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Low-energy membrane-based processes to concentrate and encapsulate polyphenols from carob pulp

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ABSTRACT

Forward osmosis (FO) and emulsification with dynamic membranes of tunable pore size (DMTS) were assessed to concentrate and encapsulate polyphenol extracts from carob pulp. In the FO step, a feed solution temperature of 40 °C resulted in the fastest concentration and the highest polyphenol yield. Moreover, FO at 35 °C enabled to concentrate up to about 20 times in 3 h using a pilot scale unit of 0.5 m^2 of membrane area. Phenolic compounds were subsequently encapsulated in the inner water phase (W_1) of water-in-oil-in-water ($W_1/O/W_2$) emulsions produced with DMTS, which enabled to obtain emulsions with a monomodal droplet size distribution (span<1, $d_{3,2}$ ≤20 μm), and polyphenol encapsulation efficiencies ranging between 87.0 ± 0.2% and 77.4 ± 0.4%. To extend the shelf-life of the encapsulated polyphenols, solid microcapsules were produced by spray drying. After rehydrating the solid microcapsules, the structure of the $W_1/O/W_2$ emulsion was partially recovered.

1. Introduction

The increasing attention towards sustainability in the food sector has led to progressive implementation of valorization strategies to yield value-added compounds, such as antioxidants, colorants, flavors and dietary fibers from agri-food wastes. This is the case of carob (*Ceratonia siliqua L.*) fruits grown in Mediterranean countries, which are pods consisting of seeds and pulp. The commercial value of the carob fruit comes from its seeds that contain a widely used food additive, locust bean gum (E−410). After removing the seeds, about 90% of the total weight of the fruit is the pulp, which is mainly used for animal feed and a few food preparations (Abu Hafsa et al., 2017; Rababah et al., 2013). However, the carob pulp contains different valuable components such as sugars, dietary fibers, and a great diversity of polyphenols and other minor components (Goulas et al., 2016). Goulas et al. (2016) have reviewed the health benefits of fibers and polyphenols from carob, reporting anti-proliferative and apoptotic activity against cancer cells, anti-diabetic effects, anti-diarrheal effects and anti-hyperlipidemia effects. The presence of fibers and polyphenols makes the carob pulp an attractive raw material to obtain extracts that can be used in gluten-free bakery products, fortified durum wheat pasta, carob spread, low lactose yoghurt, marmalades, cookies and candies (Moreira et al., 2017; Rached et al., 2016; Román et al., 2017; Sęczyk et al., 2016; Tsatsaragkou et al., 2014). A process strategy to recover the polyphenol fraction from carob pod should consist of extraction, concentration and stabilization of the biomolecules of interest. To do so, environmentally friendly technologies have evolved to increase product quality while reducing energy consumption or thermal detrimental effects.

In the conventional solid-liquid extraction process of polyphenols, a prior removal of the sugars by water extraction at room temperature is followed by several steps of polyphenols solubilization (Almanasrah et al., 2015). As for the remaining polyphenol fraction in the low-sugar-content carob pulp, it can be extracted using hot water, resulting in a water-soluble polyphenol fraction. The solid-liquid extraction process can produce high volumes of a diluted aqueous polyphenol extract that needs to be concentrated to reduce handling, storage and transportation costs and to obtain a suitable polyphenol content for its further uses. Concentration can be performed by several methods, such as evaporation, reverse osmosis and forward (or direct) osmosis. Forward osmosis (FO) is a low-energy membrane-based separation technology based on osmotic pressure difference between two solutions (Long et al., 2018; Nagy, 2019). A draw solution (DS) with very high osmotic pressure circulates on one side of a water permeable

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Abbreviations

DMTS	Dynamic membrane of tunable pore size
DS	Draw solution
EE	Encapsulation efficiency [%]
ESEM	Environmental scanning electron microscope
FO	Forward osmosis
FS	Feed solution
GAE	Gallic acid equivalent
MD	Maltodextrin
O	Oil phase
PC	Polyphenol concentrate
PE	Polyphenol extract
PGPR	Polyglycerol polyricinoleate
PR	Polyphenol re-concentrate
T_g	Glass transition temperature [°C]
TPC	Total polyphenol content [gGAE L^{-1}]
W_1	Inner water phase
W_1/O	Water-in-oil emulsion
$W_1/O/W_2$	Water-in-oil-in-water emulsion
W_2	Outer water phase
WPI	Whey protein isolate

membrane and on the other side of the membrane circulates a feed solution (FS) that has lower osmotic pressure. Under this configuration, water is driven from the FS to the DS because of osmotic pressure difference. This method prevents from applying high pressure to the solutions, since pressure is only required to circulate the draw and feed solutions, and it can be operated at mild temperatures (Cath et al., 2006). Therefore, FO is a non-thermal concentration technology very promising for the food industry since it has a minimal impact on nutritional and organoleptic quality of the products. FO can concentrate to higher soluble solids values than reverse osmosis, which is usually limited to 22–23 °Brix (Terefe et al., 2016) and it has a low irreversible fouling which decreases the costs of membrane cleaning and replacement. Food applications of FO range from water desalination, fruit and vegetable juices concentration, including the enrichment of natural antioxidants and colorants to protein concentration in fish by-products, dewatering of whey in cheese manufacturing, concentration of acid whey from Greek yoghurt and concentration of artificial sugar solutions (Haupt and Lerch, 2018; Maknakhon and Khongnakorn, 2018; Menchik and Moraru, 2019; Sant'Anna et al., 2016).

To preserve the chemical stability of polyphenols in the concentrated extract, they should be further stabilized by encapsulation in liquid or solid systems. Encapsulation in water-in-oil-in-water ($W_1/O/W_2$) emulsions, where the water-continuous system (W_2) contains oil droplets that have smaller water droplets (W_1) dispersed within, has been described as a successful system to protect and encapsulate sensitive hydrophilic compounds, such as polyphenols (Bamba et al., 2018; Berendsen et al., 2015a; Bušić et al., 2018; Estévez et al., 2019). $W_1/O/W_2$ emulsions involve the production of a W_1/O single emulsion and dispersion of the single emulsion in a W_2 continuous phase. Several emulsification techniques, such as high-pressure homogenization, rotor-stator homogenization, ultrasonication, or membrane emulsification, are used to produce the inner W_1/O emulsion, although the secondary homogenization step is usually carried out using lower energy intensity than the in the primary step so as not to break the initial W_1/O emulsion (Charcosset, 2009). Membrane emulsification, which uses low-shear stresses, has received increasing attention for producing multiple emulsions.

