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Supercritical impregnation of polyphenols from passion fruit residue in corn starch aerogels: Effect of operational parameters

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ABSTRACT

Supercritical impregnation (SFI) can carry polar compounds, such as polyphenols, in corn starch aerogels, forming new delivery systems with wide application in the food industry. This study investigated the effect of SFI pressure (22.5, 30.0, and 37.5 MPa) and temperature (45, 55, and 65 °C) on the loading of corn starch aerogels with polyphenols from passion fruit bagasse. SFI was performed in static mode with a fixed depressurization rate of 1.3 MPa/min. The best SFI condition for total phenolics and antioxidant capacity was 65 °C/37.5 MPa. The SFI efficiency was also observed from the decrease in the aerogel surface area (from 63.621 to 51.662 m^2/g), volume (from 0.285 to 0.129 cm^3/g) and particle diameter (from 8.976 to 4.788 nm). These findings may foster the use of SFI in the development of polyphenol delivery systems for nutraceuticals and food products.

1. Introduction

The advances in studies of supercritical impregnation (SFI) opened space for a potential field of application, the food industry. In this scenario, SFIhas appeared as an emerging technology to develop active materials for packaging and transporting active substances in food-grade supports, avoiding the use of organic solvents (Z. Liu et al., 2022; Rojas et al., 2020). SFI is divided into three steps: First, the target compounds are dissolved in a supercritical fluid, often carbon dioxide (CO_2), since it is non-toxic solvent, generally recognized as safe (GRAS), environmentally sustainable and with moderate critical temperature and pressure. In the second step, the mass transfer of the mixture (target compounds + solvent) to the solid material (adsorbent) takes place. Finally, the process is concluded by depressurization of the system and by dragging CO_2 and the non-impregnated compounds (Brunner, 2005; Carvalho et al., 2022). SFI has advantages such as high diffusion rate, the ability to process thermolabile substances under low temperatures and to modulate the loading of target compounds by adjusting the operating conditions (Champeau et al., 2015).

Bioactive compounds of yellow passion fruit (*Passiflora edulis* Sims) bagasse (PFB), a residue from an important crop in tropical countries, were reported in previous works as a potential source of phenolic and antioxidant compounds. Viganó et al. (2016), using pressurized liquid extraction, showed that this by-product is rich in polyphenols, mainly piceatannol and scirpusin B, and exhibits high antioxidant capacity. Dos Santos et al. (2021) identified 25 phenolic compounds in PFB and evaluated their potential to inhibit the enzymes acetylcholinesterase and lipoxygenase. The results found in their work reinforce the high antioxidant capacity of passion fruit bagasse and suggest its action against neurodegenerative diseases. As phenolic compounds are polar and CO_2 is a nonpolar molecule, it is challenging to incorporate them into food supports using SFI.

Considering the instability of polyphenols, the use of biomaterials as carriers of target compounds has been presented as an alternative to provide chemical and biological stability (Rezvankhah et al., 2020). Structured materials, such as aerogels, are excellent candidates for carriers of bioactive compounds and have aroused the interest of the scientific community and modern industry, since they combine the advantages of using sustainable raw materials with the multiple advanced physical and chemical properties of aerogels (Baudron et al., 2020; Manzocco et al., 2021; Nita et al., 2020; Singh and Lillard, 2009). Aerogels are structured solids with high surface area, high porosity, and low density, produced by the removal of agents that expand a hydrogel (e.g., solvents) while preserving its structure and volume (Smirnova and Gurikov, 2017). Aerogels are generally synthesized using inorganic or synthetic polymers, though bio-based materials, including

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polysaccharides and proteins, can also be used (Karaaslan et al., 2016).

Starch is a viable polysaccharide for producing aerogels due to its availability, sustainability, renewability, and low cost (Yixin Wang et al., 2019). Several works have used different starch sources (potato, wheat, corn, cassava, pea, and wheat) to produce aerogels for applications ranging from drug delivery systems to super-insulating materials (Fonseca et al., 2021; Mohammadi and Moghaddas, 2020; Soleimanpour et al., 2020; Ubeyitogullari and Ciftci, 2016; Zou and Budtova, 2021a, 2021b) Amongst these possible applications, the incorporation of active compounds into starch-based aerogels is an interesting approach because it preserves the compound bioavailability by protecting it from extrinsic factors, which guarantees the control of its release (Faridi Esfanjani and Jafari, 2016; Selvasekaran and Chidambaram, 2021).

There is a lack of information on using SFI to transport phenolic compounds in corn starch aerogels. Instead, most works on SFI focus on drug loading and the formulation of active packaging materials. The use of SFI to deliver nonpolar bioactive components in starch aerogels has only been reported a few times so far, mainly evaluating the loading of coffee oil, phytosterols, and fat-soluble vitamins (De Marco et al., 2018, 2019; Franco et al., 2018; Milovanovic et al., 2015; Ubeyitogullari and Ciftci, 2017; Villegas et al., 2019). Our research group has recently investigated the role of SFI variables in beta-carotene loading in corn starch aerogels (Dias et al., 2022).

