CINTIA DA SILVA ARAÚJO

OPTIMIZATION OF EXTRACTION AND MICROENCAPSULATION OF BIOACTIVE COMPOUNDS FROM SPENT COFFEE GROUNDS

LAVRAS - MG
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(Marthin Luther King)

ABSTRACT

Coffee grounds consist of a by-product produced at the time of beverage preparation. This by-product has several extractable compounds with high antioxidant action, which can be recovered and added to food and beverage formulations. In this context, this study aimed to optimize the extraction of bioactive compounds from coffee grounds and, subsequently, promote the microencapsulation of these compounds. For the extractions, the influence of different methods (extraction at room temperature, shaking incubator and soxhlet) and solvents (water, ethanol, acetone and isopropanol) was evaluated. Subsequently, using a central composite rotational design (CCRD), the effect of the water/ethanol mixture and the extraction temperature on the extraction yields were evaluated. A phenolic compounds extraction curve was built to define the ideal process time. Response surfaces were elaborated and the desirability function was applied to determine the optimal point. For the microencapsulation of the extracted bioactive compounds, drying by foam mat, spray-drying and freeze-drying of the extract and foam were used. The wall materials used were albumin, maltodextrin and gum arabic. A mixture design was used to study the concentrations of the wall materials and the desirability function was used to determine the ideal concentration. The foams were dried in a convective dryer using temperatures of 50, 60 and 70 °C and two air velocities, 1 and 2 m/s. The dried product was characterized and compared with powders produced by spray-drying and freeze-drying methods. Subsequently, a new experiment using only spray-drying and lyophilization drying was carried out. In this case, new concentrations of the wall materials were tested and the dried product was characterized and compared. The results obtained during the extraction stage indicated that the most efficient bioactive compounds extraction was achieved by using a shaker incubator and the best pure extracting agents were water and ethanol. Furthermore, according to the results of the DCCR and the extraction curve, the maximum recovery of compounds was obtained with the use of ethanol at a concentration of 45% and a temperature of 63.3 °C, for 90 min. In the microencapsulation study, the concentration of wall materials was set at 20%, consisting of 4, 6 and 10% of albumin, maltodextrin and gum arabic, respectively. The foam drying time ranged from 200 to 450 min. All drying methods resulted in products with good physicochemical properties and satisfactory encapsulation efficiency values, above 60%. In microencapsulation using spray-drying and freeze-drying the powders obtained by freeze-drying had lower moisture and water activity values and were more hygroscopic. However, the content of bioactive compounds and the encapsulation efficiency values were similar between the two methods. Among the wall materials, the use of albumin

resulted in a dried product with lower bioactive content and encapsulation efficiency for both drying methods.

Keywords: Spent coffee grounds. Bioactive extraction. Foam mat drying. Encapsulation. Encapsulation efficiency.

RESUMO

A borra de café consiste em um coproduto produzido no momento de preparo da bebida. Esse coproduto apresenta diversos compostos extraíveis de elevada ação antioxidante, que podem ser recuperados e adicionados em formulações de alimentos e bebidas. Nesse contexto, este estudo teve como objetivo otimizar a extração de compostos bioativos de borra de café e, posteriormente, promover a microencapsulação desses compostos. Para as extrações, a influência de diferentes métodos (extração em temperatura ambiente, incubadora com agitação e soxhlet) e solventes (água, etanol, acetona e isopropanol) foi avaliada. Posteriormente, por meio de um delineamento composto central rotacional (DCCR), foram avaliados os efeitos da mistura de água/etanol e da temperatura de extração sobre os rendimentos de extração. Uma curva de extração de compostos fenólicos foi construída para definição do tempo ideal do processo. Superfícies de resposta foram elaboradas e a função desejabilidade foi aplicada para determinação do ponto ótimo. Para a microencapsulação dos compostos bioativos extraídos, foram empregadas as secagens por leito de espuma, atomização e liofilização do extrato e da espuma. Os materiais de parede utilizados foram a albumina, maltodextrina e goma arábica. Um delineamento de mistura foi usado para estudar as concentrações dos materiais de parede e a função desejabilidade foi usada para determinação da concentração ideal. As espumas foram secas em secador convectivo utilizando temperaturas de 50, 60 e 70 °C e duas velocidades do ar, 1 e 2 m/s. O produto seco foi caracterizado e comparado com os pós produzidos pelos métodos de atomização e liofilização. Posteriormente, um novo experimento empregando apenas as secagens por atomização e liofilização foi realizado. Nesse caso, foram testadas novas concentrações dos materiais de parede e o produto seco foi caracterizado e comparado. Os resultados obtidos durante a etapa de extração indicaram que a extração mais eficiente dos compostos bioativos foi alcançada pelo uso da incubadora com agitação e os melhores agentes extratores puros foram a água e o etanol. Além disso, de acordo com os resultados do DCCR e da curva de extração, foi verificado que a condição de máxima recuperação de compostos era obtida com o uso de etanol a uma concentração de 45% e temperatura de 63,3 °C, durante 90 minutos. No estudo de microencapsulação, a concentração dos materiais de parede foi fixada em 20% sendo constituída por 4, 6 e 10% de albumina, maltodextrina e goma arábica, respectivamente. O tempo de secagem das espumas variou de 200 a 450 minutos. Todos os métodos de secagem resultaram em produtos com boas propriedades físico-químicas e valores de eficiência da encapsulação satisfatórios, acima de 60%. Na microencapsulação utilizando atomização e liofilização foi verificado que os pós obtidos por liofilização tinham menor valor

