Current Research in Food Science 8 (2024) 100769

Contents lists available at ScienceDirect

Current Research in Food Science

journal homepage: www.sciencedirect.com/journal/current-research-in-food-science

Microencapsulation of hop bioactive compounds by spray drying: Role of inlet temperature and wall material

Simona Tatasciore [a], Veronica Santarelli [a], Lilia Neri [a,*], Carla Daniela Di Mattia [a], Alessandro Di Michele [b], Dino Mastrocola [a], Paola Pittia [a]

[a] Department of Bioscience and Technologies for Food, Agriculture, and Environment University of Teramo, Via Renato Balzarini 1, 64100, Teramo, Italy
[b] Department of Physics and Geology, University of Perugia, Via Pascoli, 06123, Perugia, Italy

ARTICLE INFO

Handling Editor: Maria Corradini

Keywords:
Hop extract
Bioactive compounds
Spray-drying microencapsulation
β-cyclodextrin
Gum Arabic
Maltodextrin

ABSTRACT

This study explores the effect of spray-drying (SD) inlet temperatures (T_{inlet} 120 and 150 °C) and wall material on the chemical and physico-chemical properties of microencapsulated hop extracts (MHE). Hop extract was formulated with maltodextrin (MD) and gum Arabic (GA) used in single or in combination with β-cyclodextrin (βCD). MHE were evaluated for physical properties, bitter acids (BA), total polyphenol content (TPC) and encapsulation efficiency (TPC EE), and antioxidant capacity (AOC). Powders produced at T_{inlet} 150 °C exhibited the highest flowability and generally higher TPC yield. Besides T_{inlet}, MD enabled the obtaining of MHE with the highest encapsulation efficiency. Other physico-chemical and antioxidant properties differently varied depending on the T_{inlet}. Overall, the βCD addition positively affected α-acids, and β-acids of MHE obtained at T_{inlet} 120 °C. ATR-FTIR analysis showed hydrogen bond formation between hop compounds and βCD. Multifactorial ANOVA highlighted that T_{inlet}, W, and their interaction influenced almost all the chemical and physico-chemical properties of MHE.

1. Introduction

Hop cones, the female inflorescences of the plant *Humulus lupulus* L., are mostly used in the brewing industry but recently have gained considerable attention for their bioactive compounds, including bitter acids and polyphenols. Bitter acids, secreted in the lupulin glands, are prenylated derivatives of phloroglucinol (1,3,5- hydroxybenzene, $C_6H_6O_3$) and encompass two main chemical classes of compounds, i.e. α-acids (humulones) and β-acids (lupulones) (Carbone and Gervasi, 2022). Both α-acids and β-acids consist of a series of homologues i.e., humulone (35–70%), cohumulone (20–65%), and adhumulone (10–15%) for α-acids, while lupulone (30–55%), colupulone (20–65%), and adlupulone (10–15%) for β-acids (Santarelli et al., 2023).

Polyphenols are mainly present in the bracts and can account for up to 14% of the cone dry matter. Four main chemical classes have been found in hops: (I) flavan-3-ols, (II) flavonols, (III) carboxylic acids (derivatives of benzoic and cinnamic acid), and (IV) prenylflavonoids (Santarelli et al., 2021). Xanthohumol constitutes 80–90% of all prenylated flavonoids and is the most important prenylated chalcone in terms of both biological activity and concentration.

These secondary metabolites have attracted the attention of researchers thanks to their flavouring, antioxidant, anti-inflammatory, antibacterial, and food-preservative properties (Carbone and Gervasi, 2022; Santarelli et al., 2021) that may offer diverse opportunities in both food and non-food applications. Furthermore, over the last few years, the consumers' demand for clean-label, healthy, and high-quality food products has grown, and there is an increased interest from the food industry in using plant extracts as replacers of synthetic additives or ingredients (Asioli et al., 2017).

Despite the multifaceted advantages associated with hops and hop-derived bioactive compounds, their practical usage in food formulations remains limited due to various factors, including their sensitivity to environmental stresses like high temperatures, oxygen, and light during processing, storage, and transport, which can determine the loss of their biological value, bioavailability, and functionality (Carbone and Gervasi, 2022). Finally, it is worth noting that many of these molecules show a minimal solubility in water, which coupled with a pronounced astringent and bitter taste, makes their direct use in food products challenging.

To address these limitations, encapsulating the compounds of

* Corresponding author.
E-mail address: lneri@unite.it (L. Neri).

https://doi.org/10.1016/j.crfs.2024.100769
Received 7 March 2024; Received in revised form 29 April 2024; Accepted 11 May 2024
Available online 13 May 2024

interest represents a viable strategy, and various technologies are currently available for this purpose. Through diverse methods, active compounds/extracts (core material) are entrapped within a homogeneous or heterogeneous matrix (wall or coating material), creating new structures or encapsulates of varying sizes, encompassing micro- and nano-scales (Culas et al., 2023). Encapsulation technologies offer the possibility to convert unstable yet useful active molecules into stable and functional food ingredients, allowing their prolonged release and protection during food processing.

Among the microencapsulation methods, spray-drying (SD) is one of the most used by the food industry due to its scalability, cost-effectiveness, good finished product stability, versatility, and large-scale production in continuous mode (Labuschagne, 2018). SD involves atomizing a solution or dispersion of the bioactive compound and the encapsulating material, which is then dried to form microcapsules. The effectiveness of encapsulation can be affected by different variables including chemical and physico-chemical properties of the wall materials and of the active compounds to be encapsulated and, if any, their interactions (Labuschagne, 2018).

Commonly used food-grade carriers or wall materials are carbohydrates, cellulose, proteins, gums, and lipids. Carbohydrates are used extensively due to their ability to form amorphous glassy solids that provide structural support to the wall material of the delivery system. Their ability to bind active ingredients is complemented by their low cost and widespread use in foods, making them the preferred choice for encapsulation (Labuschagne, 2018). Among carbohydrates, maltodextrin (MD) has excellent encapsulation properties due to its high solubility, low viscosity, and film-forming ability. Cyclodextrins (CD), obtained by enzymatic modification of starch, have a hydrophilic outer surface and a hydrophobic inner cavity, which allows them to form inclusion complexes with a diverse range of organic compounds. In particular, as reviewed by Matencio et al. (2020) and Pinho et al. (2014), the complexation of CDs with antioxidants, also from natural extracts, allows the protection of such compounds against oxidation, light-induced decomposition, and heat-induced changes, increasing their concentration in the final ingredients that the food industry can use for products' fortification. However, most carbohydrates are not surface-active and thus have inferior emulsifying capacity. To address this shortcoming, carbohydrates can be used in combination with other ingredients with good emulsifying capacity, such as gum Arabic (GA) (Kaul et al., 2022).

To the authors' knowledge, despite a wide literature focused on the

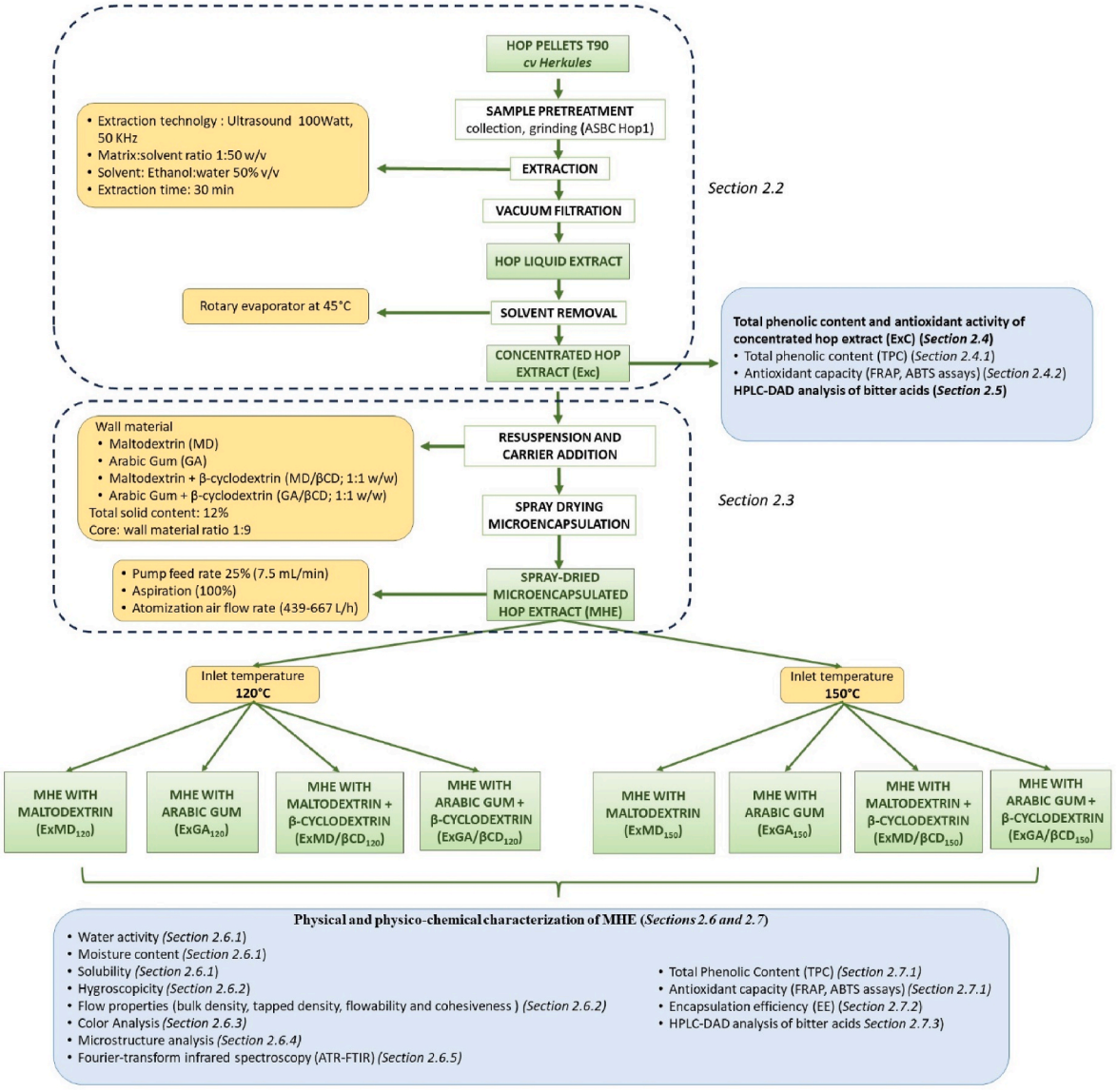

Fig. 1. Experimental plan and paper structure.

encapsulation of bioactive compounds extracted from plant matrices (de Freitas Santos, Rubio, da Silva, Pinho & Favaro-Trindade, 2021; Ribeiro et al., 2020), few studies focused on microencapsulation of hop extracts (Su et al., 2023; Tatasciore et al., 2023; Ferreira-Anta et al., 2023) for food purpose and lacking are the studies on the development of spray drying process to encapsulate hop's bioactive compounds (e.g., alfa and beta acids).

With the aim to fill this knowledge gap, this study investigated the effect of two inlet temperatures (120 °C and 150 °C) and different wall materials i.e., maltodextrin or gum Arabic used in single or in combination (ratio 1:1 w/w) with β-cyclodextrin on the chemical, physico-chemical and physical properties of the corresponding microencapsulated hop powders.

2. Materials and methods

The schematic representation of the experimental plan and paper structure is reported in Fig. 1.

2.1. Materials

Hop pellets T90 (batch E287/21/10595) of cv. Hallertau Herkules grown in Germany and harvested in 2021 were purchased from P.A.B. S. r.l. Mr. Malt (Pasian di Prato, Udine, Italy) and used in all experiments. The hop pellets were packed under vacuum in high-barrier plastic bags and stored at −40 °C until use.