Currently, no studies report the SFI impregnation of phenolic compounds into starch aerogels. A possible explanation may be the limitations thar concern the low affinity of CO_2 for polar molecules, such as polyphenols. However, the investigation of SFI operational parameters can contribute to enable and/or increase the adsorption/precipitation of polar active substances in the carrier matrix. Therefore, the present work deals with the investigation of the effect of temperature and pressure of SFI on the loading of corn starch aerogels with phenolic compounds from yellow passion fruit bagasse.

2. Materials and methods

2.1. Materials

PFB was kindly donated by Sitio do Belo (Paraibuna, São Paulo, Brazil); corn starch was supplied by Ingredion Ing. Ind. Ltda. (Brazil); commercial soybean oil (Liza, Cargill, Brazil) was purchased in a local market (Campinas, São Paulo, Brazil); absolute ethanol with purity ≥99.5% (Dinâmica, Brazil), Span® 80 surfactant (Sigma -Aldrich, USA), sintered glass beaker and CO_2 (White Martins, Brazil) were used to obtain the antioxidant extract, formulate the aerogels and in the SFI process. Potassium iodide (Farm, Brazil), iodine (Metaquímica, Brazil) and potato amylose (Sigma -Aldrich, USA) were used for amylose determination. Folin-Ciocalteu (Metaquímica, Brazil) and gallic acid (Sigma -Aldrich, USA) was used to determine the total phenolic content. 6-Hydroxy-2,5,7,8-etramethylchromane-2-carboxylic acid (Trolox), 2-2′-azobis (2-methylpropionamidene) dihydrochloride (APPH), 2,4,6-tris (2-pyridyl) -*s*-triazine (TPTZ) and fluorescein were purchased from Sigma -Aldrich (USA) and used to evaluate the antioxidant capacity. All reactants were used as received.

2.2. Production of passion fruit bagasse extract

The PFB extract was obtained following the methodology developed by Viganó et al. (2016) with some modifications. First, PFB was dehydrated in an oven (105 °C) to constant weight, grounded and stored under refrigeration and protected from light. Next, supercritical fluid extraction (SFE) with CO_2 was performed to remove the nonpolar compounds from the PFB at temperature and pressure of 35.0 ± 0.5 °C and 40 ± 1 MPa, respectively, generating the defatted passion fruit bagasse (DPFB). 10 g of DPFB were then placed in a stainless-steel cell and subjected to pressurized liquid extraction (PLE) with ethanol and water (3:1, w:w); water/ethanol) as solvent at 10 ± 1 MPa and 75.0 ± 0.5 °C, with a static time of 10 min. After the static time, the extract was collected in amber glass vials for 120 min. Finally, the total extract volume had the solvent removed in a rotary evaporator, was lyophilized, and redissolved in ethanol (99%).

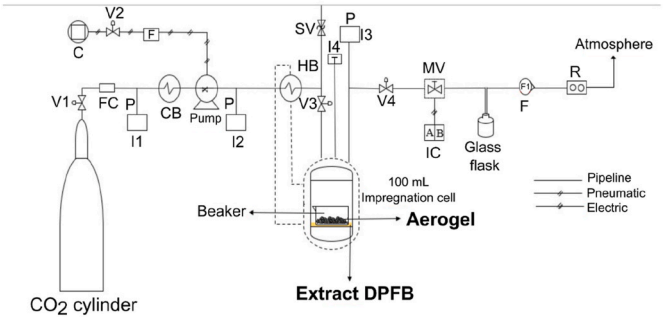

Fig. 1. Sc-CO_2 unit for impregnation. V-1 to V-4: block valves; MV: micrometer valve; SV: safety valve; C: compressor; F: air filter; FC: CO_2 filter; CB: cooling bath; HB: heating bath; I-1 to I-3: pressure indicators; I-4: temperature indicators; IC: temperature controller; F: Fluxometer; R: volumetric totalizer.

2.3. Corn starch aerogel formulation

Corn starch aerogel formulation was performed according to the method proposed by (De Marco et al., 2018), with a few modifications.

2.3.1. Preparation of the hydrogel

The corn starch hydrogel was initially prepared from two solutions. Solution I was an aqueous suspension of starch (15 wt%) prepared with a magnetic stirrer (200 rpm, 25 °C, 15 min). Solution II was prepared by mixing soybean oil and Span® 80 (2 wt%). Solutions I and II where then mixed at a volume ratio of 1:3. The emulsion gelling process started by slowly pouring solution II over solution I at 75 °C and 600 rpm. After 120 min, stirring was stopped. The emulsion was kept for 90 min at 75 °C without stirring and then stored at 4 °C for 72 h to allow retrogradation of the corn starch hydrogel. 500 mL of ethanol/water (30% v/v) was added to the retrograded solution, and the mixture was transferred to a separatory funnel to remove the oily phase, followed by vacuum filtration on filter paper to remove the excess of water.