Membrane/microporous emulsification is carried out by pressing the dispersed phase into a continuous phase through the pores of a membrane or refining a coarse pre-emulsion by pushing through the membrane pores (Güell et al., 2009). It is benefited by its low energy input and the possibility to obtain narrow droplet size distribution compared to other conventional process (Güell et al., 2009). Dynamic membranes of tunable pore size (DMTS) (Fig. 1), consisting of a bed of silica beads supported by a nickel microporous membrane, exhibit higher productivity than other membrane emulsification processes (Nazir et al., 2011), whilst maintaining its other advantages, such as a reduction of the mechanical stress and low energy consumption. Sodium chloride (Sahin et al., 2014a) and beet root juice (Eisinaite et al., 2016) were successfully encapsulated in $W_1/O/W_2$ emulsions produced with the DMTS

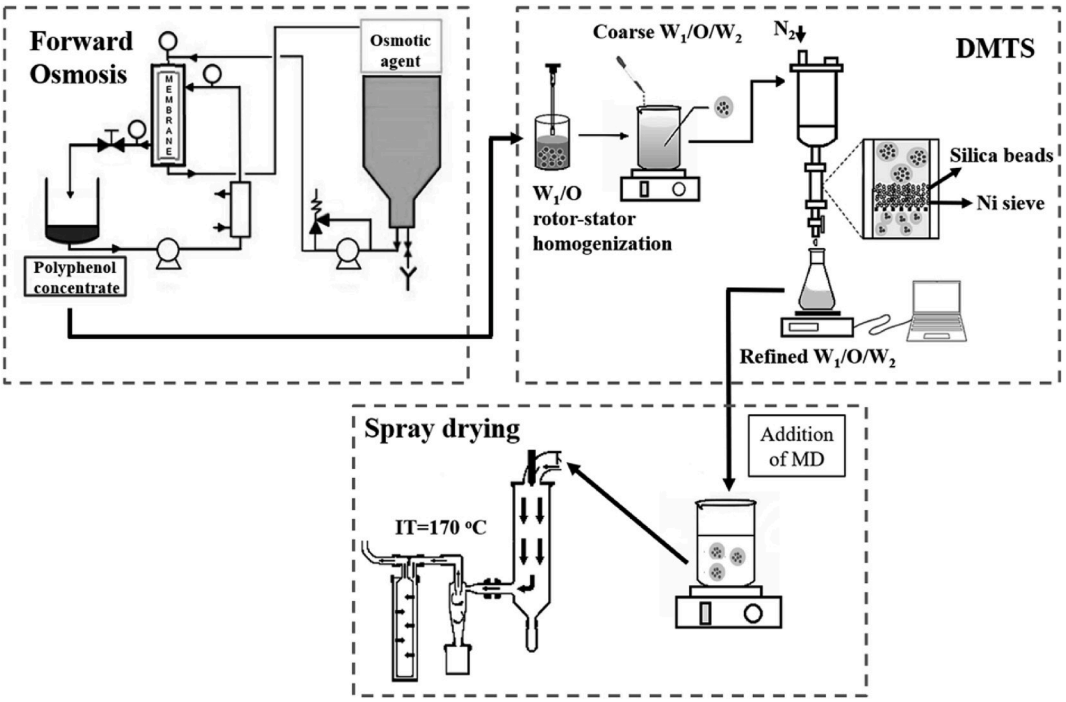


Fig. 1. Schematic diagram of the concentration and encapsulation processes for the valorization of a carob polyphenol extract.

Table 1
Operating conditions and initial and final composition during FO concentration and re-concentration.

	FS	Product	T (°C)	$V_{initial}$ (L)	V_{fianl} (L)	$TPC_{initial}$ (gGAE L^{-1})	TPC_{final} (gGAE L^{-1})	Sugar content	
								°Brix (initial)	°Brix (final)
Concentration	PE	PC	25	9.8 ± 0.8	0.9 ± 0.2	1.1 ± 0.1	6.2 ± 1.6	4.5	11.8
			35				8.9 ± 1.4		
			40				8.2 ± 0.8		
Re-concentration	PC	PR	35	2.8	0.9 ± 0.1	8.2 ± 0.1	18.4 ± 1.7	11.8	24.5

system. The operation mode consists of producing a coarse $W_1/O/W_2$ emulsion which is forced to pass through the micro-structured bed several times, decreasing the droplet size of the emulsion (Sahin et al., 2014b). During emulsion refinement, release of the entrapped compound is unavoidable as a result of droplet break-up. Therefore, operation conditions such as applied pressure, bed height, interstitial void diameter and number of cycles must be adjusted to retain the entrapped compound while reducing the droplet size distribution. Moreover, the imbalance of osmotic pressure between inner and outer water phase in $W_1/O/W_2$ emulsions is a primary source of instability during storage (Muschiolik, 2007).

Even though $W_1/O/W_2$ emulsions can protect the bioactive compounds, they have poor stability during storage, and dosage of liquid systems is more difficult to control in the production lines. Therefore, spray drying of the emulsions is a common strategy used by the food industry to produce solid microcapsules. The spray drying process requires the addition of wall-building materials, such as polysaccharides (e.g. maltodextrin), proteins (e.g. whey protein), and gums (e.g. Arabic gum), that are water soluble. Several authors have reported encapsulation of bioactive compounds by spray drying of $W_1/O/W_2$ emulsions (Berendsen et al., 2015b; Bušić et al., 2018; Esfanjani et al., 2015; Rodríduez-Huezo et al., 2004).

The objective of the study was to assess the use of membrane-based processes to concentrate and encapsulate a carob polyphenol extract. Starting from a polyphenol diluted solution from carob pulp obtained by water extraction, concentration was performed using forward osmosis (FO) in a commercial pilot unit. The effect of temperature on water flux and polyphenol concentration was studied. Moreover, to increase the stability of the extracted polyphenols, encapsulation in liquid systems ($W_1/O/W_2$ emulsions) and solid microcapsules was assessed. $W_1/O/W_2$ emulsions were produced by DMTS, while solid microcapsules were obtained by spray drying the $W_1/O/W_2$ emulsions. This study combines for the first-time concentration and encapsulation of a polyphenol extract by membrane-based processes, showing the potential of membrane technology to be implemented in bio-refinery of agri-food wastes.