The cv. Hallertau Herkules variety was chosen following preliminary tests characterizing seven varieties (Cascade, Opal, Hallertau Tradition, Perle, Magnum, Mandarina Bavaria, and Herkules) for their alpha and beta acid content, antioxidant capacity, total phenolic content, chlorophylls and carotenoids content, flavonoids and flavans content, and aromatic profile (data not shown). Since our work aims to preserve both the content of alpha and beta acids and the antioxidant properties, the Herkules variety was selected due to its favourable levels of alpha and beta acids and high antioxidant capacity compared to the other examined varieties.

For all the experiments food-grade wall materials were used i.e. maltodextrin DE12 (Glucidex®IT-12 $M_w = 18.6 \times 10^3$ Da) was purchased from Roquette Freres (Lestre, France); gum Arabic was purchased from Kerry Ingredients & Flavours Ltd. Global Technology & Innovation Centre (Millennium Park Naas, Co. Kildare, IRELAND) and β-cyclodextrin (CAVAMAX® W7 FOOD, lot.no. 701651, purity >98%) from Wacker Chemie AG (Hanns-Seidel-Platz München, Germany). All the reagents used for analysis were purchased from Sigma-Aldrich, (Steinheim, Germany).

2.2. Production of the hop extract and concentrated hop extract (ExC)

Before extraction, hop pellets were preliminarily ground to a fine powder according to the official ASBC Hops-1 method (American Society of Brewing Chemists), sieved and packed in PA/PE/PE plastic bags to protect them from light and humidity. The extraction conditions (i.e., extraction solvent, matrix:solvent ratio, method, and time) were chosen based on previous studies (Santarelli et al., 2021). Briefly, ethanol:water 50:50 (v/v) was used as extraction solvent, and 1:50 w/v was chosen as matrix:solvent ratio, then the extraction was carried out by ultrasound bath (100 W, 50 kHz; LAB SONIC) for 30 min. Then, the extract was centrifuged at 2470×*g* for 10 min at 4 °C, and the collected supernatant was filtered with a paper filter (Whatman n. 41) under vacuum. Finally, the concentrated hop extract (ExC) was obtained by the complete evaporation of the solvent by a rotary evaporator (Buchi R-100) set at 45 °C.

2.3. Production of microencapsulated hop extracts (MHE)

Microencapsulation was carried out by spray-drying (SD). To this aim, before spray-drying ExC was resuspended in a 5% (v/v) ethanol solution and formulated with three different coating materials i.e., Maltodextrin (MD), gum Arabic (GA), and β-cyclodextrin (βCD). MD and GA were used either in single or in combination with βCD (ratio 1:1 w/w). Each coating material was added to the resuspended hop extract to obtain a dispersion with a total solid content of 12% (w/v) and with an ExC:wall material ratio equal to 1:9 (w/w). For each wall material, a control sample without the extract was prepared following the same procedure.

A laboratory-scale spray dryer (Büchi Mini Spray Dryer B-290, Switzerland) operating in a co-current manner was used. The formulations were dispersed through a two-fluid nozzle with an inner diameter of 0.7 mm by using compressed air (5 bar) at 38.5 m^3h^{-1}. For each sample, two different inlet temperatures (T_{inlet}) were tested: 120 °C and 150 °C. As measured in preliminary experiments, these two T_{inlet} allowed to obtain T_{outlet} lower than about 90 °C that can prevent the isomerization of alpha acids, which present a much stronger bitterness (Jaskula et al., 2008; Malowicki and Shellhammer, 2005).

while other operating parameters were kept constant: i.e. the peristaltic pump was set at 25% of its maximum rate, the aspiration rate was set at 100%, and the atomization air flow rate was from 439 to 667 Lh^{-1}.

Each powder was produced replicating the spray drying process two times.

For each series of encapsulation trials, the outlet temperature (T_{outlet}) was registered, and the process yield was also calculated as follows (Eq. (1)):

$$\text{process yield } (\%) = m_p / m_{th,feed} \quad (1)$$

where m_p is the mass of recovered powder (g) and $m_{th,\ feed}$ is the theoretical amount of solids present in the feed (g).

After SD the hop powders were aliquoted in a glove box system under a nitrogen atmosphere and stored at − 40 °C until analysis.

2.4. Total phenolic content and antioxidant activity of concentrated hop extract (ExC)

The characterization of ExC was performed after dissolution (1:50 w/v) of the ExC in a mixture of ethanol:water:acetic acid at 50:42:8 vol ratio (Ravichai & Muangrat, 2019). This procedure was performed in duplicate.

2.4.1. Total phenolic content (TPC)

Total phenolic content was determined by using the Folin-Ciocalteu assay according to Georgé et al. (2005). Briefly, 600 μL of Folin-Ciocalteu reagent was diluted 1:10 with deionized water and mixed with 120 μL of hop extract opportunely diluted. The mixture was kept in the dark at room temperature for 2 min, and then 960 μL of Na_2CO_3 (7.5 % w/v) was added and incubated at 50 °C for 5 min. The TPC was determined at 760 nm using a spectrophotometer (UV-VIS mod. 6305 Janway, Stone, UK). The calibration curve was made using gallic acid standard solutions at different concentrations ranging between 0 and 100 ppm. Results were expressed as mg GAE g^{-1} of dry matter (dm) of ExC.

The analysis was carried out in triplicate.

2.4.2. Antioxidant capacity (AOC)

AOC was assessed accounting for both antiradical and reducing abilities using respectively the $ABTS^{\bullet+}$ and Ferric Reducing Antioxidant Power (FRAP) assays. The $ABTS^{\bullet+}$ assay was conducted according to Re et al. (1999) without modifications. Briefly, the $ABTS^{+}$ solution was prepared by reacting $ABTS^{+}$ (7 mM) with potassium persulfate (2.45 mM), and this mixture was kept at room temperature for 12–16 h before use. The assay was carried out by mixing 30 μL of the sample opportunity diluted with 2970 μL of $ABTS^{+}$ solution. The mixture was vortexed for 30 s and kept in a dark place for 7 min; thus, the absorbance of

samples was read at 734 nm. A standard curve was plotted by reacting 30 μL of Trolox at different concentrations with 2970 μL of $ABTS^{\bullet+}$ solution (Sarabandi et al., 2019). Results were expressed as Trolox equivalent antioxidant capacity (TEAC, μmol Trolox Eq g^{-1} of dm of ExC).

The FRAP assay was carried out according to Benzie and Strain (1999) without modifications. FRAP reagent that was obtained by mixing acetate buffer 300 mM (pH 3.6), and 10 mM TPTZ (2,4,6-tripyridyl-s-triazine) solubilized in HCl 40 mM and $FeCl_3$ 20 mM, in the ratio 10:1:1. An aliquot of 200 μL of extract opportunely diluted was mixed with 1.3 mL of the FRAP solution, they were mixed and incubated at 37 °C for 30 min. The absorbance was measured at 593 nm. $FeSO_4 \cdot 7H_2O$ standard solutions were used to calibrate the method, and results were expressed as μmol Fe^{2+}Eq g^{-1} of dm of ExC.

Both analyses were carried out in triplicate.

2.5. Determination of α and β-acids in concentrated hop extract (ExC) by high-performance liquid chromatography (HPLC) analysis

The determination of bitter acids in ExC was performed according to the official ASBC Hops-14 method (American Society of Brewing Chemists) by using a chromatographic system (Agilent 1100 series, Agilent, Italy) equipped with a photodiode array detector (DAD; Agilent Technologies, Milan, Italy). The analysis was carried out in triplicate.

2.6. Physical and physico-chemical characterization of microencapsulated hop extracts (MHE)

2.6.1. Water activity, moisture content and solubility

Water activity (a_w) was measured at 25 °C using the hygrometer Aqua Lab 4 TE (Aqua Lab, Decagon Devices Inc, Pullman, WA, USA).

Moisture content was determined gravimetrically at 105 °C until constant weight.

Solubility was performed according to Etzbach et al. (2020) with slight modifications. One g of the sample was mixed with 100 mL of distilled water, then the mixture was stirred for 30 min. The solution was centrifuged at 3000×*g* for 5 min and an aliquot of 4 mL was oven-dried at 105 °C for 24 h. The solubility was calculated as reported in Eq (2).

$$Solubility\ (\%) = \frac{g\ of\ solid\ in\ supernatant \times 25}{g\ of\ sample} \times 100 \quad (2)$$

All determinations were performed in triplicate.

2.6.2. Hygroscopicity and flow properties

The powder's hygroscopicity was determined by the method proposed by Bazaria & Kumar (2017). Briefly, one g of each microencapsulated sample was accurately weighed and placed at 25 °C in a desiccator with NaCl-saturated solution (75.29 % RH). After one week, the samples were weighed, and hygroscopicity was expressed as a weight (g) of adsorbed moisture per 100 g dry solids (g/100 g dm).

Bulk density, tapped density, flowability, and cohesiveness were determined according to Tatasciore et al. (2023).

All determinations were carried out in triplicate.

2.6.3. Colour

The colour of hop powders was determined by a spectrophotocolorimeter Konica Minolta Chroma Meter CR-5 (Konica Minolta, Osaka, Japan) equipped with a target mask with a measured area of 8 mm and with a D65 illuminant. The lightness (L*), hue angle (h°), and chroma (C*) values were evaluated on hop powders. The h° and C* were calculated as follows:

$$h^\circ = arctan\ \frac{b*}{a*} \quad (3)$$

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (4)$$

The results are the means of five repetitions.

2.6.4. Microstructure analysis

The morphology of the samples was analysed by field emission scanning electron microscopy FE SEM LEO 1525 (ZEISS). Each sample was deposited on an aluminium support using conductive carbon adhesive tape. Before the analysis, the samples were metalized with a thin layer of chromium (8 nm). Measurements were carried out using a secondary electron detector at 5 kV.

2.6.5. ATR-fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra analysis was carried out using a Shimadzu IR Spirit Fourier Transform Infrared Spectrophotometer (Kyoto, Japan) with QATR-S single-reflectance attenuated total reflectance (ATR) probe (diamond crystal, incidence angle of 45°).

2.7. Chemical characterization of microencapsulated hop extract (MHE)

Before analysis, 0.180 g of each microencapsulated hop extract and the corresponding controls (only carriers) were dissolved in 3 mL of distilled water by vortexing for 30 s and by using an ultrasound bath (100-Watt, 50 kHz) for 3 min (Tatasciore et al., 2023). These dispersions were used for TPC, AOC and α-acids and β-acids analysis.

2.7.1. Total phenolic content and antioxidant capacity of MHE

An aliquot of 250 μL of each aqueous dispersion was mixed with 250 μL of distilled water and 1 mL of extraction solvent (50:42:8 ethanol: water:acetic acid), vortexed for 30 s, and thus centrifugated for 10 min at 2500×*g* at 10 °C. The supernatant was recovered, opportunely diluted, and used for the TPC, ABTS, and FRAP assays (see sections 2.4.1 and 2.4.2). The same analyses were carried out on control samples to subtract to each sample the response given by interference substances possibly present in the coating material to the spectrophotometric assays. Results were expressed as mg GAE g^{-1} dm of powder for TPC; μmol Trolox Eq g^{-1} dm of powder for ABTS, and μmol Fe^{2+}Eq g^{-1} of dm of hop powder for FRAP assay.

Each analysis was carried out in triplicate.

2.7.2. Encapsulation efficiency (TPC EE) and TPC load yield (TPC Y)

TPC EE represents the percentage of phenolic compounds entrapped within the carrier with respect to the total phenolic content (surface + entrapped) and was carried out as reported by Tatasciore et al. (2023) with slight modifications. Specifically, the surface phenolic content was determined using the Folin-Ciocalteu assay as described in section 2.7.1 on the supernatant collected after resuspending 100 mg of encapsulated hop powder in 1 mL of acetone, vortexing for 1 min, and centrifuging at 2470×*g* for 15 min.

