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Spray-drying microencapsulation of tea extracts using green starch, alginate or carrageenan as carrier materials

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ABSTRACT

Tea industry generates many by-products which could be used to produce and incorporate bioactive tea extracts (TE) into nutraceuticals, cosmetics and/or clinical applications. However, sensibility to external factors is a major disadvantage hindering its utilization. This study deals with the implementation and characterization of suitable biopolymer delivery systems based on starch, carrageenan or alginate, as microencapsulation, to stabilize and protect TE through innovative thin-carbohydrate-coated formulations. TE were spray-dried and microencapsulated in recycled carrier materials (alginate, carrageenan or starch). Product yields varied from 55 to 58%. High microencapsulation and loading efficiencies were achieved (60–93% and 65–84%, respectively). Antioxidant capacity varied from 32 to 46 g Trolox/100 g extract, within different carrier-systems; which also showed promising rheological and UV-protective properties when transformed into gels. Total phenolic content, particle-size distribution, HPSEC-analysis, SEM-analysis and FTIR-analysis were also performed. In sum, this paper characterizes and discusses the high potential of these recycled carbohydrate-coated microparticles for future applications.

1. Introduction

Green tea is sourced from *Camelia sinensis* (L.), a dicot and evergreen shrub native to Southeast Asia. Today, tea plants are cultivated globally, making tea the second most consumed beverage worldwide [1]. Its leaves and buds are used in the industry at different stages of oxidation and fermentation resulting in six different categories: green, white, yellow, oolong, black and dark teas [2]. To maintain high quality, expedite harvest and maximize yields, regular pruning of tea plants is required. Depending on the climate region this process occurs throughout the year, between harvest seasons, or annually [3]. Thus, many by-products with no economic value are discarded.

The health beneficial properties associated with tea consumption are well-documented. These benefits include antioxidant, immunoregulatory, cardiovascular-protective, hepato-protective, anti-inflammatory anti-diabetic, neuro-protective, anti-obesity, gastrointestinal-protective, anti-microbial and anti-carcinogenic activities [4]. When compared, green tea has been reported to possess more health benefits than other tea types, because of its no fermentation and less oxidation [5]. Studies have shown its potential application against certain chronic and degenerative diseases, including diabetes, Alzheimer's [6], cardiovascular diseases [7], certain forms of cancer [8], even COVID-19 [9,10].

Therapeutic value of tea relies on its polyphenolic compounds (PC). Significant variation of total phenolic content occurs between green tea types depending on environmental growth conditions and processing. During processing of tea plants, phenolic content decreases as leaves undergo oxidation, hydrolysis, polymerization and transformation [3,11]. Thus, because of its sensitivity to light, heat, moisture, pH and oxygen, green tea extracts have poor stability [12,13]. These are major disadvantages hindering their effective utilization in the food industry and limiting its clinical applicability. Therefore, it is necessary to implement a suitable delivery system to stabilize and protect these bioactive compounds, and to increase its bioavailability.

Microencapsulation is a technique where an encapsulating agent is used to create a physical barrier around a sensitive compound, reducing its reactivity with external factors, providing controlled release dynamics and new properties depending on the carrier material used. Green waste-derived carbohydrate polymers as sodium alginate, starch and carrageenan, offer a unique platform for microencapsulation [14] considering all the advantages of these biopolymers (*e.g.*, sustainability, low toxicity, low cost, rheological features…), producing microcapsules

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which are stable, easily to storage [5], possible to add to food matrices and nutraceutical products [12], and even to use as 3D printing substrates [15].

Spray-drying consists in a liquid atomization through a hot gas current to directly obtain a fine and dry powder. When the atomized liquid is an emulsion of a core material plus one or more carrier materials, microencapsulation happens. Spray-drying presents advantages such as cheap large-scale production, ease of change in operating conditions and availability both under laboratory and industrial scales [16].

Nowadays, sustainable waste management is a priority in industry [17]. In addition to the "clean label" trend, the popularity and clinical value of green tea presents a great opportunity to incorporate tea extracts sourced from by-products into functional foods, beverages, nutraceuticals, cosmetics, and clinical applications.

In this sense, the main aim of this study is to revalorize these biomass by-products using clean extraction techniques in water (ultrasound bath and autohydrolysis), and to explore new sustainable applications of microencapsulated tea extracts in materials or food additives. Specifically, this paper focusses both on the preservation of the antioxidant features of bioactive tea components after encapsulation, and the characterization of recycled carbohydrate polymers as carrier materials.

2. Materials and methods

2.1. Raw materials

Tea leaves (*Camelia sinensis* L.) used in this study were kindly supplied by Orballo (Donín, A Coruña, N.W. of Spain). Samples were ground to a particle size <0.5 mm and stored in darkness at −20 °C until use. Chemical characterization was performed.

2.2. Ultrasound-assisted tea extraction

Ground tea leaves were mixed with distilled water at liquid:solid ratio of 15:1 (*w*/w). The mixture was then placed into an ultrasonic bath (P-Selecta, Spain) at 80 °C and 80 kHz for 15 min. The operation conditions were previously optimized with ethanolic extraction [18]. After the extraction process, solid and liquid phase were separated by filtration, and besides, the liquid phase was centrifuged 10 min at 9800*g* to discard remaining solid residues. Solid residue was dried 96 h at room temperature.

2.3. Autohydrolysis extraction

A stirred pressure reactor with a capacity of 3.78 L was used (Parr instruments series 4848, Il., USA), equipped with a temperature controller and a heater. Autohydrolysis extraction (AH), also known as subcritical water extraction, was used to extract remaining tea constituents from the solid residue of the ultrasound-assisted extraction (US). US-solids were placed in the reactor using distilled water as solvent. The operation conditions were liquid:solid ratio 15:1 and selected temperature was 140 °C, as previously described by Sanz et al. [19]. Liquid fraction (US-AH) were separated through filtration and solids were split. Additionally, the liquors were centrifuged for 10 min at 9800*g* to remove solid residues.

2.4. Membrane fractionation

Membranes (30, 50 and 100 kDa, Merk-Millipore, Germany) were immersed overnight in 10% ethanol at 4 °C and washed with distilled water before use.

A successive fractionation steps of the US-AH liquid phase, diluted with distilled water (1:3, *w*/w), were accomplished through different membranes. The membrane process started using a 100 kDa cut off, followed by 50 kDa and finished at 30 kDa, volume concentration ratio was 5. The retentate and permeate phases were obtained with the different membranes used. Permeates were processed in the subsequent membrane while retentates were characterized.

2.4.1. Liquid extract characterization

Total phenolic content, antioxidant capacity, carbohydrates content, proteins, yield and pH were measured for the liquid phase obtained by the extraction processes, pH of the liquid samples was measured under constant stirring and at room temperature using a Crison GLP-21 (Spain).

2.4.2. Total phenolic content

Total phenolic content (TPC) was determined by the Folin-Ciocaulteu method [20]. TPC was calculated as gallic acid (GA) equivalents, GA standard curve was performed from 0.1 to 0.8 g/L. Aliquots of 0.25 mL from liquid extract samples were mixed with 1.875 mL of distilled water. 0.125 mL of the Folin-Ciocaulteu reagent were added above, followed by 0.25 mL of a sodium carbonate solution (10%, *w/v*), the mixture was stirred in a vortex and incubated in darkness for 1 h at room temperature. The absorbance was read at 765 nm (UV–Vis spectrophotometer, Thermo Scientific Evolution 201, USA).

2.4.3. Antioxidant capacity

Antioxidant capacity of the tea leaves extracts was determined by the Trolox Equivalent Antioxidant Capacity (TEAC) assay [21]. Liquor samples (10 μL) were placed in a test tube, 1 mL of ABTS solution diluted (absorbance 0.7 ± 0.1) was added and incubated for 6 min in a water bath at 30 °C, the absorbance was measured at 734 nm. The antioxidant capacity was finally calculated using a standard curve performed with Trolox (Sigma-Aldrich, Denmark).

2.4.4. Carbohydrates and other derived groups content

Carbohydrates and other derived groups content were determined using High-Performance Liquid Chromatography (HPLC). Oligosaccharide content was calculated after a posthydrolysis process (H_2SO_4 (4%), 121 °C, 20 min). Samples were always filtered through a 0.45 μm syringe filter, and then measured on a chromatograph, using a Aminex HPX-87H column (300 × 7.8 mm, BioRad, CA, USA) operating at 60 °C being the mobile phase 0.003 M (*w*/w) H_2SO_4 at 0.6 mL/min. The HPLC was equipped with a refractive index detector.