2.3.2. Solvent exchange

The solvent exchange was carried out by immersing the particles in ethanol/water mixtures (30, 60, 90, and 100%, v/v) at a particle-to-liquid mass ratio of 1:5 and an exchange frequency of 24 h. The last solvent exchange was repeated three times, keeping the particles in ethanol to perform the supercritical drying and to obtain the aerogel.

2.3.3. Supercritical drying

Supercritical drying of the aerogels was performed as described by Hatami et al. (2020) with some modifications. 25.0 g of alcohol gel particles, packed in paper bags, were transferred to a 54.37 mL stainless steel vessel. The vessel was closed, attached to the supercritical drying unit, and kept at 40 ± 1 °C for 5 min to stabilize the system. The system was then pressurized with sc-CO_2 at 12.0 ± 0.5 MPa, keeping this pressure constant for 5 min. The sc-CO_2 flow rate was regulated at a rate of 10.0 g/min by macro and micrometric valves. The drying step was ended when an S/F (mass of consumed CO_2 [S]/mass of alcohol gel particles [F]) of 25 was reached. Finally, the system was depressurized at a rate of 1.5 MPa/min at 40 °C until atmospheric pressure. The aerogel particles were collected, packed into airtight vials, and stored in desiccators until further use.

Table 1
Surface properties of the aerogels.

	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
Corn Starch	9.873	0.016	n.d
Non-impregnated Aerogel	63.621	0.285	8.976
Impregnated corn starch aerogel (65 °C/37.5 MPa)	51.662	0.129	4.788

n.d.: not determined.

2.4. Supercritical fluid impregnation

SFI was performed in the unit shown in Fig. 1. Approximately 0.15 g of the corn starch aerogel was placed in a sintered glass beaker (25 mm diameter and 40 mm height) and transferred into a stainless-steel cell connected to the SFI unit. Immediately afterwards, 3 mL of DPFB extract was carefully placed on the cell walls, avoiding contact with the aerogel. The impregnation cell was closed, pre-heated and pressurized according to the conditions presented in Table 1. Before starting the SFI process, the system was kept static at the work pressure and temperature for 120 min. Next, the depressurization step was carried out at an average rate of 1.3 MPa/min, and finally, the impregnated particles were collected and stored protected from light until further analyses. Table 1 presents a summary of the operating conditions used in SFI.

2.5. Effect of pressure and temperature on the impregnation of polyphenols from passion fruit bagasse in corn starch aerogels

The effects of SFI temperature (45, 55 and 65 °C) and pressure (22.5, 30.0 and 37.5 MPa) were evaluated using the total phenolic content (TPC), antioxidant ferric reducing ability power (FRAP), and oxygen radical absorbance capacity (ORAC) of the impregnated aerogel particles. To recover the phenolic compounds impregnated in the aerogels, an extraction procedure was performed. This procedure consisted of the immersion of the impregnated aerogel in ethanol 50% dissolved in distilled water at a ratio of 0.05:1 (w/v), homogenization in a magnetic stirrer for 15 min, and filtration (Chormafil Xtra PA-20/25, Macherey-Nagel, Düren, Germany) to remove the aerogel particles. Finally, the extract from the impregnated aerogels was subjected to TPC, ORAC and FRAP analyses.

2.6. Total phenolics content (TPC)

The Folin-Ciocalteau method (Singleton et al., 1999) was used for the total phenolics quantification, with adaptations for microplates. Sample, standard (gallic acid 0.02–0.20 mg/mL), and blank were placed in each well of the microplate. Then, the Folin-Ciocalteau reagent was added to each sample in a 1:1 vol ratio. After 3 min, the final reaction volume of 200 μL was completed by adding a saturated solution of sodium carbonate and distilled water in a volume ratio of 1:7 at room temperature in the dark. The microplate was incubated analogously to the previous conditions for 2 h. Finally, the absorbance was read at 760 nm using a FLUOstar Omega microplate reader (Bmg Labtech GmbH, Ortenberg, Germany). The results were processed using Omega Mars 3.32R5 data analysis software and expressed as mg acid equivalent (GAE) per g of DPFB on a dry basis (d.b.).

