WALLAF COSTA VIMERCATI

OPTIMAL EXTRACTION CONDITION AND ENCAPSULATION OF BIOACTIVE COMPOUNDS FROM COFFEE SILVERSKIN

LAVRAS - MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência dos Alimentos, para a obtenção do título de Doutor.

Prof. Dr. Carlos José Pimenta

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WALLAF COSTA VIMERCATI

CONDIÇÃO ÓTIMA DE EXTRAÇÃO E ENCAPSULAÇÃO DOS COMPOSTOS BIOATIVOS DA PELÍCULA PRATEADA DO CAFÉ

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(Madre Teresa de Calcutá)

ABSTRACT

Coffee silverskin is the main co-product generated during the roasting process. This co-product has a rich nutritional composition, mainly in antioxidant compounds, and can be considered a rich natural source for the extraction of these compounds. Therefore, the aim of this study was to determine an optimal condition for the extraction of bioactive compounds from coffee silverskin and to compare different encapsulation methods (foam mat drying, spray drying and freeze drying). Initially, the effect of traditional methods of solid-liquid extraction (room temperature, with agitation and Soxhlet extraction method) and the use of more friendly solvents (water, ethanol, acetone and isopropanol) were investigated. An optimal treatment was chosen by desirability function. Afterwards, the effect of the extraction temperature and the concentration of the hydroalcoholic solution were studied. In addition, the extraction kinetics of phenolic compounds were also evaluated to determine the extraction time. The desirability function was applied to determine the optimal extraction condition of bioactive compounds from coffee silverskin. The extracted bioactive compounds were subjected to different encapsulation methods (foam mat drying, spray drying and freeze drying). Maltodextrin, gum arabic and egg albumin were used as wall materials. For foam mat drying, the agents were combined according to the treatments established by mixture design and an optimal concentration was determined. The foams were dried at temperatures of 50, 60, 70 and 80 ºC in a convective dryer. Spray drying and freeze drying of the optimal condition of the wall materials combination was also performed. The powders were characterized, and a comparison of methods was performed. For the extraction, the highest content of bioactive compounds recovered from coffee silverskin was through the method with agitation. Furthermore, ethanol was the best extraction solvent, followed by water. In the subsequent step, the optimal conditions obtained for the hydroalcoholic concentration, temperature and extraction time were 64%, 68 °C and 120 min, respectively. Regarding the encapsulation methods, the ideal condition obtained from the feed mixture for foam formation was 7.6% gum arabic, 2% maltodextrin and 10.4% egg albumin. The powders obtained by different encapsulation methods showed good quality and high encapsulation efficiency.

Keywords: Valorization. Co-products. Coffee silverskin. Extraction process. Optimization. Encapsulation methods.

RESUMO

A película prateada do café é o principal coproduto gerado durante o processo de torrefação. Este coproduto possui uma rica composição nutricional, principalmente em compostos antioxidantes, podendo ser considerada uma rica fonte natural para extração desses compostos. Portanto, o objetivo deste estudo foi determinar uma condição ótima de extração dos compostos bioativos da película prateada do café e comparar diferentes métodos de encapsulação (secagem em leito de espuma, spray drying e freeze drying). Inicialmente, o efeito dos métodos tradicionais de extração sólido-líquido (método de extração a temperatura ambiente, com agitação e em Soxhlet) e o uso de solventes mais amigáveis (água, etanol, acetona e isopropanol) foram investigados. Um tratamento ótimo foi escolhido pela função desejabilidade. Após, o efeito da temperatura de extração e da concentração da solução hidroalcóolica foram estudadas. Além disso, foi avaliada também a cinética de extração dos compostos fenólicos para determinação do tempo de extração. A função desejabilidade foi aplicada para determinar a condição ótima de extração dos compostos bioativos da película prateada do café. Os compostos bioativos extraídos foram submetidos a diferentes métodos de encapsulação (secagem em leito de espuma, spray drying e freeze drying). Maltodextrina, goma arábica e ovoalbumina foram utilizadas como materiais de parede. Para a secagem em leito de espuma, os agentes foram combinados de acordo os tratamentos estabelecidos pelo delineamento de mistura e uma concentração ótima foi determinada. As espumas foram secas nas temperaturas de 50, 60, 70 e 80 ºC em um secador convectivo. A secagem por spray e liofilização da condição ótima da combinação dos materiais de parede também foi realizada. Os pós foram caracterizados e a comparação dos métodos foi realizada. Para a extração, o maior teor de compostos bioativos recuperados da película prateada do café foi utilizando o método com agitação. Além disso, etanol foi o melhor solvente de extração, seguido da água. Na etapa posterior, a condição ótima obtida para a concentração hidroalcóolica, temperatura e tempo de extração foi de 64%, 68 °C e 120 min, respectivamente. Em relação aos métodos de encapsulação, a condição ideal obtida da mistura de alimentação para a formação de espuma foi de 7,6% de goma arábica, 2% de maltodextrina e 10,4% de ovoalbumina. Os pós obtidos pelos diferentes métodos de encapsulação apresentaram boa qualidade e alta eficiência da encapsulação.

Palavras-chave: Valorização. Coprodutos. Película prateada. Processo de extração. Otimização. Métodos de encapsulação.

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SUMMARY

FIRST SECTION

1 INTRODUCTION

Coffee is a food produced in high volumes and has high commercial importance (AMECA-VENEROSO *et al.*, 2021). The characteristic attributes of coffee, such as flavor, aroma, stimulating effect and other health benefits, are some of the factors that contribute to this beverage being widely consumed and appreciated worldwide (AÇIKALIN; SANLIER, 2021; GOKCEN; SANLIER, 2017; KHOCHAPONG *et al.*, 2021; SCHOLZ *et al.*, 2018).

According to the International Coffee Organization (ICO, 2020a), world coffee production and consumption has increased over the past 30 years. In coffee year 2020/2021, world production is estimated at 169.6 million bags, comprising 99.2 million bags of Arabica coffee and 70.4 million bags of robusta coffee. Although the COVID-19 pandemic initially influenced coffee consumption trends and patterns (ICO 2020a), world consumption is estimated to increase by 1.9% compared to last year, corresponding to 167.58 million bags. In addition, a continued growth in world coffee consumption is expected due to the relaxation of restrictions imposed by the COVID-19 pandemic and the trend towards economic recovery (ICO, 2021).

In this world scenario, Brazil ranks as the largest producer, exporter and second largest consumer of coffee (ABIC, 2021). Brazilian coffee production in the 2019/2020 harvest was estimated at 58 million bags, with 37 million bags of Arabica coffee and 21 million bags of robusta coffee (ICO, 2020b). In 2020, per capita consumption of green and roasted coffee was estimated at 6.01 and 4.81 kg of coffee/inhabitant year, respectively (ABIC, 2021).

The increase in world production and consumption of coffee consequently generates an important portion of co-products by the coffee industry (BALLESTEROS; TEIXEIRA; MUSSATTO, 2014a). Coffee silverskin (CS) is the main co-product of the coffee roasting process (IRIONDO-DEHOND *et al.*, 2019). This co-product is highly polluting and requires a high demand for oxygen to be degraded. Studies aimed at different and profitable applications must be developed in order to minimize the impact generated on the environment (MUSSATTO *et al.*, 2011). CS has been the subject of extensive research as it has a rich composition, mainly in bioactive compounds, which exert beneficial effects on health (BALLESTEROS; TEIXEIRA; MUSSATTO, 2014a; NARITA; INOUYE, 2014; NZEKOUE *et al.*, 2020).

The extraction and application of bioactive compounds are possible alternatives used to reduce the pollutant load and add value to food products (BESSADA; ALVES; OLIVEIRA, 2018). The extraction of bioactive compounds can be performed by more traditional methods

or by more recent technologies, requiring the optimization of process variables and evaluation of the possibility of use for each industry and type of food (MOHAPATRA *et al.*, 2021; OREOPOULOU *et al.*, 2020; RAHMANIAN; JAFARI; WANI, 2015). However, the extracted bioactive compounds are unstable under some factors related to food processing and storage, such as temperature, oxygen, light, among others. Therefore, other technologies must be employed to overcome these limitations (BALLESTEROS *et al.*, 2017; CHAMPAGNE; FUSTIER, 2007; LOZANO-VAZQUEZ *et al.*, 2015).

Encapsulation emerges as a potential alternative, as it makes the increase of bioactive compound stability possible. This process consists of wrapping the active material with a wall material, providing greater stability for these compounds when subjected to conditions that may degrade them. In addition, encapsulation facilitates the incorporation and controlled release of bioactive compounds into the food matrix (ARENAS-JAL; SUÑÉ-NEGRE; GARCÍA-MONTOYA, 2020; BAKRY *et al.*, 2016; BALLESTEROS *et al.*, 2017).

The composition of the wall material and the encapsulation method employed are crucial factors for the retention, solubility, stability, and controlled release characteristics of bioactive compounds. The choice of these factors will depend on the type of bioactive compound that will be encapsulated (ARENAS-JAL; SUÑÉ-NEGRE; GARCÍA-MONTOYA, 2020; MORO *et al.*, 2021). The encapsulation methods by spray drying and freeze drying are the most used (BALLESTEROS *et al.*, 2017). However, the evaluation of new encapsulation methods to overcome the limitations of existing methods, such as the high costs of equipment and processes, are always desirable (KANHA; REGENSTEIN; LAOKULDILOK, 2020). Foam Mat Drying (FMD) can be considered an alternative method, as it is simple, cheap and generates high-quality powder (HARDY; JIDEANI, 2017).

In this context, the present study aimed to evaluate the extraction and encapsulation of bioactive compounds from coffee silverskin. Therefore, this thesis was divided into two articles. In the first article, the determination of the optimal condition for the recovery of bioactive compounds was performed. Traditional solid-liquid extraction methods and friendlier solvents were evaluated. Subsequently, the extraction kinetics of total phenolic compounds and the effect of extraction temperature and solvent concentration were evaluated. In the second article, the influence of carrier agent concentration on the foam properties of CS extract and the comparison of encapsulation methods by foam mat drying with spray drying and freeze drying were studied.

2 THEORETICAL REFERENCE

2.1 Origin and commercial species of coffee

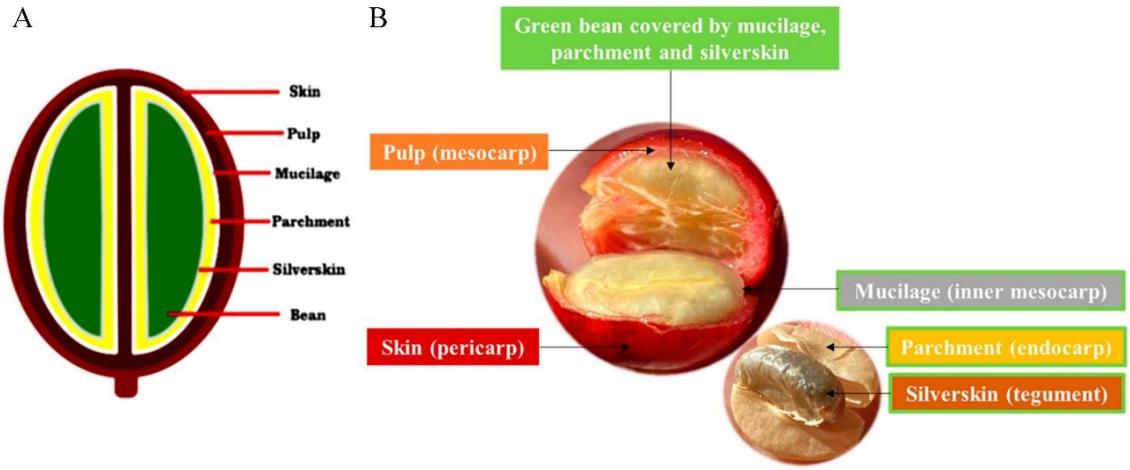
Coffee originated from Ethiopia, on the African continent, but it was the Europeans who contributed to the spread of this drink around the world (ABIC, 2021). The coffee tree belongs to the *Rubiaceae* family and the *Coffea* genus. Currently, several species have been described in the literature. However, the species with the highest economic importance are only *Coffea arabica* L. and *Coffea canephora* Pierre, known as arabica and robusta, respectively (BARREA *et al*., 2021; FERRÃO *et al*., 2015). Two other species that can also be mentioned are *C. liberica* and *C. stenophyla*, but they are of lesser commercial importance, since the international market is composed mostly (98%) of arabica and robusta coffees (ALVES *et al*., 2017).

Arabica coffee is considered of better quality, as it has a more refined and pronounced flavor, producing more appreciated beverages. Due to these characteristics, the highest market prices are found for this species (ALVES *et al*., 2009; KEIDEL *et al*., 2010; NEBESNY; BUDRYN, 2006). The drink produced from robusta coffee is less preferred, as it has a bitterer and more astringent taste, mainly due to its higher levels of caffeine, soluble solids and antioxidant compounds. In addition, robusta coffee has a lower sucrose content, which also contributes to the differentiation of beverages. Because it has a lower price and its higher yield in soluble solids, robusta coffee is used, most of the time, in the preparation of blends with arabica, being used, especially, to increase the body and the formation of foam in some coffee drinks (ALVES *et al*., 2009; LIU *et al*., 2019; NEBESNY; BUDRYN, 2006).

2.2 Anatomy and coffee processing

Coffee fruits are made up of five layers of material that protect the bean: the husk, pulp, mucilage, parchment and coffee silverskin (Figure 1).

Figure 1 – Scheme of the anatomy of the coffee fruit (A) coffee cherries with the identification of the different co-products (B).



Source: Iriondo-Dehond; Iriondo-Dehond; Del Castillo (2020); Santos *et al.* (2021).

The fruit is also known as a berry or cherry. The exocarp or epicarp (shell or skin) is the outer layer of the fruit, which is smooth, resistant and has a green color in immature fruits and red or yellow in mature fruits, depending on the variety. The second layer is the mesocarp (pulp), followed by a layer of mucilage. The pulp is fibrous, yellowish, soft and sweet. The mucilage or pectin layer is a thin, colorless, hydrated and viscous layer. The fourth layer is the endocarp (parchment), which is a thin layer of yellow-colored polysaccharides. The last layer that covers the grain is the perisperm (silverskin), a thin integument. The grain (endosperm) consists of two seeds with an elliptical shape (ALVES *et al.*, 2017; ESQUIVEL; JIMÉNEZ, 2012; FRANCA; OLIVEIRA, 2016; SANTOS *et al.*, 2021).

The coffee bean or seed, also known as green coffee, is the only part that is really used for the production of the beverage. The other parts of the fruit are considered co-products generated by the coffee sector (FRANCA; OLIVEIRA, 2016; SANTOS *et al.*, 2021)

The harvested coffee cherries undergo several unit operations until obtaining green coffee. In post-harvest processing of coffee, the main methods used are dry or wet processing, generating natural coffee and washed coffee, respectively (BRANDO; BRANDO, 2015; ESQUIVEL; JIMÉNEZ, 2012; SANTOS *et al.*, 2021). In recent years, an intermediate method has also been used, called pulped natural process or semi-dry process, resulting in pulped natural coffees (BRANDO; BRANDO, 2015).

The processing used to obtain green coffee influences the type of co-product generated (DEL CASTILLO *et al*., 2019). In dry processing, the whole cherries are immediately subjected

to sun drying or mechanical dryers after harvesting. This processing is the oldest, simpler, cheaper and commonly used in tropical regions where the harvest time coincides with the dry period. To obtain green coffee, peeling machines are used to remove the layers adhered to the dried fruit, such as dry pulp, parchment and part of the silverskin that come out together with the husk in a single fraction (BRANDO; BRANDO, 2015; SANTOS *et al*., 2021). Generally, fruits at different stages of ripeness (unripe, ripe, overripe, and partially dry fruits) are dried together. In recent years, the separation into batches has been carried out, as the different stages of maturation have different quality (BRANDO; BRANDO, 2015).

Wet processing is considered more complex, expensive and generates greater environmental problems, as a large volume of water is needed (SANTOS *et al.*, 2021). In this processing, the fruits are initially immersed in water to separate impurities and unripe and ripe fruits. The cherry coffee is then mechanically pulped, removing the husk and most of the pulp. The mucilage and a small remaining part of the pulp can be removed by fermentation, followed by washing or mechanical removal (BRANDO; BRANDO, 2015; ESQUIVEL; JIMÉNEZ, 2012).

A graphical abstract of dry and wet coffee processing is shown in Figure 2.

Figure 2 – Dry and wet coffee processing.

Source: Iriondo-Dehond; Iriondo-Dehond; Del Castillo (2020).

In the semi-dry process, the cherry coffee is pulped and most or all mucilage still remains attached to the bean, being dried together with the parchment. This allows sugars to

enter the coffee bean by osmosis and provide a sweet coffee (BRANDO; BRANDO, 2015; KLINGEL *et al*., 2020). This process started in the 90's, originally being used in Brazil, and is known as “Cereja Descascado” or CD (BRANDO; BRANDO, 2015).

The beans obtained by the different types of processing are dried to a moisture content of 10-11% and peeled to remove the parchment (endocarp), giving rise to green coffee (BRANDO; BRANDO, 2015; ESQUIVEL; JIMÉNEZ, 2012; FRANCA; OLIVEIRA, 2016).

To obtain the drink, green coffee must still undergo roasting, grinding and extraction operations. Some coffee co-products are still generated in large quantities at these stages, such as coffee silverskin (obtained during roasting) and the spent coffee grounds (obtained after extraction). The roasting process is generally carried out in the country where the beverage will be consumed and no longer in the country of origin. Roasting is crucial for the production of the beverage. At this stage, there is a series of changes in the chemical composition of the coffee beans, with some compounds being degraded and others formed. With this, the characteristic flavor, aroma, and color of the drink are formed (ESQUIVEL; JIMÉNEZ, 2012; FRANCA; OLIVEIRA, 2016; KLINGEL *et al.*, 2020).