de umidade e atividade de água e eram mais higroscópicos. No entanto, o teor de compostos bioativos e os valores de eficiência da encapsulação eram semelhantes entre os dois métodos. Entre os materiais de parede, o uso de albumina resultou em um produto seco com menor teor de bioativos e menor eficiência de encapsulação para ambos os métodos de secagem.

Palavras-chave: Borra de café. Extração de bioativos. Secagem em leito de espuma. Encapsulação. Eficiência da encapsulação.

FIGURE LIST

SECOND SECTION

ARTICLE 1

ARTICLE 2

ARTICLE 3

TABLE LIST

FIRST SECTION

SECOND SECTION

ARTICLE 1

ARTICLE 2

ARTICLE 3

SUMMARY

FIRST SECTION

1 Introduction

World coffee production has increased each year, with more than 175 million bags being produced in 2020, an increase of 6.3% compared to 2019 (ICO, 2021). In the world ranking, Brazil stands out as the largest producer and the second largest consumer market for this product. In Brazil, domestic consumption grew 1.34% in the period from November 2019 to October 2020, when compared to the same period of the previous year, reaching 21.2 million bags. Per capita consumption is estimated to be 5.99 kg/year of raw coffee and 4.79 kg/year of roasted and ground coffee. In addition to consuming traditional coffees, Brazilian consumers have shown greater interest in purchasing high quality coffees as well. Therefore, it is believed that the consumption of specialty and gourmet coffees will continue to grow and gain more and more space (ABIC, 2021).

The high popularity of the beverage means that it is produced and consumed in different regions of the world, contributing to the product playing an important role in the economy of many countries. However, together with the large production and consumption volumes, large amounts of by-products are also generated from the various processing stages. Among such by-product, spent coffee grounds deserve mention, due to the volume produced and their richness in bioactive compounds (CRUZ et al., 2012).

The ingestion of bioactive compounds can have several beneficial effects on health. However, there are many difficulties in their maintenance under food processing and storage conditions, given their instability to agents such as light, oxygen and temperature, for example. Thus, it is important to seek methods that allow to increase the stability of these compounds, allowing their incorporation and controlled release during the shelf life of the product (BALLESTEROS et al., 2017a; XU et al., 2015).

One of the most efficient and suitable methods to increase the stability of bioactive compounds is microencapsulation. In this process, bioactive compounds are involved by a polymeric matrix forming a protective layer, preventing their contact with factors capable of degrading them. In addition, the microencapsulated material is obtained in powdered form, facilitating its handling and application (LOZANO-VAZQUEZ et al., 2015).

Encapsulation can be performed using different drying methods, promoting stabilization, protection, solubility and controlled release of the encapsulated compound. The drying method and the wall material used are decisive for the characteristics of the dried particles. Thus, the choice of these parameters must be done carefully for each compound, whether they are lipids, vitamins, fatty acids, minerals, antioxidants or probiotics (RAY;

RAYCHAUDHURI; CHAKRABORTY, 2016). Considering the importance of drying for the microencapsulation process and that some disadvantages related to commonly used drying processes exist, the study of new drying technologies can be of great interest, opening up new application possibilities.