2.7. Antioxidant capacity

2.7.1. Ferric reducing ability power (FRAP)

FRAP was performed according to the procedure reported by Benzie and Strain (1996) with minor modifications. Briefly, 20 mL of acetate buffer (0.3 M) was combined with 2 mL of TPTZ solution (10 mM) and 2 mL of ferric chloride solution (20 nM) to form the FRAP solution, which was then preheated at 37 °C protected from light. In each well of the microplate, 175 μL of the FRAP solution was added to 25 μL of sample, blank or standard (Trolox solution 0.01–0.06 mg/mL) and pre-incubated in the dark at 37 °C. After 30 min, the absorbance was read at 595 nm using a FLUOstar Omega microplate reader (BMG LABTECH GmbH, Ortenberg, Germany) with Omega Mars 3.32R5 data analysis software. The results were expressed as mg Trolox equivalent (TE) per g DPFB d.b.

2.7.2. Oxygen radical absorbance capacity (ORAC)

The hydrophilic ORAC method was applied according to the protocol described by Ou et al. (2013) with some adaptations. 25 μL of sample, blank (75 mM phosphate buffer, pH 7.4), and standard (Trolox solution 0.01–0.06 μg/mL) were added to 150 μL of fluorescein working solution in each well of the black microplate, conditioned at 37 °C for 15 min. Then 25 μL of the AAPH solution was added. The fluorescence decrease (excitation at 485 nm; emission at 510 nm) was measured in a FLUOstar Omega microplate reader (BMG LABTECH GmbH, Ortenberg, Germany) for 100 min at 37 °C. Fluorescein solution was used as a positive control, and the results were processed by Omega Mars 3.32R5 data analysis software and expressed as mg Trolox equivalent (TE) per g DPFB d.b.

2.8. Physical characterization

The physical characterizations described in this section were performed on the corn starch, the raw aerogel, and the impregnated aerogel prepared following the best condition obtained from the analysis of TPC, FRAP and ORAC (results of Section 2.4).

2.8.1. Nitrogen adsorption/desorption measurements

Nitrogen adsorption/desorption measurements were carried out using 100 mg of sample. Prior to analysis, samples were heated at 60 °C under vacuum for 15 h. The nitrogen adsorption/desorption isotherms were carried out at 77.3 K (Quantachrome Instruments, Nova 2200e). BET model was used to calculate the specific surface area using a multipoint model (relative pressure range from 0.05 to 0.3). BJH model was used to calculate the pore size distribution (relative pressure of less than 0.3).

2.8.2. Field-emission scanning electron microscopy (FESEM)

Aerogel morphology was analyzed using a FESEM (Quanta 250, FEI) microscope, under vacuum and operating at 2 kV. Prior to analysis, samples were coated with iridium (Baltec, Oerlikon-Balzers) at 11.3 mV for 120 s. More than 20 images of each sample were acquired to ensure reproducibility.

2.8.3. X-ray diffraction

X-ray diffraction analysis (Philips Analytical X-Ray, X'Pert-MPD, Almelo, Netherlands) were performed using a position-sensitive detector and CuKα radiation. Diffraction was measured within the range of 10°–60°, with a step of 0.037°, and counting a time of 2 s per step.

2.8.4. Differential scanning calorimetry (DSC)

DSC curves of the aerogels before and after the impregnation were obtained in an MDSC 2910 (TA Instruments). 5 mg of each sample were placed in an aluminum pan and heated under argon from 25 to 200 °C.

2.9. Statistical analyses

The results were statistically evaluated using MINITAB® software (Version 16.1.0, Minitab Inc.). One-way analysis of variance (ANOVA) was performed using Tukey's test to evaluate significant differences at the 5% level.