2.3 Coffee co-products

Currently, a large amount of co-products are generated by industries in different fields. In the food industries, 1.6 billion tons of food co-products are generated annually as waste, with 38% generated during processing (HEJNA *et al*., 2021). Food co-products can come from various sources, such as derived from animal products (co-products from bred animals, seafood, dairy industry, among others) and vegetable origin (seeds, shells, peelings, stems, bran, trimmings residues after extraction of oil, juice, starch, and sugars) (HELKAR; SAHOO; PATIL, 2016).

Most of the time, food co-products are not properly reused and are discarded inappropriately. However, studies have highlighted the importance of valuing these co-products in order to minimize environmental contamination and additional costs for their treatment. In addition, these co-products have a high nutritional content (protein, fiber, bioactive compounds, among others) that can be used to produce functional foods. Thus, efficient waste management contributes to the growth of industries (HELKAR; SAHOO; PATIL, 2016).

In the processing of products of vegetable origin, up to 45 wt% of co-products can be produced in the processing of some fruits. However, an even higher amount is generated in coffee processing (more than 50 wt% of the fresh coffee cherry), and the coffee sector is

considered a record holder in the generation of co-products (ESQUIVEL; JIMÉNEZ, 2012; HEJNA *et al*., 2021).

In recent years, large amounts of coffee co-products have been generated (about 2 billion tons/year) (JIMÉNEZ-ZAMORA; PASTORIZA; RUFIÁN-HENARES, 2015). This is due to the increase in world production and consumption of coffee, especially in relation to specialty coffees due to increased market appreciation (ABIC, 2021; ICO, 2021).

Coffee co-products can be divided into two main classes: i) Co-products derived from production of green coffee (skin, pulp, husks, mucilage and parchment) that are generated in producing countries, and ii) Co-products obtained after the roasting process (silverskin and spent coffee grounds) being generated with a wider geographic distribution, due to the various countries that carry out the importation (DEL CASTILLO *et al*., 2019). These co-products generate an extensive environmental impact, as they have a high organic load and compounds, such as caffeine, tannins and polyphenols, that contribute to their toxic nature. Therefore, possible reuse alternatives must be evaluated. In recent decades, studies have highlighted the rich composition of coffee co-products, mainly in bioactive compounds, which are of great interest for extraction and application in the food, pharmaceutical and cosmetic industries (ALGHOONEH *et al*., 2017; ALVES *et al*., 2017; MUSSATO *et al*., 2011; SANTOS *et al*., 2021).

2.4 Coffee silverskin

Coffee silverskin (CS) is a thin integument that involves the raw coffee bean, called perisperm. The CS detachment from grain occurs during the roasting process, being separated by air flow. Therefore, this is the main co-product generated in the coffee roasting process (ALGHOONEH *et al.*, 2017; COSTA *et al.*, 2014; IRIONDO-DEHOND *et al.*, 2019; MUSSATO *et al.*, 2011; NARITA; INOUYE, 2014). In the roasting process, 60 kg of CS are produced for every eight tons of roasted coffee, corresponding to 0.75% (w/w) (ALVES *et al.*, 2017; NZEKOUE *et al.*, 2020).

Most of the time, CS is sent for composting, to landfills, or used as furnace fuel (ALGHOONEH *et al*., 2017; COSTA *et al*., 2014; MUSSATO *et al*., 2011). However, in recent years, some studies have highlighted that CS has a chemical composition of interest for application in the food, chemical and pharmaceutical industries, and is considered a potential natural source of several bioactive compounds. Therefore, several studies have reported the

importance of valuing this co-product (ALVES *et al*., 2017; NARITA; INOUYE, 2014; TOSCHI *et al*., 2014).

The wide variation in centesimal composition (Table 1) and bioactive compounds of CS is due to factors related to geographic origin, genetics, agricultural practices, climate, fruit maturation and roasting degree, post-harvest processing, and differences in analytical procedures (BARBOSA-PEREIRA; GUGLIELMETTI; ZEPPA, 2018; BESSADA *et al.*, 2018; IRIONDO-DEHOND *et al.*, 2019; SALES; MIGUEL; FARAH, 2019).

Table 1 - Centesimal composition of coffee silverskin

Centesimal composition (%) *	
Moisture	4.76 - 10.3
Carbohydrates	62.1 - 80.5
Available carbohydrates	0.25 - 6.35
Total dietary fibre	53.4 – 62.4
Insoluble dietary fibre	44.2 – 53.7
Soluble dietary fibre	3.3 – 10.95
Proteins	11.8 - 22.86
Minerals (Ashes)	5.36 - 11.58
Fats	1.32 - 3.78

*Moisture expressed in fresh weight and the other responses expressed in % dry basis (d.b.).
Source: Ballesteros; Teixeira; Mussatto (2014b); Bessada *et al.* (2018); Borrelli *et al.* (2004); Costa *et al.* (2018); Pourfarzad; Mahdavian-Mehr; Sedaghat (2013); Sales; Miguel; Farah (2019).

CS is considered the most stable material compared to other coffee co-products, as it has a low moisture content (<10%) (BESSADA *et al.*, 2018). In addition, the high temperatures used in the roasting process also contribute to the reduction or elimination of microorganisms potentially associated with the raw coffee bean (SANTOS *et al.*, 2021).

Carbohydrates are the main nutrients found in CS, followed by protein and minerals (Table 1). On the other hand, the lipid content is considered low (ARYA *et al.*, 2021; BRESCIANI *et al.*, 2014; POURFARZAD; MAHDAVIAN-MEHR; SEDAGHAT, 2013).

Dietary fiber is the major constituent of the carbohydrate fraction, being composed of ~85% insoluble dietary fiber and ~15% soluble dietary fiber. These dietary fiber values are higher than those found in other vegetables such as broccoli, apples and oat bran. Dietary fiber is of great importance for human health, as it helps to prevent various diseases, such as diabetes, cardiovascular diseases and cholesterol reduction, among others. The various physiological

effects of fiber depend on its physical and chemical properties and on the sources in which the fiber is found (BORRELLI *et al*., 2004; NARITA; INOUYE, 2014; POURFARZAD; MAHDAVIAN-MEHR; SEDAGHAT, 2013). Dietary fiber of CS is mainly composed of cellulose (17.8 - 23.8% d.b.), hemicellulose (13.1 - 16.7% d.b.), lignin (28.2 to 30% d.b.) and total pectic substances (0.02% d.b.) (DEL CASTILLO *et al*., 2019; NARITA; INOUYE, 2014; SANTOS *et al*., 2021).

Available carbohydrates are found in smaller amounts in CS, with sucrose, glucose, fructose, mannitol, inositol being some of the main soluble carbohydrates reported by Toschi *et al.* (2014). In addition, it is noteworthy that cellulose and hemicellulose are formed by glucose, fructose, xylose, galactose, mannose and arabinose (ARYA *et al.*, 2021; BALLESTEROS; TEIXEIRA; MUSSATTO, 2014b). Therefore, extraction conditions influence the actual quantification of these components, since the degree of hydrolysis of native polysaccharides will affect the final content of available carbohydrates (DEL CASTILLO *et al.*, 2019; TOSCHI *et al.*, 2014).

High amounts of protein can also be found in CS (Table 1). In addition to quantity, protein quality is also an important parameter to be considered. Therefore, amino acid composition analysis, as well as the determination of total, protein and non-protein nitrogen can be used to measure these parameters (DAMODARAN; PARKIN, 2019; MACHADO *et al.*, 2020). Machado *et al.* (2020) found that 25% of the CS nitrogen corresponded to the non-protein fraction. In this way, only the protein nitrogen was considered for the protein content calculation, in order not to overestimate the real value. The actual protein value found was 12% in fresh weigh. Regarding the amino acid profile, CS presents all essential amino acids in free form, with the exception of methionine. Regarding total amino acids, aspartic acid (10.2 mg/g) and glutamic acid (9.2 mg/g) were the main amino acids found in CS, followed by valine, isoleucine and leucine (5–8 mg/g), as well as arginine and proline (~5 mg/g) (MACHADO *et al*., 2020).

The mineral profile of CS is composed of several mineral elements, such as potassium (2.11 - 5 g/100 g d.b.), calcium (0.5 - 0.94 g/100 g d.b.), magnesium (0.31 -2 g/100 g d.b.), sulfur (0.28 g/100 g d.b.), phosphorus (0.12 g/100 g d.b.), iron (0.0418 - 0.084 g/100 g d.b.) and other minerals in quantities less than 0.047 g/100 g d.b., such as strontium, barium and manganese, among others. Some of these minerals are important for human health, being considered essential, as they contribute to various functions in the human body, such as the regulation of physiological and metabolic functions (BALLESTEROS; TEIXEIRA; MUSSATTO, 2014a; COSTA *et al*., 2018).

Regarding lipid composition, Toschi *et al*. (2014) found that the extraction method and the type of solvent used influence the lipid profile of CS. According to these authors, Soxhlet extraction using n-hexane was the most sustainable choice, with the CS lipid fraction being essentially composed of triacylglycerols (~48%), free fatty acids (~21%), esterified sterols (~ 15%), free sterols (~13%) and diacylglycerols (~4%). In addition, some authors have reported that the fatty acids profile of CS mostly presents saturated fatty acids (62-86%), followed by polyunsaturated (10-29%) and monounsaturated (5-10%), of which the main ones are palmitic acid (C16:0), linoleic acid (C18:2n6), arachidic acid (C20:0), behenic acid (C22:0), oleic acid (C18:1n9c) and linoleic acid (C18:2 n6c) (BESSADA *et al*., 2018; COSTA *et al*., 2018; TOSCHI *et al*., 2014).

2.4.1 Bioactive compounds from CS

The term "bioactive" is derived from words bio- and -active. Bio from Greek word "*bios*" refers to life and active from the Latin from "*activus*" refers to energetic, dynamic, full of energy, with energy or involves an activity, that is full of vigor. Therefore, bioactive compounds are substances that exert direct effects on living organism, on the activity or functioning of life (DHAVAL; YADAV; PURWAR, 2016; SHRINET *et al.*, 2021).

According to Vilas-Boas; Pintado; Oliveira (2021), there is still no consensus in the literature on a single definition of bioactive compounds. The definition commonly used is that "bioactive compounds are essential and nonessential compounds that occur in nature, are part of the food chain, and can be shown to have an effect on human health" (BIESALSKI *et al.*, 2009). Essen; Young; Baroutian (2020) also described that bioactive compounds "are sourced naturally from plants, algae, foods and co-products or synthetically produced and can interact with one or more components of living tissue resulting in a wide range of effects". These compounds are phytochemicals and also called "extranutritional constituents that typically occur in small quantities in foods" (SANTOS *et al.*, 2019).

The interest in bioactive compounds is due to their numerous health benefits, such as: antioxidant, hypo-cholesterolemic, anti-cancer, immunomodulatory, anti-inflammatory, anti-diabetic, anti-hypertensive, oxidative stress and metabolic disorders reduction, inhibition of receptor activities, inhibition or induction of enzymes, induction and inhibition of gene expression (BELŠČAK-CVITANOVIĆ; KOMES, 2017; BHUSHAN *et al.*, 2021; COELHO; FERNANDES; SALAS-MELLADO, 2019; SANTOS *et al.*, 2019).

Bioactive compounds include an extremely heterogeneous class of compounds, such as polyphenolic compounds, carotenoids, tocopherols, vitamins, phytosterols, organosulfur compounds, bioactive lipids, bioactive peptides, essential oils and probiotics (GALANAKIS, 2017; YUN; DEVAHASTIN; CHIEWCHAN, 2021). According to Vilas-Boas; Pintado; Oliveira (2021), these compounds "can enter the market as food additives to improve technological and sensory functions, as a supplement or being presented as a functional food".

Beyond their macro- and micronutrient contents, the coffee silverskin is a rich natural source of several bioactive compounds, mainly antioxidants, such as phenolic compounds, caffeine, melanoidins and vitamin E (BESSADA *et al.*, 2018; BORRELLI *et al.*, 2004; COSTA *et al.*, 2018; NZEKOUE *et al.*, 2020).

Nzekoue *et al*. (2020) quantified about 30 bioactive compounds present in CS extract, such as 2 alkaloids (caffeine and quinine) and 18 phenolic compounds (phenolic acids, flavonoids, xanthones). The total content of CS bioactive compounds ranged from 1.56 to 4.01% w/w, according to the type of solvent used.

2.4.1.1 Phenolic compounds

Phenolic compounds, also known as polyphenols, are defined as substances produced by the secondary metabolism of plants and are considered the most abundant natural antioxidants found in the plant kingdom, with around 10,000 different phenolic structures being isolated and identified in plants (CHIORCEA-PAQUIM *et al.*, 2020). Polyphenols are made up of one or more aromatic rings bonded (non-polar part) to one or more hydroxyl groups (polar part), generating different chemical structures. Various classifications are proposed for these compounds. Generally, they can be divided into different groups: phenolic acids, flavonoids, tannins, stilbenes and lignans, and each of these groups can be divided into other.

The polyphenols present in plants provide pigmentation, astringency and protection against UV light, parasites and insects. In addition, they are of great interest for human health, as they have antioxidant, antimicrobial, anti-inflammatory, antiproliferative effects, being potential substances for the prevention of various chronic diseases, such as cardiovascular diseases, diabetes and cancer, among others (ALBUQUERQUE *et al.*, 2021; CHIORCEA-PAQUIM *et al.*, 2020; RASHMI; NEGI, 2020). In the food industry, polyphenols have been used as natural food additives, such as antimicrobials, antioxidants and flavorings (ZEB, 2020).

Polyphenols are the most studied of the bioactives and are present in various vegetable sources, such as fruits, vegetables, spices, grains and beverages (ALBUQUERQUE *et al.*, 2021;

RASHMI; NEGI, 2020). According to Albuquerque *et al.* (2021), food co-products can also be considered a natural and cheap source for obtaining polyphenols, since these co-products generally have no economic value and are wasted.

Coffee and its co-products have relevant amounts of phenolic compounds, mainly chlorogenic acids (CGA) (BRESCIANI *et al.*, 2014; COSTA *et al.*, 2018; REGAZZONI *et al.*, 2016). CGA are esters of trans-hydroxycinnamic acids and quinic acid, with over 300 CGA major, minor, and related compounds found in coffee and other vegetables. These compounds are considered the main antioxidants in the diet, due to the high consumption of coffee (FARAH; DE PAULA LIMA, 2019). According to the chemical identity, number and position of acyl residues, CGAs can be subclassified into: caffeoylquinic acids (CQA), dicaffeoylquinic acids (diCQA), feruloylquinic acids (FQA), p-coumaroylquinic acids (pCoQA) and six mixed diesters of caffeoyl-feruloyl-quinic acids (CFAQ), where CQA, diCQA, FQA and pCoQA are formed by 3 isomers (DORSEY; JONES, 2017; FARAH *et al.*, 2005; FARAH; DONANGELO, 2006).

In the coffee silverskin, the CGA content varies from 0.6 to 3% d.b. Caffeoylquinic acids are the main CGA found in this co-product, where the highest amounts were for 5-caffeoylquinic acids (0.20-0.22%), 3-caffeoylquinic acids (0.15%) and 4-caffeoylquinic acids (0.08-0.10%), respectively. Therefore, this co-product is considered a good source for the extraction of these bioactive compounds (DEL CASTILLO *et al*., 2019). Bresciani *et al*. (2014) found a chlorogenic acid profile of CS similar to that of coffee brews. These authors identified three caffeoylquinic acid isomers (74% of the total CGA detected), three feruloylquinic acid isomers (23%) and the two coumaroylquinic acids plus the two caffeoylquinic acid lactones (3% of total hydroxycinnamates). The degree of roasting significantly influences the CGA content, since the roasting process contributes to isomerization and degradation reactions of these compounds, generating lactone (COSTA *et al*., 2018; FARAH *et al*., 2005).

2.4.1.2 Caffeine

Caffeine, also called 1,3,7-trimethylxanthine, is a purine derivative (methylxanthine) belonging to the alkaloid class, widely known and consumed throughout the world. This substance has a bitter taste and is present in small amounts in the composition of various foods, such as coffee, cocoa, tea, and yerba mate (ALVES *et al.*, 2017; BARTELLA *et al.*, 2019).

In coffee beans, the caffeine content can range from 0.9 to 2.1% d.b. Caffeine is extensively researched and used in the food, pharmaceutical and cosmetic industries due to its

stimulating effect, which enhances concentration capacity and counteracts tiredness, and for other purposes (BELŠČAK-CVITANOVIĆ; KOMES, 2017). In addition, caffeine has other interesting properties, such as antioxidant potential, immune modulator and beneficial effects on various diseases, such as Parkinson's disease, and Alzheimer's disease, among others. On the other hand, some studies describe that excessive caffeine consumption can generate undesirable effects, such as anxiety, malabsorption of some nutrients, insomnia and dependence (LIMA; FARAH, 2019).

Studies have highlighted that coffee co-products can be considered a good natural source for caffeine extraction, as they present significant amounts of this substance, as is the case with CS (BELŠČAK-CVITANOVIĆ; KOMES, 2017). The caffeine content found in CS ranges from 0.17 to 1.4%, being influenced by the type of solvent, extraction method and temperature used (ALVES *et al.*, 2017; BELŠČAK-CVITANOVIĆ; KOMES, 2017; BESSADA *et al.*, 2018; BRESCIANI *et al.*, 2014; NARITA; INOUYE, 2012), in addition to other factors previously described.

2.4.1.3 Melanoidins and Vitamin E

Melanoidins are the end products generated by the Maillard reaction. They are a group of nitrogen-containing polymeric compounds with high molecular weight, brown-coloured, with complex structure and high antioxidant activity. Their exact composition is yet unknown. Coffee and bakery products are the main sources of these compounds in the human diet (DE PEÑA; LUDWIG; CID, 2019; ESQUIVEL; JIMÉNEZ, 2012; MOREIRA *et al.*, 2012). In coffee, melanoidins are formed during the roasting process and represent about 25% of the total solids of the coffee brew (DE PEÑA; LUDWIG; CID, 2019). CS can also be considered an important source of melanoidins (DE LA CRUZ *et al*., 2019). Borrelli *et al*. (2004) found that the amount of water-soluble melanoidins in CS was 4.5%. On the other hand, Mesías *et al*. (2014) found values of 17 to 24% of melanoidins present in the CS extract. Melanoidins are formed by several compounds, mainly polysaccharides, proteins and chlorogenic acids. The types and quantities found in coffee and its co-products depend on the conditions adopted during roasting and the chemical composition of the beans (DEL CASTILLO *et al*., 2019).

