovoltaic electricity is considered. In this case, the total carbon footprint decreases to 6.1 kg CO_2 eq *per* 1 kg of tomatoes used. Finally, if the recovered ethanol is reused in the process, the carbon footprint will also decrease. For example, if 90% of the ethanol is reused, the carbon footprint of the base case would decrease to 17.0 kg CO_2 eq *per* 1 kg of tomatoes used.

3.5. Conceptual process design

Finally, a conceptual representation of the process developed in this study, envisioning its future industrial application, is depicted in Fig. 6. Ideally, all components of discarded tomatoes are blended and grounded. Subsequently, β-carotene and lycopene are recovered through a solid–liquid extraction step where the grounded tomatoes are mixed with castor oil and ethanol (100%) in a 50/50% (v/v) ratio. After removing of residual tomato components through centrifugation, ethanol is removed from the process by evaporation using low temperature (ideally room temperature or lower) to prevent carotenoid degradation. It's worth noting that ethanol, once removed, can be reused and reintroduced into the process through condensation. Finally, the resulting extract stands prepared for incorporation into future cosmetic formulations.

4. Conclusions

In this work, an innovative approach that integrates castor oil in downstream processes was accomplished. Several conventional and alternative solvents and some systems were tested to effectively recover lycopene and β-carotene from tomato pulp. Castor oil + ethanol was the chosen system to proceed with this work. Despite its lower performance compared to Castor oil + $[P_{4,4,4,14}]$Cl in ethanol, it was chosen in order to avoid IL recovery and consequently allowing to decrease both the complexity and costs of the final process. Besides, after optimizing the process, conditions the carotenoids yield of extraction becomes closer to acetone. The optimum operational conditions found by the response surface methodology are a solid–liquid ratio of 0.06 $g_{biomass}.mL^{-1}_{solvent}$ and a 50% (v/v) percentage of castor oil. From the kinetics study the optimum extraction time was discovered to be 90 min, with an extraction rate constant of $k_2 = 4.35 \times 10^{-2}$ $g_{biomass}.mg^{-1}_{Car}.min^{-1}$ describing the data fitted by a second-order model. The thermal stability assessment revealed a more stable extract, especially for 75 °C, when castor oil is the extraction solvent, showcasing its preservative qualities. The carbon footprint of the process based on castor oil + ethanol shows that electricity consumption is the principal red-flag, which may be overcome by powering the final process envisioned in this work with electricity obtained from photovoltaic renewable energy.

The findings support our working hypothesis, confirming that castor oil not only successfully recovered these natural pigments but also enhanced their stability compared to conventional acetone.

CRediT authorship contribution statement

Bárbara M.C. Vaz: Investigation, Methodology, Formal analysis, Writing – original draft. **Letícia S. Contieri:** Methodology, Investigation, Formal analysis, Writing – original draft. **Filipe H.B. Sosa:** Software, Formal analysis, Writing – original draft. **Margarida Martins:** Investigation, Formal analysis. **Alexandra Conde:** Investigation, Methodology, Formal analysis. **Ana C.R.V. Dias:** Conceptualization, Resources, Funding acquisition, Writing – original draft. **Maurício A. Rostagno:** Writing – review & editing, Supervision. **Leonardo M. de Souza Mesquita:** Writing – review & editing, Supervision. **Sónia P.M. Ventura:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision.

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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.130278.

Data availability

Data will be made available on request.

References

[1] A. Panico, F. Serio, F. Bagordo, T. Grassi, A. Idolo, M. De Giorgi, M. Guido, M. Congedo, A. De Donno, Skin safety and health prevention: an overview of chemicals in cosmetic products, J. Prev. Med. Hyg. 60 (2019) 50–57. 10.15167/2421-4248/jpmh2019.60.1.1080.

[2] R. Balwierz, P. Biernat, A. Jasinska-Balwierz, D. Siodłak, A. Kusakiewicz-Dawid, A. Kurek-Górecka, P. Olczyk, W. Ochedzan-Siodłak, Potential Carcinogens in Makeup Cosmetics, Int. J. Environ. Res. Public Health. 20 (2023) 4780. 10.3390/ijerph20064780.

[3] B. Kaličanin, D. Velimirović, A study of the possible harmful effects of cosmetic beauty products on human health, Biol. Trace Elem. Res. 170 (2016) 476–484, https://doi.org/10.1007/s12011-015-0477-2.

[4] J.-K. Liu, Natural products in cosmetics, Nat. Products Bioprospect. 12 (2022) 40, https://doi.org/10.1007/s13659-022-00363-y.

[5] K. Szabo, A.-F. Cătoi, D.C. Vodnar, Bioactive compounds extracted from tomato processing by-products as a source of valuable nutrients, Plant Foods Hum. Nutr. 73 (2018) 268–277, https://doi.org/10.1007/s11130-018-0691-0.