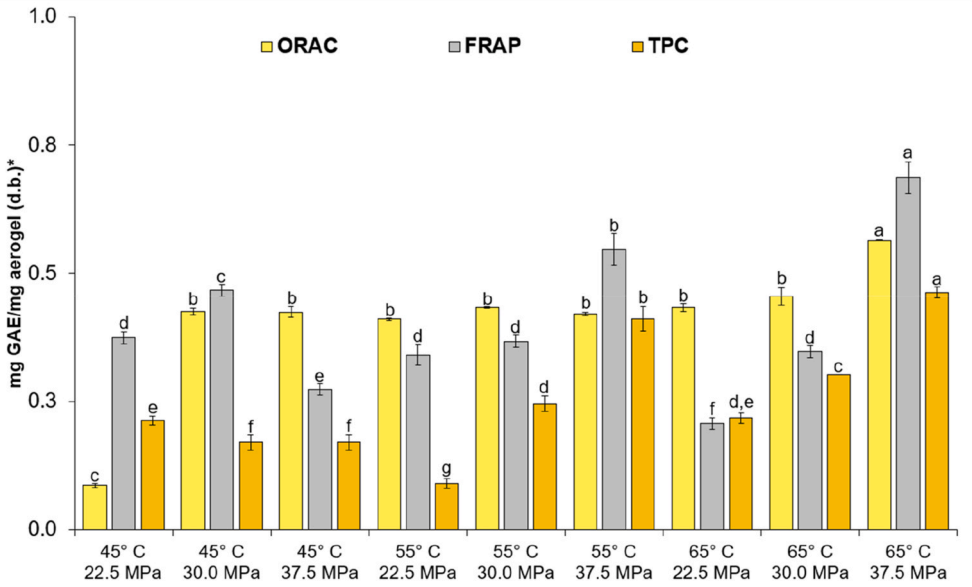

Fig. 2. Oxygen radical absorbance capacity (ORAC), antioxidant ferric reducing ability power (FRAP) and total phenolic content (TPC) of the passion fruit bagasse compounds impregnated on corn starch aerogels by SFI at different pressures (22.5–37.5 MPa) and temperatures (45–65 °C). Equal letters (a,b,c,d,e, and f) in columns that present the same color indicate no statistical difference at the 95% confidence level. *For ORAC analysis, the unit is mg GAE/g aerogel d.b.

3. Results and discussion

3.1. Effect of pressure and temperature on the supercritical fluid impregnation of polyphenols from passion fruit bagasse in corn starch aerogels

The effects of pressure and temperature on the SFI were evaluated from the results obtained in the TPC, FRAP and ORAC analyses of each experimental condition (Fig. 2). The pressure and temperature ranges were chosen to ensure the possible presence of thermosensitive polyphenols, also respecting the safety pressure limits of the unit (40 MPa). In addition, the solubility study of phenolic compounds in grape residue performed by Murga et al. (2003) was also considered. Regarding pressure, an isothermal increase from 22.5 to 37.5 MPa at 65 °C increased TPC, ORAC, and FRAP values. On the other hand, this trend was not observed at 45 and 55 °C. The positive effect of pressure on TPC, FRAP and ORAC is related to the concentration of phenolic compounds in sc-CO_2, e.g., the partition coefficient. Higher pressure increases the partition coefficient, thus favoring the impregnation of phenolic compounds in the aerogel. At higher pressures, the solubility of these compounds increases, and the diffusion of the active compound is facilitated due to the swelling of the pores of the polymer matrix (Rojas et al., 2020).

An opposite behavior was observed in TPC and FRAP results at 45 °C, in which pressure increased from 22.5 to 30.0 MPa and from 30.0 to 37.5 MPa. This behavior may have two reasons: the first one is the decrease in CO_2 diffusivity caused by the increase in pressure; and the second is given by the interactions between all the agents involved in the SFI. If the interaction between sc-CO_2 and target compounds is stronger than that of target compounds and matrix, the target compounds will be dragged in the final stage of the process and will not be impregnated in the matrix (Varona et al., 2011). A similar result was obtained by Belizón et al. (2018) when impregnating mango polyphenols in a multilayer film of polyethylene terephthalate and polypropylene, using the same temperature (45 °C), and a pressure growth from 10 to 20 MPa.

For isobaric conditions (37.5 MPa), TP and FRAP increased with temperature, though ORAC remained stable when the temperature increased from 45 to 55 °C. Opposite behaviors were observed for TPC at a pressure of 22.5 MPa when increasing temperature from 45 to 55 °C. For this same temperature range, FRAP increased at the isobaric

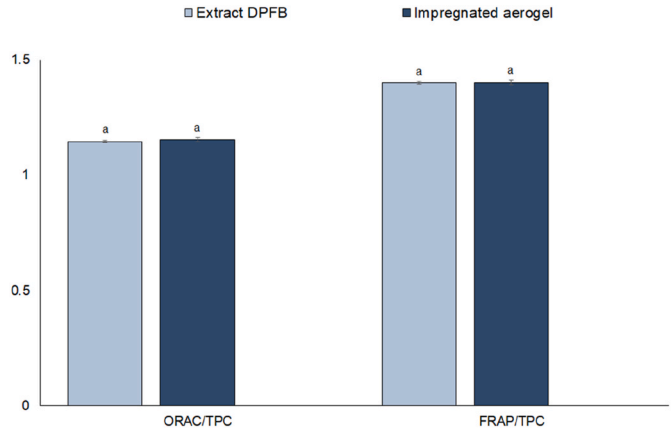

Fig. 3. ORAC/TPC and FRAP/TPC of the passion fruit bagasse extract and aerogel impregnated by SFI at 37.5 MPa and 65 °C. Equal letters in grouped columns means no statistical difference at 95% confidence level.

condition of 30.0 MPa. A possible explanation for such different behaviors is the presence of crossover regions, according to Chimowitz and Pennisi (1986). Above this region, temperature positively affects the active compound solubility, which is driven by the vapor pressure, suppressing the impact of the sc-CO2 density decrease. Similarly, below this region, the effect of decreasing density given by increasing temperature prevails. Here, the temperature/pressure combination at 65 °C/37.5 MPa provided the best impregnation, with values of 0.462 mg GAE/g for TPC, 0.687 ± 0.030 mg TE/g for FRAP and 0.564 mg TE/g for ORAC. These results suggest that the experiments were carried out above the crossover region, as also verified by Murga et al. (2003), which investigated the solubility of different phenolic compounds in sc-CO_2 and obtained the best results at 60 °C and 50 MPa.