2.4.5. Soluble protein content

Soluble protein content in the liquid phases obtained were measured by the Bradford assay [22]. A standard curve was performed using 1–10 μg/mL of bovine serum album (BSA, Sigma Aldrich, China). The protocol was 0.5 mL of sample with 0.5 mL of Bradford Reagent (Sigma Aldrich, Germany) was placed in a test tube. Subsequently, samples were incubated for 10 min and measured at 595 nm in a UV–vis spectrophotometer (Thermo Scientific Evolution 201, USA).

2.4.6. High-performance size-exclusion chromatography

The molar mass distribution of liquid extracts obtained by the extraction technologies were measured through a High Performance Size Exclusion Chromatography (HPSEC). The HPLC described above was used to determine the molar weight of the samples using two columns TSKGel G3000PW_{XL} and TSKGel G2500PW_{XL} (300 × 7.8 mm, Tosoh Bioscience, Stuttgart, Germany) and PWX-guard column (40 × 6 mm). The mobile phase was Milli-Q water at (0.6 mL/min) at 70 °C, and standard dextrans (Fluka, St. Louis, MO, USA) from 1 to 80 kDa were used.

2.4.7. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR), for the polymers and microparticles formulated were assayed. Samples were mixed with KBr, dried with an infrared lamp for 30 min, and compressed to achieve a tablet. Infrared spectra over the wavelength range 4000 to 500 cm^{-1} were recorded. The equipment used was a Bruker IFS 28 Equinox

equipment with an OPUS-2.52 software for data acquisition System 450-MT2.

2.5. Raw material and solid residues after extraction process characterization

The characterization of the raw material, solids from ultrasound-extraction process (US-solids) and the obtained after autohydrolysis treatment (US-AH-solids) was performed.

2.5.1. Determination of moisture and ash content

Both moisture and ash content were determined by a standard gravimetric method. The moisture content was carried out in a laboratory oven (105 °C; 48 h) and the ash content was determined using a muffle furnace (575 °C for 6 h).

2.5.2. Determination of protein content

The total nitrogen content was assessed following the Kjeldahl method using a FlashEA 1112 Elemental Analyzer (Thermo Fisher Scientific, Germany), and then converted to protein using the general N-protein conversion factor 6.25.

2.5.3. Determination of macroelements and microelements

The macroelements (Na, K, Ca, Mg, Fe) and microelements (Cd, Pb, Cu, Bo, Hg) were measured, as exposed in previous studies [18,19], inductively coupled plasma optical emission spectrometry (Optima 4300 DV, PerkinElmer, USA), except for Hg content which was determined using cold vapor atomic absorption spectrometry (Fernández-Fernández et al., 2007).

2.5.4. Carbohydrates and other derived groups

Dried solids were hydrolyzed with H_2SO_4 (72%) for 60 min at 30 °C in a water bath. Subsequently, the resulting solution was again hydrolyzed with H_2SO_4 (4%) in an autoclave (121 °C for 60 min). Finally, the obtained liquid phase was filtered through a 0.45 μm syringe filter and placed in an HPLC equipment to determine the content of carbohydrates as describe above in Section 2.4.4. The same retention time was obtained for xylose (xyl), galactose (gal) and mannose (man) in this case the content was measured as xyl + gal+man.

2.6. Spray-drying and preparation of microcapsules

Microencapsulation was performed through the spray-drying technique. The equipment employed was a mini spray-dryer BÜCHI B-290 (Flawil, Switzerland) equipped with a standard cyclone and a 1.5 mm nozzle. The operating conditions were assessed both according to preliminary studies found in literature [23,24] and optimal yields obtained after testing different settings. These tested parameters ranged from 105 to 150 °C inlet temperature (T_{in}), 2.5 to 9 mL/min feed solution flow rate and 439 to 1052 L/h atomization air flow rate; while air flow rate was always a fixed parameter. Operating conditions were 4 mL/min (pump at 15%) feed solution flow rate, a 38 m^3/h (100%) air flow rate, a 1052 L/h atomization air flow rate, 4.1 bar pressure and 115 °C inlet temperature. The outlet temperature was an outcome of the above mentioned parameters, ranging around 65 ± 1 °C.

Three recycled biopolymers were used as carrier materials sodium alginate, carrageenan and starch, [25–27] in order to encapsulate the US liquid extract of tea leaves and GA. Detailed information on the extraction treatment, chemical, structural and mechanical properties was provided in aforementioned studies. Microparticles with the carrier materials were also produced, and later used as control samples. US and US-AH liquid extracts were also spray-dried under the same operating conditions to use as control samples.

In order to obtain the microparticles, feed solutions for the spray-dryer were prepared using a 1:1.5 distilled water:carrier (*w*/w) ratio and stirred under dark conditions at different temperatures (70 °C for starch, 60 °C for carrageenan and sodium alginate) for 10–40 min. Afterwards, US-liquor or GA was mixed with the biopolymer solution (0.33% (*w/v*) + 0.5% (w/v) carrier material) for 15 min.

2.7. Microparticle analysis

2.7.1. Determination of product yields, microencapsulation and loading efficiencies

The product yield (%) was determined gravimetrically as grams of recovered solids/initial solid content for each microencapsulation experiment.

Microencapsulation efficiency (ME) was defined as the fraction of phenolic compounds which were coated by the carrier material and which were not washed off by a solvent, *i.e.* (total phenolics – surface phenolics)/total phenolics. The method used for its determination was adapted from [5]. Total phenolics were determined by mixing a 200 mg sample of microencapsulated particles with a 50:8:42 (*v*/v/v) solution of methanol, acetic acid, and water. The solution was vortexed for 1 min and ultrasonicated (20 min; 80 kHz). The resulting supernatant was centrifuged (9500 rpm, 10 min) and finally filtered (0.45 μm). To calculate the surface phenolic compounds, a 200 mg sample of microencapsulated particles was mixed with 2 mL of ethanol:methanol (1:1) solution, vortexed for 1 min and finally filtered (0.2 μm). Both total phenolics and surface phenolics were measured as described in Section 2.4.1.

Loading efficiency (LE) was calculated as the fraction between the total phenolics in the liquid solutions of dispersed spray-dried samples and their respective phenolic content in the initial feed solutions, as described by [28].

2.7.2. Scanning electron microscope and particle size distribution

The morphology of the microparticles were obtained using a scanning electron microscopy (JEOL JSM6010LA, Japan), samples assessed were covered by gold layer of 15 nm.

In order to obtain the particle size distribution (PSD) of the microparticles samples, SEM images were analyzed using ImageJ software. Around 500 measurements of microparticle diameters were done manually for each microparticle formulation. The final results were expressed as frequency distributions of different ranges of diameter (differential number percentage as a function of particle diameter). Using Prism GraphPad 6.0, results were graphed and adjusted to a Lorentzian distribution to visualize the distribution curve of particle sizes.

2.7.3. Release profiles

Release dynamics of the microencapsulated formulations were evaluated at room temperature under continuous stirring. Absorbance was measured every 0.2 s during 400 s in a continuous mode at 273 nm, in accordance to the peak of GA [29]. GA was used as standard release indicator because of its well-documented presence in tea extracts [30]. Briefly, a continuous and measuring method was set up using a Jasco *V*-750 UV–Vis spectrophotometer (Spain) with a SFC-712 flow cell holder coupled to a Watson-Marlow 323 pump. 0.01–0.02 g of microparticle samples were dispersed in 200 mL of a 0.1 M phosphate buffer (Sigma Aldrich, Germany) solution adjusted to pH 7.4. Additionally, some release profiles were tested in simulated gastric fluid, which consisted in a 0.1 M phosphate buffer (Sigma Aldrich, Germany) solution adjusted to pH 2.3. The sample solution was pumped through a 0.42 μm syringe filter connected to the end of the inlet tube, then passed through the flow cell and finally ejected again into the beaker, resulting in a continuously recirculating flow system.

The amount of microparticles used in the release assays was estimated by mass balance, taking into consideration the estimated amount of GA present in MT samples, in order to achieve a final concentration of the sample solution with absorbance values bellow 1.

Release profiles were always measured in triplicate, with variation

coefficients below 10%. Results were processed using the Jasco Software Analysis Program and represented as an average at intervals of 5 s.

Furthermore, the kinetic behavior of the formulated microcapsules was evaluated. Five different kinetic models (zero order, first order, Higuchi, Korsmeyer-Peppas and Weibull) were adjusted to the sampled release profiles, using the DDsolver program [31].