2. Materials and methods

2.1. Materials

Carob polyphenol extract, kindly provided by *Unió Corporació Alimentària* (Reus, Spain), had a total polyphenol content (TPC) of 1.13 g GAE L^{-1} and 4.5 °Brix with sucrose, glucose and fructose as main soluble solids (Ayaz et al., 2007; Aziz and Hicham, 2014; Goulas et al., 2016). The draw solution (DS) used during FO was composed of potassium lactate 60 °Brix supplied by Ederna SAS (Toulouse, France). P3-ultrasil 112 (ECOLAB, Finland) and acetic acid (96%, Panreac, Spain) were used for cleaning and regeneration of FO membrane. As for preparation of emulsions, sunflower oil (bought at local supermarket) with 4 wt% polyglycerol polyricinoleate (PGPR, ref-4120 Palsgaard, Denmark) was the oil phase. Whey protein isolate (WPI) with a reported protein content of 98.1% on dry basis (BiPRO, lot no. JE 034-7-440-6, Davisco Foods International. Inc., Le Sueur, MN) was used as a hydrophilic emulsifier in W_2 phase at a concentration of 1 wt%. In order to balance the osmotic pressure of two aqueous phases (W_1 and W_2), either NaCl (Panreac, Spain) or trehalose (Sosa Ingredients S.L., Spain) was added in the W_2 phase as bulk agent. Sodium azide 0.02% (w/w) (Sigma-Aldrich, USA) was added to prevent bacterial growth. Food grade maltodextrin (lot no. 219425, MD, Pral, Barcelona) with a dextrose equivalent of 16.5–19.5 was added to the $W_1/O/W_2$ emulsions as wall-building material for the microcapsules produced by spray drying. Sodium carbonate (Panreac, Spain), gallic acid monohydrate (Panreac, Spain) and Folin-Ciocalteau's reagent (Panreac, Spain) were used for total polyphenol content (TPC) quantification. Sodium hydroxide, 4M (Fisher Scientific, UK) and ethanol (96%, Scharlab S.L., Spain) were used to clean the DMTS system, that consists of a bed of silica beads (Unicorn Industrial Cleaning Solutions, the Netherlands) supported by a nickel micro-sieve (Stork Verco, Erbeek, the Netherlands).

2.2. Forward osmosis concentration

Concentration of carob polyphenol extract (PE) was carried out with FO pilot unit (EvapEOs® - Micro pilot unit) provided by Ederna SAS (Toulouse, France). The unit (Fig. 1) was equipped with a cellulose triacetate membrane module that contains a spiral wound membrane of 0.5 m^2, a feed solution (FS) reservoir, a draw solution (DS) reservoir and pumps for both solutions. The pressure inside the membrane module was controlled below 0.7 bar. A water bath was connected aside in order to control the temperature of the feed solution under 40 °C (maximum operating temperature of the membrane). For all experiments, 1 L of DS (osmotic agent) was placed initially and the transmembrane water flux (J_{FO}) was measured every 30 min by measuring the time consumed to filtrate a fixed amount of FS and calculated with equation (1),

$$J_{FO} = \frac{m}{\rho_f A_m \Delta t} \quad (1)$$

where the m is the mass of FS added in kg; ρ_f is the density of FS in kg L^{-1}; A_m is the surface area of membrane in m^2; Δt is the time duration of the process.

When the flux dropped below 4 Lm^{-2} h^{-1}, 1 L fresh osmotic agent replaced the diluted osmotic agent to continue the process. PE was firstly concentrated to obtain polyphenol concentrate (PC) at different feed temperatures (25, 35 and 40 °C); several batches of PC were collected to continue the concentration process at 35 °C to obtain a polyphenol re-concentrate (PR). The process parameters and initial and final polyphenol and sugar content during FO experiments are summarized in Table 1. The FO yield was obtained using equation (2).

$$Yield_{FO}[\%] = \frac{m_{polyPC}}{m_{polyPE}} \times 100 \quad (2)$$

Where m_{polyPC} is the amount of polyphenols in the concentrated extract and m_{polyPE} is the amount of polyphenol in the initial extract.

Experiments were run at least in duplicate. Cleaning of the membrane was carried out after each FO concentration process following the manufacturer's indications with 4%(v/v) ultrasil (pH14) and acetic acid solution (pH2). The water flux was measured after cleaning to ensure a minimum water flux value of 10 $Lm^{-2}h^{-1}$ before reusing the membrane.

Table 2
Composition of $W_1/O/W_2$ emulsions and osmolality of the two aqueous phases.

Fraction	Phase	Composition	Bulk agent	Osmolality (mOsmol/L)
6 wt %	W_1	PR	–	1200 ± 2
14 wt %	O	4 wt% PGPR	–	–
80 wt%	W_2	1 wt% WPI	i) none	40
			ii) 3.15 wt% NaCl	1055 ± 1
			iii) 28.2 wt% trehalose	1107 ± 1

2.3. Production of $W_1/O/W_2$ emulsions using DMTS

2.3.1. Production of coarse $W_1/O/W_2$ emulsions

Composition of double emulsions is presented in Table 2. Initially, W_1/O emulsion consisting of 15 g of W_1, carob polyphenol re-concentrate (PR), and 35 g sunflower oil with 1.4 g PGPR dissolved (4 wt%) (O) were homogenized (Ultraturrax, IKA® T18 Digital, Germany) at 11,000 rpm for 5 min (Fig. 1). Then, 40 g of W_1/O was added to 160 g of W_2 and mixed with a magnetic stirrer at 1600 rpm for 5 min. The high osmolality of W_1, resulting from the high sugar and polyphenol concentration in PR, was balanced by adding NaCl (3.15 wt%) or trehalose (28.2 wt%) as bulk agent in W_2 to prevent emulsion instability (Muschiolik and Dickinson, 2017). Additionally, W_2 contained 1 wt% of whey protein isolate (WPI) as hydrophilic emulsifier. Osmolality of the carob polyphenol re-concentrate solution and the W_2 aqueous phase having different compositions (Table 2) was measured using vapor pressure osmometer (K-7000, KNAUER, Germany) at 39 °C. Calibration of the equipment was done with sodium chloride solution of 400 mOsmol kg^{-1}.