These results reveal the importance of evaluating the SFI variables in the adsorption/precipitation efficiency of active compounds with small affinity to sc-CO_2, such as polyphenols from PFB. Comparing the values obtained at the worst and the best impregnation conditions, there was an increase of 270.6% in TPC content, 328.6% in FRAP antioxidant capacity, and 655.8% in ORAC antioxidant capacity.

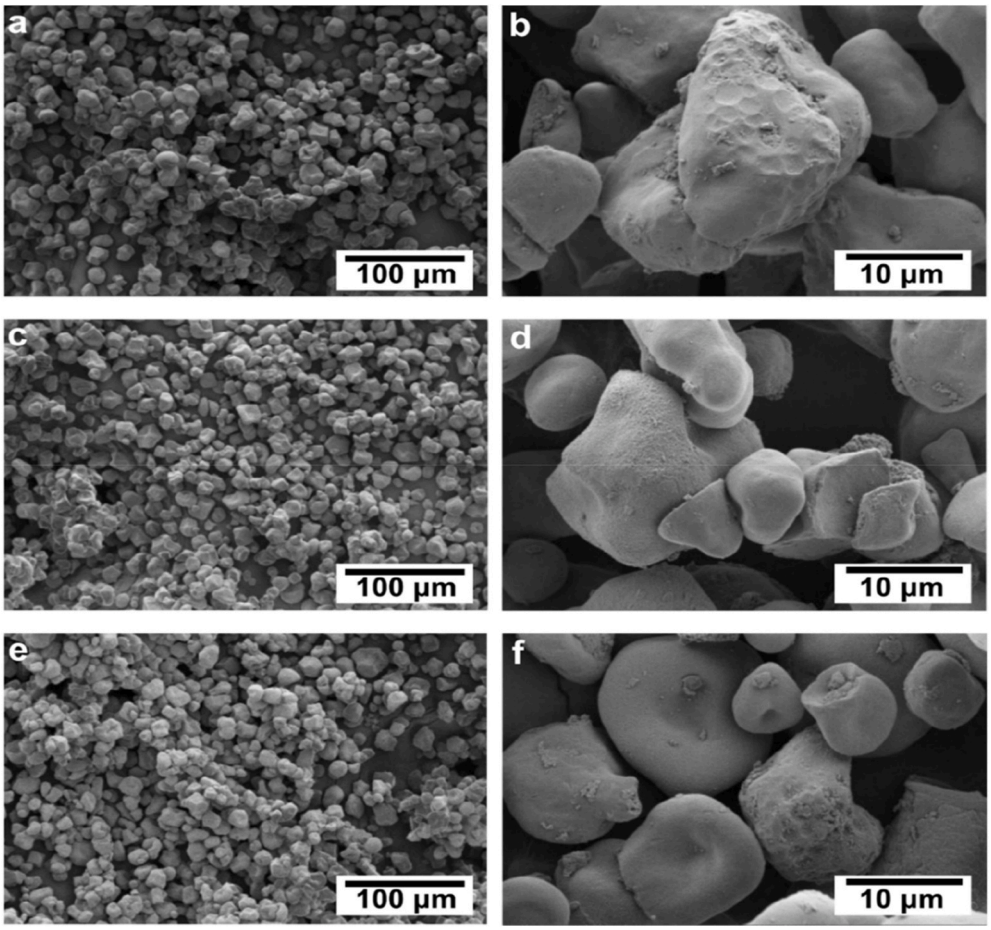

Fig. 4. Surface morphology of corn starch: (a and b), raw corn starch aerogel (c and d) and impregnated corn starch aerogels with DPFB extract (e and f) obtained by SFI at 37.5 MPa, 65 °C.

3.2. Antioxidant capacity

To verify if the antioxidant capacity of the impregnated aerogel extract remains equal to that of the DPFB extract, the ratio between h-ORAC/TPC and FRAP/TPC was calculated for the aerogels impregnated at 65 °C and 37.5 MPa (the best condition obtained in Section 3.1) and for the DPFB extract. Results in Fig. 3 indicate that SFI (65 °C, 37.5 MPa) did not decrease the antioxidant capacities, reinforcing that SFI was effective in maintaining the antioxidant capacity of the extract in corn starch aerogels. The observed antioxidant capacity is likely related to several phenolic compounds identified in passion fruit bagasse, such as phenolic acids, flavonoids, stilbenes, carboxylic acids, and phenolic aldehydes (dos Santos et al., 2021). However, the stilbene piceatannol deserves highlighting; several works performed by Viganó et al. (2016, 2020a, 2020b) report the presence of this phenolic compound that, besides having several biological activities, has an important contribution to the antioxidant capacity of the passion fruit bagasse extract.