Vitamin E is an essential micronutrient for the body. It is considered the most important fat-soluble antioxidant in the cell, as it protects the cell membrane against the action of free radicals (BESSADA *et al*., 2018; COSTA *et al*., 2018). Furthermore, it presents modulatory effects in relation to gene expression, cellular pathways and signal transduction (UNGURIANU

et al., 2021). Vitamin E is composed of eight different compounds, divided into two groups: tocopherol (α, β, ɣ and δ) and tocotrienol (α, β, ɣ and δ). Of all these components, α-tocopherol is the component with the highest biological activity (BESSADA *et al*., 2018; COSTA *et al*., 2018). In recent years, research has identified an interesting vitamin E profile of CS, with a total content ranging from 3.94 to 16.79 mg/100 g (BESSADA *et al*., 2018; COSTA *et al*., 2018). Bessada *et al*. (2018) evaluated the tocopherol profile of CS from different geographic origins and found three tocopherols present (α, β and ɣ). On the other hand, COSTA *et al*. (2018) also evaluated the vitamin E profile of CS and found a more complete profile with seven different vitamers (α-tocopherol, β-tocopherol, ɣ-tocopherol, δ-tocopherol, β-tocotrienol, ɣ-tocotrienol and δ-tocotrienol).

2.4.2 Use of the coffee silverskin

The rich composition of CS in fiber, protein, minerals and bioactive compounds justifies its potential use for application in different fields, such as the food, pharmaceutical and cosmetic industries (ALVES *et al*., 2017; COSTA *et al*., 2014; MURTHY; NAIDU, 2012). This co-product has been used as a coloring agent, source of dietary fibers and antioxidants (ARYA *et al.*, 2021; BALLESTEROS; TEIXEIRA; MUSSATTO, 2014a), application in some products to add value, such as yogurt (BERTOLINO *et al.*, 2019), cookies (GOCMEN *et al.*, 2019), cakes (ATEŞ; ELMACI, 2018, 2019), biscuits (GARCIA-SERNA *et al.*, 2014), beverages (MARTINEZ-SAEZ *et al.*, 2014) and breads (POURFARZAD ; MAHDAVIAN-MEHR; SEDAGHAT, 2013).

Some studies have also highlighted other properties of CS, such as a prebiotic, stimulating the selective growth of intestinal microflora (BORRELLI *et al*., 2004; JIMÉNEZ-ZAMORA; PASTORIZA; RUFIÁN-HENARES, 2015), a production source for fructooligosaccharides and fructofuranosidases by fermentation (MUSSATTO; TEIXEIRA, 2010), anticarcinogenic, anticariogenic, anti-inflammatory and antimicrobial effects (DE LA CRUZ *et al*., 2019; MESÍAS; DELGADO-ANDRADE, 2017), hyaluronidase inhibitory activity (FURUSAWA *et al*., 2011) and an anti-photoaging effect in human skin cells by isolation of atractyligenin (XUAN; LEE; PARK, 2019). Therefore, this co-product can be considered as a potential functional ingredient (ARYA *et al*., 2021), which can be used for direct incorporation into some foods or subjected to an extraction process so that its properties can be used separately.

2.5 Extraction process

The extraction of bioactive compounds from food matrices is an essential unit operation for maximum recovery and application of these compounds, being the first stage of isolation. Several methods and conditions of the bioactive compound extraction process have been researched in recent years, in order to obtain a higher extraction yield and find a method that is environmentally friendly, simple and accessible to industries. However, no method can be considered completely adequate, as each one has advantages and disadvantages that must be evaluated for each case. Therefore, the optimization of the extraction process for each reality is extremely important (BALLESTEROS; TEIXEIRA; MUSSATTO, 2014a; BELŠČAK-CVITANOVIĆ; KOMES, 2017; OLIVEIRA *et al.*, 2019; RAHMANIAN; JAFARI; WANI, 2015).

Solid-liquid extraction using different solvents is the most used process to isolate bioactive compounds from plant matrices (OLIVEIRA *et al.*, 2019). Generally, the extraction solvent is selected according to the polarity of the solute of interest, in order to provide migration of solutes from matrix to the extraction liquid. Studies has highlighted that the addition of water or other compounds in extraction solvents has been a common practice, as they change the viscosity of the solvent or increase its polarity and contribute to higher yields (COSTA *et al.*, 2014; LEFEBVRE; DESTANDAU; LESELLIER, 2021). Some bioactive compounds, such as phenolic compounds, have a complex and diversified composition, which are soluble in solvents with different polarities. In addition, these compounds can interact with other food components (e.g., proteins and carbohydrates) to form insoluble complexes. Therefore, the development of a single extraction method for all plant matrices is very complex (NACZK; SHAHIDI, 2006; OLIVEIRA *et al.*, 2019).

The quality and quantity of bioactive compounds present in the extract are mainly influenced by the type of solvent used and its polarity. In addition, other parameters can also affect the efficiency of the extraction process, such as the composition of the plant matrix, solid-liquid ratio, time, agitation, temperature, pressure, and the quantification test of these compounds (MOHAPATRA *et al.*, 2021; NACZK; SHAHIDI, 2006; OLIVEIRA *et al.*, 2019).

Due to the toxicity of some solvents and the greater concern for the environment, recent studies have suggested the use of green solvents to reduce or eliminate harmful substances. Therefore, solvents such as ethanol, acetone, ethyl acetate and isopropanol have been potentially considered to replace solvents that are more toxic and harmful to health, such as

hexane and methanol, among others (OLIVEIRA *et al.*, 2019; RAHMANIAN; JAFARI; WANI, 2015).

Several extraction methods are described in the literature. The methods can be divided into traditional methods, such as Soxhlet and maceration, and non-traditional methods, such as pressurized liquid extraction, subcritical water extraction, superheated liquid extraction, supercritical fluid extraction, supercritical carbon dioxide extraction, microwave assisted extraction, ultrasound assisted extraction and combined techniques (MOHAPATRA *et al*., 2021; RAHMANIAN; JAFARI; WANI, 2015).

Most industrial processes still use traditional extraction methods due to their rapid and reproducible extraction, low processing cost and ease of operation, and wide diffusion. These methods mainly use heat and/or agitation to increase the mass transfer rate (BELŠČAK-CVITANOVIĆ; KOMES, 2017; MOHAPATRA *et al.*, 2021; RAHMANIAN; JAFARI; WANI, 2015).

Non-traditional methods have received greater interest and prominence in recent years, as they are greener, safer methods, have a shorter extraction time, less thermal degradation of target compounds, better cost-benefit, less labor, higher yields and need small amounts of solvents. The combination of some of these methods has generated more satisfactory results (LEFEBVRE; DESTANDAU; LESELLIER, 2021; MOHAPATRA *et al.*, 2021; RAHMANIAN; JAFARI; WANI, 2015). However, some laboratories and industries do not have the necessary equipment available for extraction by these newer methods (COSTA *et al.*, 2014).

Ballesteros; Teixeira; Mussatto (2014a) evaluated various solid-liquid extraction conditions to maximize the recovery of antioxidant phenolic compounds from coffee silverskin. Various organic solvents (methanol, ethanol, acetone and water) were tested at different concentrations (20 - 90% v/v), solvent/solid ratio (10 - 40 mL/g of sample) and extraction time (30-90 minutes). The optimal point found by the authors was using 60% ethanol (v/v), solvent/solid ratio of 35 mL/1 g and extraction time of 30 min.

Wen *et al.* (2019) verified the effect of ultrasound-assisted extraction on extraction yield and total phenolics kinetics of the coffee silverskin. The results showed that the pretreatment with ultrasound showed the highest values of phenolic compounds compared to non-pretreated samples. Furthermore, it was also observed that the higher ultrasound power (38 W/cm²) provided the greatest recovery of phenolic compounds compared to the lowest (5 W/cm²).

Narita; Inouye (2012) used subcritical water to evaluate the extraction of antioxidant compounds in CS extract. These authors found that the antioxidant activity in the extracts

increased sigmoidly with the increase in water and subcritical water temperature from 25 to 270 ºC.

Nzekoue *et al.* (2020) found that a mixture of water and ethanol (30:70) contributed to the highest extraction of bioactive compounds from CS, identifying about 30 bioactive compounds from alkaloid and polyphenol classes, such as caffeine, quinine and 18 phenolic compounds. In addition, the mixture of these solvents contributed the highest levels of bioactive compounds (4.01%).

Machado *et al.* (2012) selected some strains of fungi with the potential to grow and release phenolic compounds from coffee silverskin and spent coffee grounds, under solid state fermentation conditions, in order to find alternatives for the reuse of these residues. The authors verified that the *Penicillium purpurogenum* GH2 strains, *Neurospora crassa* ATCC10337 and *Mucor* sp. 3P showed great capacity to grow and release phenolic compounds from coffee silverskin and spent coffee grounds.

2.6 Encapsulation

Generally, most bioactive compounds are extremely sensitive to conditions adopted during food processing, transport and storage, such as high temperatures, exposure to light, presence of oxygen and moisture, among others, limiting their application in other food matrices. Therefore, there is a need to use techniques that ensure the protection and stability of these compounds for their application (BALLESTEROS *et al.*, 2017; LOZANO-VAZQUEZ *et al.*, 2015; YUN; DEVAHASTIN; CHIEWCHAN, 2021).

Encapsulation is a technique that has been widely suggested as a promising technology to protect bioactive compounds against harmful factors (BALLESTEROS *et al.*, 2017; YUN; DEVAHASTIN; CHIEWCHAN, 2021). This process consists of packing the solid, liquid or gaseous material (known as a core) inside a wall material, forming a microparticle, also called an encapsulate. Thus, bioactive compounds are not directly exposed to external factors that affect their stability (ARENAS-JAL; SUÑÉ-NEGRE; GARCÍA-MONTOYA, 2020; BAKRY *et al.*, 2016; GHARSALLAOUI *et al.*, 2007). Encapsulation also contributes to the controlled release of compounds, increases bioavailability, acts by masking undesirable flavors (such as bitterness or astringency), improves retention time and facilitates the solubilization of insoluble compounds (AGUIAR; ESTEVINHO; SANTOS, 2016; ARENAS- JAL; SUÑÉ-NEGRE; GARCÍA-MONTOYA, 2020; BALLESTEROS *et al.*, 2017; YUN; DEVAHASTIN; CHIEWCHAN, 2021).

The encapsulate can vary in size and shape and can be produced encapsulated from 1 to 1000 µm (ARENAS-JAL; SUÑÉ-NEGRE; GARCÍA-MONTOYA, 2020). These characteristics depend on the composition of the wall and core material, and the encapsulation method. The wall material comes from different sources (carbohydrates, lipids, proteins), and a single material or a mixture of materials with different physical and chemical properties can be used, in order to overcome the limitations of using only one material. The core can also be formed by a variety of sources with different properties (ARENAS-JAL; SUÑÉ-NEGRE; GARCÍA-MONTOYA, 2020; GONÇALVES; ESTEVINHO; ROCHA, 2016; YUN; DEVAHASTIN; CHIEWCHAN, 2021).

According to Yun; Devahastin; Chiewchan (2021), every encapsulation method consists of four steps: core formation, encapsulant formation, incorporation, and solidification. Most of the time, drying processes are applied for solidification, as the bioactive compounds are present in an extract that is liquid. Several methods can be used for the encapsulation process, such as ionic gelation, spray drying, freeze drying, fluid-bed coating, coextrusion and coacervation, among others.

Encapsulation efficiency is a commonly performed analysis to assess the content of bioactive compound trapped within the encapsulate compared to the amount initially added. Several methodologies and different solvents have been used, the choice of solvent being dependent on the solubility of the wall and/or core material (YUN; DEVAHASTIN; CHIEWCHAN, 2021). For greater incorporation and encapsulation efficiency, the wall material and encapsulation methods must be carefully chosen (BALLESTEROS *et al.*, 2017; GONÇALVES; ESTEVINHO; ROCHA, 2016).

2.6.1 Wall materials

The choice of wall material must consider the properties of the core material and the desirable characteristics of the final product (BARANAUSKIENĖ *et al.*, 2006). The main functions of the wall material are to form a wrap with the core material, ensure the stabilization of the bioactive, strength and flexibility, mask aromas, colors and flavors, protect against nutritional losses (AGUIAR; ESTEVINHO; SANTOS, 2016; ANAL; SINGH, 2007).

The most used wall materials for the encapsulation of bioactive compounds are maltodextrins, modified starches, pectin, cellulose derivatives, inulin, gums and other hydrocolloids, milk proteins, soy protein and egg protein, lipids (natural oils, mono and

diglycerides, phospholipids, glycolipids and waxes and new emerging biopolymers (AUGUSTIN; HEMAR, 2009; ESTEVINHO *et al.*, 2013).

Some studies have highlighted maltodextrin, gum arabic and egg albumin as excellent wall materials obtained from natural sources for encapsulation of bioactive compounds (BALLESTEROS *et al.*, 2017; FARIA *et al.*, 2020; FERNANDES; BORGES; BOTREL, 2014; SAMBORSKA *et al.*, 2021).

Maltodextrin refers to dextrins that are obtained by acidic or enzymatic hydrolysis of starch with equivalent dextrose (DE) values of less than 20. This material is a highly water-soluble, low-viscous carbohydrate, has low cost, neutral aroma, and taste, contributes to the reduction of sticking/agglomeration of the encapsulate, being widely used in encapsulation processes. However, maltodextrin has low emulsification capacity and volatile retention as its main limitations. Therefore, blends with other polymers are commonly used (BALLESTEROS *et al.*, 2017; FERNANDES; BORGES; BOTREL, 2014; HOYOS-LEYVA *et al.*, 2018; SAMBORSKA *et al.*, 2021).

Gum arabic is a polymer produced from exudates of Acacia trees and is widely used in encapsulation processes. This ingredient is made up of D-Glucuronic Acid, L-Rhamnose, D-Galactose and L-Arabinose and about 2% protein. The main characteristics of gum arabic are good emulsifying properties and retention of volatiles. It contributes to increase the viscosity of the medium, is nontoxic, odourless and tasteless (DA SILVA *et al*., 2013; FERNANDES; BORGES; BOTREL, 2014). The main problems related to the use of this material are due to its high cost and limited availability (FERNANDES; BORGES; BOTREL, 2014; SAMBORSKA *et al.*, 2021; TONTUL; TOPUZ, 2017).

Egg albumin is the main protein present in egg whites. This ingredient is widely used in the preparation of various foods, as it has important foaming, emulsifying and gelling properties (JIA *et al*., 2019; SAMBORSKA *et al*., 2021). In addition, it can also be used as a wall material for encapsulation processes (ARZENI *et al*., 2015; KUHN; AZEVEDO; NOREÑA, 2020; TAN; ZHONG; LANGRISH, 2020). Egg albumin presents high solubility in water, biodegradability, stability in a wide pH range (pH 4-9), contributes with well-defined sizes of the encapsulates and could be used as binding or surface modifiers due to its reactive functional groups on their surface (KUHN; AZEVEDO; NOREÑA, 2020; SAMBORSKA *et al*., 2021). Tan; Zhong; Langrish (2020) verified that egg albumin can be used as a wall material to encapsulate caffeine and that the inlet temperature of the spray dryer (60–200 °C) influences the characteristics of the powder. According to these authors, low process entry temperatures generate smaller encapsulates and low yields.

2.6.2 Encapsulation methods

2.6.2.1 Spray drying

Spray drying is considered one of the oldest methods used in encapsulation, being used since 1930. This process was the first to be used in the aroma industry to produce an encapsulated aroma. The main characteristics that make spray drying the most used until today in the food industries are low cost, process simplicity, continuous flow, varieties of encapsulating matrices, compound retention and stability (GHARSALLAOUI *et al.*, 2007; MADENE *et al.*, 2007; al., 2006; REINECCIUS, 2004; RIBEIRO; ESTEVINHO; ROCHA, 2019). Therefore, this technique is widely used for the production of many encapsulated compounds, such as vitamins, minerals, flavors, polyunsaturated oils, enzymes and probiotic microorganisms (AUGUSTIN; HEMAR, 2009; FERNANDES; BORGES; BOTREL, 2014; YUN; DEVAHASTIN; CHIEWCHAN, 2021).

The spray drying method is a unitary operation in which a liquid product is atomized in a stream of hot air to obtain an instant powder. This method basically involves five steps. Initially, the material to be encapsulated must be prepared. Generally, concentration or addition processes of carrier agents are used to increase the solids content. In the second stage, the liquid is dispersed as a spray of droplets, by means of a device known as an atomizer. This spray of droplets then comes into contact with a stream of hot air, which can be used with air or an inert gas such as nitrogen. Drying of the atomized droplets occurs by evaporating water from product with a simultaneous cooling of the air due to the latent heat of vaporization. Evaporation takes place until the temperature of the drying air is equal to the temperature of the particle. Finally, the separation of air from the dry product occurs, in which the particles can be collected by gravity at the base of the drying chamber and collected by appropriate devices or can be carried by the drying air, being recovered by a system of cyclones and filters (CAL; SOLLOHUB, 2006; MURUGESAN; ORSAT, 2012; TONTUL; TOPUZ, 2017). The final powder has good quality, low water activity, facilitating storage and transport (MURUGESAN; ORSAT, 2012).

2.6.2.2 Freeze drying

Freeze drying is also a method to encapsulate bioactive compounds, being commonly used in the food and pharmaceutical industries for many years. This method is known as a premium drying, as it has greater retention of thermosensitive compounds, preservation of

sensory characteristics such as color, flavor, aroma and appearance, easy and fast reconstitution speed, low moisture content and water activity. However, it also has some disadvantages, such as more hygroscopic products, high energy consumption and long process time (ARENAS-JAL; SUÑÉ-NEGRE; GARCÍA-MONTOYA, 2020; LIU; ZHANG; HU, 2021; WAGHMARE *et al.*, 2021).

