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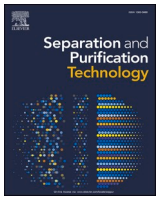

Concentration of phycocyanin and coffee extracts in aqueous solutions with osmotically-assisted membrane distillation

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ABSTRACT

Osmotic membrane distillation (OMD) is a dewatering process that exploits combined temperature and osmotic pressure gradients to drive water vapor fluxes under mild operation conditions. In this study, the feasibility of OMD is evaluated for the concentration of phycocyanin and coffee extract solutions, with the goal to safeguard the quality of the extracts. Different feed solution temperatures were studied, namely, 35 °C, 45 °C, 55 °C, while keeping a concentration of 4 M $CaCl_2$ in the extraction solution. The target concentration factor was set to 4, equivalent to a water recovery rate of 75 %. The results suggest that a temperature equal to or below 45 °C should be chosen for the concentration of phycocyanin to prevent degradation and to minimize fouling, while higher temperatures may be used for the recovery of the coffee extract. The combined gradients provided water fluxes around or above 4 L $m^{-2}h^{-1}$ with both extracts under relatively mild conditions, even at high concentration factors. Qualitative membrane fouling inspection was corroborated by estimating the fraction of productivity lost due to fouling, which was larger for higher feed temperatures and for the phycocyanin extracts, and had values between roughly 20 and 70 %. Results also suggest that the quality of the extracts was maintained, based on the measured purity and content of the target compounds in the concentrated solutions. Specifically, no trace of extraneous compounds was found, and no salt passage was observed from the extraction solution to the feed solution, suggesting that OMD has the potential to concentrate sensitive components.

1. Introduction

The extraction of bioactive compounds from natural sources, as well as from agricultural and industrial waste, has been gaining momentum in recent years [1,2]. Following the extraction process, a dewatering step is typically necessary when the extract is in aqueous form, to enhance the product stability, to reduce storage and transportation costs, and to facilitate the utilization of the valuable target compounds. Concentration and dilution processes are also important in various industrial sectors, for example, in the food & beverage field, and in the pharmaceutical, cosmetics, and nutraceutical industry. Conventional dewatering technologies often involve high temperature and pressure values, which may lead to the degradation of sensitive components and to the loss of volatile constituents [3–5]. Therefore, exploring alternative approaches that simultaneously offer high dewatering efficiency and the preservation of extract properties is important to expand the pool of available techniques aimed at improving circularity and rationally managing waste streams.

More specifically, processes that have been proposed to perform dewatering while minimizing losses and preserving the desirable extract properties include high-pressure homogenization, ion-exchange chromatography, and freeze-drying [6]. These methods are energy-intensive and generally costly, thereby affecting the commercial value of the final product [7]. Previous investigations have also involved the deployment of membrane technologies, such as nanofiltration, reverse osmosis, or membrane distillation, as alternatives to more traditional thermal evaporation and freeze-drying approaches [8–13]. However, conventional membrane technologies often lead to the degradation of

Abbreviations: OMD, Osmotic membrane distillation; PYC, Phycocyanin; CAF, Caffeine; SCGs, Spent coffee grounds; TFC, Total flavonoid content; FS, Feed solution; ES, Extraction solution.

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thermolabile or mechanically labile compounds, and they can seldom guarantee high selectivity separation between pure water and other compounds dissolved in the feed extract.

Osmotically-assisted membrane distillation (OMD) is an alternative promising concentration process, owing to its operation under mild operating conditions, such as ambient pressure and low temperatures. Differently from other membrane processes, OMD deploys both a temperature and an osmotic pressure gradient across a microporous hydrophobic membrane to drive the water vapor transfer, which is ultimately associated with the resulting vapor pressure gradient between the two sides of the membrane. Specifically, the membrane separates the warm feed solution that needs to be dewatered from an extraction solution (ES) characterized by lower water activity thanks to the presence of a solute [14]. While the application of a thermal gradient is still needed to generate feasible water fluxes, the feed temperature may be maintained at relatively low levels, since the related gradient is aided by the gradient in concentration provided by the ES [15]. Moreover, since a hydrophobic membrane is deployed for the separation, solute transfer in either direction is virtually absent. According to literature reports, several salt solutions (e.g., NaCl, $CaCl_2$, $MgCl_2$, $MgSO_4$) and organic solutions (e.g., glycerol, polyglycols) have been investigated as ES, as well as ternary mixtures, e.g., water-glycerol-salt [16]. $CaCl_2$ has exhibited remarkably effective performance, especially in terms of permeate flux, thus becoming widely employed in OMD investigations [9].

Recent investigations have demonstrated the ability of OMD of concentrating various liquid foods, including fruit and vegetable juices, which have limited stability at high temperatures and pressures [17–22]. For instance, Bahçec *et al.* carried out a comparative evaluation between different dewatering processes for the concentration of tomato juice, obtaining higher permeate flux in OMD (1.97 kg $m^{-2}h^{-1}$) with respect to osmotic distillation (1.07 kg $m^{-2}h^{-1}$) or membrane distillation (MD, 0.94 kg $m^{-2}h^{-1}$), that is, with respect to processes exploiting a driving force exerted by the gradient of one individual parameter [23]. Remarkably, the Ederna Company studied OMD in coffee processing as an alternative to conventional evaporation, projecting that it will turn into cost savings of around 30 % within five years despite the lower fluxes observed in OMD operation [24]. By employing an ultrafiltration pretreatment to minimize the unwanted material in the feed solution, Koroknai *et al.* observed higher permeate fluxes than other OMD studies, ranging from 4.5 to roughly 5.0 kg $m^{-2}h^{-1}$ (using 6 M $CaCl_2$ ES at 22 °C, and FS temperature equal to 35 °C), while preserving 97 % of the antioxidant activity of different red juices [25]. Other studies investigated the influence of thermal gradient and ES concentration on water mass transfer in OMD [26]. In particular, Babu *et al.* indicated that high concentration rates are achievable even for complex feed solutions, such as phycocyanin colorant, by tuning the vapor pressure gradient [27]. However, a thorough assessment of the role of increased temperature and osmotic pressure on concentrate quality is key to demonstrate the effectiveness of the process, especially when dealing with sensitive valuable compounds in complex and heterogeneous streams.

Among many valuable and sensitive bioactive compounds, phycocyanin (PYC) is a family of proteins found in microalgae species, such as cyanobacteria and red algae, which is gaining increasing attention as virtue of its unique beneficial properties, including antioxidant, anti-inflammatory, antidiabetic, hepatoprotective, and potentially anti-carcinogenic effects [28]. Proven to be non-toxic and safe for human consumption, PYC finds applications in various industries, such as food and beverage (primarily as a colorant), cosmetics, and pharmaceuticals [29,30]. The quality of PYC is typically assessed by means of a purity index, the ratio of its specific maximum absorbance at around 620 nm wavelength to the absorbance at 280 nm wavelength, the latter associated with total proteins [31]. Particularly, different purity index thresholds, such as ≥ 0.7 for food grade, ≥ 1.5 for cosmetics grade, and ≥ 4 for analytical grade, define its suitability for specific applications [32]. However, PYC extraction, dewatering, and general handling is challenged by its great sensitivity to many environmental conditions, such as temperature, pH, light, and mechanical stress, which can induce degradation and structural modifications that ultimately impact the quality of the PYC product [33].