Given the above, this study aimed to evaluate the potential use of espresso coffee grounds as a source of bioactive compounds. For this purpose, this thesis was divided into three articles. In the first article, a study to optimize the extraction of bioactive compounds was carried out. Different solvents and extraction methods were evaluated in order to determine a condition for maximum recovery of these compounds. From these results, new extracts were produced for the microencapsulation steps. In the second article, an alternative drying method (foam mat drying) compared to traditional microencapsulation methods (spray-drying and freeze-drying) was proposed. The dried product was characterized and compared. In the third article, spray and freeze-drying methods and three wall materials were studied. The effect of these variables in relation to the characteristics of the dried product was evaluated.

2 Theoretical reference

2.1 Coffee

Coffee originated on the African continent, more specifically in Ethiopia. Then, European peoples spread the beverage throughout the world. The popularization of the beverage took place especially after the introduction of roasting methods, around the 14th century, which resulted in a beverage similar to the one we know today (ABIC, 2021).

There are about 500 species of coffee, but only the *Coffea arabica and Coffea canephora* genera have great commercial importance worldwide. These two species differ in appearance, quality, flavor and geographic suitability (JESZKA-SKOWRON; ZGOŁA-GRZESKOWIAK; GRZESKOWIAK, 2015). Arabica coffee is generally cultivated in highlands, with an altitude of more than 600 meters, occurring mainly in Latin America, East Africa and India. Robusta coffee, on the other hand, is more adapted to lower altitudes and its production occurs in West Africa, Indonesia, Vietnam and also in Brazil (CAMPA *et al*., 2004). Although coffee is grown in several regions of the world, most of the production is due to only ten main producing countries, located in South America, Asia and Africa (MUSSATTO *et al*., 2011a).

In Brazil, among the main cultivars are *Coffea arabica* cv. Mundo Novo, Catuaí Vermelho, Bourbon and *Caffea Canephora* cv. Robusta (JESZKA-SKOWRON; ZGOŁA-GRZESKOWIAK; GRZESKOWIAK, 2015; PERRONE *et al*., 2008). Robusta coffee is considered to have the worst sensory quality. However, it has the advantage of allowing greater extraction of soluble solids. Thus, it is widely used in the formation of blends and in the soluble coffee industry (VIGNOLI; BASSOLI; BENASSI, 2011).

The quality of coffee as a beverage is closely associated with the chemical components present in green beans, which in the roasting process will be precursors of several compounds present in the beverage (RIBEIRO; FERREIRA; SALVA, 2011). Quality is influenced by several factors, including cultural practices, plant genetics, geographic location, post-harvest treatment and variables arising from the form of preparation, such as roasting and extraction profile (SUNARHARUM; WILLIAMS; SMYTH, 2014).

2.1.1 Chemical composition and quality

The chemical composition of coffee is quite complex. In the beans, lipids, proteins, amino acids, polysaccharides, oligosaccharides, alkaloids, phenolic compounds, melanoidins, minerals, aliphatic acids and volatile compounds can be found (GEORGE; RAMALAKSHMI;

RAO, 2008). Chemical constituents vary significantly among coffee species, and to a lesser extent within the same species. In Table 1, the chemical composition of arabica and robusta coffees, before roasting, is presented.

Table 1 – Chemical composition of arabica and robusta coffees, expressed in %, on a dry basis

Compounds	*Coffea arabica*	*Coffea canephora*
Polysaccharides	48 - 60	47 - 55
Lipids	7 - 20	4 - 17
Reducing sugars	0.1	0.4
Sucrose	4.7 - 12.5	2 - 6
Trigonelline	0.8 - 1.3	0.9 - 1.9
Caffeine	0.9 - 1.9	2.2 - 3.2
Chlorogenic acids	3.8 - 8.5	6.5 - 11
Proteins	11 - 15	9 - 15
Total pectin	2.7 - 6.3	2 - 5
Diterpenes	0.5 - 1.2	0.2 - 0.8
Quinic acid	0.2 - 0.5	0.4

Source: Martín; Pablos; González, 1998; Ginz *et al*., 2000; Farah *et al*., 2006; Duarte; Pereira; Farah, 2010; Joët *et al*., 2010; D'amelio *et al*., 2013; Kitzberger *et al*., 2013; Jeszka-Skowron; Stanisz; Peña, 2016; Rendón; Scholz; Bragagnolo, 2017; Caporaso *et al*., 2018; Rakocevic; Santos; Kitzberger, 2018; Worku *et al*., 2018; Oliveira *et al*., 2018.