2.3.2. Refinement of $W_1/O/W_2$ emulsions by DMTS

The setup of DMTS system is shown in Fig. 1. Freshly prepared coarse emulsion was placed into the vessel of DMTS system and it was forced to pass through the dynamic membrane consisting of a layer (4.35 mm height) of silica microbeads (101 μm diameter and 0.66 span) supported by a nickel microsieve of rectangular pores 300 μm × 25 μm (length x width) to refine the emulsions at 200 kPa by applying nitrogen gas (named as emulsification cycle 1). A digital balance coupled with a laptop was placed under the recipient in order to record the collected mass during the emulsification. The emulsion was further refined by passing through the DMTS system the second time (cycle 2). The interstitial void diameter (d_v) of the channels formed by the dynamic membrane made of silica microbeads was 59.3 μm, calculated according to equation (3),

$$d_v = \frac{4\varepsilon}{6/d_b(1-\varepsilon)} \tag{3}$$

where d_b is the bead diameter (101 μm) and ε is the bed porosity (0.47), which can be calculated by equation (4),

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p} \tag{4}$$

where ρ_b and ρ_p are the densities of silica beads measured in the bulk (1301 kg m^{-3}) and in the air (2446 kg m^{-3}) respectively.

Transmembrane flux, J_{DMTS}, during each emulsification cycle in the DMTS system can be calculated using equation (5),

$$J_{DMTS} = \frac{\varphi}{\rho_e A_v} \tag{5}$$

where φ is the mass flow rate acquired by data recorded with the electronic balance, ρ_e is the emulsion density, A_v is the effective surface area of the DMTS, calculated as equation (6).

$$A_v = \frac{6}{d_b} \tag{6}$$

The nickel sieve and silica beads were reused once they were cleaned and dried. The cleaning protocol for the nickel sieve was as described by Kaade et al. (2019). Briefly, the sieve was sonicated in the 4M NaOH solution bath for 5 min followed by rinsing under sonication in deionized water for 5 min with one replication. Silica beads were cleaned using soap and ethanol to remove the oil and dried in the oven at 100 °C.

In order to measure the polyphenol encapsulation efficiency in the emulsions, they were centrifuged for 10 min at 3000 rpm. Then, the W_2 phase was collected and analyzed as described in section 2.5.1 for total polyphenol content. The mass of polyphenols that remained encapsulated in W_1 was expressed as polyphenols encapsulation efficiency (EE) using equation (7) (Berendsen et al., 2015a),

$$EE[\%] = \frac{m^0_{poly_{W_1}} - C^n_{poly_{W_2}}\left(m^0_{W_1} + m^0_{W_2}\right)}{m^0_{poly_{W_1}} - C^n_{poly_{W_2}} m^0_{W_1}} \times 100 \tag{7}$$

where $m^0_{poly_{W_1}}$ is the initial polyphenol mass in the inner water phase (W_1), $C^n_{poly_{W_2}}$ is the concentration of polyphenols in the outer water phase (W_2), $m^0_{W_1}$ is the initial mass of the inner water phase, and $m^0_{W_2}$ is the mass of the outer water phase after n cycles.

2.4. Production of solid microcapsules by spray drying

Solid microcapsules from the $W_1/O/W_2$ refined emulsions were obtained by spray drying. Freshly prepared $W_1/O/W_2$ emulsions (cycle 1) were mixed with MD by adjusting oil to solids ratio (WPI, trehalose and MD) to 1:3 (w/w), followed by spray drying using a Büchi Mini Spray dryer B-290 (Flawil Switzerland) setting the inlet temperature at 170 °C, the outlet temperature was controlled at 100 °C, nozzle pressure of 4.5 bar, the feed flow rate of 4 $mLmin^{-1}$ and aspiration rate of 100% (35 m^3h^{-1}). Spray drying yield was calculated using equation (8),

$$Yield_{SD}[\%] = \frac{m_{capsules}}{m_{inlet\ solids}} \times 100 \tag{8}$$

where $m_{capsules}$ is the amount of spray dried powders obtained, and $m_{inlet\ solids}$ is the amount of solid compounds (trehalose, whey protein and maltodextrin) at the inlet of spray dryer.

2.5. Methods of analysis and characterization

2.5.1. Polyphenol assay

The polyphenol concentration in the initial extracts, in samples taken during forward osmosis concentration, and in the final products (PC and PR) was analyzed based on Folin-Ciocalteau colorimetric method (Tolun et al., 2016). Briefly, 100 μL of diluted sample and 100 μL of Folin reagent were mixed with 2 mL of sodium carbonate solution (75 gL^{-1}) and 2.8 mL of deionized water. After 1 h of incubation at room temperature in the dark, absorbance was measured at 750 nm by a UV–Vis spectrophotometer (Hach Lange DR5000, Hach Lange SLU, Spain). Calibration curve was made by taking gallic acid as standard, and the results were expressed as gram gallic acid equivalent per liter (gGAE L^{-1}).

2.5.2. Measurement of sugar content

The sugar content in PE, PC and PR were measured by refractometry (WAY-1S, Zuzi, Auxilab S.L., Spain). The results were given as Brix degrees (°Brix). Each sample was measured in triplicate.

2.5.3. Droplet size and distribution

Droplet size distribution of $W_1/O/W_2$ emulsions was measured after every emulsification cycle by laser diffraction using Mastersizer 2000 (Malvern Instruments). Sodium chloride solution (3.15 wt%), was used