The freeze drying process consists of the removal of water by the sublimation of ice using a reduced pressure, being considered a vacuum drying method (ARENAS-JAL; SUÑÉ-NEGRE; GARCÍA-MONTOYA, 2020). This process can be divided into freezing and drying unit operations. Initially, the material is subjected to freezing, and traditional methods can be used. Then, the frozen sample is placed in a reduced pressure chamber for the sublimation process. As the frozen product is heated, the ice crystals sublime into steam and are released, causing up to 95% of the water to be removed. At this stage, the product temperature must always be maintained. At the end of the process, residual moisture from sample surface is removed by desorption at a higher temperature (<45 ºC) and the final product moisture ranges from 0.5 to 3% (LIU; ZHANG; HU, 2021; WAGHMARE *et al.*, 2021).

2.6.2.3 Foam mat drying

Foam mat drying (FMD) consists of transforming liquid, semi-liquid or pasty foods into a stable foam by adding foaming agents and/or stabilizers and subsequent stirring. The foam, in a thin layer, is then placed on trays and subjected to drying with forced air circulation, to obtain a powder with low moisture. Generally, drying temperatures of 40 to 90 ° C are used (HARDY; JIDEANI, 2017; QADRI; SRIVASTAVA; YOUSUF, 2020; SANGAMITHRA *et al.*, 2015).

Foaming agents and stabilizers added, individually or in combination, affect foam properties such as density, porosity, overrun, and stability. These foam properties influence the drying process and the quality of the powder obtained. Therefore, optimizing the concentration of agents is a step that must be carefully determined (HARDY; JIDEANI, 2017; QADRI; SRIVASTAVA; YOUSUF, 2020). Various foaming and stabilizing agents can be used, such as whey proteins, whey protein isolate, soy and egg proteins, gum arabic, xanthan gum, methylcellulose, carboxymethylcellulose, glycerol monostearate, maltodextrin and fish gelatin (HARDY; JIDEANI, 2017; NG; SULAIMAN, 2018; SANGAMITHRA *et al.*, 2015).

FMD has been commonly applied to heat-sensitive foods, as this method uses low drying temperatures, has a shorter drying time due to the higher surface area that is exposed to

the drying air, generating an increase in drying water removal rate. FMD is considered a simple, inexpensive process, in addition to providing high powder quality and process efficiency (ARAÚJO *et al.*, 2020; KANHA; REGENSTEIN; LAOKULDILOK, 2020; MACEDO *et al.*, 2021; PAULA *et al.*, 2020; SANGAMITHRA *et al.*, 2015).

Some research has highlighted that FMD can be considered an efficient method in the encapsulation process of some compounds, such as black rice bran anthocyanins (KANHA; REGENSTEIN; LAOKULDILOK, 2020), red sorghum proanthocyanidins (SUSANTI *et al.*, 2021), pequi carotenoid (PINTO *et al.*, 2018) and protein and amino acids of moringa leaf (SUSANTI *et al.*, 2021).

3 GENERAL CONSIDERATIONS

The valorization of the coffee silverskin is very important, as this co-product represents a rich natural source for the extraction of bioactive compounds with properties beneficial to health. In addition, the reuse of CS reduces or eliminates impacts on the environment. Due to the large volumes of co-products generated by coffee processing, efficient alternatives must be studied for better reuse, such as optimizing the extraction of compounds for application in industries. Determining an optimal condition for the extraction process has been an excellent tool, as it seeks to find the most desirable condition for the various parameters studied.

The limitation of bioactive compounds extraction, such as the low stability to external factors (light, oxygen, heat, etc.), can be overcome by efficient encapsulation methods. Therefore, the suitable choice of the wall material and the encapsulation method are determining factors for the preservation of bioactive compounds.

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SECOND SECTION

ARTICLE 1 - Optimal extraction condition for the recovery of bioactive compounds and antioxidants from coffee silverskin

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Abstract

This study aimed to determine the optimal condition for the recovery of bioactive compounds from coffee silverskin. In the first step, three conventional extraction methods (at room temperature, with agitation and in Soxhlet) and four solvents (isopropanol, acetone, ethanol and water) were tested, and an ideal treatment was determined. For the second step, the extraction curve of the total phenolic compounds was evaluated to define the extraction time and the Peleg model was fitted. Sequentially, the temperature and concentration of the hydroalcoholic solution were optimized, and an optimum condition was obtained. The antioxidant activity (FRAP and DPPH assays), total phenolic content (TPC) and total flavonoid content (TFC) were influenced by the interaction between the type of solvent and the extraction method ($p<0.05$). Water and ethanol and the extraction method with agitation (EM-2) were the best operating conditions obtained in the first stage. In the second step, Peleg´s model was considered satisfactory to represent the extraction kinetics of the TPC and the extraction time determined was 120 min. Higher values of extraction temperature and ethanol concentration resulted in higher recovery of bioactive compounds. The combination of the temperature of 68 °C and ethanol concentration of 64% resulted in the best extraction condition by desirability function ($D=0.88$).

Keywords: Industrial coffee co-products, Solid–liquid extraction, Antioxidant capacity, Phenolic compounds, Flavonoids.

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1 Introduction

Coffee is a beverage globally consumed and appreciated. The growing worldwide consumption of this beverage in recent years is due to the incorporation in some formulations, development of new products, changes in the profile of consumers, new domestic coffee machines and coffee houses (Hu & Lee, 2019; Toci, Farah, Pezza, & Pezza, 2016). Consequently, an important portion of co-products is also generated by the coffee sector (Ballesteros, Teixeira, & Mussatto, 2014; Oliveira, Silva, Santos, & Queiroz, 2019).

Coffee silverskin (CS) is one of the co-products of the coffee industry and the only one produced during the roasting process. CS is generally intended for composting, landfill, or furnace fuel. However, research in recent years has highlighted its great potential for reuse and application in the food industry, as it has a varied chemical composition in its bioactive compounds (Barbero-López, Monzó-Beltrán, Virjamo, Akkanen, & Haapala, 2020; Costa et al., 2014; Del Pozo et al., 2021; Mussato, Machado, Martins, & Teixeira, 2011; Nzekoue et al., 2020; Toschi, Cardenia, Bonaga, Mandrioli, & Rodriguez-Estrada, 2014).

The extraction of bioactive compounds present in plant matrices is a unitary operation that has been extensively researched in recent years. The interest in the extraction of these compounds, such as phenolic compounds, flavonoids and other natural antioxidants, is due to their qualities regarding the offering of health benefits (Ballesteros et al., 2014; Mussato et al., 2011; Narita & Inouye, 2012). The parameters adopted in the extraction process, such as the extraction method, type of solvent, solid-liquid ratio, time, agitation and temperature, must be carefully evaluated, as they have a great effect on the extraction yield of these compounds solid matrix (Oliveira et al., 2019; Oreopoulou, Goussias, Tsimogiannis, & Oreopoulou, 2020; Peanparkdee, Yamauchi, & Iwamoto, 2018; Rahmanian, Jafari, & Wani, 2015).

The use of an extraction solvent and its polarity are considered critical parameters in the extraction process, as they influence the antioxidant activity and the total phenolic content of the food matrices (Mohapatra, Ray, Jena, Nayak, & Mohanty, 2021; Oliveira et al., 2019). Currently, green solvents, such as water and ethanol, have aroused interest in extraction processes, because they are safer, cheaper, easily obtained, non-toxic solvents and cause less, or no, risk to the environment (Oliveira et al., 2019; Rodrigues, Mazzutti, Vitali, Micke, & Ferreira, 2019).

Several extraction methods have been employed for recovery of bioactive compounds. These range from the more traditional methods mainly through the use heat, agitation and organic solvents such as Soxhlet and maceration, to the use of the latest technology (ultrasound,

supercritical fluid extraction, microwave, extraction with pressurized liquid, among others). Each method has its advantages and limitations, it being necessary to optimize the process time, the amount of solvent and the yield, in addition to assessing the possibility of use for each industry and type of food (Mohapatra et al., 2021; Oreopoulou et al., 2020; Rahmanian et al., 2015).

In the literature there can be found some studies that have evaluated different extraction methods and solvents for the recovery of bioactive compounds from coffee silverskin (Ballesteros et al., 2014; Costa et al., 2014, 2018; Narita & Inouye, 2012; Wen, Zhang, Rai, Sun, & Tiwari, 2019). Nevertheless, none of these studies found compared the effect of traditional extraction methods with friendlier solvents for the recovery of these bioactive compounds from CS. Therefore, this study aimed to (i) evaluate the influence of traditional methods of solid-liquid extraction and more friendly solvents on the recovery of bioactive compounds from coffee silverskin, (ii) study the extraction kinetics of phenolic compounds and (iii) determine the optimum condition of temperature and solvent concentration of the extraction process.

2 Materials and methods

2.1 Raw material and extraction solvents

Coffee silverskin (CS) was supplied by a local coffee shop (Cafesal) located in Lavras, MG, Brazil. The CS was dried at 60 °C until constant weight. Afterwards, the samples were milled in an electric knives mill (SL-31, Solab, Piracicaba/SP, Brazil) and packed in metallic packages for further use.

The solvents used for the extraction were deionized water, ethanol (99.5%, boiling point 78 °C, specific mass 790 kg/m^3), acetone (99%, boiling point 56 °C, specific mass of 790 kg/m^3), and isopropanol (99%, boiling point 82 °C, specific mass 790 kg/m^3).

2.2 Experimental planning

The extraction experiments were divided into two steps. In the first, the best solvents and extraction method were determined for maximum recovery of bioactive compounds from CS. In the second step, extraction kinetics of the phenolic compounds was carried out and the temperature and solvent concentration were optimized.

2.3 Extraction methods - Step 1

The extractions were carried out by different methods: extraction method at room temperature (Method 1), with agitation (Method 2) and in Soxhlet (Method 3). For all extraction methods, the solid/liquid ratio was kept fixed at 1:35 (w/v) and the extracts were filtered through a Whatman Nº. 1 filter paper and stored in amber flask at -20 °C until further use.

2.3.1 Extraction method 1 (EM-1)

The EM-1 was performed as described by Rufino et al. (2010), with some modifications. Briefly, the samples were weighed in tubes and mixed with 40 mL of each solvent (water, ethanol, acetone, or isopropanol). The mixture was kept for 60 min at room temperature and centrifuged to 2260 × g for 15 min. The supernatant was collected, and 40 mL of each solvent was added to the residue, to extract for more 60 min, followed by centrifugation. Lastly, the supernatants were combined, and the volume was made up to 100 mL with deionized water.

2.3.2 Extraction method 2 (EM-2)

The EM-2 was performed as described by Ballesteros et al. (2014), with some modifications. Sample and solvent were placed in an Erlenmeyer, duly closed to avoid solvent loss, submitted to agitation (120 rpm) on an orbital shaker (Marconi, MA830/A, Piracicaba, SP, Brazil) at constant temperature (60 ° C) for 30 min.

2.3.3 Extraction method 3 (EM-3)

Solid-liquid extraction in a Soxhlet apparatus (EM-3) was performed for 6 h with 150 mL of the solvents according to AOAC (2005). The temperature used was according to the boiling point of each solvent (Oliveira et al., 2019).

2.4 Extraction kinetics and process optimization - Step 2

Extraction kinetics of total phenolic compounds (TPC) was performed to determine the extraction time, after selecting the best solvents and extraction method from the previous step. The kinetic experiment was conducted as described by the extraction method with agitation

(EM-2, item 2.3.2), in which the temperature and solvent concentration conditions of the central point of the central composite rotational design (CCRD) (Table 1) were used (47.5 °C and 45%, v/v). The total time of the kinetics study was 24h, with aliquots (2 mL) being removed from the sample at intervals of 15 min during the first hour, 30 min during the second and third hour, 60 min until 12h and after 24h. Sequentially, the extracts obtained were centrifuged (2260 × g for 15 min), filtered through a Whatman Nº. 1 filter paper and the supernatant was destined for TPC analysis.

Table 1 – Coded and actual values of temperature and ethanol concentration for each experimental condition of the CCRD

Treatments	Coded levels		Actual levels	
	Temperature (°C)	Ethanol concentration (%)	Temperature (°C)	Ethanol concentration (%)
1	-1.00	-1.00	31.59	13.18
2	1.00	-1.00	63.41	13.18
3	-1.00	1.00	31.59	76.82
4	1.00	1.00	63.41	76.82
5	-1.41	0.00	25.00	45.00
6	1.41	0.00	70.00	45.00
7	0.00	-1.41	47.50	0.00
8	0.00	1.41	47.50	90.00
9	0.00	0.00	47.50	45.00
10	0.00	0.00	47.50	45.00
11	0.00	0.00	47.50	45.00

Peleg's model (Peleg, 1988) was used to represent the data of the solid-liquid extraction kinetics of TPC, as presented in Equation 1.

$$C(t) = C_0 + \frac{t}{K_1 + K_2 t} \quad (1)$$

where, C(t) is the concentration of analyte (mg GAE/g CS) at time t (min), C_0 is the concentration of analyte (mg GAE/g CS) at time t = 0, K_1 is Peleg's rate constant (min g/mg GAE), and K_2 is Peleg's capacity constant (g/mg GAE).

As the initial concentration of the solute is zero in the solvent ($C_0 = 0$), Equation 1 can be rewritten as shown in Equation 2 (Poojary & Passamonti, 2015).

$$C(t) = \frac{t}{K_1 + K_2 t} \quad (2)$$

The k_1 parameter of the Peleg´s model refers to extraction rate (B_0) at the beginning of the extraction ($t = t_0$) (Equation 3) and k_2 refers to the maximum extraction or equilibrium concentration (C_{eq}) of the total analyte extracted ($t \rightarrow \infty$) (Equation 4) (Poojary & Passamonti, 2015).

$$B_0 = \frac{1}{K_1} \quad (3)$$

$$C_{t \rightarrow \infty} = C_{eq} = \frac{1}{K_2} \quad (4)$$

The optimal extraction time determined by the extraction kinetics was adopted to perform the CCRD tests (Table 1).

2.5 Chemical characterization

2.5.1 FRAP assay

The antioxidant capacity by FRAP (Ferric Reducing Antioxidant Power) assay was performed as described by Rufino et al. (2010). Briefly, 2.7 mL of the FRAP reagent (TPTZ:$FeCl_3$:acetate buffer, 1:1:10) was mixed with 90 µL of the extract and 270 µL of deionized water. The mixture was vortexed and kept in a water bath for 30 min at 37 °C in the dark. Absorbance was measured at 595 nm in a spectrophotometer. FRAP reagent was used as blank. Aqueous solutions of ferrous sulfate (100–1500 µM) were used for calibration curve. The results were expressed as millimoles of ferrous equivalent per gram of coffee silverskin, in dry basis (mmol Fe (II)/g CS d.b.).

2.5.2 DPPH assay

The antioxidant capacity by free radical-scavenging (DPPH assay) was performed as described by Rufino et al. (2010). Briefly, 100 µL of extract was mixed with 3.9 mL of a methanolic solution DPPH (0.06 mM). The mixture was vortexed and kept for 40 min in darkness at room temperature. Absorbance was measured at 517 nm in a spectrophotometer. Methanol was used as blank. The results were expressed as EC_{50} (g CS d.b./g DPPH).

2.5.3 Total phenolics content

The total phenolic content (TPC) was determined by the Folin-Ciocalteau reagent method according to Waterhouse (2002), with slight modifications. For the determination, 0.5 mL of the extract was mixed with 2.5 mL of Folin-Ciocalteu reagent (10% v/v) and 2.0 mL of sodium carbonate solution (4% w/v). The mixture was vortexed and kept in the dark for 2h at room temperature. Absorbance was measured at 720 nm in a spectrophotometer. A calibration curve was made from gallic acid standard solutions (200-3000 mg/L). TPC was expressed in milligram of gallic acid equivalent per gram of coffee silverskin, on dry basis (mg GAE/g CS d.b.).

2.5.4 Total flavonoids content

Total flavonoids content (TFC) was determined according to Ballesteros et al. (2014), with some modifications. Initially, a sample aliquot (0.6 mL), properly diluted, was added to 1.8 mL methanol, 120 µL aluminum chloride (10%, w/v), 120 µL potassium acetate (1 M), and 3.4 mL deionized water. The mixture was vortexed and kept in the dark for 30 min at room temperature. Absorbance was measured at 415 nm using a spectrophotometer. A calibration curve was prepared with a standard solution of quercetin (25-200 mg/L). The results were expressed as milligram quercetin equivalent per gram of coffee silverskin, on dry basis (mg QE/g CS d.b.).

2.6 Statistical analysis

Statistical analysis was performed using the Statistica software (StatSoft Inc., Tulsa, OK, USA) at the 5% probability level. All analyzes were performed in triplicate. The experiment was carried out in a complete factorial scheme (3x4), with three repetitions (Step 1). The evaluated factors were extraction methods and solvents. Analysis of variance (ANOVA) and comparison of means by the Tukey test at the 5% probability level were performed.

Response surface methodology (RSM) was used to determine the optimal conditions for the recovery of bioactive compounds from coffee silverskin (Step 2). The second order polynomial model (Equation 5) was fitted to the experimental data to obtain the regression coefficients. Non-significant terms were removed from the final mathematical model. The t test was used to verify the significance of the regression coefficients. The coefficient of

determination (R^2) and adjusted coefficient of determination (R^2_{adj}) were used to determine the quality of the fit.

$$\hat{y} = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i<j}^{n} \sum_{j=1}^{n} \beta_{ij} x_i x_j \quad (5)$$

where $\hat{y}$ is the estimated response; β_0 is the center point of the system; β_i, β_j, and β_{ij} are the coefficients of the linear and quadratic effects and x_i and x_j are the independent variables.

The desirability function described by Derringer & Suich (1980) was used to determine the best solvents and extraction method (step 1) and to optimize the temperature and ethanol concentration (step 2) of the bioactive compounds from coffee silverskin.