2.7.4. UV-light experiments

A 8 W UV-light lamp (Vilber Loumart VL-4.LC, France) was used to generate two types of ultraviolet light (UV-A, 365 nm, with an irradiance of 0.61 mW/cm^2; and UV-C, 254 nm, with an irradiance of 0.4 mW/cm^2) in order to test the photosensitivity of resuspended microencapsulated tea particles, *i.e* bioactive tea extracts embebed in carbohydrate gel matrix. 0.02 g of each microparticle formulation were accurately weighed in 2 mL eppendorf tubes and mixed with 1 mL distilled water, resulting a final concentration of 2% (*w/v*). After measuring the initial antioxidant capacity, as described in Section 2.4.2, samples were exposed to the irradiation treatments for 90 min (in case of UV-A light) or 90 min and 72 h (in case of UV-B light), at 4 °C to exclude the thermosensitivity factor. Experiments were performed in triplicate. Afterwards, antioxidant capacity of the irradiated samples was assessed as aforementioned.

2.8. Rheological analysis

Apparent viscosity of tested microparticles using as carrier materials starch, alginate or carrageenan in the absence and presence of tea extracts is presented in Fig. 8. In all cases, flow curves were conducted at least in triplicate on a controlled-stress rheometer (MCR 302, Paar Physica, Austria) employing a sand blasted parallel plate geometry (1 mm gap, 25 mm diameter). Temperature was controlled uisng a Peltier system (±0.01). Aqueous dispersions prepared at 2% of carrier material content were tempered at room temperature for 30 min previously to rheological testing. Then, samples were placed in the plate-plate geometry, edges covered with light paraffin oil and rested for 15 min previously to steady-shear measurements to allow system equilibration. The corresponding flow curves (up/down) were run at 25 °C following a logarithmic ramp to assess the possible hysteresis phenomena.

2.9. Statistical analysis

Graphics and statistical analysis were performed using GraphPad Prism 6.0. Significant differences between means were calculated through one-way ANOVA tests, and with a p value <0.05.

3. Results and discussion

3.1. Schematic procedure

Fig. 1 summarizes the proposed extraction and microencapsulation process for the characterization and revalorization of tea waste materials.

Two different green extraction techniques were used. On the one hand, ultrasound assisted extraction (US) generated two different streams (liquid and solid phase). Secondly, US-solids were further processed through autohydrolysis (AH) generating again a liquid and a solid phase. US-AH liquids were subjected to membrane fractionation, resulting in three different retentates: 100 kDa, 50 kDa and 30 kDa. Preliminary characterization assays were performed to evaluate putative use in further spray-drying procedures of the recycled tea extracts. Once optimal extracts for the spray-drying procedure were selected, our goal was to explore the potential of three different green-sourced carbohydrate polymers (namely alginate, carrageenan, and starch) as carrier materials (*i.e.,* encapsulating agents) for the microencapsulation of bioactive tea extracts and to study its main features and putative applications.

3.2. Fundamental chemical characterization of the solid phases

Table 1 summarizes the fundamental chemical features of solids. Characterization results of tea leaves were consistent with previous studies, pointing out that in this study values were similar, but slightly lower than in [18,19]. The small differences observed could be due to intraspecific variation, different growing conditions or environmental factors [11,32]. In general terms, values between solids were similar. Tea leaves results were compared, both US and US-AH had significantly higher protein content. US solids pointed out for its significantly higher glucuronic acid content, in comparison US-AH solids had notably lower galacturonic acid values. Regarding to the macroelements, K and Mg levels were progressively lower in US and US-AH solids, compared with the raw material, while Ca levels increased. Microelements had no important differences except for Cu, which increased progressively in US and US-AH solids.

3.3. Characterization of liquid phases

3.3.1. Oligosaccharide content

Chemical characterization of liquid extracts is exposed in Table 2. Dry weight varied significantly between extracts, the highest values were measured in US liquids, being progressively lower in US-AH extract and retentates. Protein content peaked significantly at the US-AH 50 kDa fraction. The rest of the analyzed values had no notable differences between extracts. In all of the studied liquid phases, oligosaccharide content was maximum for 100 kDa retentate, except for rhamnose,

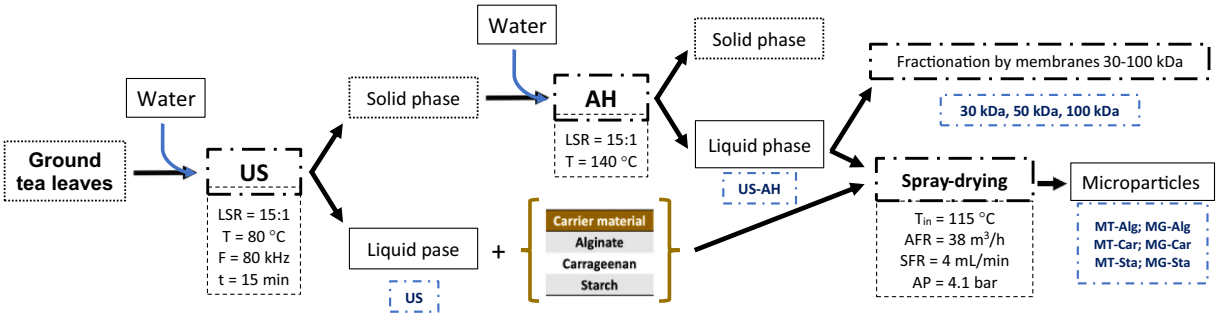


Fig. 1. Flow diagram of the processed raw material. US: ultrasound-assisted extraction technique; AH: autohydrolysis extraction technique; LSR: Liquid-solid ratio; T: temperature (°C); F: frequency (kHz); t: time (min); T_{in}: Inlet temperature (°C); AFR: air flow rate (m^3/h); SFR: feed solution flow rate (mL/min); AP: air pressure (bar). Note here that gallic acid was used as control. US: ultrasound assisted-extraction, AH: autohydrolysis, MT: tea microparticles, MG: gallic microparticles, Alg: alginate, Car: carragenate, Sta: starch.

Table 1
Chemical characterization of solids. Results are represented with standard deviations if measured in triplicate. *US solids*: Solid phase from the ultrasound-assisted extraction; *US-AH solids*: solid phase from the ultrasound + autohydrolysis assisted extraction.

		Tea leaves	US solids	US-AH solids
Macroelements (mg/kg)	Moisture (%. d. b.)	8.95 ± 0.22 $_a$	5.63 ± 0.84 $_b$	10.11 ± 1.84 $_a$
	Ash (%. d.b.)	7.46 ± 0.04 $_a$	7.33 ± 0.06 $_a$	6.71 ± 0.22 $_b$
	Protein (%. d. b.)	17.97 ± 1.51 $_a$	19.99 ± 0.07 $_b$	20.46 ± 0.17 $_b$
	Calcium	11,178	11,230	14,014
	Potassium	8268	2858	1881
	Magnesium	2320	2094	1853
	Sodium	403	442	391
	Iron	895	760	620
Microelements (mg/kg)	Cadmium	<2	<2	<2
	Cupper	7.8	9.4	9.6
	Mercury	<0.04	0.07	<0.04
	Lead	<4	<4	<4
	Boron	<20	21	<20
Carbohydrates and associated groups (%)	Total	32.83 ± 1.75 $_a$	33.28 ± 1.37 $_a$	30.99 ± 1.77 $_a$
	Glucan	11.52 ± 0.24 $_a$	11.03 ± 0.02 $_a$	11.49 ± 0.20 $_a$
	Xyl + Gal+Man	5.96 ± 0.17 $_a$	5.72 ± 0.19 $_a$	5.97 ± 0.21 $_a$
	Rhamnose	1.24 ± 0.22 $_a$	1.20 ± 0.21 $_a$	1.25 ± 0.23 $_a$
	Arabinose	2.25 ± 0.45 $_a$	2.15 ± 0.39 $_a$	2.23 ± 0.43 $_a$
	Fucose	0.03 ± 0.05 $_a$	0.03 ± 0.05 $_a$	0.03 ± 0.05 $_a$
	Ribose	0.19 ± 0.04 $_a$	0.18 ± 0.04 $_a$	0.18 ± 0.04 $_a$
	Formic acid	2.82 ± 0.09 $_a$	2.66 ± 0.13 $_a$	2.76 ± 0.1 $_a$
	Acetic acid	1.02 ± 0.04 $_a$	0.95 ± 0.02 $_a$	1.00 ± 0.04 $_a$
	Galacturonic acid	1.90 ± 0.03 $_a$	1.44 ± 0.08 $_b$	0.92 ± 0.10 $_c$
	Glucuronic acid	5.90 ± 0.41 $_a$	7.93 ± 0.24 $_b$	5.16 ± 0.37 $_a$

Data values with different subscript indicate significant ($p < 0.05$) differences between columns.

fucose, formic and galacturonic acids.