The TPC EE The encapsulation efficiency (TPC EE%) was calculated by applying the following formula (Eq. 5)

$$EE(\%) = \frac{Total\ phenolic\ content\left(\frac{mg\ GAE}{g\ powder}\right) - Surface\ phenolic\ content\left(\frac{mg\ GAE}{g\ powder}\right)}{Total\ phenolic\ content\left(\frac{mg\ GAE}{g\ powder}\right)} \times 100 \quad (5)$$

TPC Y, indicating the amount of total phenolic compound still present in the microencapsulated hop extract after the spray-drying process was determined by applying the following equation (Eq. 6):

$$Y\ (\%) = \frac{Total\ phenolic\ content\left(\frac{mg\ GAE}{g\ powder}\right)}{Calculated\ value\ of\ added\ phenolic\left(\frac{mg\ GAE}{g\ hop\ powder}\right)} \times 100 \quad (6)$$

2.7.3. Determination of α-acids and β-acids in MHE and load yield calculation

The extraction of bitter acids from the MHE aqueous dispersions (see section 2.7) was performed by mixing 0.24 mL of sample with 0.96 mL of pure methanol to reach a methanol concentration of 80 % (v/v). This solvent concentration was selected based on a set of preliminary tests aimed to optimise the methanol:water ratio of the solvent (i.e. 50:50 v/v; 60:40 v/v; 70:30 v/v; 80:20 v/v) (data not shown) to maximise the recovery of these compounds. Thus, the samples were treated by ultrasounds for 30 min and centrifuged at 12000×*g* for 10 min. The supernatants were collected, filtered with a 0.45 μm nylon filter and injected. The HPLC analysis of bitter acids was performed as reported in section 2.5. Equation (6) was used to calculate the load yield of single and total alpha and beta acids.

2.8. Statistical analysis

Data were expressed as mean and standard deviation. Significant differences among all MHE samples were calculated by LSD post hoc test at a level of $p < 0.05$ using STATISTICA for Windows (StatSoftTM, Tulsa, OK, USA) software.

Microencapsulated hop powders' data set was additionally processed by multivariate ANOVA to highlight the single and combined effects of the inlet temperature (T) and wall material (W) on the chemical and physico-chemical properties of hop powder. Effective hypothesis decomposition was further computed. The sigma-restricted coding of effects was used, and for each effect, its sum of squares is the difference between the model sums of squares for all other effects from the whole model sums of squares. As such, the effective hypothesis decomposition sums of squares provide an unambiguous estimate of the variability of predicted values for the outcome uniquely attributable to each effect (Neri et al., 2019). Data were processed using STATISTICA for Windows (StatSoftTM, Tulsa, OK, USA) software.

3. Results and discussion

3.1. Chemical characterization of concentrated hop extract (ExC)

ExC was characterised for the content of polyphenols and bitter acids, and for antioxidant capacity measured by FRAP and ABTS assay.

ExC showed a TPC of about 112 mg GAE g^{-1}. This value was similar to that reported by Wu et al. (2020) for a concentrated hop extract obtained from commercial hop pellets by 55% hydroethanolic extraction and lower than that reported by Tatasciore et al. (2023) on a concentrated hop cones extract. Regarding α-acids, a total content of 27.4 % w/w was found with n + adhumulone (17.8 % w/w) being the main representative homologue followed by cohumulone (9.6% w/w).

For β-acids, a total content of 5.9 % w/w was detected with colupulone (3.5 % w/w) being the most abundant followed by n + adlupulone (2.4%). These concentrations were lower than those reported by Pilna et al. (2015) for a supercritical CO_2 hop pellet extract of the same variety (cv Hercules).

As regards the AOC, ExC showed values of TEAC and FRAP of about 397 μmol Trolox Eq g^{-1} dm and 771 μmol Fe^{2+} g^{-1} dm, respectively; these results are lower than those reported by Mafakheri & Hamidoghli (2015) in 75 % (w/w) ethanolic extract of wild hops and by Önder et al. (2013) in hop cones concentrated extracts. All these differences, compared to the literature findings, could be due to several factors such as the initial concentration of secondary metabolites in hop cones at harvest, as well as different drying, pelletising, and extraction conditions. The comparison between the TEAC and FRAP values of ExC with those reported by Pellegrini et al. (2006) for other categories of spices and herbs generally considered rich sources of antioxidant compounds (e.g. basil, thyme, saffron, oregano, rosemary), highlights the considerable potential of this plant extract as an antioxidant ingredient.

3.2. Spray-drying process efficiency

It is well known that some process variables, such as the characteristics of the liquid feed (composition and corresponding viscosity of the initial dispersion, flow rate) and of the drying air properties (e.g. temperature, pressure) affect both the process efficiency and the chemical and qualitative properties of resulting powders.

In this study, four different carrier formulations and two different inlet temperatures (T_{inlet}) were used to produce the microencapsulated hop extract powders (Table S1).

The outlet temperature and the process yield data obtained for the production of each sample are reported in Table 1.

Process yield ranged between 46 and 77 % with $ExGA_{120}$ and ExMD/βCD_{150} showing the lowest and the highest values, respectively. According to Tonon et al. (2008), higher inlet temperatures determine an increase in the process yield irrespective of sample formulation due to the greater efficiency of heat and mass transfers. Moreover, at equal formulation, the increase of the T_{inlet}, as expected, caused the increase of the T_{outlet}. This parameter is a result of the heat and mass balance in the drying chamber, which in turn is influenced by the T_{inlet} and the feed flow rate. Overall, as the effect of the carrier is concerned, no significant differences were evidenced on T_{outlet} data.

3.3. Physico-chemical properties of powders

3.3.1. Moisture content, water activity, solubility, and hygroscopicity

All microencapsulated powders showed a_w values lower than 0.150, and moisture content lower than 3% which ensure the reduction of microbial risk, enhance their solubility, improve their overall storage stability, and make them well-suited for industrial applications (Dobroslavić et al., 2023).

Solubility is an important quality factor influencing the reconstitution behaviour of microencapsulated extracts and the release of the core material (Dobroslavić et al., 2023). In general, all MHE presented a very high solubility (~99%) (Table 1). These results are higher than those found by Cano-Chauca et al. (2005) on mango juice encapsulated by spray-drying using maltodextrin (DE-20) and gum Arabic. In general, despite its low solubility in water, β-cyclodextrin did not decrease the solubility of the powders, and this result agrees with those observed by Yang et al. (2012) on whey proteins hydrolysate encapsulated by SD using sole maltodextrin or maltodextrin in combination with β-cyclodextrin.

In terms of hygroscopicity, values between 7.5 and 14 g H_2O/100 g of powder were found, with $ExGA_{120}$ and $ExGA_{150}$ showing the lowest and the highest values, respectively. In general, it can be noted that at the equal carrier, samples obtained at T_{inlet} 150 °C showed the highest ($p < 0.05$) hygroscopicity. As already observed for solubility, the nature and composition of the carrier affected hygroscopicity, with a T_{inlet} co-effect. In particular, for βCD, a significant decrease ($p < 0.05$) of hygroscopicity was evidenced when it was coupled with MD at both T_{inlet} and when it was used in combination with GA at T_{inlet} 150 °C. As explained by Yang et al. (2012), these results could be due to the higher hydrophobicity of βCD compared to the other investigated wall materials.

Data related to solubility, and hygroscopicity were analysed by multifactorial ANOVA (Table 2) and effective hypothesis decomposition (data not shown) analyses. Results highlight a significant effect ($p < 0.001$) on hop powders hygroscopicity for the individual W and T_{inlet} factors, where $T_{inlet} > W$, and of their interaction ($W \times T_{inlet}$) ($p < 0.001$). As concerns the solubility, it was significantly influenced ($p < 0.001$) by the individual T_{inlet} factor, and the combined $W \times T_{inlet}$ factor ($p < 0.001$), whilst the effect of W was not significant ($p > 0.05$).

3.3.2. Bulk density, tapped density, flowability, and cohesiveness

Bulk density, tapped density, flowability (Carr Index, CI), and cohesiveness (Hausner ratio, HR) of hop powders are reported in

Table 1
Process parameters and physico-chemical properties of the differently microencapsulated hop extract (MHE).

	$ExMD_{120}$	$ExMD/\beta CD_{120}$	$ExGA_{120}$	$ExGA/\beta CD_{120}$	$ExMD_{150}$	$ExMD/\beta CD_{150}$	$ExGA_{150}$	$ExGA/\beta CD_{150}$
Outlet temperature (°C)	$74.7^{b} \pm 1.2$	$72.3^{bc} \pm 0.6$	$73.7^{bc} \pm 1.2$	$71.3^{c} \pm 1.5$	$91.0^{a} \pm 1.0$	$89.7^{a} \pm 1.2$	$92.7^{a} \pm 2.1$	$91.3^{a} \pm 0.6$
Process yield (%)	$63.9^{c} \pm 1.7$	$46.4^{f} \pm 2.9$	$66.5^{bc} \pm 3.1$	$58.3^{d} \pm 1.8$	$69.5^{b} \pm 2.6$	$52.4^{e} \pm 2.1$	$77.2^{a} \pm 1.7$	$68.1^{b} \pm 2.5$
Solubility (%)	$99.1^{a} \pm 0.0$	$98.8^{ab} \pm 0.1$	$99.0^{bc} \pm 0.0$	$99.0^{bc} \pm 0.0$	$99.0^{d} \pm 0.1$	$99.0^{cd} \pm 0.2$	$99.1^{ab} \pm 0.0$	$99.0^{cd} \pm 0.0$
Hygroscopicity (g H_2O/100 g dm)	$9.6^{d} \pm 0.3$	$7.9^{e} \pm 0.0$	$7.5^{e} \pm 0.3$	$9.5^{d} \pm 0.2$	$10.1^{c} \pm 0.1$	$9.4^{d} \pm 0.4$	$14.0^{a} \pm 0.5$	$11.5^{b} \pm 0.3$
Bulk density (g mL^{-1})	$0.25^{c} \pm 0.00$	$0.23^{d} \pm 0.00$	$0.26^{bc} \pm 0.01$	$0.27^{a} \pm 0.00$	$0.26^{b} \pm 0.00$	$0.18^{e} \pm 0.00$	$0.27^{a} \pm 0.00$	$0.26^{b} \pm 0.08$
Tapped density (g mL^{-1})	$0.36^{a} \pm 0.00$	$0.32^{d} \pm 0.01$	$0.33^{c} \pm 0.01$	$0.32^{cd} \pm 0.00$	$0.35^{b} \pm 0.01$	$0.19^{f} \pm 0.00$	$0.34^{b} \pm 0.00$	$0.29^{e} \pm 0.00$
Carr Index (CI)	$30.4^{a} \pm 1.0$	$27.5^{b} \pm 0.5$	$21.3^{cd} \pm 0.5$	$15.5^{e} \pm 1.9$	$23.9^{c} \pm 2.2$	$7.26^{f} \pm 2.3$	$21.1^{d} \pm 0.0$	$8.04^{f} \pm 2.5$
Hausner Ratio (HR)	$1.44^{a} \pm 0.33$	$1.38^{b} \pm 0.01$	$1.27^{d} \pm 0.01$	$1.18^{e} \pm 0.03$	$1.32^{c} \pm 0.04$	$1.08^{f} \pm 0.03$	$1.26^{d} \pm 0.01$	$1.09^{f} \pm 0.03$
Lightness (L*)	$89.9^{a} \pm 0.2$	$89.1^{a} \pm 0.2$	$82.7^{d} \pm 0.4$	$84.2^{c} \pm 0.6$	$88.4^{b} \pm 0.3$	$88.4^{b} \pm 0.3$	$82.2^{d} \pm 0.4$	$83.7^{c} \pm 0.8$
Chroma (C*)	$21.3^{e} \pm 0.3$	$23.8^{cd} \pm 0.8$	$19.1^{g} \pm 0.3$	$23.6^{d} \pm 0.6$	$24.2^{bc} \pm 0.5$	$24.4^{b} \pm 0.3$	$20.4^{f} \pm 0.2$	$25.1^{a} \pm 0.5$
Hue angle (h°)	$101.3^{b} \pm 0.3$	$102.3^{a} \pm 0.4$	$97.5^{f} \pm 0.2$	$99.8^{d} \pm 0.3$	$100.4^{c} \pm 0.3$	$101.6^{b} \pm 0.1$	$96.8^{g} \pm 0.3$	$98.9^{e} \pm 0.4$

Ex: hop extract; MD: Maltodextrin; GA: gum Arabic; βCD: beta cyclodextrin; 150 and 120 in subscript stand for inlet temperatures. Data on rows with different letters are statistically different at p level <0.05. Different letters are significantly different by the LSD-test at the 95% level of significance.