[6] FAO, Food wastage footprint, in: Impacts Nat. Resour. Summ. Report; FAO, Rome, Italy, 2013. www.fao.org/publications.

[7] V.N. Madia, D. De Vita, D. Ialongo, V. Tudino, A. De Leo, L. Scipione, R. Di Santo, R. Costi, A. Messore, Recent advances in recovery of lycopene from tomato waste: A potent antioxidant with endless benefits, Molecules 26 (2021) 4495, https://doi.org/10.3390/molecules26154495.
[8] M. Michalak, Plant-derived antioxidants: Significance in skin health and the ageing process, Int. J. Mol. Sci. 23 (2022) 585, https://doi.org/10.3390/ijms23020585.
[9] L.M. Alda, I. Gogoasa, D.-M. Bordean, I. Gergen, S. Alda, C. Moldovan, L. Nita, Lycopene content of tomatoes and tomato products, Agroaliment. Process. Technol. 15 (2009) 540–542.
[10] M. Bin-Jumah, S.S. Alwakeel, M. Moga, L. Buvnariu, N. Bigiu, M. Zia-Ul-Haq, Application of Carotenoids in Cosmetics, in: M. Zia-Ul-Haq, S. Dewanjee, M. Riaz (Eds.), Carotenoids Struct. Funct. Hum. Body, springer, 2021: pp. 747–756. 10.1007/978-3-030-46459-2.
[11] A.M. Marchena, L. Franco, A.M. Romero, C. Barriga, A.B. Rodríguez, Lycopene and melatonin: Antioxidant compounds in cosmetic formulations, Skin Pharmacol. Physiol. 33 (2020) 237–243, https://doi.org/10.1159/000508673.
[12] E.N. Story, R.E. Kopec, S.J. Schwartz, G.K. Harris, An update on the health effects of tomato lycopene, Annu. Rev. Food Sci. Technol. 1 (2010) 189–210, https://doi.org/10.1146/annurev.food.102308.124120.
[13] M. Baranska, W. Schutze, H. Schulz, Determination of lycopene and β-carotene content in tomato fruits and related products: Comparison of FT-Raman, ATR-IR, and NIR spectroscopy, Anal. Chem. 78 (2006) 8456–8461, https://doi.org/10.1021/ac061220j.
[14] L. Bogacz-Radomska, J. Harasym, β-Carotene-properties and production methods, Food Qual. Saf. 2 (2018) 69–74, https://doi.org/10.1093/fqsafe/fyy004.
[15] J. Nagarajan, H.P. Kay, N.P. Krishnamurthy, N.R. Ramakrishnan, T.M. S. Aldawoud, C.M. Galanakis, O.C. Wei, Extraction of carotenoids from tomato pomace via water-induced hydrocolloidal complexation, Biomolecules 10 (2020) 1019, https://doi.org/10.3390/biom10071019.
[16] R. Cortez, D.A. Luna-Vital, D. Margulis, E.G. de Mejia, Natural pigments: Stabilization methods of anthocyanins for food applications, Compr. Rev. Food Sci. Food Saf. 16 (2017) 180–198, https://doi.org/10.1111/1541-4337.12244.
[17] E. Reverchon, M. Scognamiglio, L. Baldino, Lycopene extract from tomato concentrate and its co-precipitation with PVP using hybrid supercritical processes, J. CO2 Util. 64 (2022) 102157, https://doi.org/10.1016/j.jcou.2022.102157.
[18] N.K. Arora, I. Mishra, United Nations Sustainable Development Goals 2030 and environmental sustainability: Race against time, Environ. Sustain. 2 (2019) 339–342, https://doi.org/10.1007/s42398-019-00092-y.
[19] 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.
[20] K.R. Kunduru, A. Basu, M. Haim Zada, A.J. Domb, Castor oil-based biodegradable polyesters, Biomacromolecules 16 (2015) 2572–2587, https://doi.org/10.1021/acs.biomac.5b00923.
[21] A. Yari, H. Yeganeh, H. Bakhshi, R. Gharibi, Preparation and characterization of novel antibacterial castor oil-based polyurethane membranes for wound dressing application, J. Biomed. Mater. Res. - Part a. 102 (2013) 84–96, https://doi.org/10.1002/jbm.a.34672.
[22] E.B. Mubofu, Castor oil as a potential renewable resource for the production of functional materials, Sustain. Chem. Process. 4 (2016) 1–12, https://doi.org/10.1186/s40508-016-0055-8.
[23] A. Herman, A.P. Herman, B.W. Domagalska, A. Młynarczyk, Essential oils and herbal extracts as antimicrobial agents in cosmetic emulsion, Indian J. Microbiol. 53 (2013) 232–237, https://doi.org/10.1007/s12088-012-0329-0.