3.3.2. Total phenolic content and antioxidant capacity

Fig. 2 shows the TPC and scavenging capacity against ABTS (expressed as TEAC, or Trolox equivalent antioxidant capacity value) of the obtained liquid tea extracts. In Fig. 2a the TPC of US liquors is depicted. Significant differences were observed before and after the spray-drying process. US-extracts presented slightly lower TPC after the spray-drying process (14.02 ± 0.16 g GAE/100 g extract) compared to before (14.83 ± 0.81 g GAE/100 g extract). In case of US-AH liquid extracts, slightly higher levels of TPC were observed after spray-drying (9.87 ± 0.81, compared to 8.98 ± 0.20 g GAE/100 g extract). Nevertheless, considering the overlap of the standard deviations, these differences could be due to experimental inaccuracies or low precision of the used equipment. Fig. 2b shows TEAC values of the produced liquid extracts. No significant difference was observed before and after spray-drying of US liquid extracts (83.16 ± 5.82 and 84.46 ± 5.48 g Trolox/100 g extract, respectively). In case of US-AH extracts, the difference was significant comparing before and after spray-drying (75.75 ± 2.44 and 69.76 ± 3.90 g Trolox/100 g extract, respectively).

Results show that the temperature of the spray-drying process did not affect, or minimally affect, the polyphenol integrity and/or the antioxidant capacity, since the temperature in the atomized droplets is reported to remain below 40 °C as long as the drying air flow does not exceed 150 °C. This occurs due to the heat loss from evaporation that reduces the temperature inside the atomized droplets [33]. These results are consistent with similar studies found in literature [34,35].

US-AH liquors had always significantly lower TPC and TEAC values, when compared with US liquid extracts. These results indicate that a greater amount of phenolic compounds and antioxidant capacity are released in the first extraction step, although the following autohydrolysis extraction still yields considerable levels of TPC and antioxidant capacity.

US-liquid extract presented about the half of polyphenolic content achieved in similar studies with green tea extracts (30.0 g GAE/ 100 g extract, by [28]; 27.5 g GAE/ 100 g extract, by [5]). It should be noted that the raw material used in this study is sourced from pruning by-products, unlike in the aforementioned studies, where fresh tea leaves with higher TPC were used. Therefore, taking into consideration the lower quality of the raw material, our results stand out for its moderately high TPC and TEAC values, being higher than those achieved with similar raw material (13 g GAE/100 g extract, [18,19]).

In Fig. 2c-d TPC and TEAC of US-AH retentates are exposed. When comparing with the original US-AH liquid extract (8.98 ± 0.20 g GAE/ 100 g and 75.75 ± 2.44 g Trolox/100 g extract) results show that both TPC and TEAC start with significantly lower values in the 100 kDa retentate (5.37 ± 0.09 g GAE/100 g and 34.17 ± 1.13 g Trolox/100 g extract), but progressively increase, with 9.93 ± 0.38 g GAE/100 g and 76.89 ± 5.68 g Trolox/100 g extract in the 50 kDa retentate, reaching 14.79 ± 0.29 g GAE/100 g and 82.56 ± 1.81 g Trolox/100 g extract in the 30 kDa retentate. Hence, the final retentate, concentrated high amounts of TPC and antioxidant capacity within its dry extract.

The molar mass distribution (Fig. S1) was also evaluated for all the liquid samples obtained after extraction processes and from membranes. The extract obtained by US exhibit an important peak under 1 kDa, but also other peaks at largest molecular weight were observed. Fig. S1 shows a big peak above 80 kDa for the profile of US and AH processes, this result was in consistence with those published by [36], where the polysaccharide fraction was found close of 100 kDa. These results were according to other work where polysaccharides of the tea were analyzed (Tsubaki et al., 2008). This performance could be explained by the degradation of the molecules after a sequence of extraction processes. Retentate of 100 kDa shows a possible isolate of the biggest peak observed for the mass distribution AH-US, also smaller molecules were found. Retentates of 50 and 30 kDa also display slight peaks above 80 kDa and also under 1 kDa, therefore an effect after membrane fractionation was observed.

Fig. S2 represents the FTIR profiles of the extracts from tea leaves, polymers used as carriers, and the microparticles formulated with gallic acid and tea extracts. Starch showed the main bands at 1645 cm^{-1} related to C—O bending associated with OH group and also C-O-C ring vibration of carbohydrate was observed at 920 cm^{-1}. These peaks were also observed in the microparticles formulated with this carrier. For carrageenan, a band observed at 930 cm^{-1} reveal 3,6-anhydro-galactose, and the peaks showed at 1100 cm^{-1} could be due to C—O stretching vibrations. These representative bands were identified in the particulate systems were carrageenan was used. Also, alginate polymer profile was represented also in the Fig. S2. In this case, the characteristic bands were obtained at 1020 and 1030 cm^{-1}, these latter wavenumbers represent the mannuronic and guluronic acids existent in this natural polymer. Above results are consistent with those previously reported for biopolymers used as carriers [25,26,37].

3.4. Microparticles formulations: development and characterization

3.4.1. Encapsulation with green sourced carbohydrate polymers

Compared to other encapsulation materials, green sourced carrier systems represent a sustainable alternative for the industry in a global context were green transition and circular economics are gaining attention [14]. Additionally, the proposed carbohydrate polymers

Table 2
Chemical characterization of liquids. Results are represented with standart deviations if measured in triplicate. US: Liquid phase from the ultrasound-assisted extraction; US-AH: Liquid phase from the ultrasound+autohydrolysis assisted extraction; 100, 50, 30 kDa: fractions of US-AH.

	Parameters	US	US-AH	100 kDa	50 kDa	30 kDa
Carbohydrates and associated groups (%)	Dry weight (%)	1.43 ± 0.02 $_a$	0.71 ± 0.01 $_b$	0.33 ± 0.02 $_c$	0.15 ± 0.03 $_d$	0.1 ± 0.02 $_d$
	pH	5.54	5.34	5.56	5.89	5.9
	Proteins (%. d.b.)	2.18 ± 0.16 $_a$	2.45 ± 0.26 $_a$	2.82 ± 0.10 $_a$	6.22 ± 1.05 $_b$	2.87 ± 0.05 $_a$
	Total	42.06 ± 1.53	59.96 ± 0.94	72.07 ± 3.55	47.00 ± 3.63	32.17 ± 0.78
	Glucose	4.53	3.42	1.14	1.85	2.02
	Xylose	–	–	0.84	1.25	1.92
	Rhamnose	2.72	1.58	0.49	0.55	0.64
	Arabinose	–	1.51	0.38	0.63	0.58
	Fucose	1.15	2.17	0.33	1.03	1.68
	Maltose	5.39	1.80	1.32	2.04	2.35
	Ribose	0.62	–	–	–	–
	Acetic acid	–	0.93	–	–	–
	Galacturonic acid	–	–	1.54	2.30	–
	Glucuronic acid	–	–	0.71	0.93	–
	O-Glucose	12.25 ± 0.43	3.78 ± 0.05	17.66 ± 0.85	11.53 ± 0.73	0.87 ± 0.23
	O-Gal+Xyl + Man	7.26 ± 0.21	10.70 ± 0.02	11.89 ± 0.53	–	7.19 ± 0.05
	O-Rhamnose	2.33 ± 0.10	4.92 ± 0.03	1.35 ± 0.42	8.97 ± 0.83	5.90 ± 0.13
	O-Arabinose	2.04 ± 0.14	8.24 ± 0.02	13.79 ± 0.57	4.32 ± 0.39	3.39 ± 0.06
	O-Fucose	–	–	–	5.7 ± 0.51	3.46 ± 0.04
	O-Ribose	0.20 ± 0.06	1.49 ± 0.02	3.16 ± 0.11	2.2 ± 0.63	0.63 ± 0.03
	O-Maltose	–	–	2.69 ± 0.18	–	–
	Formic acid	1.99 ± 0.26	3.42 ± 0.12	–	–	–
	Acetyl groups	0.88 ± 0.23	3.14 ± 0.23	4.91 ± 0.15	0.41 ± 0.21	–
	Galacturonic acid	–	3.46 ± 0.08	0.53 ± 0.07	0.28 ± 0.05	0.45 ± 0.07
	Glucuronic acid	0.69 ± 0.10	9.40 ± 0.37	12.03 ± 0.85	3.01 ± 0.28	1.09 ± 0.17

Different letters indicate significant ($p < 0.05$) differences between columns.