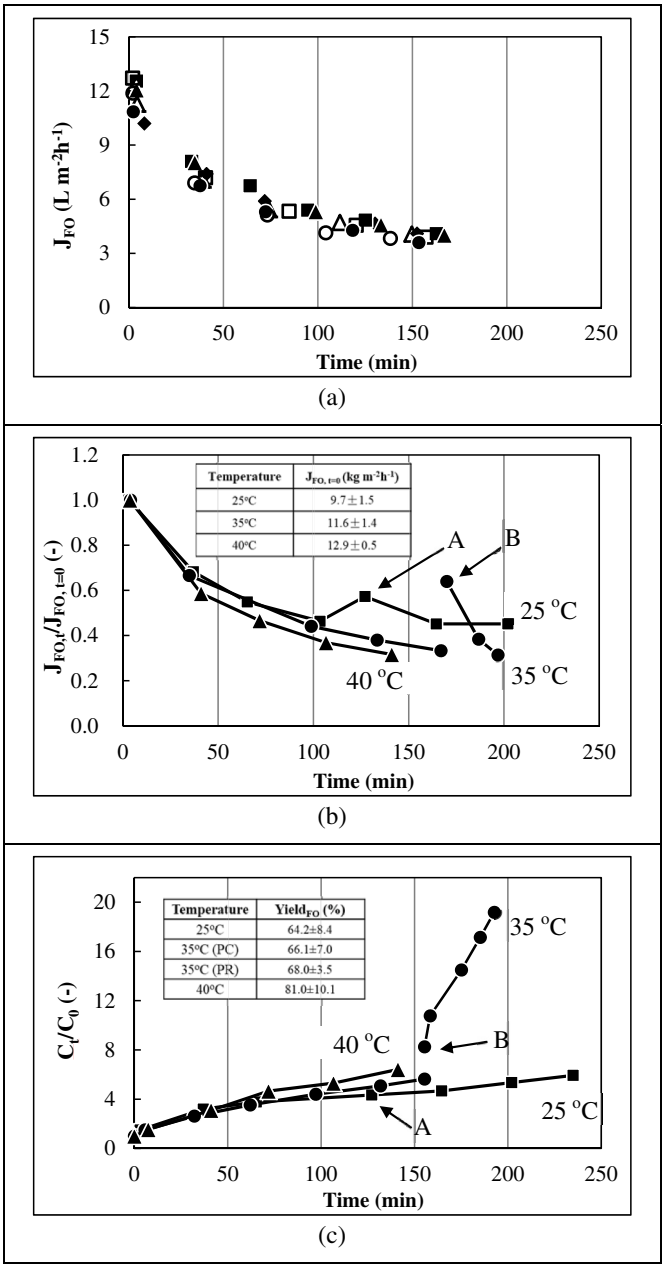


Fig. 2. Effect of feed solution temperature on FO performance: (a) progress of water flux at 35 °C for 7 runs; (b) normalized flux ($J_{FO,t}/J_{FO,t=0}$) to obtain PC at 25 °C, 35 °C and 40 °C; (c) normalized TPC (C_t/C_0) in the feed solution. Arrow A is pointing the replacement of DS during FO, and arrow B indicates both the use of a clean membrane and new DS to continue concentration process.

as the continuous phase in Mastersizer Hydro 2000G accessory in order to disperse the emulsion in a solution with similar osmotic pressure. Mean droplet size and droplet size distribution can be calculated, which were expressed as Sauter mean diameter $d_{3,2}$ (equation (9)) and the relative span factor (equation (10)), respectively.

$$d_{3,2} = \frac{6}{S_v} = \left(\sum_{i=1}^{n_s} \frac{v_i}{d_i} \right)^{-1} \quad (9)$$

S_v is the droplet surface area per unit volume, v_i is the volume fraction of droplets in the i^{th} size class of the discretized distribution, d_i is the mean droplet diameter in that class, and n_s is the number of size classes.

$$\delta = \frac{d_{90} - d_{10}}{d_{50}} \quad (10)$$

d_x is the droplet diameter corresponding to x% volume on a cumulative droplet size distribution curve.

2.5.4. Morphology of solid microcapsules

Outer and inner morphology of the capsules was observed through FEI Quanta 600 Environmental scanning electron microscope (ESEM). Accelerating voltage was set to 20 kV. Rehydrated emulsion capsules in 3.15 wt% NaCl solution was observed under the optical microscope (Leica DM 2500) at 1000×.

2.5.5. Moisture content of solid microcapsules

Moisture content of solid capsules was measured by titration method using Karl Ficsher (TitroMatic 1S, Crison Intruments S.A., Spain) using solvent and titrant for Karl Fischer (Aquametric, Panreac Spain). Calibration was done using a water standard 1% (Aquastar™, Merck KGaA, Germany) and the results were expressed as mass per 100 g of powder (wet basis). Measurements were done in triplicate.

3. Results and discussion

3.1. Forward osmosis concentration: effect of temperature on water flux and concentration

Forward osmosis experiments were carried out using a carob polyphenol extract and a food grade osmotic agent as feed solution (FS) and draw solution (DS), respectively. The effect of feed temperature, 25 °C, 35 °C and 40 °C, on the transmembrane flux (J_{FO}) and polyphenol concentration is shown in Fig. 2.

Regardless the initial concentration of the carob polyphenol extract (PE) (Table 1), a high reproducibility and the same trend on transmembrane flux reduction can be observed from the seven experiments conducted at 35 °C (Fig. 2-a). For clarity purposes, from this point on the results of FO will be shown as average values without the error bars. Fig. 2-b shows that the overall processing time required for concentrating decreased by increasing the FS temperature. This was mainly attributed to the decrease of FS viscosity as temperature increases, which enhanced the mass transfer coefficient and, in turn, the water flux through the membrane (Babu et al., 2006; Hameed, 2013; Nayak and Rastogi, 2010). The rise of water flux during the concentration at 25 °C (at around 130 min) in Fig. 2-b (point A) was due to the replacement of the diluted DS by new osmotic agent to recover the flux which had dropped below 4 Lm^{-2}h^{-1}. Despite the replacement of the DS in the FO system, there was only a slight increase in the water flux on account of (1) the fouling of the membrane, since the FO system had been running for more than 2 h, and (2) by the increase in the polyphenol/sugar concentration of the FS. When the replacement of the DS was accompanied by the use of a clean membrane, as can be seen for the FO concentration at 35 °C (Fig. 2-b, point B), water flux reached the same value as the one obtained after the initial 40 min of concentration. This is a clear indication that both membrane fouling and water activity gradient between FS and DS are key parameters controlling water flux.

The increase rate of polyphenol content (Fig. 2-c) in PC showed no difference within the first hour at different FS temperature. From this point on, the increase rate was directly related to temperature. This is in agreement with higher water fluxes across the membrane obtained when the temperature of the FS increased, being an effective way in FO to accelerate the concentration process. As for obtaining the PR (FO of several PC batches) at 35 °C, the use of a clean membrane and new DS resulted in high water fluxes and consequently a fast increase in the polyphenol content. Significant loss of polyphenols during FO experiments was observed from the calculated yields (Fig. 2-c). This loss could be caused either by polyphenols retention in the membrane or by their