3 Results and discussion

3.1 Influence of extraction conditions - Step 1

The interaction between the extraction method and type of solvent was significant, indicating that these factors acted in a dependent manner ($p<0.05$) in the extraction of bioactive compounds from coffee silverskin. The results of FRAP, DPPH, TPC and TFC of the extracts obtained from CS ranged from 0.03 to 0.06 mmol Fe (II)/g CS d.b., 919.13 to 13735.90 g DPPH/g CS d.b., 1.49 to 5.68 mg GAE/g CS d.b., and 0.20 to 1.23 mg QE/g CS d.b., respectively (Figure 1).

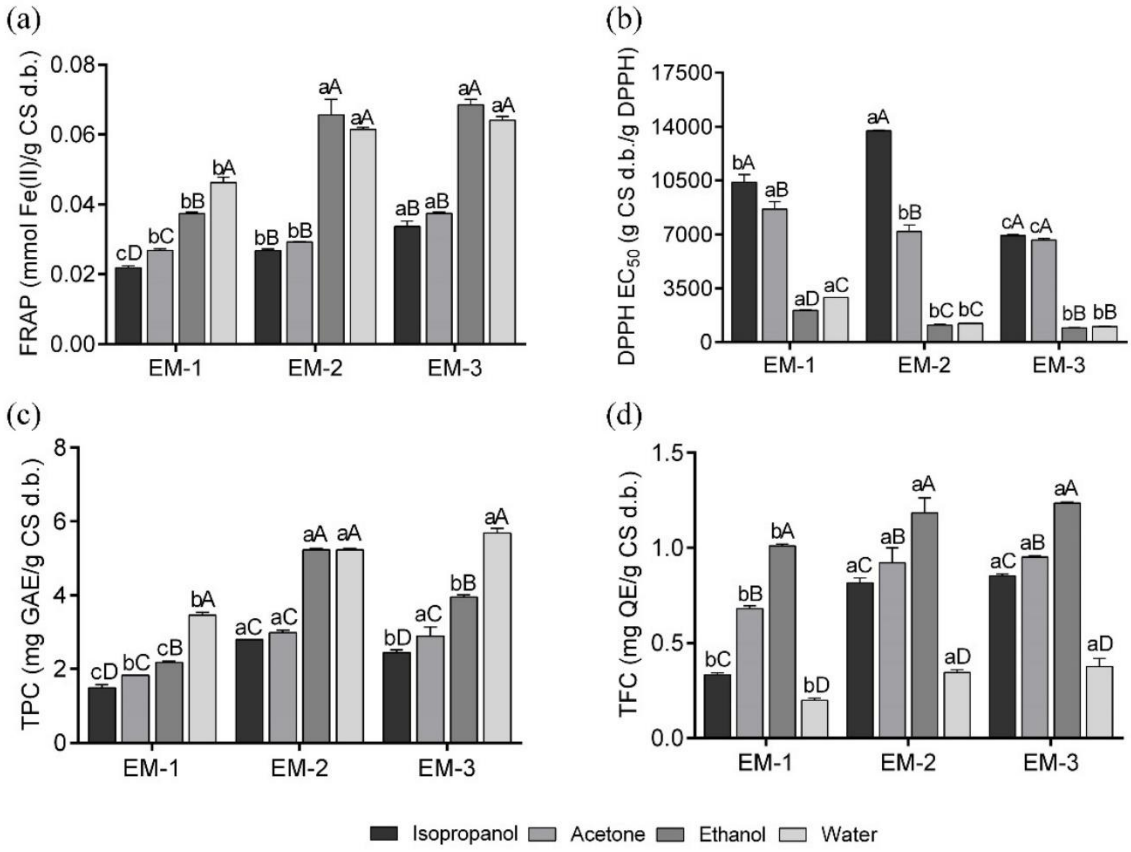

Fig. 1 – Antioxidant activity by FRAP assay (a) and DPPH assay (b), TPC: Total phenolics content (c) and TFC: Total content flavonoids (d) from CS extracts.

Results are expressed as mean ± standard deviation of three repetitions. EM-1, EM-2 and EM-3 are extraction methods at room temperature, with agitation and in Soxhlet, respectively. Different lower case letters indicate a significant difference between the extraction methods and different capital letters indicate a significant difference between the extraction solvents according to the Tukey test ($p < 0.05$).

For all solvents, EM-1 contributed to the lowest extraction potential of antioxidant compounds, TPC and TFC ($p<0.05$), as shown in Figure 1. The higher extraction yields of bioactive compounds and antioxidant activity by EM-2 and EM-3 can be explained by the use of higher temperatures and agitation, compared to an extraction process at room temperature and without constant agitation (EM-1). Gerke, Hamerski, Scheer, & Silva (2018), also found that agitation and temperature are important parameters in the extraction process of bioactive compounds from yerba mate, as they significantly affect the extraction yield of these compounds. According to these authors, the turbulence of the system caused by agitation and the increase in temperature favor the mass transfer phenomenon.

Regarding the evaluated solvents, water and ethanol were the solvents that had the highest extraction potential of the antioxidant compounds and TPC from CS ($p<0.05$), for all

extraction methods (EM-1, EM-2 and EM-3). The lowest extraction yields of these compounds were obtained when acetone and isopropanol were used (Figure 1), which can be explained by the lower relative polarity of these solvents, 0.355 and 0.390, respectively, compared to ethanol (0.654) and water (1.0) (Reichardt, 2003). On the other hand, water had the lowest TFC extraction potential (Figure 1d), and the highest values were obtained when organic solvents were used (ethanol> acetone> isopropanol). The small difference observed between antioxidant activity by FRAP and DPPH assays (Figures 1a and 1b) can be explained by the different target species and reaction mechanisms involved in each method (Ballesteros, Ramirez, Orrego, Teixeira, & Mussatto, 2017). Ballesteros et al. (2014) also found differences in the antioxidant activity of CS extracts by the FRAP and DPPH assays when using the same solvent.

The type of solvent used and its polarity are some of the factors that have a great influence on the efficiency of the extraction of a bioactive compound (Mohapatra et al., 2021), as verified in this study. Costa et al. (2018) found that ethanol was the best extraction solvent for TPC and TFC of CS. Oliveira et al. (2019) found that different solvents and extraction period had a significant effect ($p<0.05$) on the extraction yield of soluble solids, bioactive compounds and antioxidant activity of green coffee beans and their pressing bran. These authors also reported that ethanol was the most recommended solvent for the extraction of bioactive compounds these materials.

3.1.1 Determination of the extraction method and solvent ideals

Based on the data obtained in this study, different conditions for the evaluated responses were obtained. Therefore, the desirability function was applied to determine the ideal condition of the extraction process of the bioactive compounds and antioxidant activity from CS. The global desirability values for the treatments are shown in Table 2. The results indicated that EM-2 had the highest global desirability values in relation to the other methods, for most of the evaluated solvents, except for isopropanol. For this method, ethanol (D = 0.941) followed by water (D = 0.581) had the highest global desirability values.

Table 2 - Values of global desirability for the treatments in step 1

Extraction methods (EM)	Solvents			
	Isopropanol	Acetone	Ethanol	Water
EM-1	0.002	0.217	0.454	0.039
EM-2	0.020	0.460	0.941	0.581
EM-3	0.373	0.377	0.875	0.427

Some studies have observed that the mixture of water and ethanol was more efficient for the extraction of bioactive compounds than when these solvents were used alone (Ballesteros et al., 2014; Costa et al., 2014). Therefore, EM-2, ethanol and water were chosen for the next step. Different proportions of these solvents were evaluated to obtain the maximum recovery of the bioactive compounds from CS.

3.2 Kinetic behavior and Peleg's model - Step 2

In the second step of this study, extraction kinetics of the total phenolic compounds from CS was performed to define the ideal extraction time. The extraction method was determined in the previous step (EM-2). The extracted TPC was plotted as a function of the extraction time (Figure 2). The operating conditions adopted for temperature and ethanol concentration were 47.5 °C and 45% (central point of the CCRD).

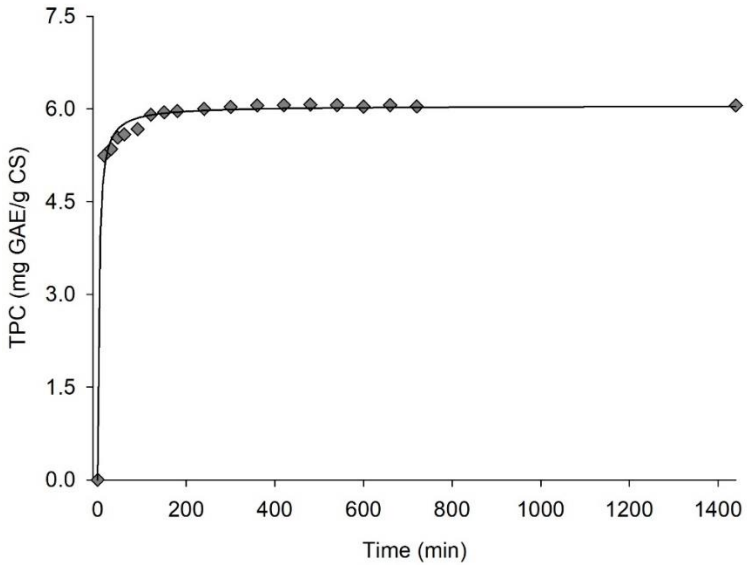

Fig. 2 - Extraction kinetics of total phenolics and Peleg’s model (line) fitted to the experimental data.

As shown in Figure 2, the extraction yield of TPC increased significantly in the initial times of the process. With the progress of the extraction, the yield becomes slower, and the process continues until a maximum concentration is reached, indicating the equilibrium condition of the system. This classic behavior of the extraction kinetics was also verified for the extraction of lycopene (Poojary & Passamonti, 2015), bioactive compounds of yerba mate (Gerke et al., 2018), anthocyanins of hibiscus (Cissé et al., 2012) and phenolic compounds of oregano (Oreopoulou et al., 2020). This occurs because in the initial periods of extraction the solvent comes in contact with the compounds present on the sample surface, being easily extracted, generating high rates of mass transfer to the liquid phase. As the process progresses, the intraparticle diffusion mechanism controls the extraction rate and, with this, the extraction occurs more slowly until reaching a maximum (Gerke et al., 2018; Oreopoulou et al., 2020; Poojary & Passamonti, 2015). According to Viganó et al. (2020), the determination of the ideal condition of an extraction process must consider the shortest time necessary for the highest recovery of the compounds of interest, in addition to the costs of the process. Therefore, in the present study, the ideal extraction time was set at 120 min, since most of the TPC extraction occurred within that period, with 97% of TPC extracted from CS compared to the total process (1440 min).

The Peleg model has been commonly adopted to represent the extraction kinetics of bioactive compounds from food sources (Gerke et al., 2018; Poojary & Passamonti, 2015). For this study, the Peleg model presented a good fit to the experimental data, being considered a satisfactory model to represent the TPC extraction kinetics of CS (Figure 2), with a high determination coefficient value (R^2 = 0.9952) and low error (SE = 0.0978). The model parameters showed values of 0.5011 min g/mg GAE and 0.1653 g/mg GAE for K_1 and K_2, respectively. Subsequently, the values calculated for the initial extraction rate (B_0) and the equilibrium concentration (C_{eq}) were 1.9957 mg GAE/min g and 6.0497 mg GAE/g, respectively.

3.3 Effect of temperature and ethanol concentration - Step 2

As previously reported, several factors can affect the extraction of compounds from food matrices, such as temperature and solvent concentration (Oliveira et al., 2019; Oreopoulou et al., 2020). Therefore, it is necessary to evaluate how these factors influence the extraction of bioactive compounds and antioxidant activity, in order to optimize the extraction process (Ballesteros et al., 2014). In this step, an optimization of the operational variables (temperature

and ethanol concentration) was performed, using the extraction time of 120 min. The temperature and ethanol concentration levels evaluated were 25 to 70 °C and 0 to 90% v/v, respectively, according to the tests defined by the CCRD.

The response surfaces of antioxidant activity (FRAP and DPPH assays), TPC and TFC are shown in Figure 3 and the values of the parameters of the regression model that describe these responses are shown in Table 3. The non-significant parameters of the models ($p > 0.05$) were removed, and a simplified model was adjusted to the experimental data. The coefficients β_0, β_1, β_2 and β_{22} were significant ($p<0.05$) for all responses. The models were considered satisfactory to represent the experimental data, as can be verified by the high values of the coefficient of determination (R^2) and adjusted coefficient of determination (R^2_{adj}).

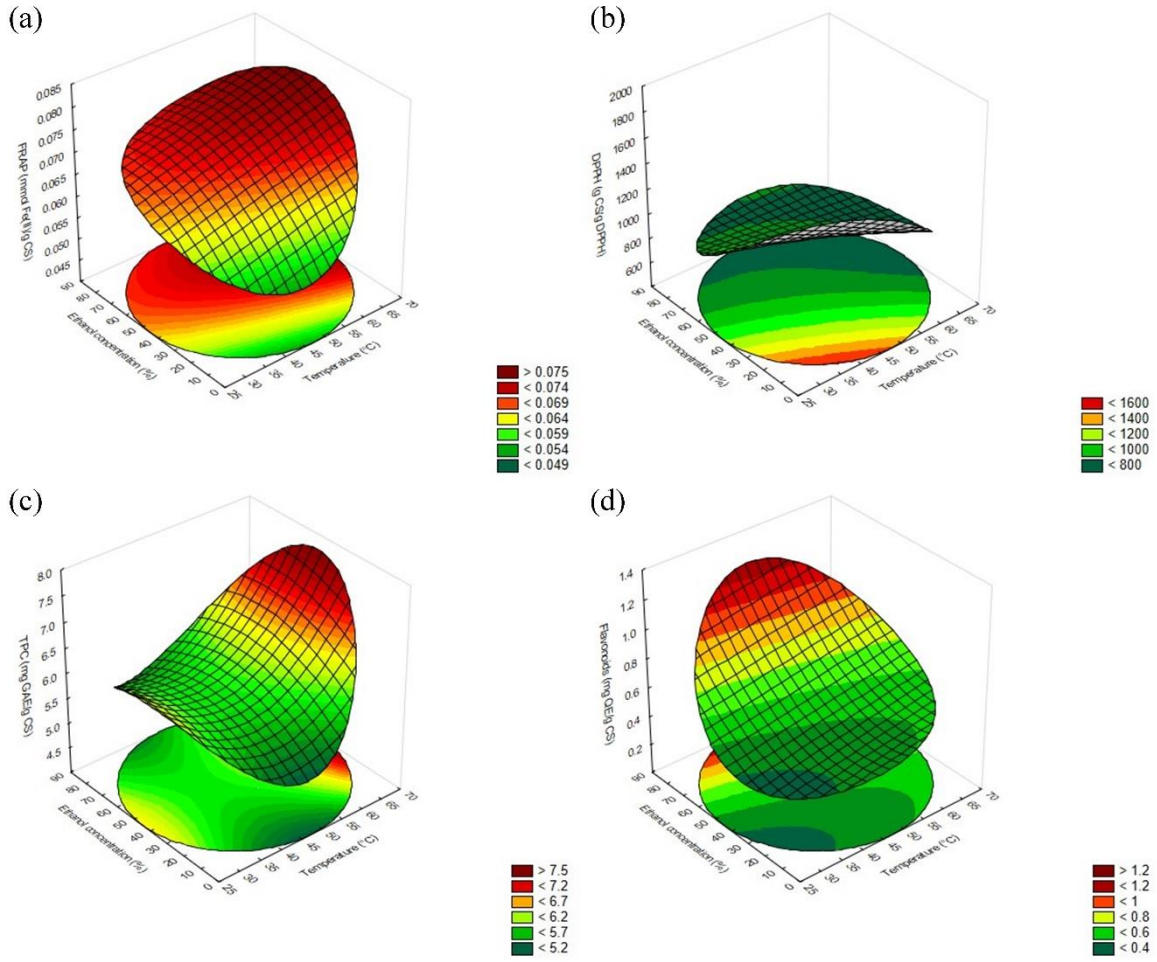

Fig. 3 - Influence of temperature and ethanol concentration on antioxidant activity by FRAP assay (a), DPPH assay (b), TPC: Total phenolics content (c) and TFC: Total flavonoids content (d) from CS extract.

Table 3– Values of parameters of the regression model, coefficients of determination (R^2) and adjusted coefficients of determination (R^2_{adj})

Coefficient	FRAP	DPPH	TPC	TFC
β_0	4.205×10^{-2}	2306.340	9.824	2.330×10^{-1}
β_1	2.536×10^{-4}	-18.836	-2.092×10^{-1}	5.133×10^{-3}
β_{11}	-	-	2.320×10^{-3}	-
β_2	5.800×10^{-4}	-27.179	1.490×10^{-2}	-4.011×10^{-3}
β_{22}	-4.276×10^{-6}	1.020×10^{-1}	-2.878×10^{-4}	1.299×10^{-4}
β_{12}	-	2.360×10^{-1}	3.333×10^{-4}	-
R^2	0.890	0.920	0.980	0.910
R^2_{adj}	0.850	0.865	0.966	0.866

As verified in Figure 3, the extraction temperature and ethanol concentration had a significant effect ($p<0.05$) on the evaluated responses. The increase in temperature and ethanol concentration contributed to the higher antioxidant activity (FRAP and DPPH assays) of CS extracts, with the highest value obtained for treatment 4 (63.41 °C and 76.82% ethanol concentration). The lower results obtained for DPPH (Figure 3b) indicate a higher antioxidant activity, since the results are expressed in EC_{50} (Mohapatra et al., 2021). Regarding the TPC, the increase in temperature (25-70 °C) and the ethanol concentration (up to about 45%) contributed to the best TPC extraction yields. For TFC, it was found that the highest ethanol concentrations (90%) and temperatures up to 47.5 °C generated the highest extraction yields for these compounds.