Table 2
Multifactorial analysis of variance (MANOVA) of the individual and interactive effects of wall material (W) and inlet temperature (T_{inlet}) of chemical and physicochemical properties of hop powders.

	F		
	W	T_{inlet}	W × T_{inlet}
Solubility	n.s.	17***	11***
Hygroscopicity	62***	497***	117***
Bulk density	313***	37***	74***
Tapped density	363***	330***	166***
Carr Index (CI)	96***	167***	40***
Hausner ratio (HR)	108***	195***	40***
Lightness (L)*	614***	23***	n.s.
Chroma (C*)	201***	111***	11***
Hue angle (h°)	477***	70***	n.s.
Total polyphenols content (TPC)	104***	77***	71***
Encapsulation efficiency (EE)	618***	281***	306***
Cohumulone	137***	22***	260***
n + adhumulone	141***	23***	211***
Total α-acids	139***	23***	228***
Colupulone	47***	n.s.	73***
n + adlupulone	67***	5*	82***
Total β-acids	98***	n.s.	138***
Ferric reducing antioxidant power	134***	n.s.	21***
ABTS radical scavenging activity	36***	n.s.	19***

*p < 0.05; **p < 0.01; ***p < 0.001; n.s. not significant.

Table 1. Bulk density values ranged between 0.180 and 0.270 g mL^{-1} with $ExMD/\beta CD_{150}$ and $ExGA/\beta CD_{120}$ samples showing the lowest and the highest values, respectively. These values are similar to those reported by Nadeem et al. (2011) on spray-dried mountain tea (*Sideritis stricta*) encapsulated with MD, GA and βCD. The T_{inlet} differently affected ($p < 0.05$) the bulk density of the hop powders depending on the carrier composition. In particular, the bulk density of samples formulated with sole MD and GA increased with the increase of the T_{inlet}.

Flowability, expressed as Carr index (CI), is the relative movement of the particles between themselves or along the surface of a vessel wall, while cohesiveness, measured as a Hausner Ratio (HR) is an internal property of the powder indicating the retentive forces of the particle together. The lower the Carr index and Hausner ratio, the better the flow, and the less cohesive the powder (Hadree et al., 2023). The CI of the hop powders ranged from about 7% to 30% and the HR between 1.08 and 1.44 with $ExMD/\beta CD_{150}$ and $ExMD_{120}$ showing the lowest and the highest values, respectively (Table 1). Hop powders showed diverse flowability and cohesiveness depending on the T_{inlet} and carrier formulation used. Regarding T_{inlet}, it had a positive influence on both the overmentioned physical parameters, except for the ExGA samples in agreement with findings reported by Hadree et al. (2023). The presence of βCD significantly decreased the HR and CI of the microencapsulated hop powder, i.e., increased the flowability and decreased the cohesiveness.

Data of bulk and tapped density, cohesiveness, and flowability were computed by multifactorial ANOVA (Table 2) and effective hypothesis decomposition analyses (data not shown). The results showed a significant effect ($p < 0.001$) of both the individual W and T_{inlet} factors, as well as their interaction (W × T_{inlet}) ($p < 0.001$) on all the mentioned physical properties.

3.3.3. Colour

The lightness (L*), chroma (C*) and hue angle (h°) of the differently microencapsulated hop powders are reported in Table 1. Overall, samples showed h° values ranging between 97 and 102, and L* and C* varying between 82 and 90, and 19 and 25, respectively. In general, MD-based powders resulted more yellow, brighter and with a higher chroma than powders made with GA, which, in turn, were greenish, darker, and less saturated colour. The mixing of both MD and GA with βCD, slightly increased h° while L* and C* parameters varied depending on the carrier composition and the T_{inlet}. By comparing the samples produced using the same carrier but different spray-drying T_{inlet}, it can be observed that, in general, those obtained at T_{inlet} 150 °C presented h° and C* values respectively higher and lower than those obtained at T_{inlet}120 °C.

In general, the differences in the colour of the powders are influenced by the different colourimetric properties of the carrier materials themselves (Tatasciore et al., 2023).

The effect of W and T_{inlet} factors on the colorimetric characteristics of powder was analysed by multivariate ANOVA (Table 2) and effective hypothesis decomposition analyses (data not shown) and a significant ($p < 0.001$) effect of single W and T_{inlet} factors was observed, with W > T_{inlet}. The combined effect of W × T_{inlet} had a significant effect ($p < 0.01$) only on the C* parameter.

3.4. Particle morphology

In Fig. 2 the SEM micrographs of the differently microencapsulated hop powders are shown and compared with the corresponding control samples (i.e. wall materials spray-dried without hop extract).

It can be observed that irrespective of the feed composition and the operating temperature, powders are composed of microparticles of variable diameter (2–10 μm) showing typical morphologies of polymeric spray-dried powders appearing as shrivelled spheres (Di Battista, Constenla, Ramírez-Rigo & Piña, 2015) characterized by numerous and large concavities formed during the rapid evaporation of the liquid droplets. The outer surfaces of the dry particles were free of cracks and disruptions which suggests a good film-forming ability of the carrier materials. By comparing the hop powders to the respective control samples, a very notable difference in the particles' morphology was observed. More specifically, microencapsulated hop extract particles were more crumpled, and characterized by more numerous, larger, and deeper concavities. This result could be due to a decrease in the evaporation rate of water during the drying process due to the hydrophobic nature of ExC (Tatasciore et al., 2023; Nadeem et al., 2011).

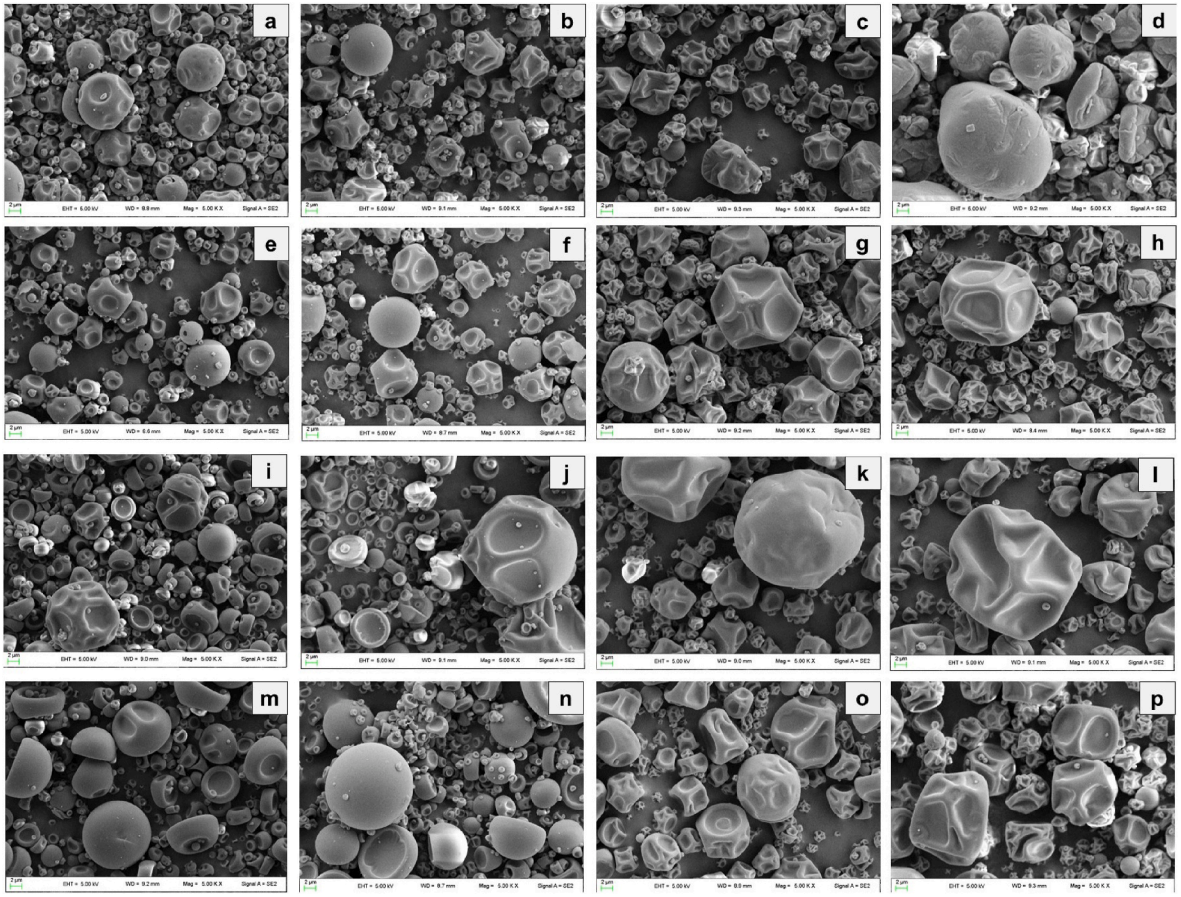

Fig. 2. Micrographs of different microencapsulated hop extracts. In detail: a) MD_{120}; b) MD_{150}; c) $ExMD_{120}$; d) $ExMD_{150}$; e) MD/βCD_{120}; f) MD/βCD_{150}; g) ExMD/βCD_{120}; h) ExMD/βCD_{150}; i) GA_{120}; j) GA_{150}; k) $ExGA_{120}$; l) $ExGA_{150}$; m) GA/βCD_{120}; n) GA/βCD_{150}; o) GA/βCD_{120}; p) GA/βCD_{150} where Ex: hop extract; MD: Maltodextrin; GA: gum Arabic; βCD: β-cyclodextrin; 120–150 in subscript stands for inlet temperature.

By comparing the differently formulated hop powders, it can be noted that irrespective of the T_{inlet}, those produced with GA showed a more continuous structure and a smoother surface than those containing MD. According to Tatasciore et al. (2023), this result could be due to the higher emulsifying properties of GA than MD. The different surface morphology could explain the higher flowability and lower cohesiveness of ExGA powders compared to the ExMD ones. The T_{inlet} and the use of βCD did not affect the particle morphology.

3.5. ATR-Fourier transform infrared spectroscopy (ATR-FTIR)

FT-IR spectra of the wall materials (GA, MD, MD/βCD, and GA/βCD), hop extract (ExC), different MHE (ExMD, ExGA, ExMD/βCD, and ExGA/βCD) produced at two inlet temperatures (120 °C and 150 °C) were obtained to evaluate the characteristics of the different wall materials and their interactions with the hop extract (Figs. 3–5).