Another noteworthy aqueous stream containing highly valuable compounds is that obtained using spent coffee grounds (SCGs). SCGs represents one of the main by-products generated in the industrial processing of coffee, accounting for almost 6 million tons every year [34,35]. SCGs contain polysaccharides, lipids, amino acids, alkaloids (e.g., caffeine), flavonoids and phenolic acids, which are recognized for their beneficial health properties and can be used as antioxidants, anti-inflammatory, and nutraceutical agents [36].

In this study, the feasibility of OMD for the dewatering of PYC and SCGs extracts is assessed. The role of the feed solution temperature and of the $CaCl_2$ extraction solution concentration is preliminary evaluated to understand the relative contribution of the two parameters on the driving force and on the distillate flux. The thermolability of valuable components, such as PYC, CAF and flavonoids is also discussed, based on liquid chromatography and colorimetric analyses. The OMD performance is evaluated also considering fouling and the degradation of target components. Finally, optimal conditions for maximizing concentration yields while preserving the quality and the bioactivity of target compounds (i.e., PYC, CAF, and flavonoids), are proposed. The underlying hypothesis of this study is that, under certain conditions of feed temperature and extraction solution concentration, the OMD process effectively concentrates valuable and thermolabile compounds and maintains their high quality.

2. Materials and methods

2.1. Feed solutions preparation for the osmotic membrane distillation tests

2.1.1. Preparation of phycocyanin extract

Phycocyanin (PYC) was obtained from *Galdieria sulphuraria*, a red unicellular microalga cultivated under controlled conditions in a photobioreactor designed and operated at Politecnico di Torino (Department of Environment, Land and Infrastructure Engineering) [37]. *G. sulphuraria* is a polyextremophilic microalga that can tolerate harsh temperature and pH conditions. In autotrophic cultivations, *G. sulphuraria* expresses high PYC contents ($\geq$10 % by weight), similarly to the values generally obtained with *Arthrospira platensis*, currently the most widely used biological platform for commercial PYC production [38,39]. Nevertheless, PYC from *Galdieria* genus has been shown to possess greater stability at low pH and high temperatures, thus expanding the potential industrial uses of this pigment [40–42]. PYC was extracted from the microalgal suspension with a process consisting of: (i) biomass harvesting through centrifugation (10000 × *g*; 20 min; CLARA 20 – Alfa Laval, Sweden); (ii) freezing at − 85 °C of recovered biomass concentrate and subsequent lyophilization (ScanVac CoolSafe Touch 55–4 Freeze Dryer, LaboGene, Denmark); (iii) approximatively 20 g of the obtained *Galdieria sulphuraria* powder was resuspended in a 100 mM sodium phosphate buffer, pH 7; (iv) bead milling (breakage of cellular walls) through addition of micro glass beads and horizontal agitation (30 Hz, 2 × 10 min, with 5 min break on ice; Mixer Mill MM 400, Retsch, Germany). Finally, (v) the lysate was centrifuged at 10000 × *g* for 20 min and the supernatant was collected in fresh tubes, resulting in a final aqueous suspension (crude extract) that requires dewatering before the final high-purity PYC recovery. A photograph of the final extract, i.e., the PYC feed solution for the OMD tests, is provided in Fig S.1a in the Supporting Information (SI).

2.1.2. Preparation of coffee extract

Spent coffee grounds (SCGs) used in this study were collected from a local cafeteria in the city of Turin. The coffee powder was processed with a professional espresso machine and was composed of 50 % Arabica and 50 % Robusta. After the collection, the SCGs batch was immediately

dried at 25 °C and stored in hermetic containers at room temperature until use, to prevent microbial growth. Dried SCGs were subjected to a simple rinsing process to obtain the coffee extract. More in detail, 10 g of dried SCGs were mixed with 200 mL of deionized water. The obtained suspension was stirred at room temperature for 24 h and then filtered under vacuum through a net filter characterized by a mesh size of 11 μm (Merck Millipore, Milan, Italian branch). A photograph of the final extract, i.e., the coffee extract feed solution for the OMD tests, is provided Fig S.1b of the SI.

2.2. Osmotic membrane distillation systems

OMD tests were carried out in two different systems: a clear glass diffusion cell (membrane area: 1.8 cm^2) and a bench scale system (21 cm^2), the latter involving the use of centrifugal pumps for the recirculation of both the feed solution (FS) and the extraction solution (ES). Schemes of the two systems are found in Figure S.2 of the SI. The diffusion cell was used for the concentration of PYC, which is particularly sensitive to mechanical stress, while the coffee extract was concentrated in the bench-scale system. All tests were performed with a commercially available hydrophobic polytetrafluoroethylene (PTFE) membrane (Aquastill, Sittard, Netherlands), with the specifications provided by the manufacturer listed in Table 1. The water contact angle of the membrane active surface was determined through a sessile drop method using a Drop Shape Analyzer DSA100 (KRÜSS GmbH, Germany). Specifically, the measurements were carried out immediately after the deposition of deionized water onto a leveled membrane, revealing an average water contact angle of roughly 127°.

The diffusion cell (Side-By-Side class, PermeGear, Hellertown, USA) comprised two specular halves, each one composed of a jacket and an internal chamber. The internal chambers were filled one with 25 mL FS and the other with 25 mL ES. The temperature of each respective stream was kept constant by circulating water at the desired temperature in the heat-exchanging jackets. The circulating water temperature was regulated by two different thermostatic baths (AMETEK Brookfield, USA). The entire system was placed on a magnetic stirrer (PermeGear, Hellertown, USA) used to mix both the FS and the ES. Water flux through the membrane was measured evaluating the volume variation of the extraction solution over time.

A two-plate cell module was used in the bench scale system. Two centrifugal pumps were used to recirculate the streams inside the module in counter-current mode. For each stream, the flow rate was kept at 25 L/h during the test and controlled by means of two flowmeters (ASA, Sesto San Giovanni, Italy). The initial volumes in both the FS and ES tanks were 1.2 L. In this system, heat was exchanged directly inside the thermostatic baths before entering the module to achieve the desired temperature. The ES solution was placed on a computer-interfaced scale to retrieve the water flux every 20 min during the tests.

2.3. Tests protocols

Preliminary tests were performed in the diffusion cell by using pure water as FS to assess the influence of the FS temperature and of the ES concentration on the vapor flux. In the ES, calcium chloride ($CaCl_2$) at different concentrations, namely, 0 M, 3 M, 4 M, 5 M, was used to provide the concentration difference between the two streams. Its temperature was kept at 25 °C. In the FS, for each concentration of the ES, the effect of temperature on flux was investigated in the 25–55 °C range, increasing by 10 °C the FS temperature between the different steps. The saline solution was always replaced between different steps and steady-state flux data were averaged to retrieve the value of distillate flux.

The vapor pressure difference Δp (Pa) generated between the FS and ES solutions was calculated with the Antoine's equation [43]:

$$p = e^{\left(23.238-\frac{3841}{T-45}\right)} \quad (1)$$

where T is the absolute temperature (K). The Δp between the two solution was then calculated with the following expression, also considering the influence of the salt in the ES:

$$\Delta p = p_{FS} - a_w p_{ES} \quad (2)$$

where p_{FS} is the feed vapor pressure and p_{ES} is the extraction solution vapor pressure. The a_w coefficient may be estimated considering the salt concentration in the ES:

$$a_w = 1 - 0.03112 \cdot m - 0.001482 \cdot m^2 \quad (3)$$

where m is the molality (mol/kg) of the extraction solution.