In general, the use of a hydroalcoholic solution and the increase in temperature up to a certain point were more efficient for the extraction of compounds than when using pure water (treatment 7) and lower temperatures. According to Kashaninejad, Sanz, Blanco, Beltrán, & Niknam (2020), the increase in temperature in the extraction process improves the extraction yield, as it generates more diffusion and solubility of the compounds. However, an optimal condition must be determined, since high temperatures can also contribute to the degradation of some target compounds (Kashaninejad et al., 2020). Narita & Inouye (2012) studied the antioxidant potential of CS extracts obtained with subcritical water at different temperatures. These authors also reported that the increase in temperature resulted in an increase in antioxidant activity, with the highest value obtained at 270 °C. Ballesteros et al. (2014) and Costa et al. (2018) found that the aqueous extracts of CS had less antioxidant activity and content of bioactive compounds compared to extracts obtained with some organic solvents, as

ethanol. According to Ballesteros et al. (2014), this may be due to the influence of the polarity and viscosity of the solvent on the extraction of antioxidant compounds and the higher solubility of phenolic compounds in solvents less polar than water.

Some studies with other food sources have also found that higher extraction temperatures and a combination of solvent and water were more efficient for extracting bioactive compounds. Bucić-Kojić, Planinić, Tomas, Jakobek, & Šeruga (2009) found that 50% ethanol and increased extraction temperature contributed to the highest values of antioxidant activity and TPC in grape seed. The use of higher extraction temperatures also generated the greatest antioxidant potential of mango co-products (Dorta, Lobo, & Gonzalez, 2012). Kashaninejad et al. (2020) described that 80% ethanol was the best solvent for extraction of TPC and oleuropein from the lyophilized extract of olive leaves.

The results obtained for the FRAP, DPPH, TPC and TFC were in the range of 0.056 to 0.079 mmol Fe (II)/g CS, 689.40 to 1513.13 g CS/g DPPH, 5.70 to 7.77 mg GAE/g CS and 0.44 to 1.32 mg QE/g CS, respectively. The results of FRAP and TPC are within the range found by Ballesteros et al. (2014), in which values of 0.031 to 0.088 mmol Fe (II)/g CS and 5.26 to 13.53 mg GAE/g CS were obtained. Bessada, Alves, Costa, Nunes, & Oliveira (2018) verified that the geographic origin of CS significantly influenced its chemical composition. Wen et al. (2019) performed the ultrasound-assisted extraction of bioactive compounds from CS using different ultrasound intensity and water and 80% methanol as solvents, with TPC values ranging from 5.80 to 8.94 mg TPC/g CS. According to Bucić-Kojić et al. (2009), although some authors have also evaluated a problem similar to that reported by our study, the results are, in most cases, not comparable, since differences are found among the conditions of obtaining samples, extraction process, methodologies and presentation of results.

3.4 Optimization and validation of results

The optimal temperature and ethanol concentration condition to maximize the antioxidant activity and the content of bioactive compounds was obtained by the desirability function. The values established for calculation the individual desirability of the responses is shown in Table 4.

Table 4 – Established values of each response for the desirability function

Parameters	DPPH	FRAP	TPC	TFC
L	-	0.0535	5.1235	0.2331
T	714.0399	0.0789	7.7096	1.1719
U	1510.3357	-	-	-

L is the lower acceptable limit; U is the higher acceptable limit and T is the desired ideal value.

After determining the limit values, the overall desirability was calculated, and a response surface was obtained (Figure 4). The maximum value obtained for the global desirability was 0.88, corresponding to a temperature of 68 °C and an ethanol concentration of 64%.

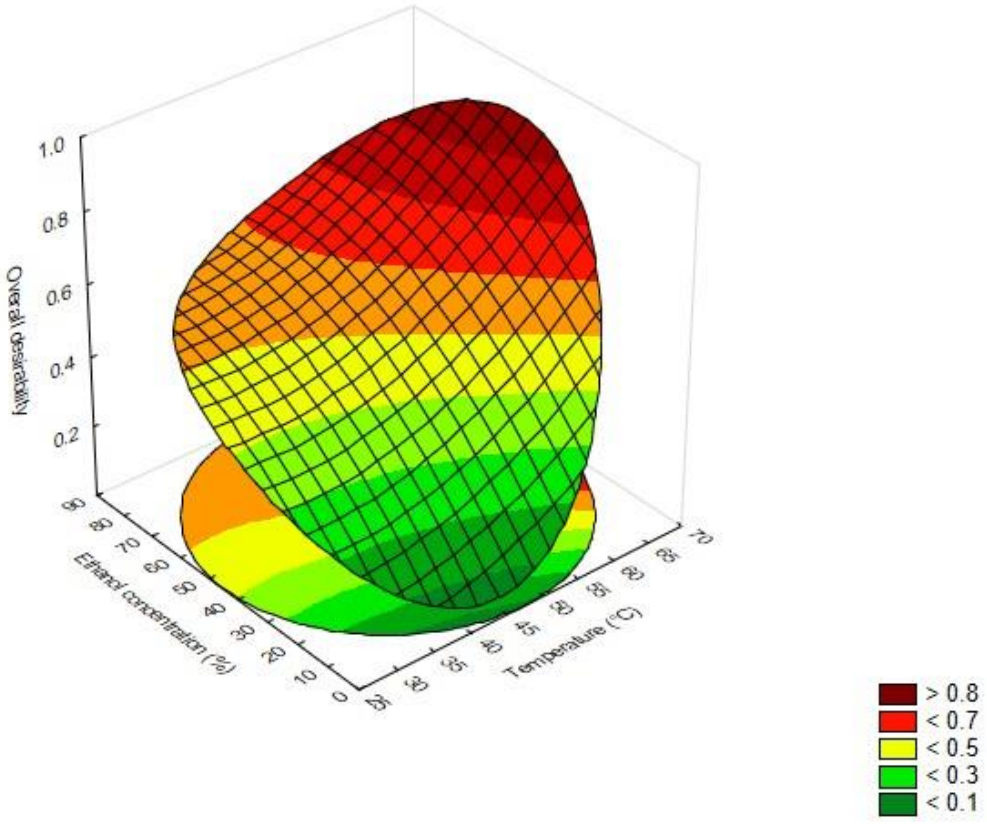

Fig. 4 - Overall desirability for ethanol concentration (%) and temperature (°C).

Additionally, the experiment was repeated in this condition determined for validation. The experimental and predicted results (Table 5) showed a good agreement, indicating that the models used to predict responses were considered adequate.

Table 5 – Results obtained for the validation of the optimal extraction condition

Results	FRAP (mmol Fe (II)/g CS)	DPPH EC_{50} (g CS/g DPPH)	TPC (mg GAE/g CS)	TFC (mg QE/g CS)
Predicted	0.079	733.21	7.55	0.86
Experimental	0.071	706.74	7.22	0.81

Costa et al. (2014) described that the use of a hydroalcoholic solution 1:1, 40 °C and 60 min was the condition that best contributed to maximize the content of bioactive compounds and antioxidant activity in CS extracts. On the other hand, Ballesteros et al. (2014) found an ideal extraction condition for bioactive compounds and greater antioxidant activity of CS using 60% ethanol, solid/solvent ratio of 1/35 (w/v) and 30 min, where the values obtained for FRAP, TPC, TFC were 0.098 mmol Fe (II)/g CS, 12.81 mg GAE/g CS and 1.68 mg QE/g CS, respectively. These results were superior to those obtained under the optimum conditions of the present study. This may be due to the different parameters used for the extraction process (temperature, time, and ethanol concentration) and the factors that can influence the composition of the coffee (genetic, geographic, agricultural practices, climate, type of post-harvest processing and roasting degree) (Pereira et al., 2019; Scholz, Kitzberger, Durand, & Rakocevic, 2018).

4 Conclusion

The operational conditions adopted in this study (extraction methods and solvents) had a significant effect on the extraction potential of the bioactive compounds present in coffee silverskin. The results indicated that water and ethanol and the extraction method with agitation (EM-2) were efficient in the recovery the bioactive compounds. The ideal condition obtained for hydroalcoholic mixture and the temperature for maximize antioxidant activity, TPC and TFC was 68 °C and 64% ethanol. This research also found that knowledge of the extraction kinetics of TPC from CS is extremely important for determining the ideal extraction time.

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Conflicts of interest

The authors declare that there are no conflicts of interest.

Availability of data and material

Research data are not shared.

Ethics approval

Ethics approval was not required for this research.

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ARTICLE 2 - Encapsulation of coffee silverskin extracts by foam mat drying: Combination of carrier agents for foam production and comparison with powders obtained by spray drying and freeze-drying

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Abstract

Coffee silverskin (CS) is a co-product that has been considered a rich natural source for the extraction of bioactive compounds. However, most of these compounds are susceptible to the conditions used during food processing and storage. Encapsulation is a process of great interest to increase the stability of these bioactive compounds and facilitate their application in other products. This study aimed to evaluate the encapsulation methods by foam mat drying (FMD), spray drying (SD) and freeze drying (FD) for producing powder from coffee silverskin extracts. Foam properties were evaluated and the characteristics of powders were determined. The ideal condition obtained of the feed mixture for foam formation was 7.6% GA, 2% MD and 10.4% EA. All methods presented powders with desirable values of water activity, moisture content and hygroscopicity, being considered stable for storage, and high content of bioactive compounds. Higher temperatures for FMD produced powders with higher encapsulation efficiency (EE >77%) and longer wettability than lower temperatures (50 and 60 °C). However, the powders obtained by SD, followed by FD showed higher EE results than FMD.

Keywords: Coffee co-products, Valorization, Bioactive compounds, Encapsulation methods.

1 Introduction

The coffee sector is considered a record holder in the generation of co-products, with amounts exceeding 50% of the coffee fruit discarded during processing (Esquivel & Jiménez, 2012; Hejna et al., 2021). Coffee silverskin (CS) is one of these co-products and consists of a thin integument that surrounds the coffee bean, which is detached during the roasting process and separated by the air flow (Costa et al., 2014; Mussato et al., 2011). Some studies have shown that CS extracts have a high antioxidant potential (Ballesteros et al., 2014; Costa et al., 2014; Mussato et al., 2011) and about 30 bioactive compounds (Nzekoue et al., 2020).

The extraction and application of CS bioactive compounds is of great interest, as they contribute to add value to other products and offer several health benefits (Fernandez-Gomez et al., 2016). However, most of these compounds are susceptible to the conditions used during food processing and storage, and may be influenced by several factors, such as oxygen, moisture, temperature and exposure to light, limiting their application in food matrices. In this context, encapsulation methods emerge as a promising technology to minimize these limitations, promoting higher stability to the bioactive compound and masking unpleasant tastes (Ballesteros et al., 2017; Yun et al., 2021).

Encapsulation technology basically consists of using a wall material, coating or encapsulant, to envelop sensitive compounds, namely the core, protecting them from adverse conditions (Yun et al., 2021). Several methods can be applied for the encapsulation of bioactive compounds, with spray drying (SD) and freeze drying (FD) being the most used methods (Ballesteros et al., 2017). On the other hand, the evaluation of new encapsulation methods to overcome the limitations of existing methods, such as the high costs of equipment and processes, are always desirable (Kanha et al., 2020).

Foam mat drying (FMD) arises as a potential alternative to SD and FD, as it has lower cost and ease of operation, in addition to providing high powder quality and process efficiency (Kanha et al., 2020; Sangamithra et al., 2015). This method consists of transforming solid-liquid food into a stable foam by mixing it with foaming agents and/or stabilizers, drying temperatures ranging from 40 to 90 °C being commonly used to obtain the powder. Foaming agents and stabilizers added, singly or in combination, affect foam properties such as density, porosity, overrun and stability. In turn, these foam properties also influence the drying process and the quality of the powder obtained. Therefore, these properties must be carefully determined (Hardy & Jideani, 2017; Qadri et al., 2020).

Some recent studies have described that FMD can be considered an efficient method in the encapsulation process of some compounds, such as black rice bran anthocyanins (Kanha et al., 2020), red sorghum proanthocyanidins (Susanti et al., 2021), pequi carotenoid (Pinto et al., 2018) and protein and amino acids of moringa leaf (Wahyuni et al., 2021). However, no work has verified the effect of FMD and traditional methods for CS extract encapsulation. In this context, this study aimed to (i) determine the effect of the concentration of carrier agents (gum arabic, maltodextrin and egg albumin) on the foam properties of CS extract and (ii) compare the encapsulation methods by spray drying (SD) and freeze drying (FD) with foam mat drying (FMD).

2 Materials and methods

2.1 Materials

Coffee arabica silverskin was supplied by local coffee shop in Lavras-MG, Brazil, and dried in an oven at 60 °C until constant weight. The carrier agents used for the encapsulation process were: Gum arabic (GA) (Synth, Diadema, SP, Brazil), maltodextrin (MD) (DE< 20, Cassava S.A., Maripá, PR, Brazil), and egg albumin (EA) (Naturovos, Salvador do Sul, RS, Brazil).

2.2 Extract preparation

The coffee silverskin (CS) extract was obtained by solid-liquid extraction in an Erlenmeyer, duly closed, submitted to agitation (120 rpm) on an orbital shaker (Marconi, MA830/A, Piracicaba, SP, Brazil) at 68 °C for 2 h. Deionized water was used as a solvent in a ratio of CS:water of 1:35 (w/v), according to preliminary tests (data not shown). The extract obtained was filtered through a Whatman No. 1 filter paper and stored in an amber flask at -20 °C until further use. The extract was previously characterized, in triplicate, the values being: total polyphenolic content (TPC), 5.93 ± 0.04 mg GAE/g CS d.b.; antioxidant activity by FRAP, 0.055 ± 0.0015 mmol Fe (II)/g CS d.b.; and antioxidant activity by DPPH, 8.38 ± 0.06 μmol TE/g CS d.b.

2.3 Foam preparation and experimental planning

The feed mixture was prepared by adding carrier agents (GA, MD and EA) to the extract using a homogenizer (Ultra-Turrax IKA T18 basic, Wilmington, USA) at 6000 rpm for 5 min. Afterwards, the feed mixture was stirred in a planetary mixer (ARNO, BPA KJ 280W, São Paulo, Brazil) for 20 min at full speed.

A simplex-centroid mixture design was used to evaluate the influence of GA (X_1), MD (X_2) and EA (X_3) on the density, stability, porosity, and overrun of the foam. For each independent variable (X_1, X_2 and X_3), a minimum restriction of 2% (w/v) was adopted (Table 1), as defined in preliminary tests for foam formation. The total concentration of the carrier agents was fixed at 20% (w/v) ($\sum_{i=1}^{3} X_i = 20\%$).

Table 1 - Coded values and real concentrations of carrier agents for each assay of the mixture design

Assay	Coded values			Real concentrations (%)		
	GA (X_1)	MD (X_2)	EA (X_3)	GA (X_1)	MD (X_2)	EA (X_3)
1	0.0000	0.0000	1.0000	2.0000	2.0000	16.0000
2	0.0000	1.0000	0.0000	2.0000	16.0000	2.0000
3	1.0000	0.0000	0.0000	16.0000	2.0000	2.0000
4	0.0000	0.5000	0.5000	2.0000	9.0000	9.0000
5	0.5000	0.0000	0.5000	9.0000	2.0000	9.0000
6	0.5000	0.5000	0.0000	9.0000	9.0000	2.0000
7	0.1667	0.1667	0.6667	4.3338	4.3338	11.3338
8	0.1667	0.6667	0.1667	4.3338	11.3338	4.3338
9	0.6667	0.1667	0.1667	11.3338	4.3338	4.3338
10	0.3333	0.3333	0.3333	6.6667	6.6667	6.6667
11	0.3333	0.3333	0.3333	6.6667	6.6667	6.6667
12	0.3333	0.3333	0.3333	6.6667	6.6667	6.6667

GA: Gum Arabic; MD: Maltodextrin; EA: Egg albumin.

The polynomial model (Eq. 1) was fitted to the data obtained of the foam properties.

$$\hat{y} = \sum_{i=1}^{3} \beta_i X_i + \sum \sum_{i<j}^{3} \beta_{ij} X_i X_j + \sum \sum \sum_{i<j<k}^{3} \beta_{ijk} X_i X_j X_k \quad (1)$$

Where $\hat{y}$ is the estimated response; β_i, β_j, β_k are the regression coefficients and X_i, X_j and X_k are the concentrations of GA, MD and EA, respectively.

2.4 Foam properties

Foams were evaluated for density, porosity, and overrun, in triplicate. The foam was placed in a graduated cylinder (50 mL), the mass (m) and the volume (v) being measured to calculate the density (ρ) at 25 °C (Eq. 2) (Macedo, Corrêa, Araújo, et al., 2021).

$$\rho\left(\frac{g}{mL}\right) = \frac{m}{v} \quad (2)$$

Porosity (φ) and overrun were calculated according to Eqs. 3 and 4, respectively (Macedo, Corrêa, Araújo, et al., 2021).

$$\varphi = 1 - \frac{\rho_{foam}}{\rho_{extract}} \quad (3)$$

$$\text{Overrun } (\%) = \frac{\frac{1}{\rho_{foam}} - \frac{1}{\rho_{extract}}}{\frac{1}{\rho_{extract}}} \times 100 \quad (4)$$

To determine stability, the foam was placed in a graduated cylinder and the initial volume (Vi) was measured. The foam was left at 30 °C for 1 h and the reduced volume (V_f) was measured to calculate the stability (Eq. 5) (Kanha et al., 2020).

$$\text{Stability } (\%) = \frac{V_f}{V_i} \times 100 \quad (5)$$

2.5 Encapsulation methods

The ideal condition of the carrier agents (GA, MD and EA) obtained in the formation of the foam was used for comparison between FMD, SD and FD. The feed mixture was prepared by adding carrier agents (GA, MD and EA) to the extract using a homogenizer (Ultra-Turrax IKA T18 basic, Wilmington, USA) at 6000 rpm for 5 min. The powders obtained by all methods were packed in a metallic package and kept at -20 °C until further analysis.

2.5.1 Foam mat drying

The foam was placed in a dish (160 mm diameter and 15 mm height) and dried in a tunnel dryer (Eco Engenharia Educacional, MD018 model, São José, SC, Brazil) with forced air circulation (1.0 m/s) at temperatures of 50, 60, 70 and 80 °C. The drying was performed until samples reached a moisture content of 5% w.b.