Hop extract (Fig. 3) showed three absorption bands between 2800 and 3000 cm^{-1} associated with C–H stretching vibrations in aliphatic and aromatic compounds, and a shoulder band at 3330 cm^{-1} due to O–H stretching in agreement with Masek et al. (2014). The aromatic structures were confirmed by the C═C skeleton vibration bands between 1300 and 1600 cm^{-1}. Between 1050 and 1200 cm^{-1} the stretching absorption band of C–O for phenols was observed, while in the region between 1100 and 985 peaks from carbohydrates and vibrational frequency of the CH_2OH groups of carbohydrates were noted (Masek et al., 2014).

As concerns the wall materials (Fig. 4), both GA_{120} and GA_{150} showed absorption bands from 3200 to 3500 cm^{-1} (O–H stretching), at 2910 cm^{-1} (C–H stretching from the carboxylic group), 1608 cm^{-1}

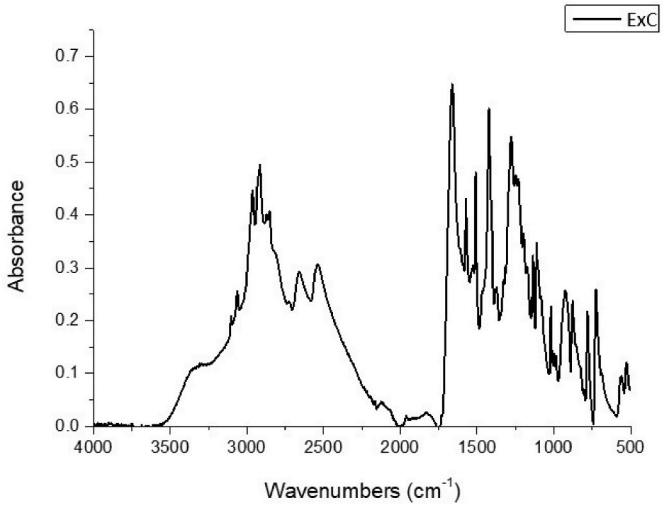

Fig. 3. ATR-FTIR spectra of concentrated hop extract (ExC).

(C═O stretching or N–H bending), 1404 cm^{-1} (CH_3 bending and C–H bending), and 1041 cm^{-1} (C–O stretching), and this result is similar to Chew et al. (2018). Comparing the FTIR spectra of GA and GA/βCD samples, a shift of the OH stretching peak (Fig. 4b–c) was observed and associated to the perturbation of hydrogen bonds, and of C═O stretching and N–H bending peaks (Fig. 4d–e). Moreover, the GA/βCD spectra highlighted an increase of the shoulder at 1350 due to an increase of

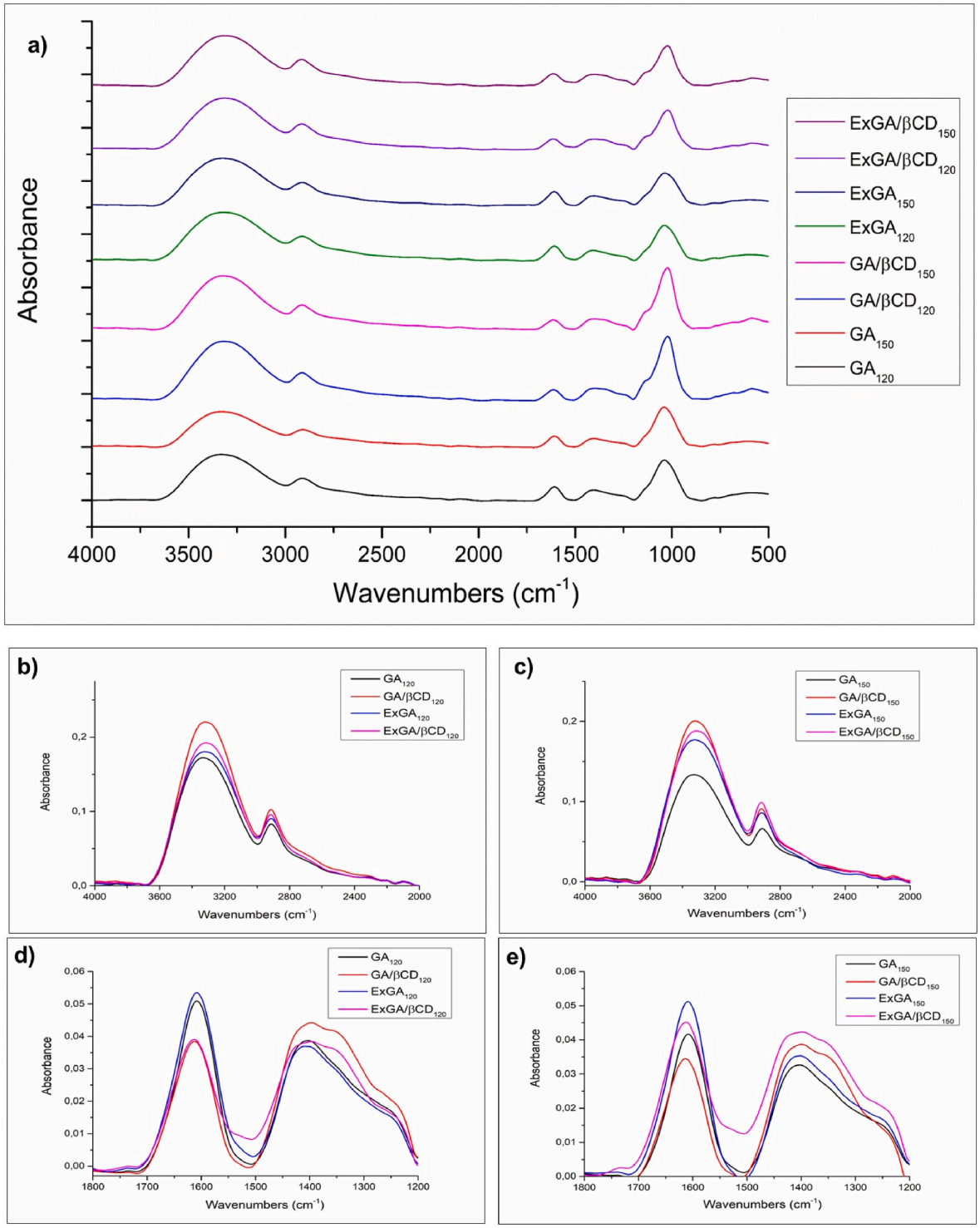

Fig. 4. ATR-FTIR spectra of differently microencapsulated hop extracts and their respective control samples between 4000 and 500 cm^{-1} (a); spectra region between 4000 and 2000 cm^{-1} (b, c); spectra region between 1800 and 1200 cm^{-1} (d, e). Ex: hop extract; GA: gum Arabic; βCD: β-cyclodextrin; 150-120 in subscript stands for inlet temperatures.

O–H bending. In both ExGA and ExGA/βCD samples, the presence of the extract determined a shift of the OH stretching bands toward lower frequencies. This effect can be ascribed to the interaction between the wall materials and the components of the hop extract through the formation of hydrogen bonds. In samples containing βCD, this interaction was more pronounced in $ExGA/\beta CD_{150}$ and it is possibly ascribed to the inclusion of hydrophobic hop compounds into the cyclodextrin hydrophobic cavity (Crupi et al., 2007). Conversely, the peak associated with C–H stretching was not disturbed by changes in the composition of the mixture.

Spectra of MD_{120} and MD_{150} (Fig. 5) showed characteristic absorption bands at 3320 cm^{-1} (O–H stretching), 2925 cm^{-1} (C–H stretching from the carboxylic group), 1644 cm^{-1} (C═O stretching), 1352 cm^{-1} (O–H bending), and 1150 cm^{-1}, 1078 cm^{-1}, 1001 cm^{-1} (C–O stretching and C–O –H bending), according to what reported by Kang et al. (2019).

Comparing the FTIR spectra of the MD and MD/βCD mixture, a slight

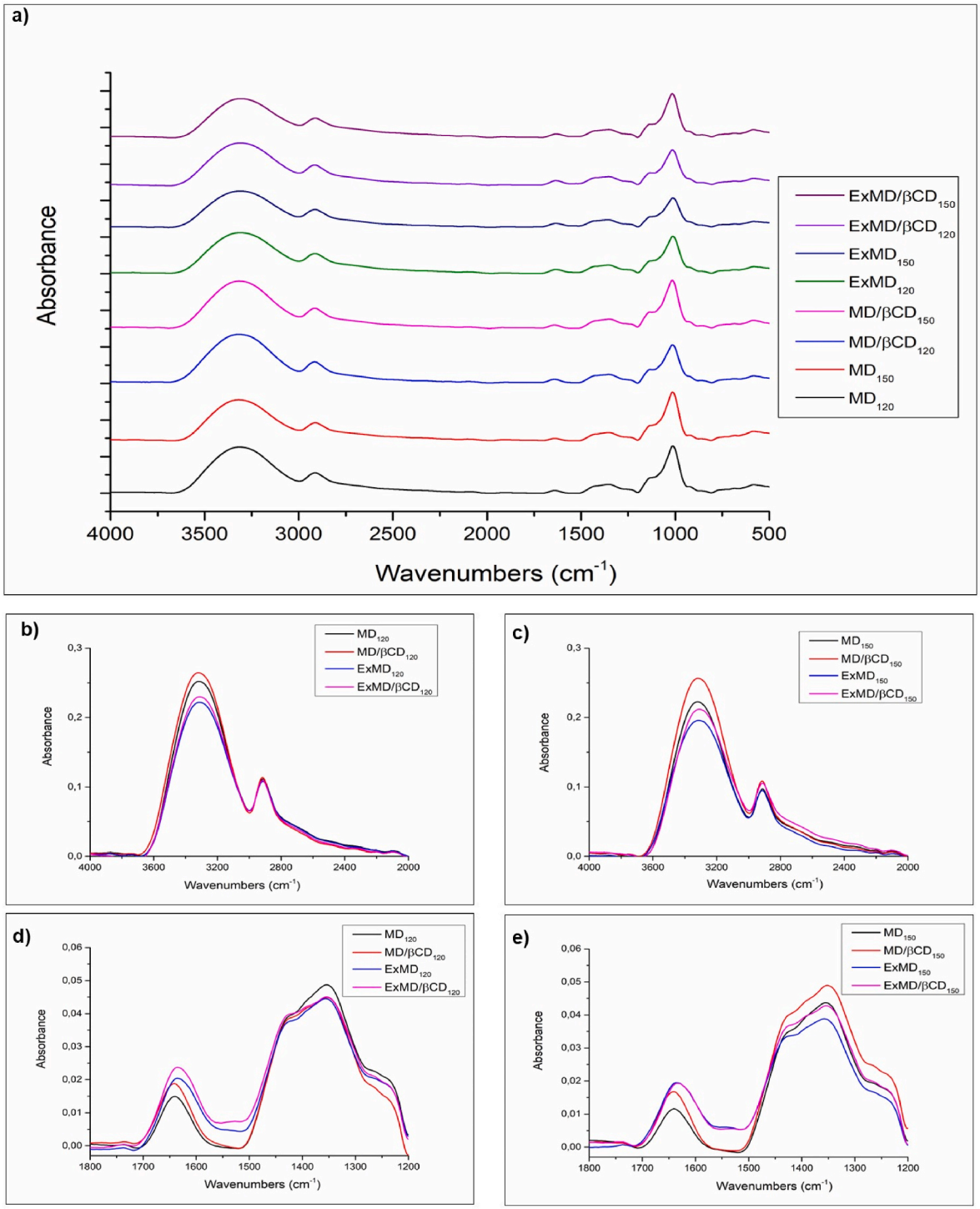

Fig. 5. ATR-FTIR spectra of differently microencapsulated hop extracts and their respective control samples between 4000 and 500 cm^{-1} (a); spectra region between 4000 and 2000 cm^{-1} (b, c); spectra region between 1800 and 1200 cm^{-1} (d, e). Ex: hop extract; MD: Maltodextrin; βCD: beta-cyclodextrin; $_{150\text{-}120}$ in subscript stands for inlet temperatures.

shift of the OH stretching peak (Fig. 5b) and C═O stretching band (Fig. 5d) was noted but only to the spray-dried powders at T_{inlet} 120 °C. When the hop extract was used (ExMD and ExMD/βCD samples a shift of both the OH stretching peak and C═O stretching band toward lower frequencies due to the formation of hydrogen bonds occurred. These results again highlight the interaction between the wall materials and the components of the hop extract and, for samples containing βCD, the possible formation of inclusion complexes.