After assessment of the driving force influence on flux in OMD, high recovery tests with PYC and SCGs extracts were performed. All the tests were performed with a 4 M $CaCl_2$ ES, under the same FS temperature range investigated in the preliminary tests. The final target recovery rate was always 75 % (concentration factor equal to 4) and water flux was computed by measuring the change in volume of the ES over time. For each test, the loss of water flux only due to the dilution effect of the extraction solution was assessed by using the correlation between water flux against the FS-ES vapor tension difference (see Table S.1 of the SI), the latter retrieved from Eq. 1–3. In turn, this allowed estimation of the sole flux decline contribution due to fouling.

The feed content was analyzed to assess the achieved concentration yield and concentrate quality. Specifically, PYC concentration and a standard purity index for the same compound were monitored at the beginning and at the end of each test, while caffeine (CAF) concentration and total flavonoid content (TFC) were measured for the SCGs extract. Additionally, total organic carbon (TOC) measurements were performed both for the FS and ES solutions.

2.4. Assessment of feed solution quality during OMD test: Analytical methods

To assess the performance of the OMD system, quantitative and qualitative analyses were conducted on the extracts (feed solution) at the beginning and at the end of the process. In particular, the concentration yield was evaluated by choosing PYC and CAF as representative compounds, for the phycocyanin extract and for the SCGs extract, respectively. PYC concentration was determined by spectrophotometry, whereas CAF concentration by chromatographic analyses. On the other hand, the quality of the final concentrate was estimated spectrophotometrically using the standard purity index (see below) for PYC in the related extract and assessing the TFC in the SCGs extract samples. The overall assessment on the process effectiveness in terms of mass balance and organic compounds transfer were evaluated trough total organic carbon (TOC) measurements.

2.4.1. Total organic carbon

Total organic carbon (TOC) measurements were conducted on the FS and on the ES solutions at the beginning and at the end of each test with a TOC analyzer (TOC-LDSH FA, E200, Shimadzu, Milan, Italian branch). Analyses were performed on 40 mL samples in non-purgeable organic carbon mode, preceded by appropriate calibration.

Table 1
Characteristics provided by the manufacturer of the PTFE membrane used for the osmotic membrane distillation tests.

Parameter	Value	Units
Thickness	77	μm
Mean pore size	0.17	μm
Porosity	0.83	–

2.4.2. Colorimetric analysis of phycocyanin

PYC concentration was evaluated by means of a spectrophotometer (Analytik Jena AG). In this study, the maximum absorbance of PYC was observed at 619 nm, in good agreement with previous reports [28]. This wavelength was therefore used as reference for the evaluation of PYC concentration. A calibration curve was obtained by measuring the maximum absorbance of PYC in solutions at different known concentrations (60, 80, 100, 120 mg/L; $R^2 = 0.998$), which were prepared by diluting a concentrated crude extract. The PYC content of the crude extract was calculated measuring the absorbance at 620 and 652 nm and converting the measured absorbance to concentration using the Kursar and Alberte equation [44]. The obtained calibration curve was then used to retrieve the concentration of the PYC solutions from light absorbance. Spectrophotometry was also used for the evaluation of PYC purity index, a key parameter to determine PYC quality, assumed as ratio between the absorbance at 619 nm and the absorbance at 280 nm [28,31,32]. Purity index values were normalized with respect to the value measured for the initial feed solution.

2.4.3. Colorimetric analysis of total flavonoid content

The TFC of coffee extract samples was estimated according to the colorimetric assay described by Shraim et al., with slight modifications [45]. A 1 mL aliquot of appropriately diluted sample or standard solutions of rutin (50, 70, 100, 150, and 300 mg/L) was added to a 10 mL volumetric flask containing 4 mL of deionized water, followed by a 0.3 mL of 5 % sodium nitrite solution. The mixture was stirred at ambient temperature for 5 min. Then, 0.3 mL 10 % of aluminum chloride solution was added. After 5 min, 2 mL of 1 M sodium hydroxide solution was added. The final volume solution of 10 mL was than reached by adding the remaining aliquot with deionized water. Absorbance of the mixture was determined at 510 nm. The results were expressed as rutin equivalent (RE) through the calibration curve of rutin ($R^2 = 0.998$).

2.4.4. HPLC/UV–Vis caffeine detection

CAF concentration in coffee extract was measured through a high-performance liquid chromatography system (HPLC) purchased from Shimadzu (Milan, Italian branch). The HPLC is equipped with a UV–Vis photodiode array detector (SPD-M40), a system controller (SCL-40), a dual solvent pump (LC-40D), an injection valve (DGU-405), an on-line solvent degasser (DGU-14A), a column oven (CTO-40C), and an autosampler (SIL-40). The injection volume was set at 10 μL A reverse phase C18 column (ROC C18, 150 m × 4.6 mm, pore size 100 Å, 5 μm packing, RESTEK, Milan, Italian branch) was used at 40 °C. The chromatographic separation was performed using a binary gradient elution described in Table S.2 (SI), at a flow rate of 1 mL/min. The mobile phase was as follows: phosphoric acid solution 1×10^{-2} M (solvent A) and acetonitrile (solvent B). The detection of CAF was performed at 272 nm wavelength and retention time of 3.6 min. CAF concentration was obtained from a calibration curve prepared with standard water solutions of caffeine (50, 75, 100, 150, and 200 mg/L; $R^2 = 0.999$). All samples were filtered with a syringe filter (pore size 0.45 μm, cellulose acetate (CA) membrane, Merck Millipore, Milan, Italian branch) before the HPLC/UV–Vis analysis.

3. Results and discussion

3.1. Effect of the feed temperature and extraction solution concentration on permeate flux

Preliminary tests were conducted with pure water as feed solution to evaluate the contribution on water flux of each individual gradient, one associated with the ES solute concentration and the other with the temperature difference across the membrane. Fig. 1a shows the steady-state flux as a function of the ES concentration ($CaCl_2$ at 0, 3, 4, 5 M), for the various investigated FS temperatures (25, 35, 45, 55 °C). Overall, despite the major influence of temperature, the role of ES concentration was generally not negligible [46,47]. In detail, an increment of 3.6 L $m^{-2}h^{-1}$ (LMH) was observed when increasing the ES concentration from 0 M to 5 M, while keeping the same temperature in the ES and FS at 25 °C, i.e., in osmotic distillation mode driven solely by a concentration gradient. This effect of flux, provided by the ES concentration, was gradually more relevant when increasing the FS temperature [21,48]. Related results are also reported in Figure S.3 of the SI, which shows the same water flux data plotted as a function of the FS temperature for the different tested ES concentrations. Specifically, an increase of almost 7 LMH was observed at the highest tested FS temperature of 55 °C when increasing the $CaCl_2$ from 0 to 5 M in the ES solution. The more pronounced effect observed at higher FS temperature (7 LMH vs. 3.6 LMH) may be rationalized with the higher diffusion coefficient and with the higher water vapor pressure at increasing value of the temperature (Eq. 1) for the same ES concentration values, making osmotic membrane distillation (FS temperature higher than ES temperature) potentially more convenient than pure osmotic distillation (same FS and ES temperature), especially when low-grade energy is available [21].