2.5.2 Spray drying

Spray drying was performed using a mini spray dryer (Yamato Scientific Co., Model ADL-311S, Japan). The drying parameters were: air pressure (0.1 MPa), drying airflow (0.21 m^3/min), inlet air temperature (160 ± 1 °C), outlet air temperature (60 ± 2 °C) and feed rate (2.3 mL/min).

2.5.3 Freeze drying

The feed mixture was frozen at -20 °C for 48 h in a freezer. Subsequently, the samples were placed in a freeze dryer chamber (FreeZone 2.5, Labconco, USA) under a pressure of 0.010 mbar at -50 °C for 48 h.

2.6 Physicochemical characterization

2.6.1 Water activity

The water activity (a_w) was determined by direct reading on a water activity meter (Aqualab, 3-TE model Washington, USA) at 25 °C (Araújo et al., 2020).

2.6.2 Moisture content

The moisture content was determined by the gravimetric method in an oven at 70 °C, under vacuum, according to method 934.06 according to the methodology of the Association of Official Analytical Chemists (AOAC, 2010).

2.6.3 Wettability

The wettability of the powders was determined as described by Jinapong, Suphantharika, & Jamnong (2008). Briefly, 0.1 g of powder was poured into a beaker (250 ml) containing 100 ml of distilled water at 25 °C. The time required for all particles to get wet was recorded and the results were expressed in seconds.

2.6.4 Hygroscopicity

The hygroscopicity was determined by spreading each sample (1 g) in Petri dishes. Subsequently, Petri dishes were stored in a desiccator at 20 ± 1 °C with saturated solution of NaCl (75% relative humidity and a_w = 0.75) for 7 days. The results were expressed in grams of absorbed moisture per 100 g dry solids (Sun-Waterhouse & Waterhouse, 2015).

2.6.5 Solubility

The solubility was determined according to Kanha et al. (2020), with a slight modification. Briefly, sample (0.5 g) was mixed with distilled water (10 mL) and stirred for 30 min. The mixture was centrifuged at 2260 × g for 15 min at room temperature. The supernatant was transferred to Petri dishes and dried at 105 °C. Solubility (%) was calculated as the ratio between the mass of dried solids and the mass of the initial sample.

2.6.6 Color

The colorimetric parameters were determined by direct reading on colorimeter (Konica Minolta, Spectrophotometer model CM-5). The parameters obtained were L* (lightness), a* (redness), b* (yellowness), C* (chroma) and hº (hue angle)(Macedo, Corrêa, Araújo, et al., 2021).

2.6.7 Antioxidant activity

The antioxidant activity was determined by the ferric reducing antioxidant power (FRAP) assay and DPPH radical scavenging activity assay methods. The FRAP assay was performed as described by Vimercati et al. (2020) and the results were expressed as millimoles

of ferrous equivalent per gram of sample, on a dry basis (mmol Fe(II)/g d.b.). The DPPH assay was performed according to Ballesteros et al. (2014) and the results were expressed as micromoles of trolox equivalents (TE) per gram of sample, on a dry basis (μmol TE/g d.b).

2.6.8 Total phenolic content

The total phenolic content (TPC) was determined by the Folin-Ciocalteau reagent method according to Waterhouse (2002), with slight modifications. Briefly, an aliquot of the extract (0.5 mL), properly diluted, was mixed with 2.5 mL of Folin-Ciocalteu reagent (10% v/v) and 2.0 mL of sodium carbonate solution (4% w/v). The mixture was stirred in a vortex and kept for 2 h at room temperature protected from light. Absorbance was measured at 720 nm in a spectrophotometer. TPC was expressed in milligrams of gallic acid equivalent per gram of sample, on a dry basis (mg GAE/g d.b.).

2.7 Encapsulation efficiency

The encapsulation efficiency (EE) was determined according to Kanha et al. (2020), with some modifications. Samples (0.1 g) were placed in tubes and 10 mL of deionized water were added. The mixture was vortexed for 10 s, for the determination of total phenolics on the surface (TPC_{sur}), and until the complete dissolution of the particles, for the determination of total phenolics (TPC_{Tot}). The solutions were then centrifuged at 2260 × g for 15 min at room temperature and filtered through 0.45 μm Millipore filter. The final volume was completed with deionized water to 50 mL in a volumetric flask. These solutions were used to determine the total phenolic content (item 2.4.8). The encapsulation efficiency was calculated according to Eq. 6.

$$EE\ (\%) = \left(\frac{TPC_{Tot} - TPC_{sur}}{TPC_{Tot}}\right) \times 100 \quad (6)$$

2.8 Statistical analysis

The linear, quadratic and special cubic models were tested for mixture design and generation of the response surface. The models with the highest R^2_{adj} and lowest mean absolute percentage (MAPE, %) were chosen (Cornell & Berger, 1987). Desirability function was used

for optimization (Derringer & Suich, 1980). The drying experiments were carried out in three repetitions. Analysis of variance (ANOVA) and significant differences between the means using the Tukey test were performed. The Pearson's correlation coefficient was calculated to determine the correlations among the TPC and antioxidant activity. Statistics software (StatSoft, Tulsa, USA) was used for all statistical analyzes, adopting a 5% level of significance. All analyses were performed in triplicate.

3 Results and discussion

3.1 Foam properties

Based on preliminary tests to determine the proportion of carrier agents for foam formation and stability (data not shown), a minimum restriction (2% w/v) of each agent was employed. This minimal restriction was adopted since MD and GA, individually, are not able to form foam, being more used as foam stabilizers and also contribute to increasing the viscosity of the medium. On the other hand, EA is a good foaming agent (Hardy & Jideani, 2017a; Qadri et al., 2020; Sangamithra et al., 2015). These agents are commonly used in FMD and can also act as excellent wall materials for encapsulating bioactive compounds (Arzeni et al., 2015; Ballesteros et al., 2017). Therefore, the determination of an ideal condition of the proportion of these agents was evaluated in this study.

The response surfaces for the foam properties are shown in Fig. 1. The predicted equations to represent these properties, p value, coefficient of determination (R^2) and MAPE (%) are described in Table 2. The different concentrations of the agents GA, MD and EA had a significant effect ($p<0.05$) on the foam properties. The results obtained for density, porosity, overrun and foam stability ranged from 0.15 to 0.33 g/cm³, 0.66 to 0.85, 196.68 to 562.61% and 79.14 to 99.72%, respectively. The adjusted models were considered adequate to explain the effect of the addition of different proportions of GA, MD and EA on the behavior of the foams ($p<0.05$), as it presented non-significant lack of adjustment, high R^2 values (>0.9) and low MAPE values (<6%). Non-significant terms were removed from the models, such as GA and EA interaction (X_1X_3) for all responses and GA, MD and EA interaction ($X_1X_2X_3$) for porosity and overrun.

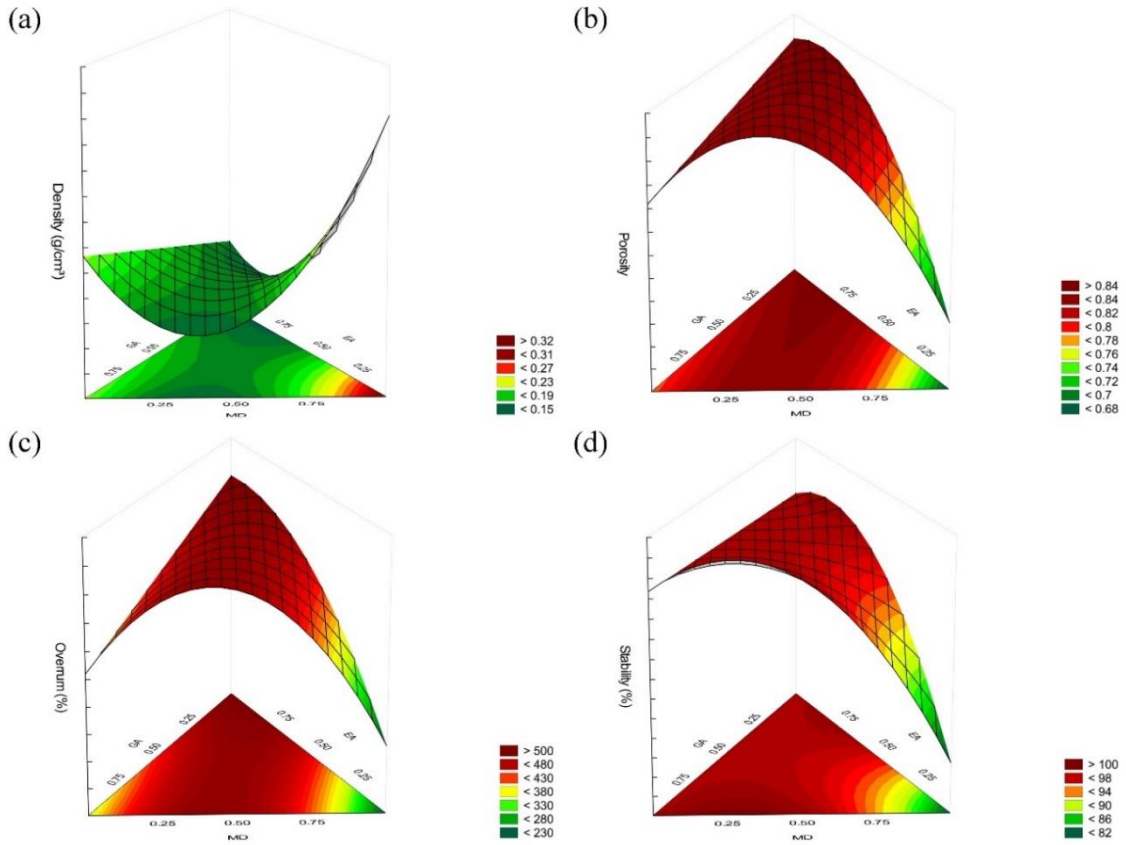

Fig. 1. Surface response graph of the foam properties. Density (a), porosity (b), overrun (c) and stability (d).

Table 2 - Predicted equations for experimental data of foam properties

Response	Coded equation in terms of pseudo components	p-value	R^2	MAPE (%)
Density	$\hat{y} = 0.2132\ X_1 + 0.3217\ X_2 + 0.1591\ X_3 - 0.4446\ X_1X_2 - 0.2859\ X_2X_3 + 0.4136\ X_1X_2X_3$	<0.01	0.9164	5.35
Stability	$\hat{y} = 98.7241\ X_1 + 81.1773\ X_2 + 98.1543\ X_3 + 39.2907\ X_1X_2 + 31.0255\ X_2X_3 - 71.0327\ X_1X_2X_3$	<0.01	0.9134	1.11
Overrun	$\hat{y} = 359.6540\ X_1 + 224.3256\ X_2 + 529.5958\ X_3 + 857.9890\ X_1X_2 + 346.5657\ X_2X_3$	<0.01	0.9032	5.16
Porosity	$\hat{y} = 0.7836\ X_1 + 0.6788\ X_2 + 0.8380\ X_3 + 0.4088\ X_1X_2 + 0.2492\ X_2X_3$	<0.01	0.9041	1.36

X_1: Gum arabic; X_2: Maltodextrin; X_3: Egg albumin.

As observed, the mixtures with the highest amounts of MD and with the lowest amounts of EA and GA (near the MD vertex) resulted in the most unsatisfactory conditions for the foam properties, with high density values (Fig. 1A) and low values of porosity (Fig. 1B), overrun (Fig. 1C) and stability (Fig. 1D). On the other hand, the highest contents of EA or GA combined with the lowest contents of MD showed a trend towards the ideal condition of the foam properties, with the lowest density values and the highest values for the other responses. Li, Sulaiman, Rukayadi, & Ramli (2021) verified that the best properties of the cantaloupe puree foam were obtained by increasing the concentration of GA by up to 10%. Benković et al. (2019) described that the lowest density values of cocoa foam enriched with peppermint extract were obtained with the highest addition of egg white (80 g), with a higher incorporation of air in the foam. For the production of instant coffee by foam mat drying, Maciel, Teixeira, Della Lucia, & Saraiva (2021) verified that different concentrations (0 to 6%) of MD and whey protein isolate (WPI) influenced some properties of foams and powders. These authors found an ideal condition at 1.32% of MD and 2.64% of WPI.

In some cases, the use of foaming agent alone is not sufficient or does not provide the most desirable characteristics for the foam properties, requiring the addition of stabilizers. Such stabilizers increase the viscosity of the solution or form a three-dimensional network that reduces the mobility of the material within its structure (Dehghannya et al., 2018; Qadri et al., 2020). This fact was verified in our study, since the combination of the foaming agent (EA) with the foam stabilizers (MA and GA) resulted in the best foam properties.

3.2 Ideal condition and validation of foam properties

The ideal condition of the proportion of carrier agents (GA, MD and EA) to obtain the most desirable foam properties, such as low density and high values of porosity, overrun and stability, was obtained by the desirability function. Foam density has been minimized and other responses maximized. Minimum and maximum values for each response were established and individual desirability was obtained. The overall desirability was then calculated and a response surface that presents its profile was generated (Fig. 2).

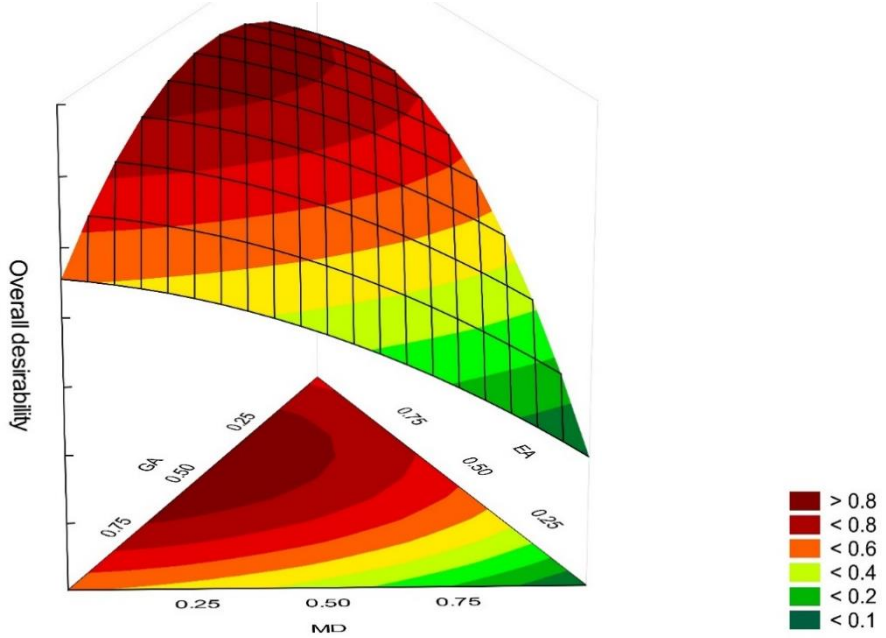

Fig. 2. Surface response graph of the overall desirability for gum arabic (GA), maltodextrin (MD) and egg albumin (EA) concentrations.

The maximum value of overall desirability found was 0.93, being obtained as a function of the coded variables X_1, X_2 and X_3, with values of 0.4, 0 and 0.6, respectively. This ideal condition corresponds to 7.6% GA (X_1), 2% MD (X_2) and 10.4% EA (X_3). The values predicted by the models for the responses of density, porosity, overrun and stability in this ideal condition were 0.1808 g/cm³, 0.8163, 461.6191% and 98.3838%, respectively. The experiment was repeated in this ideal condition for the validation process of the results. Mean values of 0.1787 ± g/cm³ for density, 0.8202 ± 0.0012 for porosity, 456.4489 ± 3.9765% for overrun and 99.0477 ± 0.0560% for stability were found. Therefore, the mathematical models used to describe the foam properties were considered satisfactory, as the predicted results were close to the experimental values and low mean relative deviation values were obtained (<5%).

Some studies have verified that the mixing design has been an efficient statistical tool to determine the optimal combination of carrier agents for the production of powder particles by freeze drying (Aksoylu Özbek & Günç Ergönül, 2020) and spray drying processes (Souza et al., 2018). According to our results, this tool can also be used satisfactorily in the FMD process to determine the ideal proportion of carrier agents to obtain a stable foam.

3.3 Comparison of powder properties

3.3.1 Water activity, moisture content and hygroscopicity

The values of aw, moisture content and hygroscopicity of the powders for the different methods ranged from 0.16 to 0.23, 1.57 to 4.99% and 12.42 to 18.20%, respectively (Table 3). The lowest values of aw and moisture content and the highest powder hygroscopicity values were obtained by the FD method ($p<0.05$). The powders produced by FMD at different temperatures and by SD showed no significant difference ($p>0.05$) for aw and hygroscopicity.

Determining the water present in dehydrated foods is an extremely important parameter, as it influences the shelf life and some reconstitution properties of these foods. Biochemical reactions and microbiological stability of foods are influenced by available water, denominated aw (Kanha et al., 2020; Li et al., 2021). Values of aw between 0.2 and 0.3 limit the growth of most microorganisms and the occurrence of chemical and enzymatic reactions, contributing to higher stability during the storage of powders (Franco et al., 2016). In addition, the reduction in the total water content of the food (moisture content) makes it easier to transport and generates lower costs with packaging and storage, as there is a significant reduction in weight and volume (Brar et al., 2020). The powders obtained in our study can be considered an unfavorable medium for the growth of microorganisms and biochemical reactions and with a long shelf life.

Hygroscopicity is a property that also affects powder stability, being defined as the water absorption capacity of powders in environments with high relative moisture (Dadi et al., 2020). In our study, all values obtained for hygroscopicity of powders were considered relatively low (<19%) (Table 3), which is a desirable characteristic, as low hygroscopicity contributes to low risk of handling issues, such as stickiness and agglomeration (Sun-Waterhouse & Waterhouse, 2015). Hygroscopicity is influenced by the type of carrier agent and the drying conditions and methods employed (Dadi et al., 2020; Franco et al., 2016). According to Tonon, Brabet, & Hubinger (2008), the higher hygroscopicity values of the powders are related to the lower moisture content and this is due to the higher water gradient between the environment and the product.