(alginate, carrageenan, and starch) present some advantages over others. Gelatinized starch has good film-forming properties and it is easily convertible into a paste. Moreover, starch has a low price and a high consumer acceptance because of its presence in foods and extended use as additive [38]. Sodium alginate is derived from brown seaweeds, which allows a simple and cheap production. Its high versatility and low toxicity make it a suitable choice for microencapsulation experiments (Dias et al., 2017; Rezaul et al., 2018). It is also successfully used as protective agent in microencapsulation assays with polyphenols, making it a good choice for this study [39]. Moreover, its thickening properties are interesting in order to find applicability in the food industry [15]. Carrageenan, derived from red seaweeds, has proved to be an effective microencapsulation polymer, standing out for its gel-forming properties, low toxicity and applicability as pharmaceutical excipient [40]. Thus, six different microcapsulation systems were proposed: tea US-liquid extracts with sodium alginate (MT-Alg), carrageenan (MT-Car) and starch (MT-Sta) as carrier materials; and gallic acid, with the same polymer carbohydrates as encapsulating agents (MG-Alg, MG-Car and MG-Sta). In addition, sodium alginate (alg), carrageenan (car) and starch (sta) empty microparticles were formulated as negative controls.

Considering the inevitable losses produced through the exhaust of the spray-dryer, notably high yields for a laboratory scale were attained. Spray-dried US and US-AH liquid extracts achieved a 80.56% and 78.38% product yield respectively, doubling yields obtained in similar studies [28].

During the microencapsulation assays through spray-drying, the following product yields were achieved: 55.3% MT-Alg, 50.03% MG-Alg, 38.03% Alg, 45.86% MT-Car, 56.82% MG-Car, 48.53% MT-Sta and 58.57% MG-Sta.

These yields were higher compared to those reported in similar studies for the same carrier carbohydrates and core materials [14], even using different operating conditions and core:carrier ratio, but identical equipment [28].

US-AH liquid extracts, and its fractions were excluded from the microencapsulation assay because of its very low dry weight values, while higher values in US liquid extracts were considered more adequate for this experiment (see Section 3.3).

Due to the high 1:1.5 core:carrier ratio used, the microcapsules generated in this study will be designated as thin-polysaccharide-coated tea extracts, compared to other studies where low core:carrier ratios (1:3 or lower) were preferred [5,28,41], based on the assumption that lower carrier concentrations provide lower polyphenol entrapment [28]. Nevertheless, our results show high TPC and antioxidant capacity in thin-coated microcapsules (Fig. 3), calling into question the supposition that higher concentrations of polysaccharide carriers are essentially required to achieve an efficient entrapment of tea polyphenols.

Microencapsulation efficiencies (ME) were tested for MT-Alg, MT-Car and MT-Sta. A ME of 76.63 ± 1.52% was achieved for MT-Alg, 92.72 ± 1.8% for MT-Car, and 60.25 ± 7.14% for MT-Sta. In case of MT-Car, our results more than duplicated the ME reported in similar studies found in literature (42.56 ± 2.81%), and where notably higher in case of MT-Alg (69.81 ± 3.33%). Nevertheless, ME of MT-Sta was lower, when compared to modified corn starch (80.03 ± 5.31%) [28].

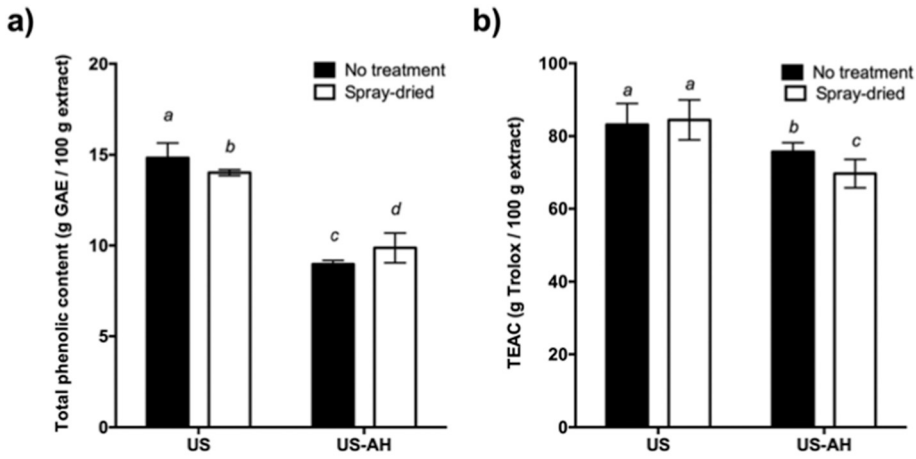
As reported by other studies [5], our results show that ME is affected by the carrier material used. Viscous feed solutions are not appropriate for spray-drying and hinder the formation of well-coated microcapsules [42]. Because of this, always low concentrations in the feed solution were used. However, higher viscosity of starch dispersions could be reason of its lower ME.

Note that: 1. Low concentrations of feed solutions were used to reduce the emulsion viscosity, and thus, the putative moisture content in the spray-dried powder [43]. 2. A relatively high core:carrier ratio was used with the aim of maximizing the concentration of bioactive compounds in the spray-dried product.

3.4.2. Morphology and size distribution

Solidification mechanisms during spray-drying are influenced by chemical characteristics and interactions of core and carrier materials. Evaporation rate is mainly determined by the feed solution viscosity, T_{in}, and air flow rate. Particle size is mostly affected by atomization air flow rate. Together, solidification mechanisms, evaporation rate and particle size, determine the morphology of the spray-dried particles in the final stages of the drying process [44].

SEM micrographs of the spray-dried microparticles are shown in Fig. 4. Structural differences between different carrier carbohydrates (*i.e.*, encapsulating agents) and different core materials were observed,



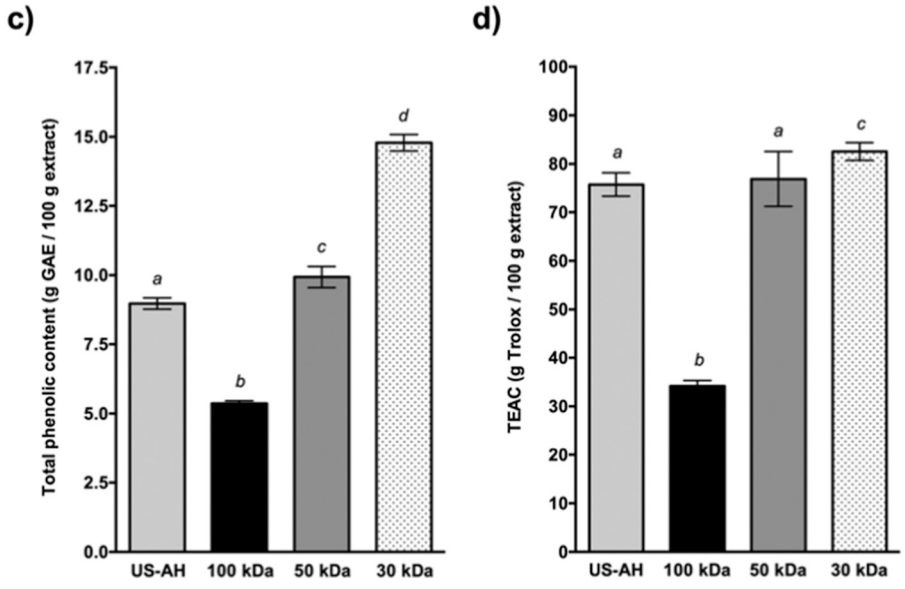


Fig. 2. Total phenolic content (TPC) and scavenging capacity against ABTS (expressed as TEAC value) of liquid tea extracts: a) and b) represent TPC and TEAC (respectively) of US and US-AH extracts before and after spray-drying; c) and d) show TPC and TEAC (respectively) of membrane-fractionated US-AH extracts. US: Ultrasound-assisted extraction; AH: Autohydrolysis extraction. Note that different letters indicate significant ($p < 0.05$) differences between means. The values are represented as means. Standard deviations are depicted as error bars.