[24] G. Alvarez-Rivera, M. Llompart, M. Lores, C. Garcia–Jares, Preservatives in Cosmetics: Regulatory Aspects and Analytical Methods, in: A. Salvador, A. Chisvert (Eds.), Anal. Cosmet. Prod., Second Edi, Elsevier B.V., 2018: pp. 175–224. 10.1016/b978-0-444-63508-2.00009-6.
[25] S.A.S. Mapari, A.S. Meyer, U. Thrane, Photostability of natural orange-red and yellow fungal pigments in liquid food model systems, J. Agric. Food Chem. 57 (2009) 6253–6261, https://doi.org/10.1021/jf900113q.
[26] L.M. de S. Mesquita, M. Martins, É. Maricato, C. Nunes, P.S.G.N. Quinteiro, A.C.R. V. Dias, J.A.P. Coutinho, L.P. Pisani, V.V. de Rosso, S.P.M. Ventura, Ionic liquid-mediated recovery of carotenoids from the *Bactris gasipaes* fruit waste and their application in food-packaging chitosan films, ACS Sustain. Chem. Eng. 8 (2020) 4085–4095. 10.1021/acssuschemeng.9b06424.
[27] B.M.C. Vaz, M. Kholany, D.C.G.A. Pinto, I.P.E. Macário, T. Veloso, T. Caetano, J. L. Pereira, J.A.P. Coutinho, S.P.M. Ventura, Recovery of bacterioruberin and proteins using aqueous solutions of surface-active compounds, RSC Adv. 12 (2022) 30278–30286, https://doi.org/10.1039/d2ra02581g.
[28] B.M.C. Vaz, M. Martins, L.M. de Souza Mesquita, A.P.M. Fernandes, D.C.G.A. Pinto, M.G.P.M.S. Neves, M.C. Neves, J.A.P. Coutinho, S.P.M. Ventura, Using aqueous solutions of ionic liquids as chlorophyll eluents in solid-phase extraction processes, Chem. Eng. J. 428 (2022) 131073, https://doi.org/10.1016/j.cej.2021.131073.
[29] M. Martins, C.M. Albuquerque, C.F. Pereira, J.A.P. Coutinho, M.G.P.M.S. Neves, D. C.G.A. Pinto, M.A.F. Faustino, S.P.M. Ventura, Recovery of Chlorophyll *a* derivative from *Spirulina maxima*: Its purification and photosensitizing potential, ACS Sustain. Chem. Eng. 9 (2021) 1772–1780, https://doi.org/10.1021/acssuschemeng.0c07880.
[30] M. Martins, A.P.M. Fernandes, M.A. Torres-Acosta, P.N. Collén, M.H. Abreu, S.P. M. Ventura, Extraction of chlorophyll from wild and farmed *Ulva* spp. using aqueous solutions of ionic liquids, Sep. Purif. Technol. 254 (2021) 117589, https://doi.org/10.1016/j.seppur.2020.117589.
[31] M. Kholany, P. Trébulle, M. Martins, S.P.M. Ventura, J.-M. Nicaud, J.A. P. Coutinho, Extraction and purification of violacein from *Yarrowia lipolytica* cells using aqueous solutions of surfactants, J. Chem. Technol. Biotechnol. 95 (2020) 1126–1134, https://doi.org/10.1002/jctb.6297.
[32] TURBOMOLE V4.5.2, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989−2007, TURBOMOLE GmbH. (2007). https://www.turbomole.org (accessed February 23, 2024).
[33] BIOVIACOSMOtherm, DassaultSystèmes. (2021). https://www.3ds.com/products/biovia/cosmo-rs/cosmotherm (accessed February 23, 2024).
[34] F. Eckert, A. Klamt, Fast solvent screening via quantum chemistry: COSMO-RS approach, AIChE J. 48 (2002) 369–385, https://doi.org/10.1002/aic.690480220.
[35] A. Dean, D. Voss, Design and Analysis of Experiments, 1st edn, Springer, New York, 1999. 10.1007/b97673.
[36] M.I. Rodrigues, A.F. Lemma, Planejamento de Experimentos e Otimização de Processos, 3rd ed., Casa do Pão Editora, 2014.
[37] H.S. Kusuma, M. Mahfud, The extraction of essential oils from patchouli leaves (*Pogostemon cablin* Benth) using a microwave air-hydrodistillation method as a new green technique, RSC Adv. 7 (2017) 1336–1347, https://doi.org/10.1039/c6ra25894h.
[38] L.M. de Souza Mesquita, L.S. Contieri, F.H.B. Sosa, R.S. Pizani, J. Chaves, J. Viganó, S.P.M. Ventura, M.A. Rostagno, Combining eutectic solvents and pressurized liquid extraction coupled in-line with solid-phase extraction to recover, purify and stabilize anthocyanins from Brazilian berry waste, Green Chem. 25 (2023) 1884–1897, https://doi.org/10.1039/d2gc04347e.