As for samples containing gum Arabic, the peaks associated with C–H stretching were not disturbed by the components of the hop extract.

3.6. Chemical characterization of encapsulated hop extracts

3.6.1. Total phenolic content (TPC), TPC yield (Y), TPC encapsulation efficiency (EE)

In Fig. 6 the TPC (a), TPC Y (insert in Fig. 6a), and TPC EE (b) of the different hop powders are shown. TPC ranged from 4.7 mg GAE g^{-1} to 10.5 mg GAE g^{-1} with $ExGA_{120}$ and $ExMD_{150}$ showing the lowest and

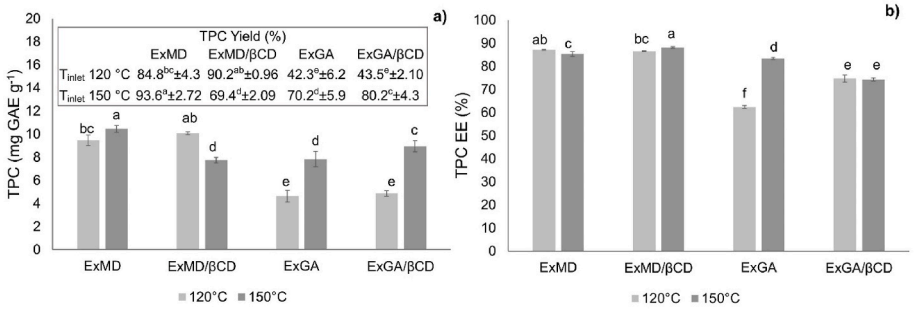

Fig. 6. TPC: Total phenolic content (a); total phenolic content yield (insert a); TPC EE: polyphenol encapsulation efficiency (b). Different letters are significantly different by the LSD-test at the 95% level of significance. Ex: hop extract; MD: Maltodextrin; GA: gum Arabic; βCD: β-cyclodextrin.

highest values, respectively.

At equal carrier type, powders produced at T_{inlet} 150 °C generally showed a higher phenolic compounds retention (insert Fig. 6a) than those at T_{inlet} 120 °C, and consequently, the highest TPC. Similar results were also observed by Chong and Wong (2017) who studied the effect of spray dryer inlet temperature on the total phenolic content of Sapodilla fruit (*Manilkara zapota*) powder, and could be ascribed to the faster drying process occurring at the highest inlet temperatures, which cause shorter exposure time and consequently, a lower degradation of the heat-sensitive phenolic compounds.

As regards the effect of the carrier composition, it can be noted that irrespective of the spray-drying T_{inlet}, the powders produced solely with MD presented higher TPC values compared to those made of the GA alone. This result is in accordance with what was observed by Sarabandi et al. (2019), who encapsulated eggplant peel extract using MD and GA as wall materials. As regards the βCD, it showed a positive effect on the retention and content of phenolic compounds ($p < 0.05$) only when it was used in combination with GA and when spray-drying was performed with T_{inlet} 150 °C. As highlighted by ATR-FT-IR analysis, this result could be ascribed to the inclusion and protection of some prenylated flavonoids into the cyclodextrin hydrophobic cavity.

The total phenolic compounds encapsulation efficiency (TPC EE) of the powders (Fig. 6b) ranged from 62 to 88% with samples $ExGA_{120}$ and $ExMD/\beta CD_{150}$ showing the lowest and the highest values, respectively.

Comparing these data with those obtained by Tatasciore et al. (2023) (64–79%) on microencapsulated hop extracts by freeze-drying with the same carriers, it can be concluded that spray-drying technology, under optimized conditions, can represent a valuable alternative to the expensive and time-consuming technique commonly adopt for the encapsulation of thermosensitive compounds. The T_{inlet} differently influenced ($p < 0.05$) the TPC EE depending on the type of carrier used, while regarding the effect of the carrier material, the highest encapsulation efficiency values were achieved with MD, according to other authors (Tatasciore et al., 2023; Ballesteros et al., 2017). βCD differently influenced the TPC EE depending on the T_{inlet} and the carrier material to which it was mixed. More specifically, it showed a positive effect ($p < 0.05$) when used in combination with MD and spray dried at T_{inlet} 150 °C, or mixed with GA and spray dried at T_{inlet} 120 °C. These results point out a strict dependence of TPC EE on both the process temperature and wall material, corroborating the findings reported in other studies (Marcillo Parra, Tupuna-Yerovi, González & Ruales, 2021).

The effect of W and T_{inlet} factors on TPC, TPC EE was also analysed by multifactorial ANOVA (Table 2) and hypothesis decomposition analyses (Fig. 7), which pointed out a significant effect ($p < 0.001$) of W and T_{inlet} factors, with $W > T_{inlet}$, and of $W \times T_{inlet}$ ($p < 0.001$) on all the investigated parameters.

3.6.2. α and β acids content and yield

The total and single content of α-and β-acids and the corresponding yield (see inserts) of the hop powders are reported in Fig. 8.

It can be observed that among the investigated samples, $ExGA_{150}$ showed the highest retention and, consequently, the highest content of the detected bitter acids, while the samples $ExGA/\beta CD_{150}$ and $ExMD_{120}$ showed the lowest one.

The T_{inlet} showed a positive effect on α-acids (Fig. 8a-8b-8c) and β-acids (Fig. 8d-8e-8f) content only on samples formulated with MD or GA alone. βCD enhanced ($p < 0.05$) the retention and content of α-acids in all the hop powders except for $ExGA/\beta CD_{150}$. For β-acids, this positive effect was observed only at T_{inlet} 120 °C. In agreement with the ATR-FT-IR data, these results could be ascribed to the formation of inclusion complexes between bitter acids and βCD.

The results of the MANOVA (Table 2) and effective hypothesis decomposition (Fig. 9) analyses on bitter acids data showed a significant effect ($p < 0.001$) of both W and T_{inlet}, where $W > T_{inlet}$, and of their combined effect ($W \times T_{inlet}$) for cohumulone, n + adhumulone, and total α-acids content. As regards β-acids, a significant ($p < 0.001$) effect of both W and $W \times T_{inlet}$ factors, ($p < 0.001$) was observed on colupulone, n + adlupulone and total β-acids content; conversely, the individual T_{inlet} factor had a significant effect ($p < 0.05$) only on n + adlupulone content (Table 2).

To the author's knowledge, the lack of literature studies on the encapsulation of α and β acids makes difficult the comparison of the

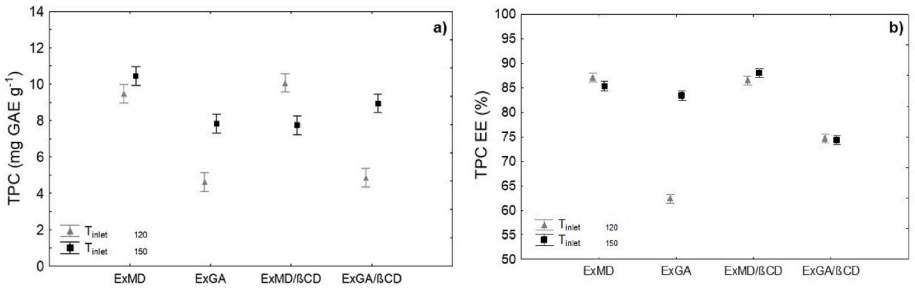

Fig. 7. Effective hypothesis decomposition of factorial ANOVA for the combined effects of wall material (W) × inlet temperature (T_{inlet}) on TPC (a) and TPC EE (b) data. Vertical bars denote 95% confidence. Ex: hop extract; MD: Maltodextrin; GA: gum Arabic; βCD: β-cyclodextrin.

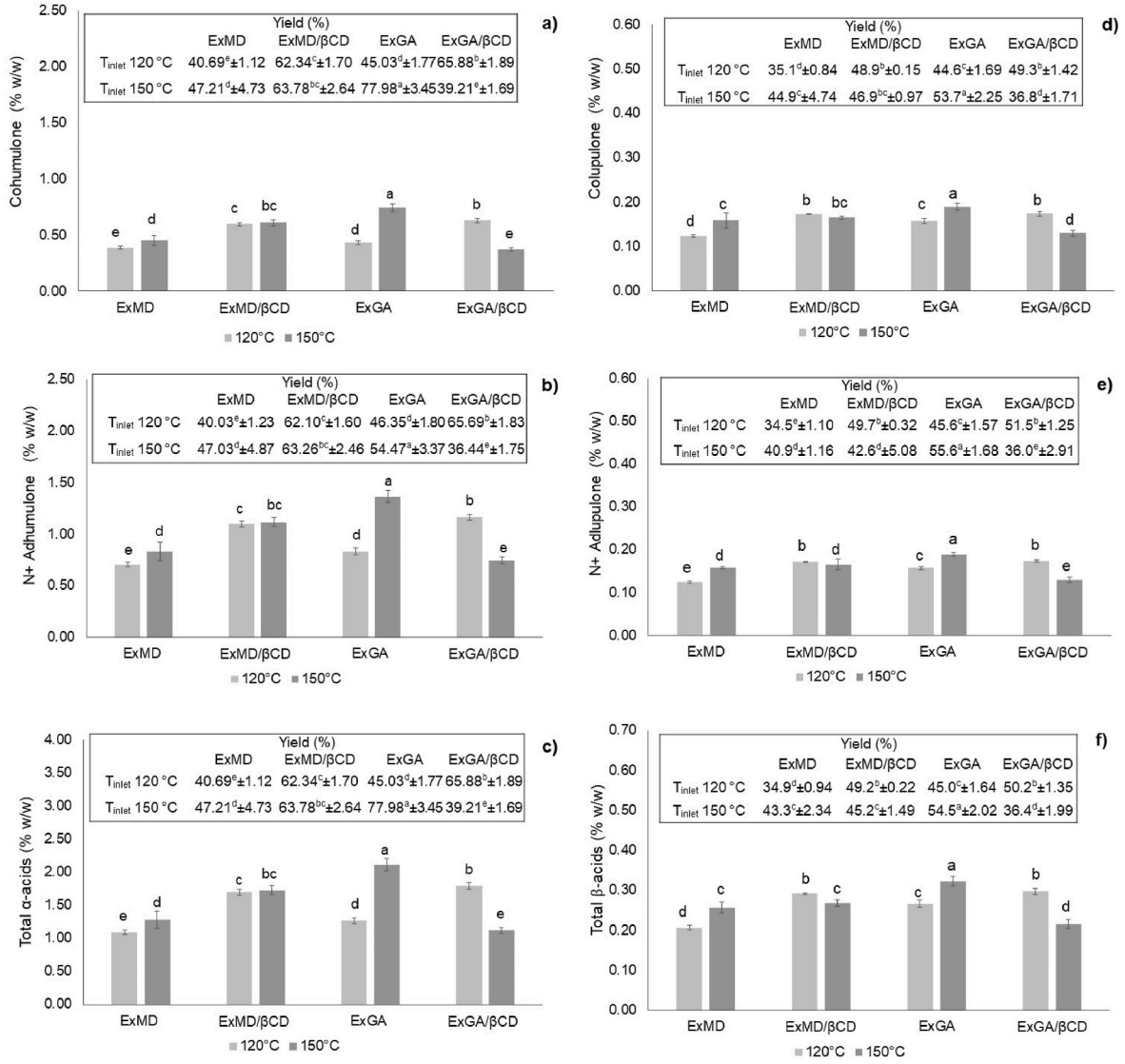

Fig. 8. Cohumulone content (a); Cohumulone yield (insert a); N + Adhumulone content (b); N + Adhumulone yield (insert b); Total α-acids content (c); Total α-acids yield (insert c); Colupulone content (d); Colupulone yield (insert d); N + Adlupulone content (e); N + Adlupulone yield (insert e); Total β-acids content (f); Total β-acids yield (insert f). Different letters are significantly different by the LSD-test at the 95% level of significance. Ex: hop extract; MD: Maltodextrin; GA: gum Arabic; βCD: β-cyclodextrin.

results obtained in this study with current literature data.