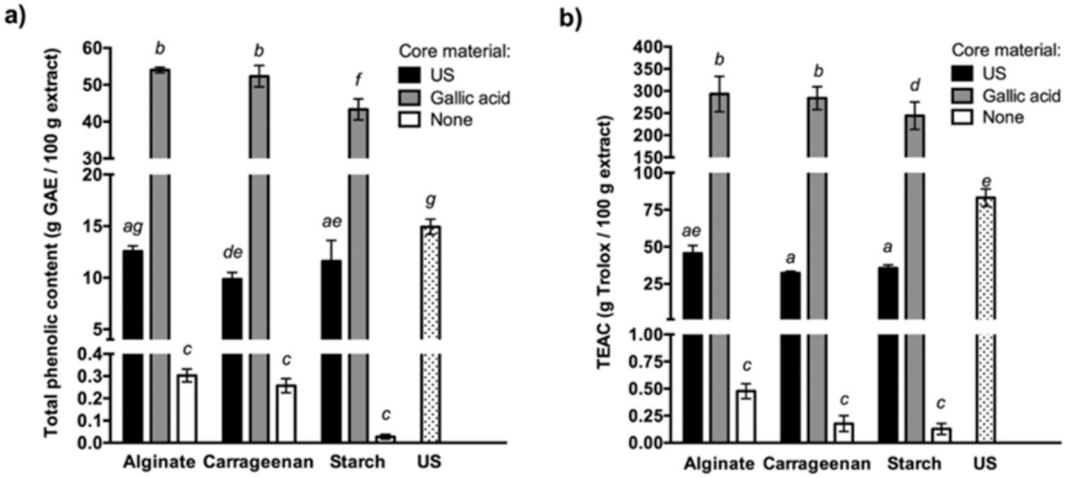


Fig. 3. Microparticle analysis. a) Total phenolic content (TPC) and b) scavenging capacity against ABTS (expressed as TEAC value), of spray-dried microparticles. Gallic acid and empty microencapsulates were used as control. US: spray-dried liquid phase from the ultrasound-assisted extraction technique. Note that different letters indicate ($p < 0.05$) differences between means. The values are represented as means. Standard deviations are depicted as error bars.

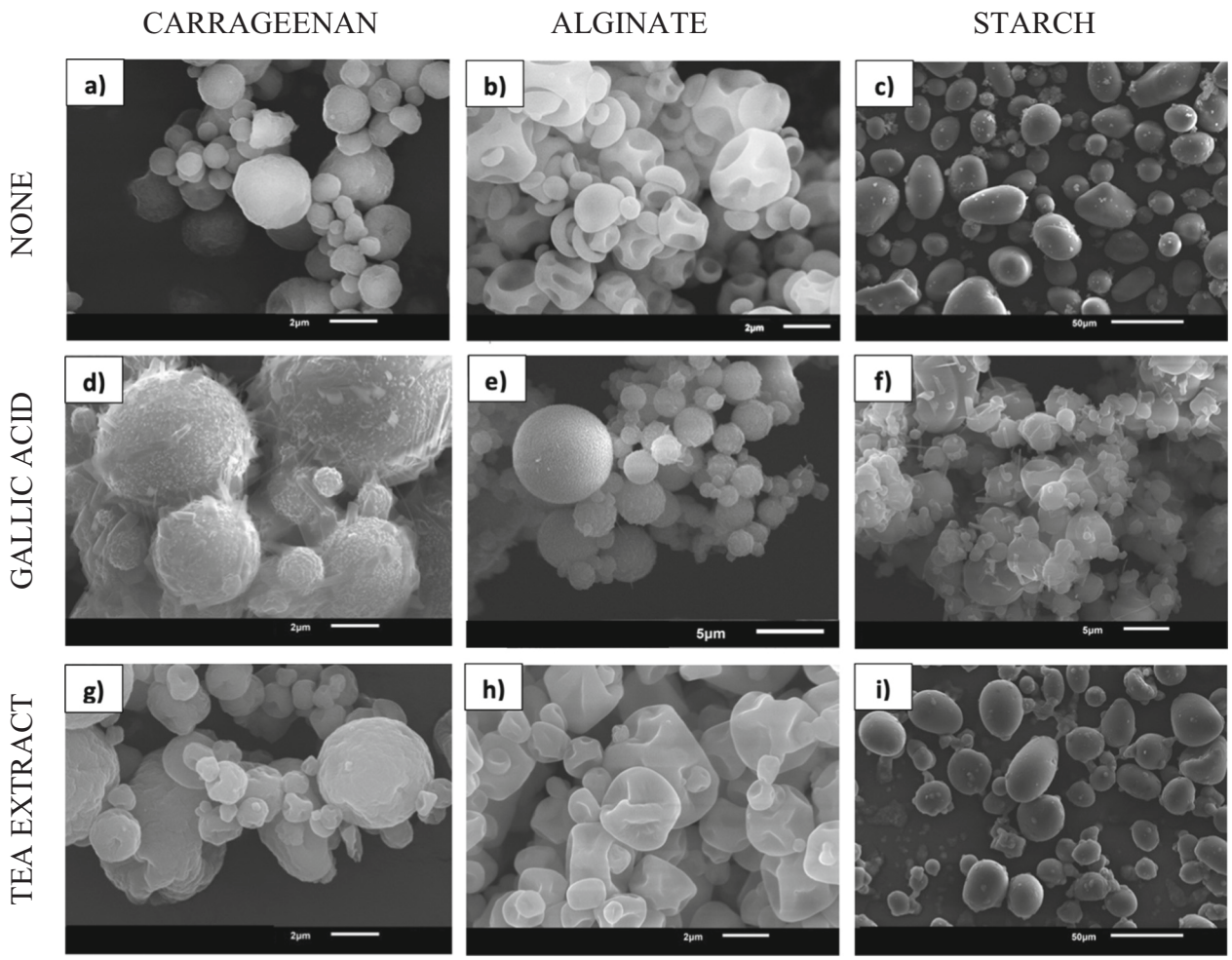


Fig. 4. Scanning electron microscopy images of spray-dried microparticles. Horizontal text refers to the encapsulating polymer, vertical text indicates the core material used. Scale bars represent a) 2 µm, b) 2 µm, c) 50 µm, d) 2 µm, e) 5 µm, f) 5 µm, g) 2 µm, h) 2 µm, i) 50 µm.

pointing out the fact that the spray-dried microcapsule morphology could be affected by the interactions between core and carrier materials, as already exposed by [45]. In general terms, results show a particle population with moderate size polydispersity and spherical shape, with the exception of starch based formulations which showed slight ovoid morphologies. Important surface indentation was observed in MT-Alg and MG-Alg, which is common in carbohydrate- and specially alginate formulations [23,46]. Starch-based formulations presented smooth surfaces, while carrageenan-based formulations presented rough surfaces.

In some MG, GA crystallization was observed, which may cause disaggregation of MG-Sta microparticles during the spray-drying process, involving notably smaller particle sizes than MT-Sta and empty starch microparticles. SEM analysis of the spray-dried US liquid extract showed that bridging of the particles occurred.

Particle size distribution results of MT and MG are shown in Fig. 5.

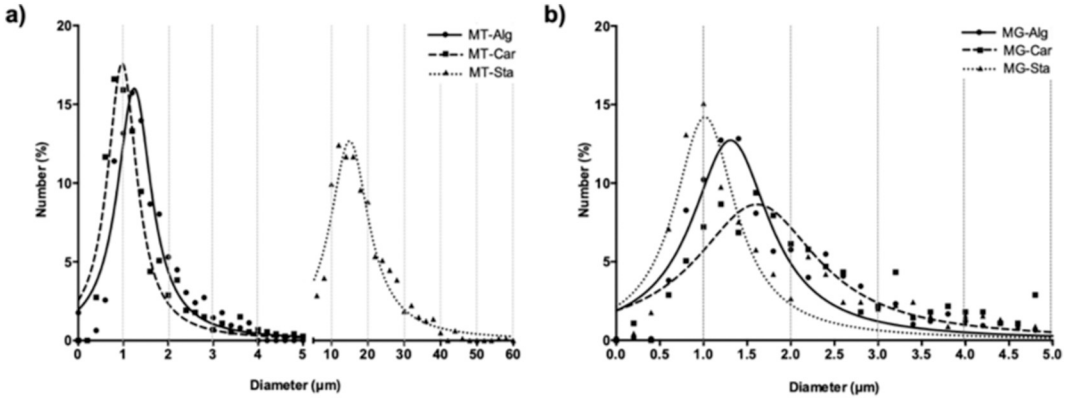


Fig. 5. Particle size distributions of the formulated microparticles: a) microencapsulated tea (MT); b) microencapsulated gallic acid (MG). Alginate (Alg), carrageenan (Car) or starch (Sta) were used as carrier materials. Results were adjusted to a Lorentzian distribution.

MT-Alg and MT-Car frequency distributions were almost identical, peaking at 1.2 and 1 μm respectively. MT-Sta presentenced notably larger diameters, around 15 μm. On the other hand, very similar distributions of particle sizes, in the range of 0.5–2.5 μm, were reported in case of MG. MG-Alg frequency distribution peaked at 1.3 μm, MG-Car at 1.6 μm and MG-Sta at 1 μm.