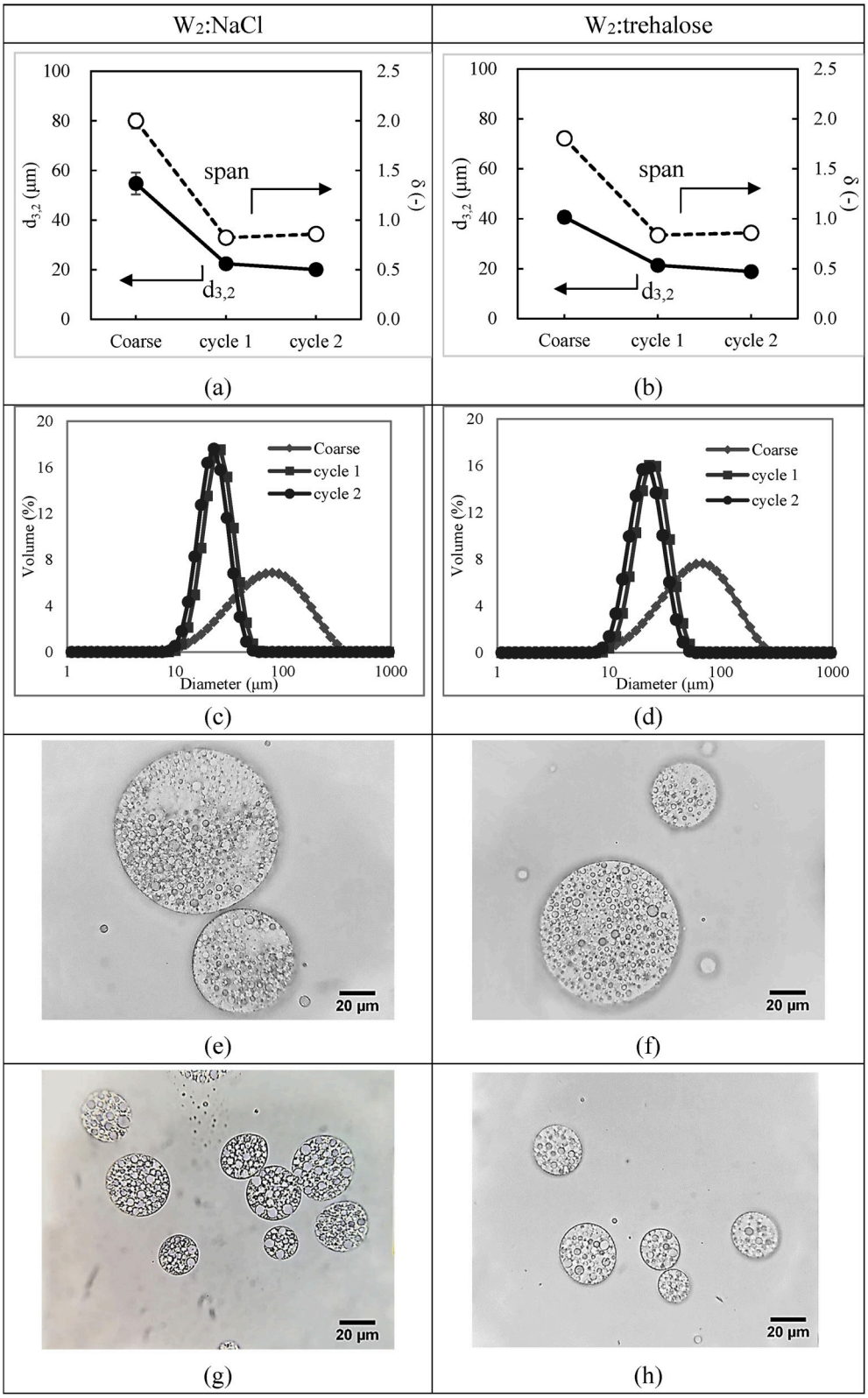


Fig. 3. Results of $W_1/O/W_2$ coarse emulsion and refined emulsions formulated by adding NaCl or trehalose as bulk agent in W_2: (a)(b) sauter mean diameter ($d_{3,2}$) and span (δ) of $W_1/O/W_2$ as a function of emulsification cycle with error bars representing standard deviation (n = 18); (c)(d) droplet size distribution of $W_1/O/W_2$ as a function of emulsification cycle; (e)(f) optical microscope images of coarse $W_1/O/W_2$ emulsions; (g)(h) optical microscope images of $W_1/O/W_2$ emulsions after 2 cycles of emulsification in DMTS. Lines are guides to the eyes.

pass from the FS to the DS. The noticeable color change in DS was a clear indication that some phenolic compounds had diffused through the membrane. The higher yield of FO at 40 °C could be linked to a shorter operation time. In this study, 18-fold increase of carob polyphenol content (1.1 gL^{-1} to 18.4 gL^{-1}) was achieved by 3.3h of FO concentration at 35 °C. It has shown a higher efficiency compared to studies concentrating anthocyanins from red radish (Rodriguez-saona et al., 2001), red cabbage (Jampani and Raghavarao, 2015) and grape (Nayak et al., 2011) extracts. In these studies, they reported 6.8 to 14-fold increase in anthocyanin contents (from 0.22 gL^{-1} to 8.19 gL^{-1}) during 11–24 h of FO concentration at temperatures ranging from 25 °C to 60 °C. Moreover, Nayak and Rastogi (2010) achieved 54-fold increase in

anthocyanin content (0.05 gL^{-1} to 2.69 gL^{-1}) concentrating a kokum extract during 18 h at 25 °C. In the present case, the concentration process was fast at mild temperature conditions also because of the large membrane area (0.5 m^2) of the pilot FO unit.

On the other hand, the fouling of the FO membrane must be considered. Even though high temperatures may trigger the increase of total polyphenol content by structural changes such as disruption, polymerization and re-synthesis of phenolic compounds (Tolun et al., 2016), studies on reverse osmosis have shown that there was no difference in polyphenol concentration and antioxidant properties at temperatures between 20 °C and 40 °C (Gunathilake et al., 2014). Moreover, Kim et al. (2015) pointed out that FO membrane was less fouled with increasing the FS temperature due to the enhanced back diffusion of organic compounds from membrane surface, what would explain the higher polyphenol yield obtained at 40 °C. Despite these results, experiments to obtain PR extracts were run at 35 °C, because the maximum operating temperature of the membrane is 40 °C being not advisable for long-running processes.

3.2. Encapsulation of polyphenols in $W_1/O/W_2$ double emulsions

For producing $W_1/O/W_2$ emulsions able to entrap the carob polyphenol re-concentrate in W_1, the formulation of the several phases had to be set up. In this kind of systems, the internal (W_1 in O) and external interfaces (W_1/O in W_2) require to be stabilized by surface active compounds. In this case, PGPR and WPI were used as lipophilic and hydrophilic emulsifiers, respectively (Berendsen et al., 2015a; Eisinaite et al., 2016; Muschiolik and Dickinson, 2017; Sahin et al., 2014a). Another important factor to maintain $W_1/O/W_2$ emulsions stable is to prevent any significant imbalance of the osmotic pressure between W_1 and W_2, that could induce any mass transport between the two water phases. This phenomenon, facilitated by the inverse micelles formed by the lipophilic emulsifier, can end up in the transformation of $W_1/O/W_2$ in a single emulsion or, further on, in phase separation.