In all membrane-based processes exploiting distillation, e.g., osmotic distillation, osmotic membrane distillation, and membrane distillation,

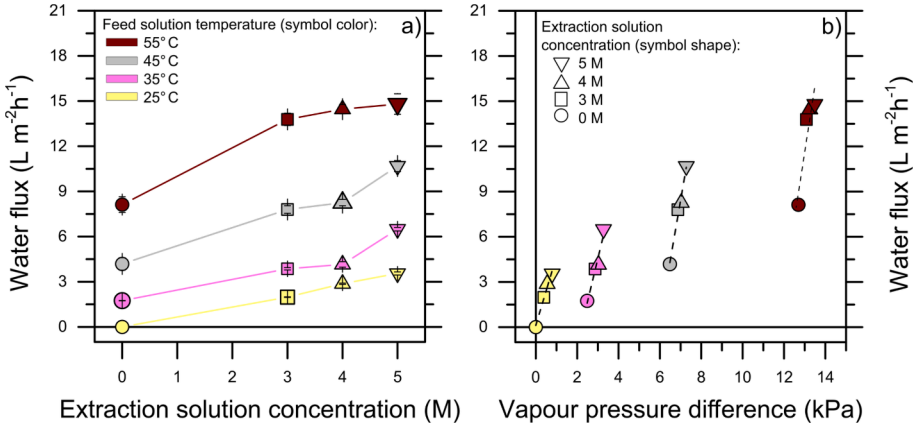

Fig. 1. Observed water fluxes in osmotic membrane distillation under different conditions of feed temperature and extraction solution concentration. Pure water was used as feed solution while different concentrations of $CaCl_2$ were used in the extraction solution. The feed temperature range was 25–55 °C, while the extraction solution temperature was kept at 25 °C in all tests. The distillate water flux is represented as a function of: a) the extraction solution concentration; b) the vapor pressure difference between the feed solution and the extraction solution. In b), the dash trend lines are the results of the model describing the effect of the extraction solution concentration while keeping the feed solution temperature constant. Colors refer to different feed temperatures as shown in the legend of the left-hand graph, while data point shapes refer to different extraction solution concentrations, as shown in the legend of the right-hand graph.

the driving force of the process is ultimately provided by the water vapor pressure difference between the two streams in contact with the membrane [16,47,49]. As expressed by Eq. 1–3, this driving force is predominately influenced by the temperature difference and in lesser magnitude by the concentration difference between the FS and ES solutions, reflecting the experimental results reported in Fig. 1 [21,48]. To better stress out this crucial point, Fig. 1b reports the same flux data presented in Fig. 1a, but as a function of the vapor pressure difference (Eq. 2). The dash trend lines are the results of the model predicting the effect of the ES concentration while keeping the FS temperature as constant; equations are listed in Table S.1 of the SI. The vapor tension value was retrieved with the Antoine equation (Eq.1), which considers the effect of both temperature and concentration. Consistent with experimental data, the slope of the dash lines increases gradually when increasing the feed temperature; see Fig. 1b. Slope values are reported in Table S.1 of the SI. This result highlights the beneficial use of a more concentrated ES when operating at medium–high FS temperatures, as the concentration gradient is exploited in a more efficient way. It is also important to note that no reverse flux from the ES to the FS was observed in any of the tests, owing to the barrier to liquid passage provided by the hydrophobic membrane, which represents an important advantage for long-term OMD processes [50].

The experimental water fluxes also indicate the detrimental effects of concentration and temperature polarizations, which limit the flux in this process below 15 LMH under the tested conditions. In particular, the results of the tests performed at 55 °C FS temperature show a near-asymptote in flux values when using the ES with concentrations higher than 3 M, corresponding to values of the water flux of roughly 13.5 LMH. Above this value of ES concentration, a further increase up to 5 M only allowed a growth in flux of roughly 1 LMH. A similar behavior was observed by Ravindra Babu et al. [46]. This result may be explained by the ES dilution in proximity of the membrane surface, due to the passage of the water distillate, and by the temperature polarization effects due to both heat conduction and of the latent heat of vaporization/condensation as water evaporates in the feed solution and condenses in the extraction solution, thus cooling the former and warming the latter at the respective membrane/solution interfaces [46,51]. Indeed, previous investigations highlighted the importance of increasing the cross-flow velocity to keep a sustainable flux [27,46,51].

Based on the results of this preliminary investigation, an ES concentration of 4 M $CaCl_2$ was regarded as efficacious for OMD processes, due to the observed feasible water flux values achieved under manageable concentrations, well below the salt solubility [52]. A concentration of 4 M was thus adopted for the higher-recovery tests aimed at dewatering PYC and CAF solutions.

3.2. Degradation of the valuable compounds: Effect of feed temperature

Before discussing the results of the high recovery tests, it is worth describing the effect of temperature alone on the PYC and SCGs extract feed solutions. While temperature has an important, positive, influence on OMD productivity, the thermolability of valuable food and pharmaceutical substances is precisely the reason OMD is a competitive process in as much as it allows utilizing lower values of the feed solution temperature compared to other evaporative processes. The sensitivity of PYC to heat is well known from previous studies [33,53–55]. In fact, even medium–high temperatures (i.e., 35–55 °C) cause degradation of the molecular structure [56]. This phenomenon is particularly evident when dealing with PYC extract obtained from cyanobacteria, e.g. *Spirulina platensis*, while a potential improvement in thermostability has been observed when PYC is extracted from *Galdieria sulphuraria* [41]. On the other hand, in relation to SCGs extracts, temperature substantially influences its organoleptic characteristics (i.e., aroma, flavor, color). While an increase in temperature promote the extraction of organic compounds during coffee brewing [57], exposure to medium–high temperatures during long-term filtration can cause the loss of volatile and bioactive compounds of coffee extracts, thus compromising the quality of the final concentrate [58]. PYC is the main component of the phycocyanin extract while SCGs extract is a heterogeneous matrix, from which both CAF and TFC were selected as representative indicators of the stream quality. Therefore, CAF and TFC were systematically monitored as targets in degradation tests at different temperatures. Degradation tests were conducted at 35 °C, 45 °C, and 55 °C, and samples were taken at 0, 4, 8, 12, 16, and 24 h.

In Fig. 2, visible spectra (400–800 nm wavelength range) obtained over time are reported for PYC and TFC. The temperature affected the characteristic peak of PYC at 619 nm, which decreased with time, highlighting the occurrence of a substantial degradation. At higher temperature values, the trend was more apparent; see Fig. 2a-c. The effect was particularly visible at 55 °C, especially within the first 4 h, corroborating that PYC is subject to more rapid and extensive degradation as the temperature rises. Almost complete degradation was reached after 8 h operation, implying that 55 °C is surely too high an operating temperature when dealing with PYC extracts. On the other hand, results related to TFC revealed that the characteristic peak at 510 nm did not vary appreciably over time and that no noteworthy degradation occurred at 55 °C; see Fig. 2e-f. The influence of different temperatures was qualitatively noticeable also in the extract appearance. Photographs of the samples taken at the end of the degradation tests are reported in Figure S.4 of the SI. For PYC samples at 35 °C and 45 °C, the initial characteristic blue color was preserved after 24 h, while at 55 °C the solution turned into a greyish color. Instead, no color variation was observed in TFC solutions during the experiments, i.e., all the solution maintained the same pinkish color, typical of the TFC once isolated from the SCGs extract solution.