[39] Z. Yang, Y. Han, Z. Gu, G. Fan, Z. Chen, Thermal degradation kinetics of aqueous anthocyanins and visual color of purple corn (*Zea mays* L.) cob, Innov. Food Sci. Emerg. Technol. 9 (2008) 341–347, https://doi.org/10.1016/j.ifset.2007.09.001.
[40] S. Bhatnagar, H. Aoyagi, Thermal and UV degradation kinetics of water-soluble extracellular pigment produced by *Talaromyces purpurogenus*, Food Bioprocess Technol. 15 (2022) 606–619, https://doi.org/10.1007/s11947-021-02733-9.
[41] E.E. Badin, R. Quevedo-Leon, A. Ibarz, P.D. Ribotta, A.R. Lespinard, Kinetic modeling of thermal degradation of color, lycopene, and ascorbic acid in crushed tomato, Food Bioprocess Technol. 14 (2021) 324–333, https://doi.org/10.1007/s11947-021-02579-1.
[42] I.O. for Standardization, ISO 14067:2018 Greenhouse gases – Carbon footprint of products – Requirements and guidelines for quantification, 2018.
[43] G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz, B. Weidema, The ecoinvent database version 3 (part I): Overview and methodology, Int. J. Life Cycle Assess. 21 (2016) 1218–1230, https://doi.org/10.1007/s11367-016-1087-8.
[44] L. Pari, E. Alexopoulou, W. Stefanoni, F. Latterini, C. Cavalaris, N. Palmieri, The eco-efficiency of castor supply chain: A greek case study, Agriculture 12 (2022) 206, https://doi.org/10.3390/agriculture12020206.
[45] V. Masson-Delmotte, P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, B. Zhou, (eds.), Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, 2021.
[46] M. Martins, L.M. de S. Mesquita, B.M.C. Vaz, A.C.R.V. Dias, M.A. Torres-Acosta, B. Quéguineur, J.A.P. Coutinho, S.P.M. Ventura, Extraction and Fractionation of Pigments from *Saccharina latissima* (Linnaeus, 2006) Using an Ionic Liquid + Oil + Water System, ACS Sustain. Chem. Eng. 9 (2021) 6599–6612. 10.1021/acssuschemeng.0c09110.
[47] Maurice L. Huggins, The Solubility of Nonelectrolytes. By Joel H. Hildebrand and Robert S. Scott., in: J. Phys. Chem., 1951: pp. 619–620. 10.1021/j150487a027.
[48] I. Montes, C. Lai, D. Sanabria, Like dissolves like: A classroom demonstration and a guided-inquiry experiment for organic chemistry, J. Chem. Educ. 80 (2003) 447–449, https://doi.org/10.1021/ed080p447.
[49] I. Gheonea (Dima), I. Aprodu, E. Enachi, G. Horincar, C.A. Bolea, G.E. Bahrim, G. Râpeanu, N. Stănciuc, Investigations on thermostability of carotenoids from tomato peels in oils using a kinetic approach, J. Food Process. Preserv. 44 (2020) 14303. 10.1111/jfpp.14303.
[50] P.P. Valério, A.L.T. Brandão, J.M.F. Celayeta, E.C. Cren, Thermal degradation of β-carotene from macauba palm: Mathematical modeling and parameter estimation, Int. J. Food Stud. 10 (2021) 161–172, https://doi.org/10.7455/IJFS/10.1.2021.A3.
[51] M. Honda, Carotenoid isomers: A systematic review of the analysis, biological activity, physicochemical property, and methods for isomerization, in: Stud. Nat. Prod. Chem., 2021: pp. 173–220. 10.1016/B978-0-12-819485-0.00002-5.
[52] J. Cerezo, J. Zúñiga, A. Bastida, A. Requena, J.P. Cerón-Carrasco, L.A. Eriksson, Antioxidant properties of β-carotene isomers and their role in photosystems: Insights from Ab initio simulations, J. Phys. Chem. a. 116 (2012) 3498–3506, https://doi.org/10.1021/jp301485k.
[53] C.S. Boon, D.J. McClements, J. Weiss, E.A. Decker, Factors influencing the chemical stability of carotenoids in foods, Crit. Rev. Food Sci. Nutr. 50 (2010) 515–532, https://doi.org/10.1080/10408390802565889.
[54] E.M. Yahia, J. de J. Ornelas-Paz, T. Emanuelli, E. Jacob-Lopes, L.Q. Zepka, B. Cervantes-Paz, Chemistry, Stability, and Biological Actions of Carotenoids, in: E.M. Yahia (Ed.), Fruit Veg. Phytochem. Chem. Nutr. Value, Stab., 2nd ed., 2017: pp. 285–345. 10.1002/9781119158042.ch15.