3.6.3. *Antioxidant capacity of hop powders*

In Fig. 10, data related to the antioxidant capacity (AOC) of the MHE tested by FRAP (a) and ABTS (b) assays and their respective results of effective hypothesis decomposition analysis (Fig. 11) are reported.

Results of the FRAP assay of MHE (Fig. 10a) showed values ranging between 84 and 144 μmol Fe^{2+}Eq g^{-1} with $ExGA_{120}$ and $ExGA/\beta CD_{150}$ presenting the lowest and the highest values, respectively. Regarding the scavenging capacity against $ABTS^{\bullet+}$ (Fig. 10b), values ranging between 48 and 87 μmol Trolox g^{-1} were obtained with $ExGA_{150}$ and $ExGA/\beta CD_{150}$ having respectively the lowest and the highest AOC. Overall, irrespective of the method of analysis used, the AOC of the powders turns out dependent on both the carrier formulation and T_{inlet}. Noteworthy is the effect of βCD that, when added to the formulation, caused a significant AOC increase ($p < 0.05$) in all the samples except for $ExMD/\beta CD_{150}$.

The different results obtained by ABTS and FRAP assay could be due to the different mechanisms of action of the two assays towards polyphenols (e.g. xanthohumol and isoxanthohumol), bitter acids and other antioxidant compounds (e.g., chlorophylls, carotenoids) generally found in hop concentrated extracts (Popoola et al., 2015; Kontek et al., 2021; Santarelli et al., 2021; Santarelli et al., 2023) or their oxidation products possibly produced during the spray-drying process, as well as due to their possible interactions with the coating/carrier materials (Nilsson et al., 2005).

Multifactorial ANOVA analysis (Table 2) and effective hypothesis decomposition were carried out on AOA data. No significant effect ($p > 0.05$) for the T_{inlet} factor was evidenced; conversely, the single W factor, and the interaction W × T statistically influenced ($p < 0.001$) the AOC of the powders (Table 2 and Fig. 11).

4. Conclusion

The experimental results show that spray-drying can be successfully used to encapsulate hop extract and that different process conditions and carriers affect the composition of hop microencapsulated powders leading to hop products with different chemical and physicochemical properties.

Spray-drying T_{inlet} influenced the physicochemical properties of

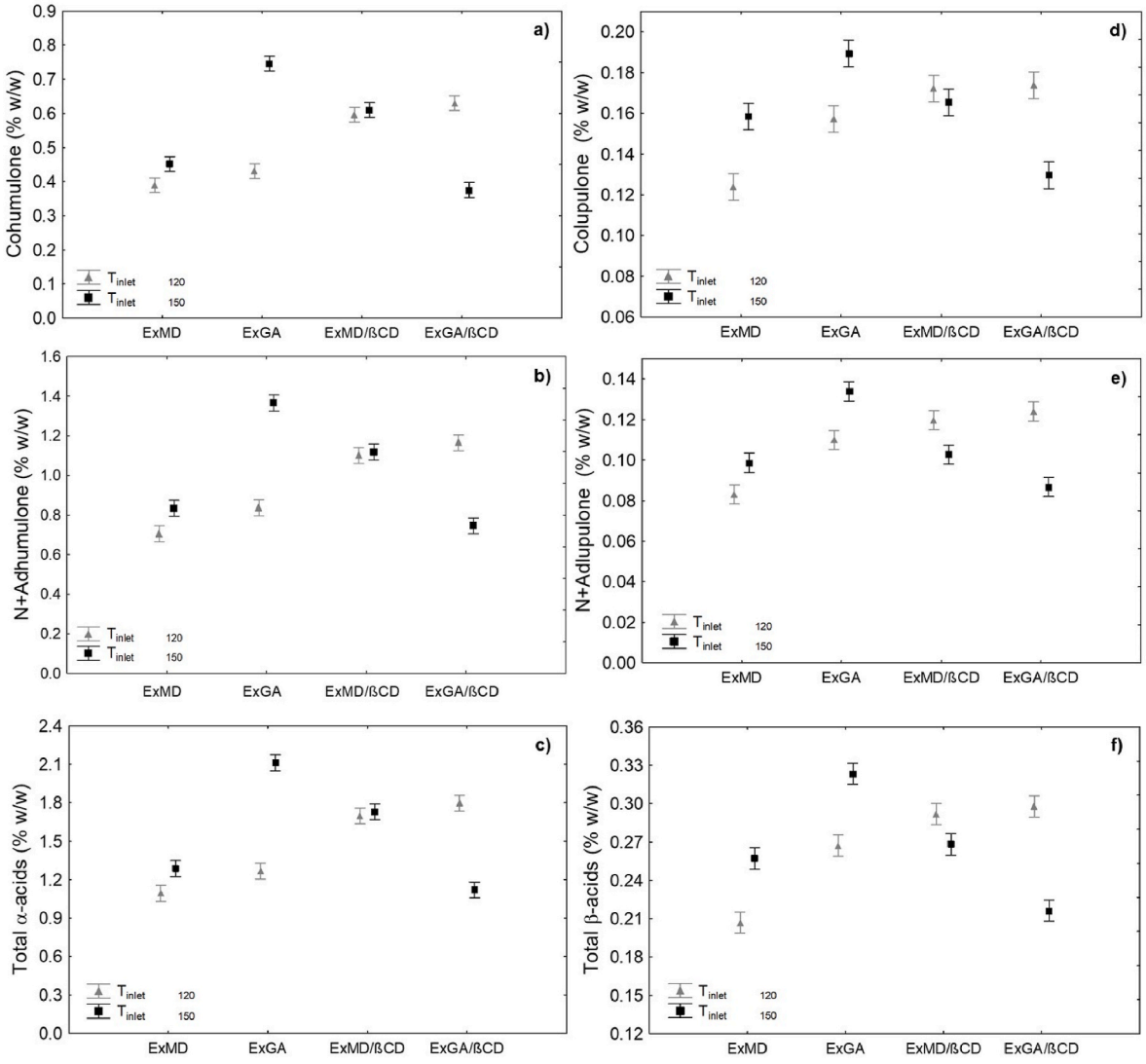

Fig. 9. Effective hypothesis decomposition of factorial ANOVA for the combined effects of wall material (W) × inlet temperature (T_{inlet}) on Cohumulone content (a); N + Adhumulone content (b); Total α-acids content (c); Colupulone content (d); N + Adlupulone content (e); Total β-acids content (f). Vertical bars denote 95% confidence. Ex: hop extract; MD: Maltodextrin; GA: gum Arabic; βCD: β-cyclodextrin.

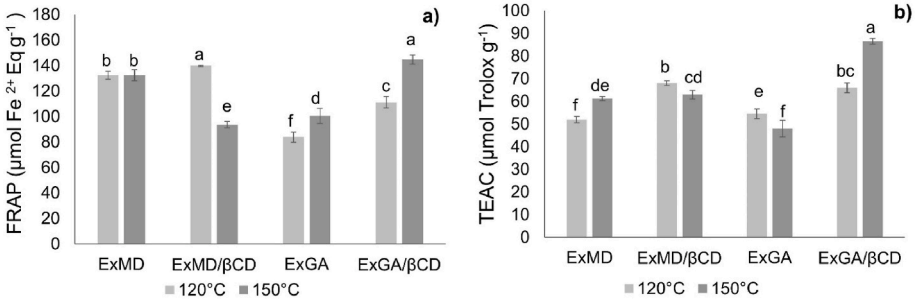

Fig. 10. FRAP: Ferric reducing antioxidant power (a); TEAC: Trolox equivalent antioxidant capacity (b). Different letters are significantly different by the LSD-test at the 95% level of significance. Ex: hop extract; MD: Maltodextrin; GA: gum Arabic; βCD: β-cyclodextrin.

powders, the content and encapsulation of phenolic compounds, and the α-acid content whilst it had no effect on the colupulone and total β-acids content and on the antioxidant capacity. The use of MD and GA as wall material, in single or in combination with βCD significantly affected the process yields and all the investigated chemical and physico-chemical parameters except for the solubility. In particular, the presence of MD in the formulation positively affected the process yield and generally led to high TPC and TPC EE values. When βCD was added to the formulation, a positive effect was observed only for α-acids content while a combined effect between carrier and T_{inlet} was observed for the other physicochemical parameters. These results suggest that the choice of the carrier and process parameters must be made based on the desired

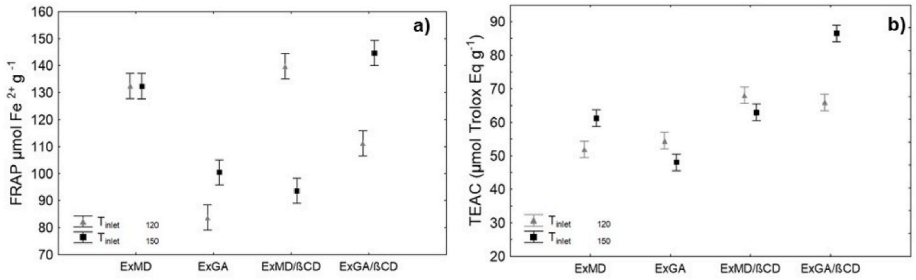

Fig. 11. Effective hypothesis decomposition of factorial ANOVA for the combined effects of wall material (W) × inlet temperature (T_{inlet}) on FRAP (a) and ABTS (b) data. Vertical bars denote 95% confidence. Ex: hop extract; MD: Maltodextrin; GA: gum Arabic; βCD: β-cyclodextrin.

physical properties and chemical characteristics of the resulting hop-based ingredient.

To the authors' knowledge, this study could be of main relevance as the basis for the scaling up, development and production of new hop-based ingredients. Further investigations will be focused on the evaluation of the storage stability of MHEs as well as their techno-functional, sensory and functional properties in model and real food systems in order to assess their possible use as natural ingredients/additives in food formulations and products.

CRediT authorship contribution statement

Simona Tatasciore: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Veronica Santarelli:** Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Lilia Neri:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Carla Daniela Di Mattia:** Methodology, Formal analysis, Writing – review & editing. **Alessandro Di Michele:** Investigation, Writing – original draft, Writing – review & editing. **Dino Mastrocola:** Conceptualization. **Paola Pittia:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition, All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

Data availability

Data will be made available on request.

Acknowledgements

This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy – VITALITY.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2024.100769.

References

American Society of Brewing Chemists (ASBC). Methods of Analysis, Hops-1 Sampling (International Method) .

American Society of Brewing Chemists (ASBC). Methods of Analysis, Hops-14 α-Acids and β-acids in Hops and Hop Extracts by HPLC. (International Method).

Asioli, D., Aschemann-Witzel, J., Caputo, V., Vecchio, R., Annunziata, A., Næs, T., Varela, P., 2017. Making sense of the "clean label" trends: a review of consumer food choice behavior and discussion of industry implications. Food Res. Int. 99, 58–71.