In the present work, the ORAC (564.47 μg TE/g) and FRAP (687 μg TE/g) antioxidant capacities of the aerogels impregnated at 65 °C and 37.5 MPa were higher than those found in works that used different systems. However, they had a similar objective, to carry bioactive compounds. Luo et al. (2020) used the dispersion method to load liposomes with procyanidins from the lychee pericarp and obtained ORAC antioxidant capacities of 238.28 μg TE/g and FRAP of 119.4 μg TE/g. Arango-Ruiz et al. (2018), from the encapsulation of curcumin using the supercritical antisolvent (SAS) method, obtained ORAC antioxidant capacity of 119.4 μg TE/g.

3.3. Nitrogen adsorption/desorption

Surface area, pore volume and average pore diameter calculated by nitrogen adsorption/desorption measurements of corn starch before and after aerogel preparation (Table 1) indicated the production of starch aerogels. The aerogel production from raw corn starch revealed a 6.4-fold increase in surface area and a 17.8-fold increase in pore volumes. The increased surface area and pore volume of the aerogel make it possible to use it as a carrier for bioactive compounds using SFI. These results were similar to those of Dias et al. (2022) on corn starch aerogel, certifying the achievement of a porous network from starch gelling followed by drying with sc-CO_2. The average pore diameter (8.98 nm) of the corn starch aerogel is typical of mesoporous structures. Similar surface areas (50–100 m^2/g) and pore diameters (5–20 nm) were obtained by Mehling et al. (2009) and Soleimanpour et al. (2020) for aerogels synthesized from raw corn starch and with high amylose content.

Moreover, the adsorption/desorption analysis revealed that SFI of phenolic compounds from PFB was achieved (Table 1). The decreases in surface area (from 63.621 to 51.662 m^2/g), volume (from 0.285 to 0.129 cm^3/g) and diameter (from 8.976 to 4.788 nm) of the pores indicate the loading of phenolic compounds into the mesopores of the corn starch aerogel by SFI. In addition, the similarity of the hysteresis loop shapes of the aerogel before and after the SFI process (Fig. a.1, supplementary material) indicated no drastic change in the pore channel during the impregnation of the phenolics from the DPFB extract.

Higher surface area (247 ± 12 m^2/g) and pore volume (0.84 ± 0.04 $cm^3\ g^{-1}$) were obtained by García-González et al. (2012) for native corn starch when studying the effect of gelling temperature. According to

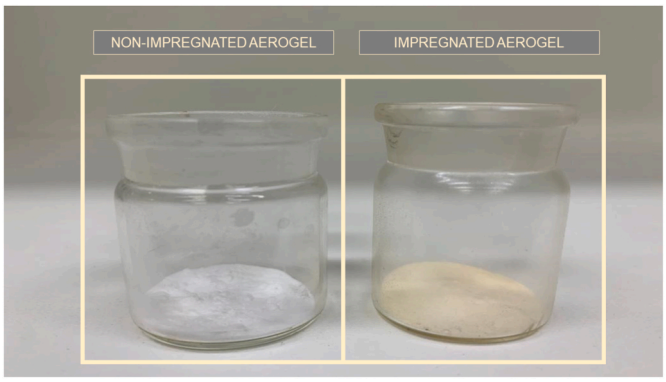

Fig. 5. Color difference between non-impregnated and impregnated aerogel (SFI at 65 °C and 37.5 MPa).

these authors, the structural aspects of the starch particles were improved at 120 °C. The impact of the gelling temperature on aerogel processing was not the focus of this work, though structural improvements could be achieved using higher temperatures. It is important to note that the applied conditions, despite not resulting in surface areas similar to those of García-González et al. (2012), confirmed the success of SFI in loading phenolic compounds of the DPFB extract into the aerogels.

3.4. Scanning electron microscopy (FESEM)

Morphological analysis by FESEM of raw starch and starch aerogel before and after the impregnation at 37.5 MPa and 65 °C are shown in Fig. 4. The irregular, granular structure of the starch remained after the aerogel and SFI production processes, suggesting that the main modifications take place inside the particles, as indicated by the increase in pore size and surface area. Moreover, the impregnation process did not change the overall aerogel morphology. The visible color change of the impregnated aerogel (Fig. 5) and the results discussed in the previous sections are evidence of the transfer of phenolic compounds from the DPFB extract mainly to the inner part of the corn starch aerogel particles.