In the current scenario, W_1 phase, consisting of carob re-concentrate, exhibited an osmolality of 1200 mOsmol kg^{-1} which can be explained by its high solid soluble content which were mainly sugars (24.5 °Brix). The water extraction process produced a polyphenol extract containing sugars (4.5 °Brix) that was also concentrated during FO and possibly as well as low amount of soluble fibers such as pectin (Goulas et al., 2016; Nasar-Abbas et al., 2016). On account of the huge difference (1160 mOsmol kg^{-1}) of the osmolalities between the W_1 and W_2 phases (no bulk agent added) (Table 2), water from W_2 phase can diffuse quickly to W_1 phase which leads to the swelling of the inner water droplets (W_1) and eventually they burst and release the compounds to W_2 phase. This phenomenon was observed in the pre-trial of $W_1/O/W_2$ emulsions formulated without bulk agent in W_2 phase, which resulted in a polyphenol EE of 35% and 30% after first and second emulsification cycle, respectively in the DMTS system.

As reviewed by Muschiolik and Dickinson (2017), salt and sugars are most commonly used bulk agents added in the external aqueous phase in order to counter with the imbalance of osmotic pressure difference between two aqueous phases. Therefore, to balance the osmotic pressure of W_1, NaCl and trehalose were added to W_2 at a concentration of 3.15 wt% and 28.2 wt%, respectively, leading to the osmolalities reported in Table 2, balancing the osmotic gradient. Osmolality in W_2 phase was adjusted a little less than W_1 phase referring to the study by Pawlik et al. (2010), whom observed lowest release of W_1 fraction when the W_2 phase was less than required for equilibrating the osmotic pressures.

The droplet size distribution of the coarse and refined emulsions (cycle 1 and 2) were measured right after emulsification. Fig. 3 shows $d_{3,2}$ evolution during DMTS emulsification which sustains the feasibility of using this emulsification system to refine $W_1/O/W_2$ emulsions. As expected, a significant droplet reduction occurs during the first emulsification cycle followed by a minor decrease during the second emulsification cycle. After the first cycle, the span value was on the range of 0.8–0.9 which is an indication that the emulsions are in narrow size distribution. It is important to note that no significant effect of W_2 composition was observed on the droplet size distribution during DMTS emulsification.

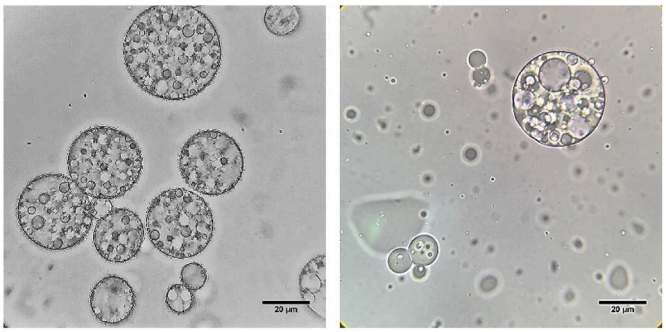
Table 3
Progress of droplet size, encapsulation efficiency and transmembrane flux of $W_1/O/W_2$ emulsions prepared with NaCl and trehalose in W_2 before and after each emulsification cycle.

	W_2: NaCl			W_2: trehalose		
	$d_{3,2}$ (μm)	Flux (L $m^{-2}h^{-1}$)	EE (%)	$d_{3,2}$ (μm)	Flux (L $m^{-2}h^{-1}$)	EE (%)
Coarse	54.7 ± 4.4	–	95.2 ± 1.0	40.6 ± 2.3	–	92.7 ± 6.3
Cycle 1	22.4 ± 0.4	135.9 ± 24.9	87.3 ± 0.7	21.3 ± 0.1	148.2 ± 8.6	79.4 ± 0.1
Cycle 2	20.0 ± 0.2	163.8 ± 18.4	87.0 ± 0.2	18.8 ± 0.2	120.4 ± 19.9	77.4 ± 0.4

Regarding encapsulation efficiency (EE), a reduction with each emulsification cycle was observed (Table 3). Apparently, the release of the inner encapsulate was caused by droplet breakup during emulsification. Part of the inner aqueous fraction was released to W_2 phase when droplets were broken up in the microchannels of the DMTS system. These results agree with previous findings encapsulating anthocyanin in $W_1/O/W_2$ by SPG membrane (Berendsen et al., 2015a) and during encapsulation of concentrated beet root juice with a DMTS system (Eisinaite et al., 2016). In the present study, the composition of W_2 seems to influence the EE, obtaining values of 87.0 ± 0.2% and 77.4 ± 0.4% after two emulsification cycles for NaCl and trehalose, respectively. Moreover, the $W_1/O/W_2$ emulsions maintained the EE above 50% for 14 days, with minor changes in $d_{3,2}$ (±1 μm) and span (±0.1). This behavior agrees with previous results from Pawlik et al. (2010) for the physical stability of $W_1/O/W_2$ emulsions over 60 days with minor droplet size increase and 30% reduction of EE.

Considering the implementation of emulsification technology at industrial scale, both the emulsion properties (droplet size distribution and EE) and productivity are of importance. The results show that DMTS emulsification allows to produce monomodal and narrow droplet size distribution $W_1/O/W_2$ emulsions with high EE (Table 3). As the flux during the process can be the indicator of productivity, results showed that the fluxes obtained at 200 kPa are well above 100 $Lm^{-2}h^{-1}$. These flux values are slightly higher or similar to the ones reported for $W_1/O/W_2$ emulsification at lower pressures using SPG membranes (Surh et al., 2007; Vladisavljević et al., 2004, 2006). Moreover, they were 30 times higher than the ones reported for a similar emulsification system to encapsulate concentrated beetroot juice in $W_1/O/W_2$ emulsions, which had flux of 5 $m^3m^{-2}h^{-1}$ at second cycle (Eisinaite et al., 2016), and in the range (100–800 $m^3m^{-2}h^{-1}$) reported by Sahin et al. (2014a) for the encapsulation of NaCl in $W_1/O/W_2$ emulsions at pressure range of 200 kPa–600 kPa and silica beads size of 30–90 μm.