3.4.3. Rheological features

Rheological analysis of the microparticles formulated using starch, alginate or carrageenan as carriers, both unloaded and loaded with tea extracts, exhibited different apparent viscosity profiles (Fig. 6). Microparticles prepared using alginate carriers showed Newtonian behavior, whereas those developed employing carrageenan or starch carriers presented shear-thinning behavior with a clear decrease of the apparent viscosity with increasing shear rate. Latter behavior is distinctive of macromolecules dispersions and suggests that there was an alignment of the molecules at the largest shear rates, promoting the fluid flow [47]. This viscous tendency is consistent with a characteristic non entangled biopolymer performance in the dilute regime [48]. The observed apparent viscosity drop was larger for carrageenan microparticles (about 3 decades) when compared with those made with starch (about 1.5 decades). At fixed shear rate, the presence of tea extracts slightly decreased the apparent viscosity of microparticle systems. The highest apparent viscosity values was identified for microparticles encapsulated using carrageenan followed by those made with alginate and starch, which tended to common apparent viscosity values at the lowest tested shear rates (0.1 s). Note here that systems formulated with carrageenan or starch could be satisfactorily described by the well-known power law model ($R^2 > 0.992$). It should be highlighted that tested systems did not show hysteresis loops, which signifies a relevant advantage from the processing point of view. To sum up, tested carbohydrate biopolymers offer a diverse palette of carrier materials for bioactive components, which could be useful in further research on the potential application of microcapsules as ready-to-use substrates for 3-D printing applications or gel-matrices for nutraceuticals and/or pharmacological applications.

3.4.4. Release dynamics of the microencapsulated formulations

The thin-coated nature of the formulated microcapsules allowed a rapid release and dispersion of the core materials, promoted of the use of water soluble polysaccharide carriers. MT showed extremely fast release profiles. Tea extract components are very soluble in water, mainly because of the polar nature of its polysaccharides [35], enhancing rapid release dynamics. Even MT-Sta had fast release dynamics, despite its higher surface-volume ratio compared to MT-Alg and MT-Car. Rough or indented surfaces, as observed in MT-Alg (and more slightly in MT-Car), are also supposed to increase release dynamics (again, because of its higher surface-volume ratios. See Section 3.6), but our results did not show this effect. Thus, surface-volume ratios may not play such an important role in release dynamics as has been assumed so far by others [49–51].

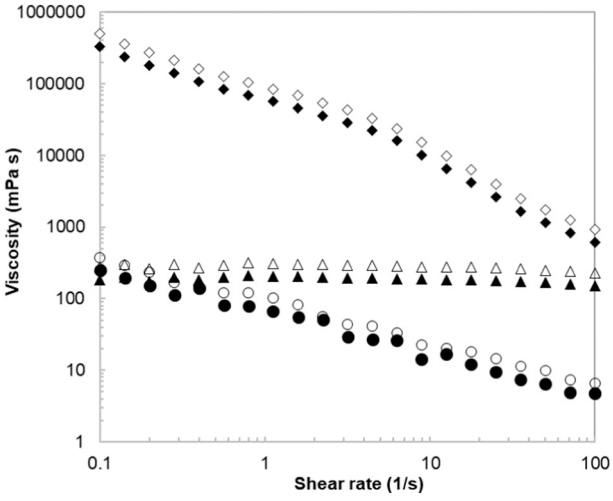


Fig. 6. Apparent viscosity profiles of dispersed alginate (▲), carrageenan (◆) and starch (●) microcapsules in the absence (open symbols) and presence (closed symbols) of tea extract as core material.

MG had fast release profiles, but in this case, the core material (GA) is moderately soluble in water [52]. MG-Sta presented the slowest release profile, probably due to the low solubility of starch compared to alginate and carrageenan.

In MG formulations, the surface-volume ratio was very similar between carrier materials (see Section 3.6), excluding the effect of this factor on the release dynamics. Thus, our results showed that the chemical nature of the core and carrier materials affected the release profiles, rather than size and morphology. However, the carbohydrate carriers compared in this study induced only slight differences in the release dynamics, without affecting its putative applications. Note here that pH effect was also analyzed without notably modifications (representative examples in Fig. S3).

Kinetic modeling is essential regarding to the design of a system with predictable and specific behavior. Thus, five different models (zero order, first order, Higuchi, Korsmeyer-Peppas and Weibull) were adjusted to the release profiles in order to analyze the kinetic behavior of thin-carbohydrate-coated microparticles. Our results (Fig. 7) showed that the Weibull model accurately predicted the release dynamics of MT-Alg ($\alpha = 170.87$, $\beta = 1.371$, $R^2 = 0.992$), MG-Alg ($\alpha = 712.52$, $\beta = 1.874$, $R^2 = 0.997$), MG-Car ($\alpha = 185.19$, $\beta = 1.215$, $R^2 = 0.993$), MT-Sta ($\alpha = 231.43$, $\beta = 1.653$, $R^2 = 0.999$) and MG-Sta ($\alpha = 536.71$, $\beta = 1.366$, $R^2 = 0.998$), while a First order equation predicted slightly better the MT-Car release profile ($k_1 = 0{,}026$, $R^2 = 0.974$). These results are consistent with the predominantly Weibull-model adequacy observed by [23].

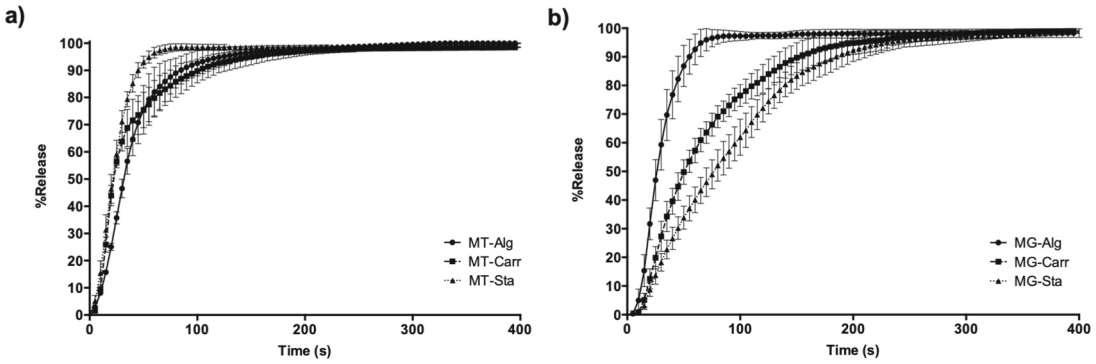
3.4.5. Total phenolic content and antioxidant capacity assays

Fig. 8 depicts TPC and TEAC values of the spray-dried microparticles. Note here that during the experiments spray-dried tea was resuspended in water. Results show high loading efficiencies (LE), with small differences between the TPC and TEAC values of the original liquid US-extract and the microencapsulated tea, due to the thin-coated nature of the microparticles. These formulations surpassed the results of similar studies [5,14,28], obtaining LE of 84,19% (MT-Alg), 65,91% (MT-Car) and 77,63% (MT-Sta). LE of tea extract as core material were higher than those with GA as loading material (data not shown), pointing out a possible interaction between tea components and the proposed carriers. Overall, thin coated formulations allowed to maximize the bioactive content concentration of bioactive tea components in the carbohydrate matrix of microparticles.

3.4.6. UV light experiments

UV-light is one of the foremost physical factors involved in the degradation of tea constituents. Specifically, tea polyphenols present a high photosensitivity [53]. Because of its rapid degradation the applicability of tea polyphenols is limited. Catechins have its absorption maximum in the range of 250–360 nm [54]. This corresponds to the UV-B spectra, and thus, this range is normally related to photodegradation processes of tea polyphenols. But in this study, we wanted to focus on less attended parts of the UV spectrum and to evaluate its effects. Two types of UV-lights were tested: UV-A (365 nm) and UV-C (254 nm). In order to assess the photosensitivity of tea extracts embebed in different carbohydrate polymer matrix, samples were exposed to different irradiation treatments for 90 min (in case of UV-A light) or 90 min and 72 h (in case of UV-C light).

The dispersion in distilled water of the formulated microcapsules made from bioactive tea extracts embebed in different carbohydrate matrix. The proposed hypothesis were: 1. The studied UV wavelengths did have an effect on the antioxidant properties of green tea extracts, 2.