3.5. X-ray diffraction and differential scanning calorimetry

XRD and DSC were used to characterize the materials and to verify the presence of DPFB extract from the SFI (65 °C, 37,5 MPa). The XRD patterns of corn starch, non-impregnated aerogel and impregnated aerogel are shown in Fig. 6(A). The peaks for corn starch showed a profile characteristic of type A starches, with clear peaks at 15°, 17°, 18°, 23° (2 θ) (Yiwei Wang et al., 2021). The preparation of the aerogel caused the disappearance of the peak at 18° (2 θ), a decrease in the intensity of the peaks at 15° and 17° (2 θ) and the appearance of the peak at 20° (2 θ). The disappearance or decrease in the intensity of the peaks is possibly related to starch gelatinization, which promotes crystal dissolution and granule disruption (H. Liu et al., 2009). The appearance of the characteristic 20° peak (2 θ) is related to the formation of the amylose-lipid complex and crystallites from retrogradation. Considering that the water-in-oil emulsion technique was used in this work for the formation of aerogels, the residual oil phase possibly formed a complex with amylose, promoting the appearance of the 20° peak (2 θ). A similar behavior was observed by Ubeyitogullari & Ciftci (2016) and B. Wang et al. (2021). After SFI of the DPFB extract, the peak at 15° (2θ) moderately decreases. This slight decrease in crystallinity can be attributed to the presence of phenolic compounds from the DPFB extract in the aerogel, which would be preventive, as this decrease indicates prevention of crystallization by the presence of the active compound (De Oliveira et al., 2020). DSC thermograms of the corn starch, aerogel, and impregnated aerogel samples are presented in Fig. 6 (B). The samples showed similar behavior in the heat flow profile as temperature increased, with endothermic peaks around 139° for starch and 125 °C for non-impregnated aerogel and impregnated aerogel. It was possibly related to dehydration and gelatinization of the starch.

4. Conclusion

SFI was successful in the loading of corn starch aerogel particles with DPFB extract. The combination of 65 °C and 37.5 MPa obtained the best results for TPC, ORAC and FRAP antioxidant capacities. Compared to the non-impregnated aerogels, the surface area and pore volume and diameter of the impregnated aerogels decreased by 11.96 m^2, 0.16 cm^3/g, 4.19 nm, respectively. These results confirm that the phenolic compounds from DPFB extract were successfully impregnated into the corn starch aerogels by SFI. The antioxidant capacities evaluated from the ORAC/TPC and FRAP/TPC ratio of the DPFB extract were not modified by SFI at 65 °C and 37.5 MPa. The impregnated aerogels demonstrated their potential to carry the target compounds, such as polyphenols, and SFI did not modify their structure. Future works should investigate other SFI conditions and possible applications of aerogels impregnated with DPFB extract as delivery systems for bioactive compounds to be used in nutraceutical and food products.

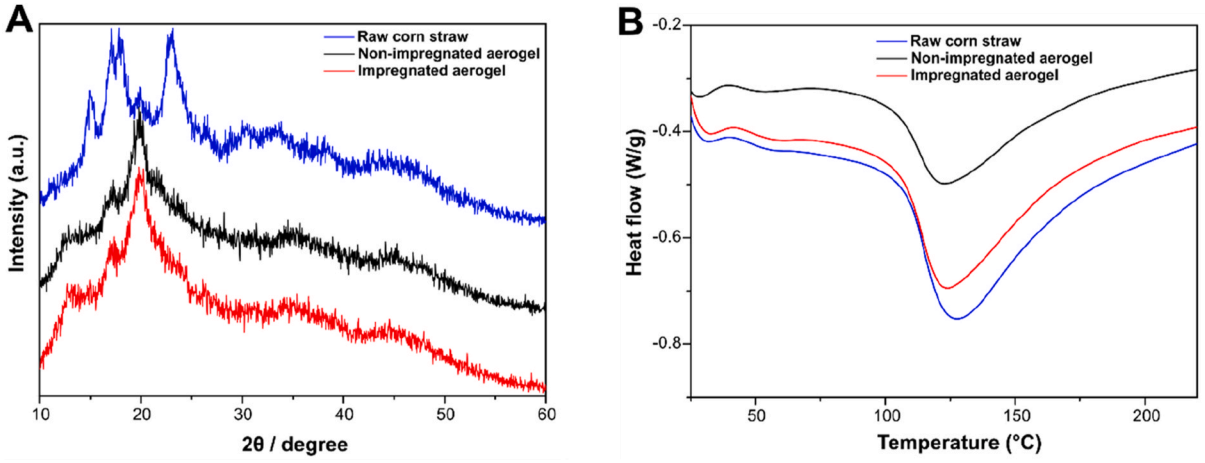

Fig. 6. A) X-ray diffraction pattern; and B) DSC thermograms of the corn starch, non-impregnated corn starch aerogel and impregnated corn starch aerogel (impregnation conditions: 37.5 MPa and 65 °C).

Credit author statement

Erick Jarles de Araújo: Definition, Conceptualization, Validation, Writing, Visualization, Supervision, Project administration. **Eupidio Scopel:** Conceptualization, Investigation. **Camila Alves de Rezende:** Formal analysis, Investigation, Funding acquisition. **Julian Martínez:** Definition, Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jfoodeng.2022.111394.

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