In Fig. 3, PYC and TFC degradation results are shown in terms of normalized concentration profiles over time and compared with those obtained for CAF, differently derived by means of HPLC/UV–Vis analysis due to its characteristic transparency. For both feed streams, two replicate tests were carried out for each temperature; the plots report the average values and the error bar represents one standard deviation. Differently from TFC, the CAF seemed to be prone to some degradation within the tested temperature range, especially at 55 °C. At this temperature, a decrease of 25 % in CAF concentration was observed after 4 h, which then stabilized through the rest of the test. On the other hand, negligible or little degradation was observed at 35 °C or 45 °C, the latter condition producing a loss of less than 15 % of the initial concentration, similarly to what observed for PYC at 35 °C. These results are in good agreement with previous studies [41,59]. As also suggested by the results reported in Fig. 2, the concentration of TFC did not vary appreciably during the tests for all the three investigated temperatures, suggesting that temperature limitations for coffee extract management and concentration is mainly constrained by CAF thermolability.

In summary, batch degradation tests confirmed the important heat sensitivity of PYC, while proved SCGs extract to be more resistant to temperature degradation, at least in terms of TFC. CAF was observed to be more sensitive than flavonoids to temperature, albeit with appropriate resilience up to 45 °C. In particular, results suggested that the optimal FS temperature in OMD could possibly be in the 35–40 °C range for PYC, as higher temperature quickly degraded this substance. Other than temperature, PYC is well known to be sensitive to other environmental factors, such as light and shear stress [60]. Indeed, mechanical stress under cross-flow conditions may induce an additional PYC decomposition, negatively affecting the quality of the final concentrate. On the other hand, SCGs extract may be suitable for operation in a higher temperature range. Below, the OMD performance and impact of OMD conditions are further evaluated by discussing high-recovery experimental results, with the additional aim to identify the conditions resulting in the best compromise between productivity and the quality of the final concentrated solution.

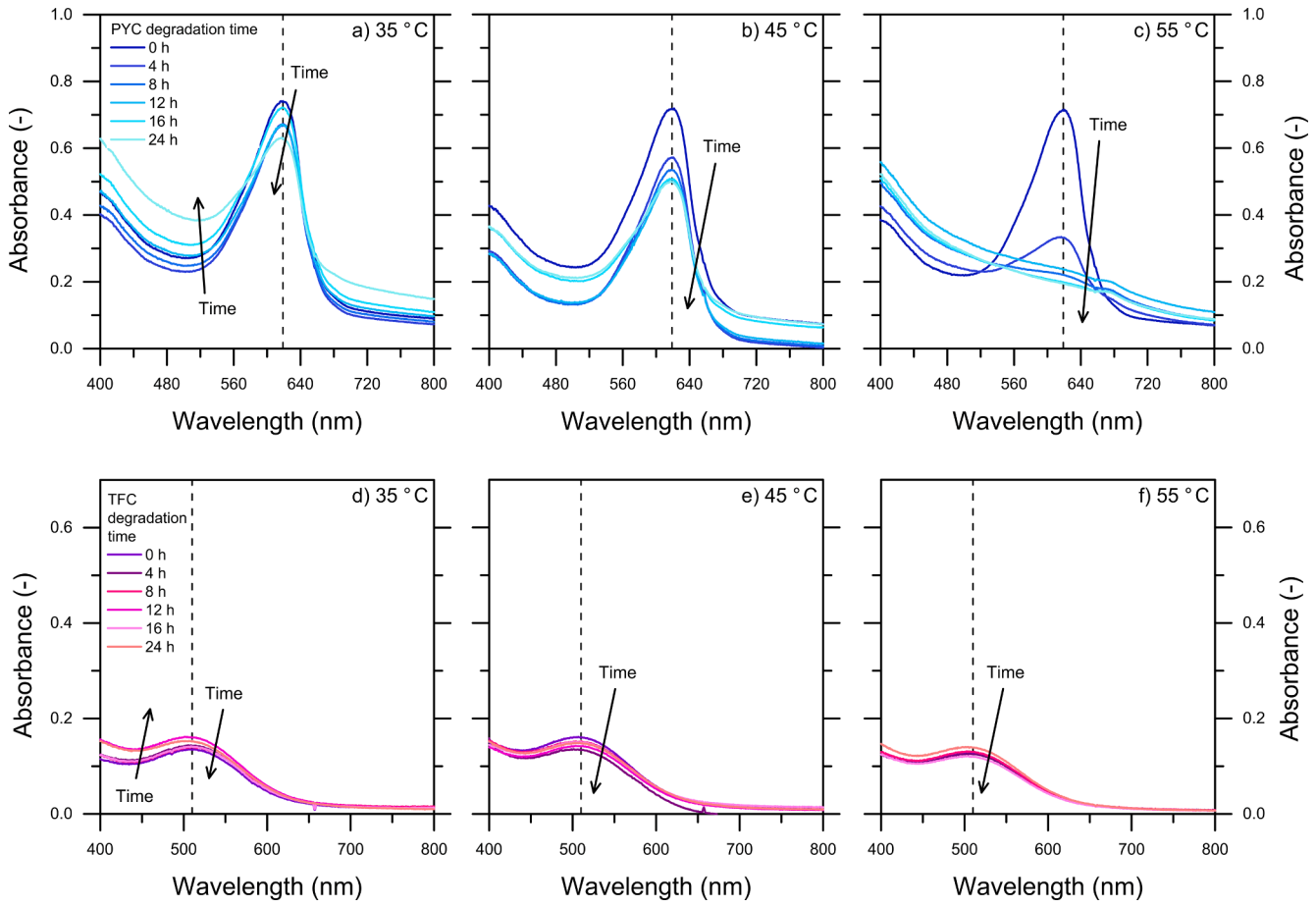

Fig. 2. Effect of temperature on the content of (above, a-c) phycocyanin (PYC) and (below, d-f) total flavonoids (TFC) during 24-h batch tests. Three feed temperatures were tested, namely, 35 °C, 45 °C, 55 °C (from left to right). Absorbance values between 400 nm and 800 nm are reported for both solutions. The vertical dash line indicates the maximum absorbance, measured at 619 nm for the phycocyanin extract and at 510 nm for the SCGs extract. In all charts, the arrow qualitatively indicates the influence of time on the absorbance values. Representative photographic images of the solutions at the end of each degradation test are reported in Figure S.4 of the SI.

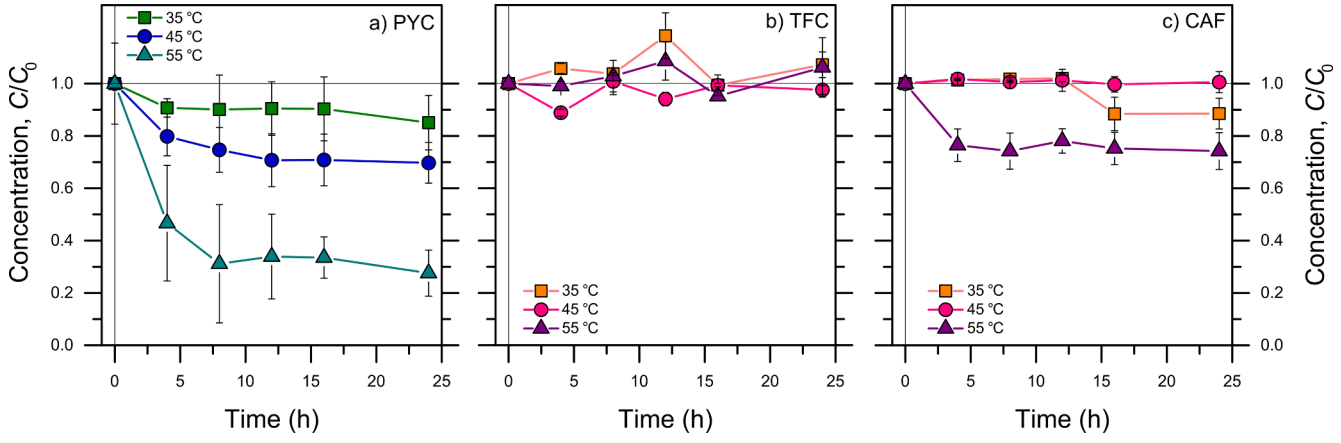

Fig. 3. A) PYC, b) TFC, c) CAF normalized concentration profiles as a function of time (0, 4, 8, 12, 16, 24 h), measured at the three temperatures (35 °C, 45 °C, 55 °C, referring to squares, circles, and triangles, respectively).