Ballesteros, L.F., Ramirez, M.J., Orrego, C.E., Teixeira, J.A., Mussatto, S.I., 2017. Encapsulation of antioxidant phenolic compounds extracted from spent coffee grounds by freeze-drying and spray-drying using different coating materials. Food Chem. 237, 623–631.

Bazaria, B., Kumar, P., 2017. Effect of dextrose equivalency of maltodextrin together with Arabic gum on properties of encapsulated beetroot juice. J. Food Meas. Char. 11 (1), 156–163.

Benzie, I.F.F., Strain, J.J., 1999. Ferric reducing/antioxidant power assay: direct measure of total antioxidant activity of biological fluids and modified version for Simultaneous measurement of total antioxidant power and ascorbic acid concentration. Methods Enzymol. 299, 15–27.

Cano-Chauca, M., Stringheta, P.C., Ramos, A.M., Cal-Vidal, J., 2005. Effect of the carriers on the microstructure of mango powder obtained by spray drying and its functional characterization. Innovative Food Sci. Emerging Technol. 6 (4), 420–428.

Carbone, K., Gervasi, F., 2022. An updated review of the genus Humulus: a valuable source of bioactive compounds for health and disease prevention. Plants 11 (24), 3434.

Chew, S.C., Tan, C.P., Nyam, K.L., 2018. Microencapsulation of refined kenaf (Hibiscus cannabinus L.) seed oil by spray drying using β-cyclodextrin/gum Arabic/sodium caseinate. J. Food Eng. 237, 78–85.

Chong, S.Y., Wong, C.W., 2017. Effect of spray dryer inlet temperature and maltodextrin concentration on colour profile and total phenolic content of Sapodilla (Manilkara zapota) powder. Int. Food Res. J. 24 (6), 2543–2548.

Culas, M.S., Popovich, D.G., Rashidinejad, A., 2023. Recent advances in encapsulation techniques for cinnamon bioactive compounds: a review on stability, effectiveness, and potential applications. Food Biosci. 103470.

Crupi, V., Ficarra, R., Guardo, M., Majolino, D., Stancanelli, R., Venuti, V., 2007. UV–vis and FTIR–ATR spectroscopic techniques to study the inclusion complexes of genistein with β-cyclodextrins. J. Pharmaceut. Biomed. Anal. 44 (1), 110–117.

de Freitas Santos, P.D., Rubio, F.T.V., da Silva, M.P., Pinho, L.S., Favaro-Trindade, C.S., 2021. Microencapsulation of carotenoid-rich materials: a review. Food Res. Int. 147, 110571.

Di Battista, C.A., Constenla, D., Ramírez-Rigo, M.V., Piña, J., 2015. The use of Arabic gum, maltodextrin and surfactants in the microencapsulation of phytosterols by spray drying. Powder Technol. 286, 193–201.

Dobroslavić, E., Elez Garofulić, I., Zorić, Z., Pedisić, S., Roje, M., Dragović-Uzelac, V., 2023. Physicochemical properties, antioxidant capacity, and bioavailability of laurus nobilis L. Leaf polyphenolic extracts microencapsulated by spray drying. Foods 12 (9), 1923.

Etzbach, L., Meinert, M., Faber, T., Klein, C., Schieber, A., Weber, F., 2020. Effects of carrier agents on powder properties, stability of carotenoids, and encapsulation efficiency of goldenberry (Physalis peruviana L.) powder produced by co-current spray drying. Curr. Res. Food Sci. 3, 73–81.

Ferreira-Anta, T., Torres, M.D., Vilarino, J.M., Dominguez, H., Flórez-Fernández, N., 2023. Green extraction of antioxidant fractions from Humulus lupulus varieties and microparticle production via spray-drying. Foods 12 (20), 3881.

Georgé, S., Brat, P., Alter, P., Amiot, M.J., 2005. Rapid determination of polyphenols and vitamin C in plant-derived products. J. Agric. Food Chem. 53 (5), 1370–1373.

Hadree, J., Shahidi, F., Mohebbi, M., Abbaspour, M., 2023. Evaluation of effects of spray drying conditions on physicochemical properties of pomegranate juice powder enriched with pomegranate peel phenolic compounds: modeling and optimization by RSM. Foods 12 (10), 2066.

Jaskula, B., Kafarski, P., Aerts, G., De Cooman, L., 2008. A kinetic study on the isomerization of hop α-acids. J. Agric. Food Chem. 56 (15), 6408–6415.

Kang, Y.R., Lee, Y.K., Kim, Y.J., Chang, Y.H., 2019. Characterization and storage stability of chlorophylls microencapsulated in different combination of gum Arabic and maltodextrin. Food Chem. 272, 337–346.

Kaul, S., Kaur, K., Mehta, N., Dhaliwal, S.S., Kennedy, J.F., 2022. Characterization and optimization of spray dried iron and zinc nanoencapsules based on potato starch and maltodextrin. Carbohydr. Polym. 282, 119107.
Kontek, B., Jedrejek, D., Oleszek, W., Olas, B., 2021. Antiradical and antioxidant activity in vitro of hops-derived extracts rich in bitter acids and xanthohumol. Ind. Crop. Prod. 161, 113208.
Labuschagne, P., 2018. Impact of wall material physicochemical characteristics on the stability of encapsulated phytochemicals: a review. Food Res. Int. 107, 227–247.
Mafakheri, M., Hamidoghli, Y., 2015. Effect of different extraction solvents on phenolic compounds and antioxidant capacity of hop flowers (Humulus lupulus L.). IV International Humulus Symposium 1236, 1–6.
Malowicki, M.G., Shellhammer, T.H., 2005. Isomerization and degradation kinetics of hop (Humulus lupulus) acids in a model Wort-boiling system. J. Agric. Food Chem. 53 (11), 4434–4439.
Marcillo-Parra, V., Tupuna-Yerovi, D.S., González, Z., Ruales, J., 2021. Encapsulation of bioactive compounds from fruit and vegetable by-products for food application–A review. Trends Food Sci. Technol. 116, 11–23.
Masek, A., Chrzescijanska, E., Kosmalska, A., Zaborski, M., 2014. Characteristics of compounds in hops using cyclic voltammetry, UV–VIS, FTIR and GC–MS analysis. Food Chem. 156, 353–361.
Matencio, A., Navarro-Orcajada, S., García-Carmona, F., López-Nicolás, J.M., 2020. Applications of cyclodextrins in food science. A review. Trends Food Sci. Technol. 104, 132–143.
Nadeem, H.Ş., Torun, M., Özdemir, F., 2011. Spray drying of the mountain tea (Sideritis stricta) water extract by using different hydrocolloid carriers. LWT–Food Sci. Technol. 44 (7), 1626–1635.
Neri, L., Santarelli, V., Di Mattia, C.D., Sacchetti, G., Faieta, M., Mastrocola, D., Pittia, P., 2019. Effect of dipping and vacuum impregnation pretreatments on the quality of frozen apples: a comparative study on organic and conventional fruits. J. Food Sci. 84 (4), 798–806.
Nilsson, J., Pillai, D., Önning, G., Persson, C., Nilsson, Å., Åkesson, B., 2005. Comparison of the 2,2′-azinobis-3-ethylbenzotiazoline-6-sulfonic acid (ABTS) and ferric reducing antioxidant power (FRAP) methods to asses the total antioxidant capacity in extracts of fruit and vegetables. Mol. Nutr. Food Res. 49 (3), 239–246.
Önder, F.C., Ay, M., Sarker, S.D., 2013. Comparative study of antioxidant properties and total phenolic content of the extracts of Humulus lupulus L. and quantification of bioactive components by LC–MS/MS and GC–MS. J. Agric. Food Chem. 61 (44), 10498–10506.
Pellegrini, N., Serafini, M., Salvatore, S., Del Rio, D., Bianchi, M., Brighenti, F., 2006. Total antioxidant capacity of spices, dried fruits, nuts, pulses, cereals and sweets consumed in Italy assessed by three different in vitro assays. Mol. Nutr. Food Res. 50 (11), 1030–1038.
Pinho, E., Grootveld, M., Soares, G., Henriques, M., 2014. Cyclodextrins as encapsulation agents for plant bioactive compounds. Carbohydr. Polym. 101, 121–135.
Popoola, O.K., Marnewick, J.L., Rautenbach, F., Ameer, F., Iwuoha, E.I., Hussein, A.A., 2015. Inhibition of oxidative stress and skin aging-related enzymes by prenylated chalcones and other flavonoids from Helichrysum teretifolium. Molecules 20 (4), 7143–7155.
Pilna, J., Vlkova, E., Krofta, K., Nesvadba, V., Rada, V., Kokoska, L., 2015. In vitro growth-inhibitory effect of ethanol GRAS plant and supercritical CO2 hop extracts on planktonic cultures of oral pathogenic microorganisms. Fitoterapia 105, 260–268.
Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M., Rice-Evans, C., 1999. Antioxidant activity applying an improved ABTS radical cation decolorization assay. Free Radic. Biol. Med. 26 (9), 1231–1237.
Ribeiro, A.M., Estevinho, B.N., Rocha, F., 2020. Microencapsulation of polyphenols-The specific case of the microencapsulation of Sambucus Nigra L. extracts-A review. Trends Food Sci. Technol. 105, 454–467.
Ravichai, K., Muangrat, R., 2019. Effect of different coating materials on freeze-drying encapsulation of bioactive compounds from fermented tea leaf wastewater. J. Food Process. Preserv. 43 (10), e14145.
Santarelli, V., Neri, L., Carbone, K., Macchioni, V., Pittia, P., 2021. Use of conventional and innovative technologies for the production of food grade hop extracts: focus on bioactive compounds and antioxidant activity. Plants 11 (1), 41.
Santarelli, V., Neri, L., Carbone, K., Macchioni, V., Faieta, M., Pittia, P., 2023. Conventional and innovative extraction technologies to produce food-grade hop extracts: influence on bitter acids content and volatile organic compounds profile. J. Food Sci. 88 (4), 1308–1324.
Sarabandi, K., Jafari, S.M., Mahoonak, A.S., Mohammadi, A., 2019. Application of gum Arabic and maltodextrin for encapsulation of eggplant peel extract as a natural antioxidant and color source. Int. J. Biol. Macromol. 140, 59–68.
Su, X., Xu, Y., Xu, Z., Hurley, K., Feng, Y., Yin, Y., 2023. Encapsulation of hop (Humulus lupulus L.) essential oil for controlled release in the non-alcoholic beverage application. Food Hydrocolloids 134, 108039.
Tatasciore, S., Santarelli, V., Neri, L., González Ortega, R., Faieta, M., Di Mattia, C.D., Di Michele, A., Pittia, P., 2023. Freeze-drying microencapsulation of hop extract: effect of carrier composition on physical, techno-functional, and stability properties. Antioxidants 12 (2), 442.
Tonon, R.V., Brabet, C., Hubinger, M.D., 2008. Influence of process conditions on the physicochemical properties of açai (Euterpe oleraceae Mart.) powder produced by spray drying. J. Food Eng. 88 (3), 411–418.
Wu, C.N., Sun, L.C., Chu, Y.L., Yu, R.C., Hsieh, C.W., Hsu, H.Y., Hsu, F.C., Cheng, K.C., 2020. Bioactive compounds with anti-oxidative and anti-inflammatory activities of hop extracts. Food Chem. 330, 127244.
Yang, S., Mao, X.Y., Li, F.F., Zhang, D., Leng, X.J., Ren, F.Z., Teng, G.X., 2012. The improving effect of spray-drying encapsulation process on the bitter taste and stability of whey protein hydrolysate. Eur. Food Res. Technol. 235 (1), 91–97.