Table 3 - Physicochemical characterization of the powders produced by foam mat drying (FMD) at different temperatures, freeze drying (FD) and spray drying (SD)

Responses	FMD 50 °C	FMD 60 °C	FMD 70 °C	FMD 80 °C	FD	SD
a_w	0.22 ± 0.01 a	0.21 ± 0.02 a	0.20 ± 0.01 a	0.20 ± 0.01 a	0.16 ± 0.01 b	0.23 ± 0.02 a
Moisture content (g/100 g)	4.99 ± 0.13 a	4.89 ± 0.35 a	4.83 ± 0.25 a	4.89 ± 0.14 a	1.57 ± 0.10 c	3.57 ± 0.16 b
Hygroscopicity (g/100 g)	12.59 ± 0.29 b	12.57 ± 0.09 b	12.74 ± 0.05 b	12.42 ± 0.29 b	18.20 ± 0.26 a	12.44 ± 0.06 b
Wettability (s)	207.33 ± 7.02 b	204.50 ± 8.1 b	256.67 ± 8.39 a	248.5 ± 6.50 a	83.00 ± 1.00 e	134.00 ± 3.61 d
Solubility (g/100 g)	73.40 ± 1.06 a	73.42 ± 0.16 a	72.95 ± 1.00 a	71.54 ± 0.88 a	74.34 ± 1.24 a	72.46 ± 1.53 a

Results are expressed as mean ± standard derivation, n=3. Different letters in each line indicate significant differences by Tukey test ($p<0.05$).

3.3.2 Wettability and solubility

The reconstitution properties of powders are commonly evaluated by wettability and solubility times. The rapid and complete reconstitution of dehydrated products is an important quality indicator considered by consumers (Forny et al., 2011). The ability of the powder to rehydrate in water is known as wettability, and a shorter rehydration time (i.e., faster wettability) is desirable for powdered products (Figueiredo et al., 2020). In the present study, the encapsulation method influenced ($p<0.05$) the wettability of the powders, with values between 83 and 256.67 seconds being found (Table 3). The powders with the lowest moisture content (FD and SD) showed a rapid and complete reconstitution than the powders with the highest moisture content (FMD). For FMD, the lowest drying temperatures (50 and 60 °C) produced powders with a shorter wettability time compared to the higher drying temperatures (70 and 80 °C).

Regarding the solubility of the powders, the values obtained ranged from 71.54 to 74.34%, with no significant effect ($p>0.05$) of the encapsulation method on this response (Table 3). These values are within the range found by Souza et al. (2018) for tomato extract (68 to 77%), being considered powders with good solubility. According to these authors, high solubility values of powders are associated with high solubility of carrier agents. Darniadi, Ho, & Murray (2018) and Maciel et al. (2021) also verified that the carrier agents and the drying method did not influence the solubility of blueberry and instant coffee powders, respectively. On the other hand, Kanha et al. (2020) found that black rice bran anthocyanin powders obtained by FD and SD had higher solubility than powders obtained by FMD. These authors verified that the higher temperatures for FMD (70 and 80 °C) contributed to the higher solubility of the powders than the powders obtained by the lower drying temperature (60 °C).

3.3.2 Color

Color is an important attribute of food quality and is used by consumers as a first attribute to determine the acceptance or rejection of a product. Generally, consumers have a specific color pre-established for a certain product, and colors different from the expected can affect acceptance. The color of a food can be affected by several changes that occur from growth, harvesting to processing (Pathare et al., 2013). According to Koç, Yüksel, Baş, & Erdoğan (2020), different pre-treatments and drying methods can influence the color of the products. In our study, the different colors of the powders are shown in Fig. 3A. FMD produced

darker powders (lower L*) (Fig. 3B), with a more intense or vivid color (higher C*) (Fig. 3C), and a lower hue value (lower h°) (Fig. 3D), than the powders obtained by FD and SD ($p<0.05$). The hue of all powders (°h) was between red (0°) and yellow (90°) (Fig. 3D). The powders obtained by SD exhibited the highest values of h° and L* (lighter color) and the lowest value of C* (pale color) ($p<0.05$). The higher L* values for the powders obtained by SD can be correlated with the higher encapsulation efficiency by this method ($r=0.80$), in which, probably, the higher encapsulation efficiency by SD contributed to the formation of a capsule with spherical shape, making the extract color less visible. This behavior for the L* and h° parameters was also observed by Kanha et al. (2020) for encapsulation of black rice bran anthocyanin by FMD, SD and FD. Regarding the temperatures used in FMD (50 to 80 °C), a significant difference ($p<0.05$) was found only for the L* parameter, in which the use of lower temperatures produced darker powders. This can be due to the oxidation reactions that occur in the product, in which the lower temperature for FMD takes longer to reduce moisture and, consequently, is exposed to oxygen longer. The drying time for FMD ranged from 130 to 360 min, for the lower (50 ºC) and higher (80 ºC) temperature, respectively.

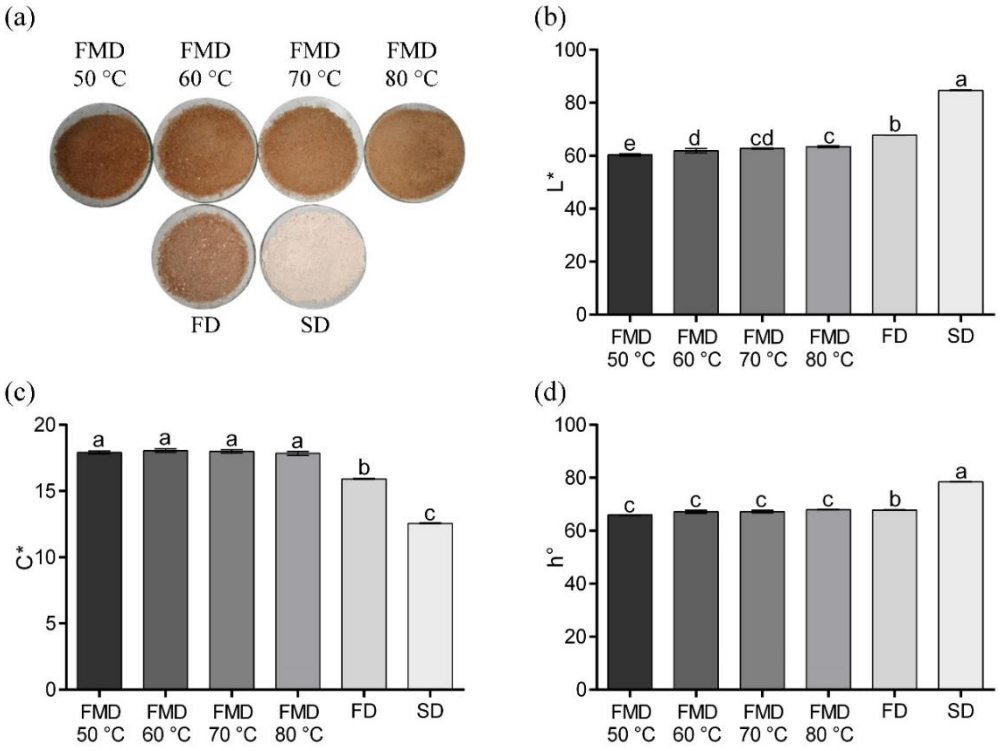

Fig. 3. Images (a) and colorimetric parameters of the powders obtained by foam mat drying (FMD) at different temperatures, freeze drying (FD) and spray drying (SD). L* (Luminosity) (b), C* (chroma) (c) and h° (hue) (d).

Results are expressed as mean ± standard derivation, n=3. Different letters above columns indicate significant differences by Tukey test ($p< 0.05$).

3.4 TPC and antioxidant activity

The results of TPC and antioxidant activity (FRAP and DPPH assays) for powders are shown in Fig. 4. CS can be considered a potential source for the extraction of functional compounds such as phenolic compounds and antioxidants (Ballesteros et al., 2014; Costa et al., 2014; Mussato et al., 2011). According to Bessada, Alves, Costa, Nunes, & Oliveira (2018), these functional compounds of CS are related to the presence of their natural constituents and those formed in the coffee roasting process, and can be used for application in the pharmaceutical, food and cosmetic industries.

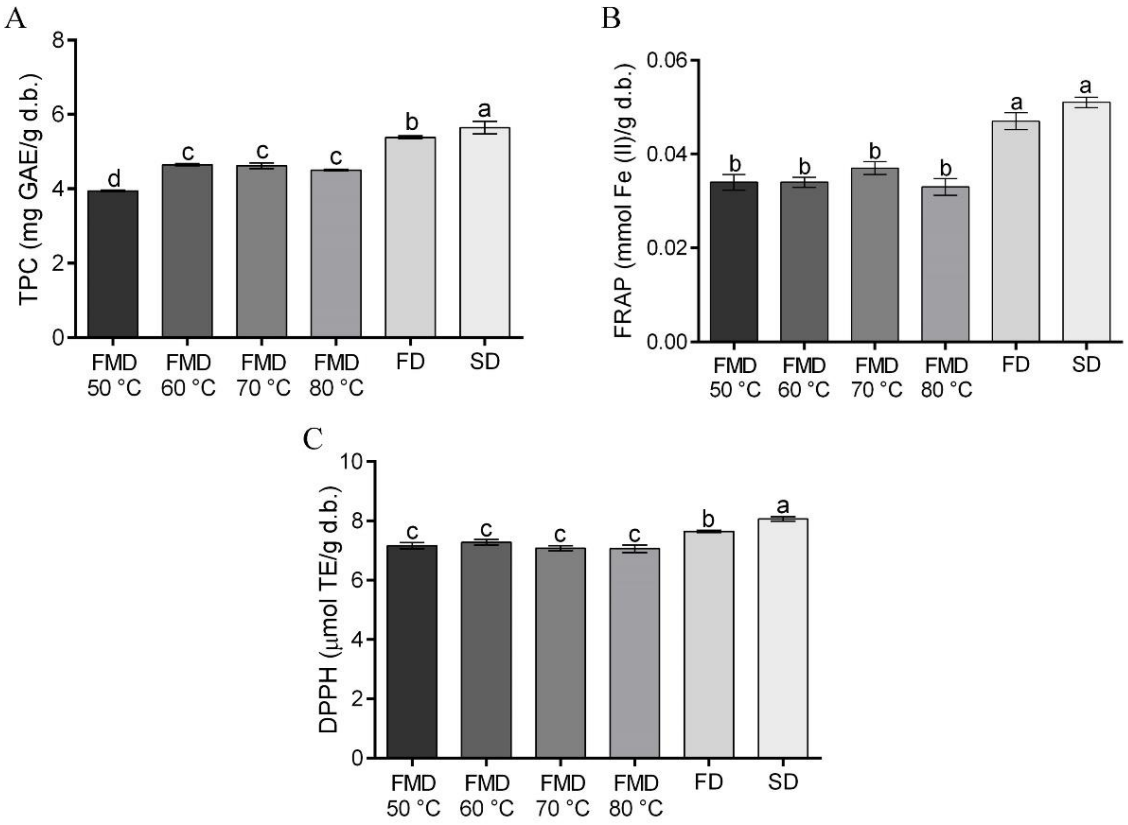

Fig. 4. Total phenolic content (TPC) (A) and antioxidant activity by FRAP (B) and DPPH (C) of powders obtained by foam mat drying (FMD) at different temperatures, freeze drying (FD) and spray drying (SD).

Results are expressed as mean ± standard derivation, n=3. Different letters above columns indicate significant differences by Tukey test ($p<0.05$).

In general, the drying temperatures used for FMD (50 to 80 °C) had no significant effect ($p>0.05$) on the results of TPC, FRAP and DPPH, with the exception of FMD at 50 °C which

had the lowest value of TPC in relation to other temperatures ($p<0.05$) (Figs. 4A, 4B and 4C). Compared with FD and SD, the results showed that FMD (50 to 80 °C) produced powders with the lowest values of TPC, FRAP and DPPH ($p<0.05$) (SD>FD>FMD), with retention of TPC, FRAP and DPPH ranging from 66.46 to 78.38%, 58.85 to 65.79% and 84.15 to 86.76%, respectively. The highest antioxidant capacity result by the FRAP and DPPH assays was obtained for the powder with the highest TPC value (Figure 3). This is due to the significant positive correlation of the FRAP assay with TPC ($r = 0.90$) and with DPPH ($r = 0.85$). This result was consistent with those obtained by Dadi et al. (2020), who also observed a strong positive correlation between the antioxidant activity and TPC of microencapsulated bioactive products from *Moringa stenopetala* leaf extract.

No studies were found in the literature for the encapsulation of CS bioactive compounds for comparison with our study. The results obtained in our study are different from those found by Kanha et al. (2020), who found that increasing the temperature for FMD (60 to 80 °C) contributed to the increase in the total anthocyanin content of the powder. Furthermore, these authors verified that the total anthocyanin content of the powder obtained by FMD at 80 °C did not present any significant difference from the powder obtained by SD and was higher than the results obtained for FD ($p<0.05$). Maciel et al. (2021) also verified that FMD at 60 °C was efficient for the retention of bioactive compounds from instant coffee. Ballesteros et al. (2017) found that the best condition for encapsulation of antioxidant phenolic compounds extracted from spent coffee grounds was obtained using the FD method and maltodextrin as wall material, with retention of 62% and 73-86% for TPC and antioxidant activity, respectively. These retention results are close to those obtained in our study for FMD.

The drying methods used for the encapsulation process of bioactive compounds from foods affect the retention of these compounds. The degree of retention of bioactive compounds depends on the drying method and conditions used, the material to be encapsulated and the wall material. Among the drying methods, the use of high temperatures, long drying times and oxidation reactions are the main factors that contribute to the highest bioactive compound losses. Therefore, the comparison and optimization of different encapsulation methods and wall material that provide the best retention of these compounds is desirable and should be evaluated for each type of food (Ballesteros et al., 2017; Hardy & Jideani, 2017; Kanha et al., 2020).

3.5 Encapsulation efficiency

The TPC encapsulation efficiency results of the samples were influenced ($p<0.05$) by the encapsulation method (Fig. 5). For FMD, the temperatures of 70 and 80 °C resulted in the highest EE values (>77%) in relation to the lowest temperatures (50 °C and 60 °C). This result is in accordance with Kanha et al. (2020). Higher drying temperatures can contribute to the carrier agent to form a faster wall structure to protect the compounds, contributing to higher EE (Kanha et al., 2020). These authors also found that FMD at 70 or 80 °C provided higher EE than the powders obtained by DF and that they did not differ from the powders obtained by SD ($p>0.05$). Distinct results were obtained in our study, and it was verified that FMD had lower EE values in relation to FD and SD (FMD<FD<SD) (Fig. 5).

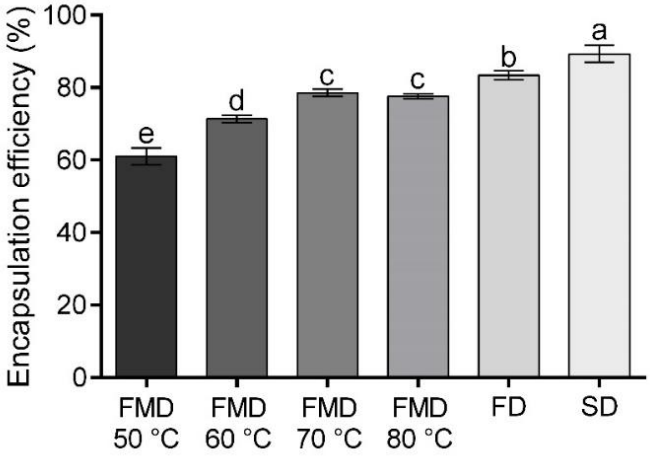

Fig. 5. Encapsulation efficiency of TPC of powders obtained by foam mat drying (FMD) at different temperatures, freeze drying (FD) and spray drying (SD).

Results are expressed as mean ± standard derivation, n=3. Different letters above columns indicate significant differences by Tukey test ($p<0.05$).

The EE of a particular bioactive compound is an important characteristic commonly evaluated. The highest values obtained for this parameter indicate that the bioactive compound is in smaller amounts on the surface and more retained within the particle. Therefore, the bioactive compound would be less affected by some external conditions during storage, contributing to its longer shelf life (Idham et al., 2012; Kanha et al., 2020). The EE can be influenced by several factors, such as the properties and amounts of carrier agents and the material to be encapsulated, and by different encapsulation methods (Dadi et al., 2020). Overall,

our study found that FMD using temperatures above 70 °C can be considered an efficient method for encapsulating TPC of CS, as it presented high EE.

4 Conclusion

This study evaluated, for the first time, the comparison among different methods encapsulation from CS extract. Different combinations of carrier agents (GA, MD and EA) had a significant effect on the foam properties. The ideal condition for foam formation was 7.6% GA, 2% MD and 10.4% EA. The encapsulation by FMD, SD and FD methods also influenced the physicochemical properties and efficiency of the powders. FMD of CS extract using drying temperatures above 70 °C produced powders with higher encapsulation efficiency than powders obtained by lower temperatures (FMD at 50 and 60 °C) but showed the lowest results when compared to SD and FD. The powders obtained by FMD had a darker color (smaller L*) and more intense (higher C*) than those obtained by SD and FD. There was no statistical difference between the powders obtained by SD and FMD for aw, hygroscopicity. Furthermore, the solubility of the powders obtained by all methods were statistically equal. The values of TPC and antioxidant activity of the powders showed a significant difference. FMD can be considered an efficient and promising method for encapsulating bioactive compounds from CS extract and other food matrices, generating quality powders. Future studies should be carried out with other types and proportions of carrier agents, as well as the combination with other drying methods, such as foam mat vacuum drying, foam mat freeze drying and microwave foam mat drying, in order to optimize the drying process and contribute with the highest efficiency and quality of powders.

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Author contributions

W. Vimercati designed the study, collected test data, interpreted the results and drafted the manuscript. C. Araújo and L. Macedo collected test data and interpreted the results. J. Corrêa and C. Pimenta designed the study and reviewed the manuscript

Conflicts of interest

The authors declare that there are no conflicts of interest.

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