3.3. Osmotic membrane distillation for the concentration of phycocyanin and coffee feed solutions: Flux and fouling investigation

Fig. 4a and 4b present the water flux values obtained from OMD high-recovery tests with the PYC extract and the SCGs extract feed solutions, respectively. All the tests were conducted with 4 M $CaCl_2$ ES concentration and at 25 °C ES temperature. Consistent with the discussion of Fig. 1, the FS temperature played a key role in system productivity. Initial water flux values measured at 55 °C were more than double those observed at 35 °C. In particular, for PYC extract and for SCGs extract, initial water fluxes were 5.5–12 LMH and 6–16.5 LMH in the 35–55 °C FS range, respectively. The SCGs extract showed higher

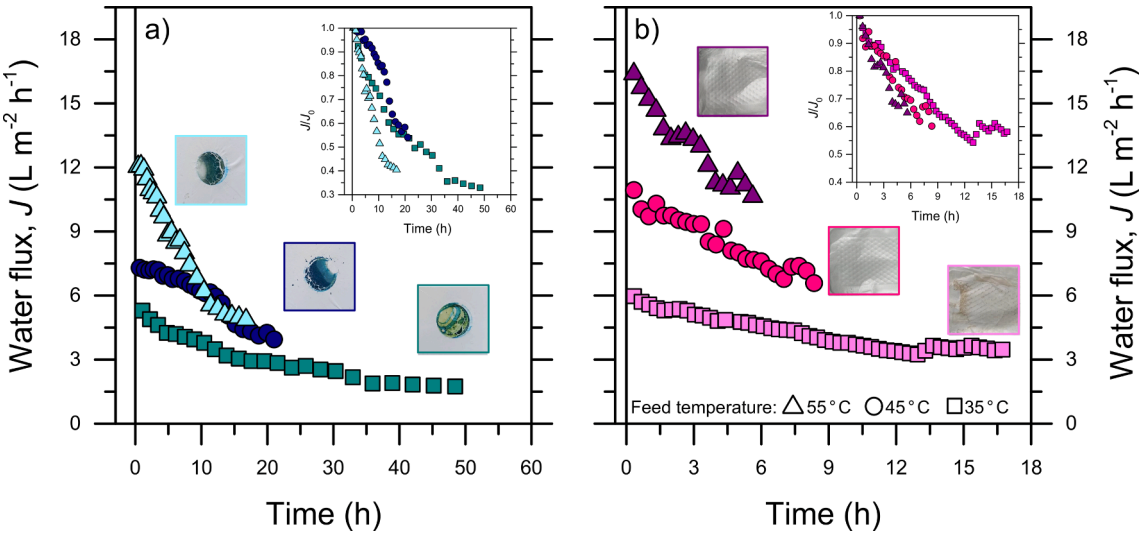

Fig. 4. Development of water flux, J, as a function of time observed with (a) phycocyanin and (b) coffee extract feed solutions during osmotic membrane distillation tests. For each feed solution, tests were conducted at three distinct feed temperatures, namely, 35 °C, 45 °C, 55 °C, while the extraction solution temperature was always kept at 25 °C. The extraction solution was 4 M of $CaCl_2$ in all tests. The final target recovery rate was 75 % (feed solution concentration factor of 4). A representative photographic image of the active surface of the membrane at the end of each test is also shown next to the respective data. In the top right corner of each plot, inset graphs report the same flux data as normalized flux (J/J_0) with respect to the initial flux value for each curve, to allow for a better comparison among the decline observed at the various conditions.

initial fluxes. Since foulant accumulation may be reasonably assumed negligible at the very beginning of the test, this phenomenon was possibly due to the absence of a cross-flow rate when using the diffusion cell [27,61].

For all experiments, productivity decreased with time (hence, recovery rate) proportionally to the initial water flux. In general, PYC solutions showed a faster and deeper drop compared to the SCGs extract, again attributed to the absence of a cross-flow and to larger fouling in the system used for PYC solution dewatering. Fouling has been reported as a limiting factor in OMD industrial implementation [16,21,62,63]. According to fouled membrane pictures collected at the end of the experiments, higher fouling load on the membrane surface was observed when dewatering PYC solutions, in good agreement with the more pronounced flux decline observed in the OMD tests. Membranes showed a deposited colored layer of PYC, with increasing visible deposition when operating at higher temperature, highlighting the correlation between fouling and water fluxes, well reported also for other membrane processes [64–66]. Fouling effects were also monitored during the process by isolating the sole contribution to water flux decline due to ES dilution. In Figure S.5 of the SI, dash lines implement the correlation between water flux and the ES concentration retrieved from the preliminary test results (Fig. 2b and respective equations in Table S.1). Thus, the difference between the dash and the experimental lines may be attributed to fouling alone [43]. Higher fouling rates were estimated with the PYC solutions compared to SCGs extracts and, more in general, for higher FS temperature. Specifically, the loss of productivity due to fouling was estimated to be between roughly 50 % and 75 % for tests involving PYC solutions and between roughly 30 and 45 % for SCGs extracts. We hypothesize that the organic molecules present in the coffee extract might be characterized by lower molecular weight and higher hydrophilicity compared to phycocyanin protein molecules, especially when the latter are degraded and denatured, which may also lead to their aggregation and coagulation and to a lower water solubility. Qualitative partitioning tests performed using cyclohexane and water preliminarily corroborated this hypothesis; see Supporting Information, Figure S.6. These characteristics would increase the likelihood of fouling of the hydrophobic membrane by the PYC feed stream, compared to the fouling propensity of the spent coffee ground extract solution.

In summary, SCGs extract showed higher initial fluxes and a slower flux decline than the PYC solutions during the OMD tests. The configuration of the system may partially influence the process since better feed channel mixing helps in both reducing fouling and temperature polarization, hence maintaining higher productivity. However, avoiding shear stress when treating PYC is mandatory to preserve the integrity of the final product. Overall, fouling was evidently more pronounced for PYC than for SCGs extract as supported by combined productivity profiles, membrane images, and flux analysis. To reduce both fouling and temperature degradation mechanisms, based on the combined results of degradation tests and high-recovery OMD dewatering, it may be concluded that: (i) a feasible FS temperature in OMD could be set around 35 °C and not higher than 45 °C to dewater PYC extracts, (ii) while a higher FS temperature, around or above 45 °C, may be suitable to dewater the SCGs extracts.