Kinetic models	Equations	Parameters	Alginate		Carrageenan		Starch	
			TE	GA	TE	GA	TE	GA
Zero order	$y = k_0 \cdot x$	*k0 (mg/min)*	0.641	0.659	0.633	0.576	0.669	0,523
		R^2	0.637	0.501	0.615	0.844	0.440	0.945
First order	$y = 100(1 - e^{-k_1 \cdot x})$	*k1 (min^{-1})*	0.024	0.031	0.026	0.014	0.039	0.010
		R^2	0.980	0.960	0.974	0.993	0.972	0.993
Higuchi	$y = k_h \cdot \sqrt{x}$	*kh (mg min$^{-0.5}$)*	8.049	8.359	8.192	7.059	8.549	6.298
		R^2	0.816	0.699	0.734	0.946	0.650	0.976
Korsmeyer-Peppers	$y = k_{KP} \cdot x^n$	*kkp (min^{-n})*	15.25	21.09	19.73	5.37	28.70	1.98
		n	0.369	0.310	0.315	0.556	0.251	0.736
		R^2	0.853	0.770	0.869	0.940	0.765	0.976
Weibull	$y = 100\,(1 - e^{-\frac{x^\beta}{\alpha}})$	*α (min)*	170.9	712.5	30.9	185.2	231.4	536.7
		β	1.371	1.874	0.946	1.215	1.653	1.366
		R^2	0.992	0.997	0.973	0.993	0.999	0.998

Fig. 7. Release profiles of the studied microcapsules. Absorbance was read at 273 nm; GA was used as standard release indicator. Results were expressed in percentage (%), being 100% the maximum absorbance measured for each sample. a) Release profiles of microencapsulated tea (MT); b) release profiles of microencapsulated gallic acid (MG). Alginate (Alg), carrageenan (Car) or starch (Sta) were used as carrier materials. Standard deviations are represented as error bars.

The formulated gel-matrix would be able to maintain the antioxidant capacity of the tea extract and 3. It would present protection against UV-light treatments.

Results exposed in Fig. 8a show that surprisingly UV-A light depleted antioxidant capacity of non-encapsulated tea extracts after 90 min of treatment, while microencapsulated tea (MT) did not show this effect. Gallic acid, used as control sample, also showed a slight decrease in exposure to this wavelength, which did not occur in the microencapsulated samples (MG), except for the microencapsulation with alginate (MG-Alg).

UV-C light is used in food-sterilization processes. Previous studies showed that UV-C irradiation did not significantly deplete catechins neither produce harmful by-products [55], this results are consistent with Fig. 8b, where a short-time exposure to UV-C light did not produced significant change. Nevertheless, a long-time exposure (72 h) to UV-C light caused depletion of the antioxidant properties of tea extracts and GA, as exposed in Fig. 8c, which in turn were avoided in the encapsulated samples (MT and MG). This small decrease compared to the UV-A light could be explained by the fact that the UV-C lamp has a 35% lower irradiance level than the UV-A lamp. Thus, it was necessary to expose samples to longer irradiance times in order to show some degradation.

Designing a system which could protect bioactive tea constituents could open an array of possible applications. Our approach on the preservation of these antioxidant properties is based on the formulation of thin-carbohydrate-coated microparticles as precursors of gels, taking into account its hygroscopic features [56,57], which form a matrix with UV-light protecting features. Thus, the microencapsulated particles could work as ready-to-use precursors in the formulation of the above-mentioned carbohydrate gels, which could be extended to other systems, foreseeing chemical protection from light-dependent degradation in case of cosmetics or pharmacological applications.

4. Conclusions

Our approach demonstrated that green-sourced materials and non-contaminating extraction techniques were effective for the formulation of thin-carbohydrate-coated microencapsulation systems, that could be considered as “natural” and “recycled” for the industry. The spray-drying technique showed to be successful, resulting in high yields, high loading efficiencies for all of the studied carriers (alginate, carrageenan, and starch) and outstanding microencapsulation efficiencies in case of carrageenan and alginate. Together with the green-extraction trend, these are promising results for scaling up the process in industry. SEM-imaging showed adequate properties of the formulated

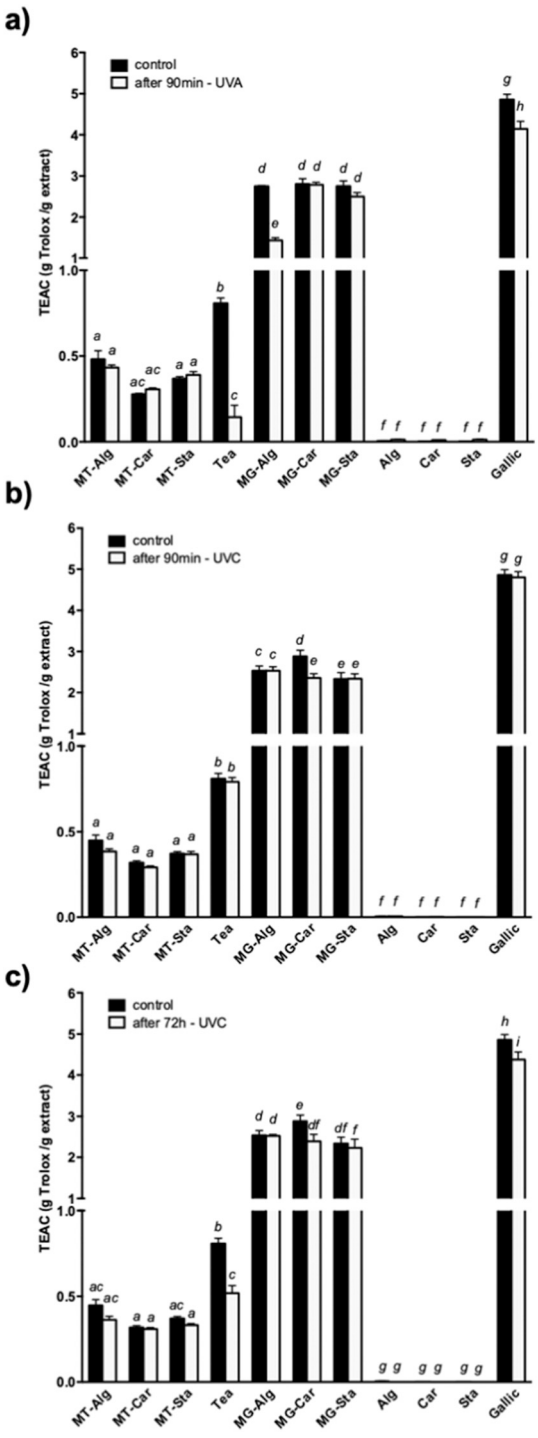


Fig. 8. Antioxidant capacity (expressed as TEAC) of an array of gel formulations obtained through dispersion of microparticles in de-ionized distilled water, exposed to different UV-light treatments. a) 90 min UVA light (356 nm), b) 90 min UVC light (254 nm), c) 72 h UVC light (254 nm). Note that different letters indicate significant ($p < 0.05$) differences between means. The values are represented as means. Standard deviations are depicted as error bars.

powders, shedding light on the microparticle forming mechanisms. Highly efficient release profiles were achieved, due to the thin-coated nature of the microparticles, independently of the carrier material used. Furthermore, our results proved the presence of phenolic compounds in the carbohydrate matrix of the spray-dried microparticles and showed that the antioxidant capacity was conserved after the spray-drying process. Extended shelf-life and protective properties of microencapsulation systems for tea extracts are well-known. But its applications are not presented and/or tested very often. One of the innovative aspects of this study is that its next-step application was analyzed. After in-depth characterization of the microparticles, rheological analysis and UV-light experiments were performed on generated gel-matrix to assess the potential application of the formulated microparticles, with promising results relating on the conservation of is antioxidant effect and gel-forming properties. UV-A and UV-C irradiance depleted antioxidant capacity of tea extracts. The analyzed carbohydrates polymers showed to be effective as UV-protective encapsulating agents. Together with rheological features, our results point out the technological potential of the proposed thin-coated microparticle systems and open the door for its applicability as green sourced/recycled precursors of edible gels, functional foods, or new drug delivery systems of bioactive tea components. Further research has to be done to analyze the shelf-life behavior of these thin-coated microparticles and to investigate its integration and behavior in functional foods, cosmetics and/or pharmaceuticals.

CRediT authorship contribution statement

conceptualization, H.D., M.D.T and N.F.F.; experimental work, K.L.B.; data curation, K.L.B., N.F.F. and M.D.T.; writing—original draft preparation, K.L.B., N.F.F., M.D.T. and H.D., and M.D.T.; writing—review and editing, H.D., N.F.F. and M.D.T.; funding acquisition, H.D., and M.D.T.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijbiomac.2022.01.129.

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