It seems that the composition of the W_2 phase affects the flux progress during emulsification. For the $W_1/O/W_2$ emulsions produced with trehalose in the W_2 phase, the flux slightly decreases during emulsification, possibly due to the accumulation of droplets in or before the micro-structured silica bed. However, when NaCl was used to balance the osmotic pressure in the $W_1/O/W_2$ emulsions, the flux slightly increased from cycle 1 to cycle 2. This trend has already been reported during the production of O/W emulsions by membrane emulsification which is attributed to both the lack of fouling and the endpoint of droplet breakup, that enables to use all the energy (pressure applied) in flowing the emulsion through the system (Nazir et al., 2010; Ribeiro et al., 2005). The difference in viscosity of the W_2 phase when it contains NaCl or trehalose is thought to be responsible of the different behavior in flux progress, even though there was no effect on droplet breakup with a minor impact in the EE.



(a) (b)

Fig. 4. Microscopic images of $W_1/O/W_2$ emulsions with 28.2 wt% trehalose in the external aqueous phase after one cycle of emulsification in DMTS: (a) freshly prepared and (b) rehydration of $W_1/O/W_2$ spray dried capsules.

3.3. Solid microcapsules production by spray drying

Although $W_1/O/W_2$ emulsions are suitable systems to encapsulate and protect the carob polyphenols, solid microcapsules can extend the shelf-life of the product and facilitate its dosage for industrial applications. Spray drying has been selected to turn the emulsions into solid microcapsules, following the methodology described in section 2.4. Refined $W_1/O/W_2$ emulsions by DMTS after cycle 1 were selected for spray drying since the main droplet size reduction happened during the first emulsification cycle, as explained in section 3.2 (Fig. 3). From the two different formulations, only the ones with trehalose in the W_2 phase have been dried. This is mainly because the use of a 3% NaCl solution as outer water phase, even though balances the osmotic pressure and leads to high fluxes during emulsification, will affect the taste of the product. Besides, the emulsion with trehalose in W_2 requires addition of lower amounts of wall-building materials such as maltodextrin.

In the selection process for a sugar to balance the osmotic pressure, due attention was paid to the glass transition temperature (T_g) of several edible sugars. Materials with high T_g are easy to dry, whereas those with low T_g are impossible to dry since they remain in the fluid state under normal drying conditions. Trehalose with a T_g of 115 °C is a much more suitable sugar than glucose (T_g = 30 °C) and sucrose (T_g = 60 °C) (Simperler et al., 2006). By adjusting the inlet and outlet temperatures at 170 and 100 °C, respectively, solid microcapsules were produced. The yield of the drying process (calculated using equation (8)) was 32.7 ± 1.3% and the moisture content of the microcapsules 3.9 ± 0.5 wt %. A freshly prepared $W_1/O/W_2$ emulsion was analyzed by an optical microscope at 1000× magnification before spray drying (Fig. 4-a). The inner aqueous droplets containing the carob polyphenols entrapped by big oil droplets can be clearly seen from the figure. Once dried, the morphology of the solid microcapsules was analyzed by ESEM. As can be seen in Fig. 5, spray dried capsules are spherical with smooth surface that is related to a rapid drying velocity. The similar inner surface of the capsules can be noticed by breaking them (Fig. 5-c). The structure of $W_1/O/W_2$ emulsions was partially recovered after rehydration of the solid microcapsules, as can be seen in Fig. 4-b. This figure shows W_1 droplets within large oil droplets, as well as small oil droplets, suggesting that some entrapped polyphenols in the inner water phase were released.

4. Conclusions

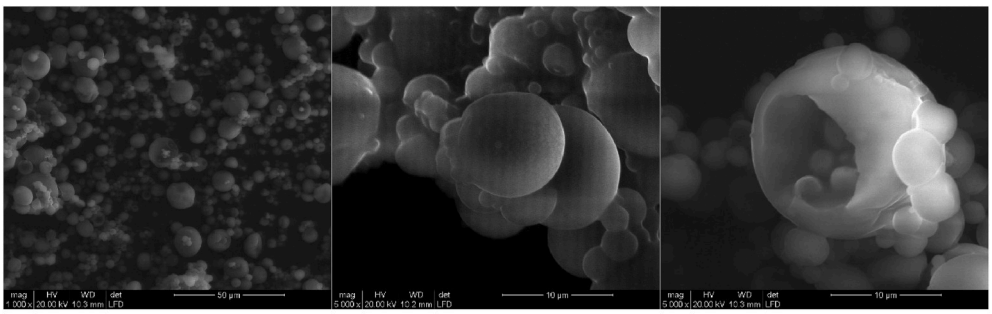
Forward osmosis is a suitable method to concentrate bioactive compounds such as polyphenols extracted from carob pulp. The highest feed solution temperature was more effective in terms of process time and polyphenol yield due to the increase in mass transfer coefficient. To protect the polyphenols obtained after FO, encapsulation in $W_1/O/W_2$ emulsions was proven feasible using a low \energy high throughput emulsification system (DMTS), based on a microporous bed of silica beads. Regardless of the bulk agent (NaCl or trehalose) used to balance the osmotic pressure, encapsulation efficiency was between 77 and 87%, and emulsions showed a narrow droplet size distribution. In terms of productivity, the fluxes were significantly higher than the ones reported for different applications using DMTS. To extend the shelf-life of the encapsulated polyphenols, solid microcapsules were successfully produced by spray dying $W_1/O/W_2$ emulsions containing a mixture of trehalose and maltodextrin as a wall material. After rehydrating the solid microcapsules, the structure of the $W_1/O/W_2$ emulsion was partially recovered. The results of this study show the potential of combining membrane-based processes to concentrate and encapsulate bioactive compounds as a strategy to valorize agri-food by-products under mild process conditions.

Declaration of competing interest

None.

CRediT authorship contribution statement

Junjing Wang: Conceptualization, Formal analysis, Investigation, Methodology, Data curation, Writing - original draft, Writing - review & editing. **Andrea Martínez-Hernández:** Conceptualization, Formal analysis, Investigation, Methodology, Data curation, Writing - original draft. **Sílvia de Lamo-Castellví:** Investigation, Methodology. **Maria-Paz Romero:** Investigation, Methodology. **Wael Kaade:** Investigation, Methodology. **Montse Ferrando:** Conceptualization, Formal analysis, Investigation, Supervision, Funding acquisition, Writing - original draft, Writing - review & editing. **Carme Güell:** Conceptualization, Formal analysis, Investigation, Supervision, Funding acquisition, Writing - original draft, Writing - review & editing.



(a) (b) (c)

Fig. 5. ESEM images of spray dried $W_1/O/W_2$ emulsion capsules: (a) at magnification of 1000×; (b) at magnification of 5000× and (c) after mechanical break.

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