3.4. Osmotic membrane distillation for the concentration of phycocyanin and coffee feed solutions: Evaluation of the concentrated solution quality

So far, possible ranges of operative conditions in terms of FS temperature and ES concentration have been discussed, but without considering the final concentrated solution quality. However, determination of concentration yields is a key step in assessing the effectiveness of the OMD process when dealing with valuable and sensitive compounds. At the end of each test, PYC and CAF concentrations were compared to the final expected concentration value based on the effective concentration factor, which may have differed slightly from the set target of 4 for some tests due to experimental variability. Because of such differences, error bars from replicate tests were not reported in Fig. 5, whereby only the results from one representative test are plotted. Data for all the replicate tests, namely, two tests with PCY and three tests with the coffee extract, can be found in the SI (Figure S.7) and imply adequate repeatability of the tests. Regarding the PYC feed solution (Fig. 5a), no increase in the concentration of PYC was found in the FS at 55 °C, despite feed stream dewatering, while the final concentrations were higher than the initial values when operating at 45 °C and 35 °C. This difference in behavior may be indeed attributed to the thermolability of PYC observed in the degradation tests (Fig. 3), since the solution was instead effectively concentrated in terms of organic content, as will be discussed below. In particular, at 55 °C the advantage of lower

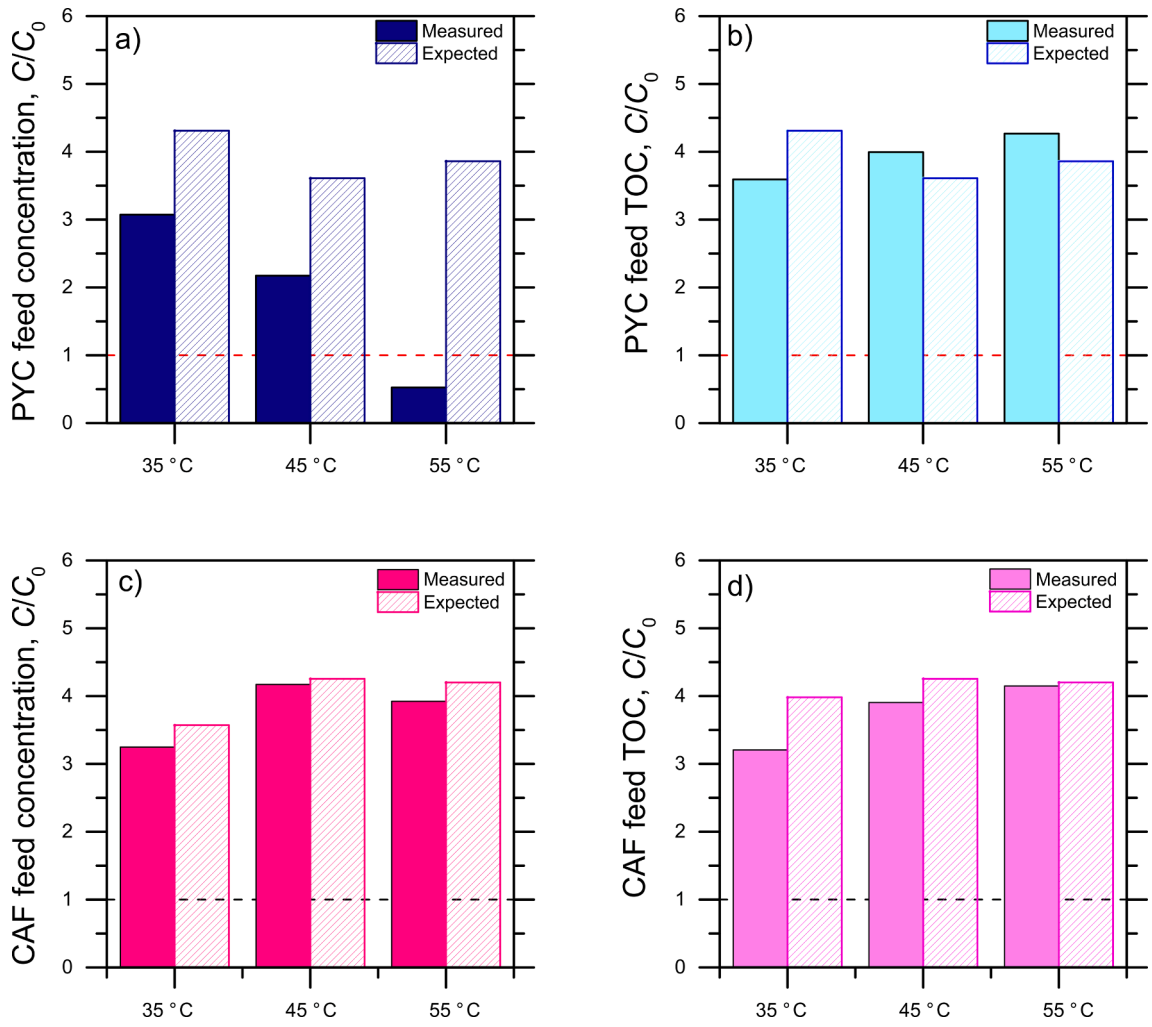

Fig. 5. Assessment of the process feasibility through analysis of the feed content observed in tests using (above, a-b) phycocyanin and (below, c-d) coffee extract as feed solutions at different temperature values: (solid bar) measured and (patterned bar) expected values at the end of each test performed at distinct feed solution temperature for, (a, c) the concentration of the target compounds and (b, d) the total organic carbon (TOC) content. The expected values were calculated from the actual recovery rate achieved during each test, which may be slightly different from the target rate, i.e., 75%. All concentration values were normalized with respect to the initial concentration and the horizontal dash line indicates the starting point.

filtration time required to reach the target recovery was defeated by the faster degradation exerted at this temperature, resulting in an observed decrease in PYC concentration of approximately 48 %. At 35 °C and 45 °C, adequate concentration yields were achieved. The final PYC concentration was almost tripled in the 35 °C test, while it doubled at 45 °C. That being said, in both cases the final concentration did not reflect the target value, intended to be roughly four times higher than the initial one under ideal conditions (patterned bars in Fig. 5a). This result indicates that degradation occurred even at medium temperatures. According to these additional results and, further corroborating the data discussed above and related to degradation and water flux tests, the optimal temperature for PYC processing may be identified around 35 °C, at which thermal degradation occurred slowly enough to allow suitable concentration even under low OMD productivity.

Fig. 5c shows the concentration results obtained for CAF at the end of each recovery test. As opposed to the PYC case, the measured final concentrations well reflected the expected final values based on the amount of water extracted from the FS. Nevertheless, a slight CAF degradation was observed at 35 °C and 55 °C, corresponding to 9 % and 7 %, respectively. In particular, at 55 °C the degradation may be related to the sole temperature effect, as suggested by the degradation tests conducted at this temperature (Fig. 3b). At 35 °C, the extended residence time within the cross-flow system may have produced some degradation. However, the limited concentration losses imply that the process can be carried out successfully under a wider range of FS temperatures.

A positive control of the FS quality and of the effective concentration effect of the OMD process was obtained through TOC measurements, performed on both the FS and ES in the beginning and at the end of the tests. This method provides an understanding of the process in terms of organic mass balance, while also allowing detection of any potential transfers of organic substances from the FS to the ES. Since PYC represent the main constituent of the related extract, the occurrence of a degradation phenomenon across all temperatures was further confirmed by the difference between normalized TOC and PYC concentration in the FS, i.e., data reported in Fig. 5a and Fig. 5b, accounting for approximately 15 %, 46 %, 88 % at 35 °C, 45 °C, 55 °C, respectively. That is, the TOC content increased with FS dewatering consistent with the concentration factor, while PYC concentration did not or did at a slower pace: this discrepancy may be rationalized and quantified in terms of PYC degradation.

Differently, the SCGs extract is a mixture of various organic compounds [67], with TOC providing information on the overall organic mass balance of the process rather than on the two selected CAF and TFC components. As shown in Fig. 5d, in all tests the organic content in the FS showed a near four-fold increase compared to the initial values,

indicating an adequate mass balance upon solution dewatering and being consistent with the CAF results discussed above and presented in Fig. 5c. That is, TOC was a good indicator for the behavior of CAF, and organic substances in general underwent no or only slight mineralization during the OMD tests. Only a slight decrease in measured TOC was observed at lower temperatures, confirming the susceptibility of SCGs extract when exposed to a prolonged mechanical stress in the cross-flow system. With respect to the ES solutions, the TOC content was found to be negligible for all tests (see Table S.3 of the SI), thereby implying that no transfer of organic matter occurred from the FS to the ES and further confirming the advantage of OMD process in reducing liquid-based *trans*-membrane transport.

To complete the evaluation of the effectiveness of OMD in the recovery of highly valuable PYC and coffee components, quality markers of the final products were assessed and are reported in Fig. 6. For PYC, the final product quality was effectively increased only at 35 °C, of about 30 %, corroborating the conclusion that this condition is the most appropriate for PYC concentration. Clearly, the unfeasibility of the process carried out at 55 °C is evident in the drop of purity, while at 45 °C the PYC concentration increased to some extent in the FS, although accompanied by a loss of about 25 % in the purity index. At 45 °C the process might be feasible for applications in which a high purity of PYC is not crucial and whereby rapid production is necessary, e.g., as additive in the food and beverage industry [31]; note that at 45 °C the time needed to achieve a concentration factor of ~ 4 was half that required at 35 °C (Fig. 4a). SCGs extract quality was not affected by operating conditions. The TFC quality always increased in agreement with the achieved water recovery rate. These trends, along with the concentration of CAF, further corroborate that the OMD process may be feasible in terms of product quality even at 45–55 °C for the concentration of SCGs extracts.

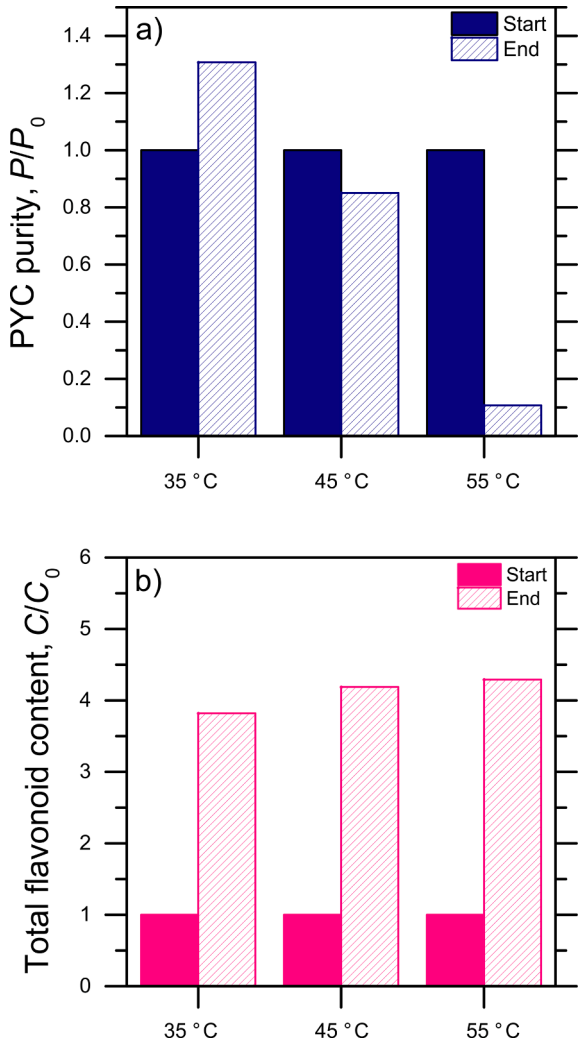

Fig. 6. Evaluation of the final product quality obtained with the OMD process at different temperature values shown through a key parameter for each feed solutions, specifically, (a) the purity index for phycocyanin and (b) the total flavonoid content for coffee extracts. In both graphs, the data are reported as normalized values with respect to the starting value and the adjacent bars presents values (solid bar) at the start, equal to 1 in all cases, and (patterned bar) at the end of each test, for the three investigated temperature values.

4. Conclusions

The OMD process was evaluated for the concentration of phycocyanin and spent coffee grounds extracts with the aim of preserving the final products quality. Preliminary tests with deionized water revealed the interplay between temperature and concentration gradients in determining water flux. They also allowed identification of a range of operating conditions for the tests conducted with complex feed solutions. Specifically, the operative conditions for recovery tests were selected at 35 °C, 45 °C, and 55 °C, while keeping the extraction solution concentration at 4 M $CaCl_2$.

Results of the PYC and SCGs extract dewatering tests suggested the OMD capability to concentrate both targets, although with limitations for PYC extracts. In fact, the OMD process was effective in achieving high-purity PYC concentration at 35 °C FS temperature, albeit with a productivity of approximately 2 LMH. The temperature range may be increased to 45 °C for some specific applications, thus doubling the productivity value at the possible expense of some loss in final product yield and quality if the process requires maintaining this temperature for several hours. The dewatering was deemed not feasible at 55 °C due to the rapid PYC degradation. PYC extracts also exhibited a relatively quick flux decline, largely due to fouling. Note that in this study, PYC fouling and low flux may have been exacerbated by the use of a non-cross-flow system (diffusion cell), which however was necessary to avoid mechanical degradation of PYC (preliminary results using a cross-flow systems produced near total degradation of the PYC even at ambient temperature). PYC sensitivity to thermal and mechanical stress limits productivity and needs to be carefully considered in industrial applications. On the other hand, no important restrictions were observed for SCGs extract in terms of FS temperature, indicating that the OMD process may be effective for its concentration even at medium–high temperatures (i.e., 45–55 °C), without strongly compromising the quality of the final products.

Finally, in all tests, negligible organic compound transfer to the extraction solution, as well as negligible salt passage in the other direction, highlighted the possibility of further ES reuse and the practical absence of cross-contamination between the two streams separated by the membrane. Note the heat spared by the OMD process in the dewatered FS solution may be used in a separate thermally driven step to partially reconcentrate the ES solution and for its ideal reuse in a closed loop system. In fact, the recovery of the diluted ES still represents one of the main drawbacks of the OMD process that should be evaluated in future investigations.

CRediT authorship contribution statement

Erica Bertozzi: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Lorenzo Craveri:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Marco Malaguti:** Methodology, Formal analysis, Investigation. **Francesco Ricceri:** Investigation, Methodology, Supervision, Writing – original draft. **Michele Carone:** Investigation, Writing – review & editing. **Vincenzo Riggio:** Supervision, Methodology, Writing – review & editing. **Alberto**

Tiraferri: Funding acquisition, Project administration, Resources, Supervision, Visualization, Writing – review & editing.

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

Data will be made available on request.

Acknowledgments

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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.2023.125360.

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