The coffee beverage is recognized for its stimulating effect, mainly attributed to caffeine. However, several other compounds have already been identified and many have beneficial effects on the body. Such effects may vary from individual to individual and also depend on the quantity and quality of the beverage (ESQUIVEL; JIMÉNEZ, 2012; GEORGE; RAMALAKSHMI; RAO, 2008).

The various chemical constituents combined provide the sensory quality of the coffee. Thus, some sensory attributes may be more noticeable when they are in the presence or absence of another particular compound (SCHOLZ *et al*., 2018). Farah *et al*. (2006) found that some chemical components such as trigonelline, 3,4-dicaffeoylquinic acid and caffeine had a good association with the quality of the beverage in green and roasted beans. On the other hand, higher contents of caffeoylquinic acids, feruloylquinic acids and their oxidation products were associated with low quality beverages.

The acids present in the green beans, together with those formed during the roasting process, give the beverage's acidity, an important quality attribute. In green coffee beans, the main acids found are citric, malic, chlorogenic and quinic. In roasted coffee, the main ones are formic, acetic, glycolic and lactic (GINZ *et al*., 2000). The acidity presented by the beverage depends on the degree of roasting adopted. Thus, determining the content of these acids becomes a useful tool to develop the best roasting conditions that green coffee should be subjected to in order to obtain a desirable acidity (RODRIGUES *et al*., 2007). As reported by Bicho *et al*. (2011), during roasting, volatilization, degradation and formation of various acids occur. Gloess *et al*. (2014) observed a decrease in acidity in medium and dark roasted coffees, this reduction being attributed to the degradation of citric, malic and chlorogenic acids.

According to França; Mendonça; Oliveira (2005), higher quality coffees tend to have lower acidity as well as higher pH value. Thus, prolonged storage of coffee beans can cause loss of sensory quality due to increased acidity due to fermentation. Ramalakshmi; Kubra; Rao (2007) reported higher acidity in defective grains, which can be attributed to the occurrence of undesirable fermentations during drying or even to harvest while the grains were still immature.

Sucrose is the sugar found in higher quantity in green grains. On the other hand, fructose and glucose are found in amounts about 20 times lower than sucrose and stachyose and raffinose oligosaccharides are in amounts about 100 times lower than that of the predominant sugar. In addition to these carbohydrates, other monosaccharides can be found, albeit in very low amounts, such as galactose, arabinose, rhamnose and mannose (KNOPP; BYTOF; SELMAR, 2006). Higher sucrose contents are reported for arabica coffee beans, which contain approximately twice as much as robusta coffee. However, the latter has a higher content of reducing sugars (CAPORASO *et al*., 2018; MURKOVIC; DERLER, 2006). Sugars act as flavor precursors giving rise to compounds such as furans, aldehydes and carboxylic acids (PERRONE; DONANGELO; FARAH, 2008). During roasting, the sucrose levels in the grain decrease sharply and losses of up to 98% can occur as a consequence of chemical reactions (Farah *et al*., 2006).

The lipid fraction of coffee consists predominantly of triacylglycerols (75%). However, it also has diterpenic esters (approximately 20%), sterols (2-3%), free fatty acids (1%) and tocopherols (0.05%), which are mainly concentrated in the endosperm. Vasconcelos *et al*. (2007), evaluating green arabica coffee beans, found lipid levels ranging between 8.1 and 10.2%. Some changes in lipids that are mainly related to hydrolysis and oxidation processes can lead to decreased coffee quality (NIKOLOVA-DAMYANOVA; VELIKOVA; JHAM,

1998). Oliveira *et al*. (2006) and Mazzafera (1999) found that healthy coffee beans had higher lipid content compared to defective beans.

2.1.2 Phenolic compounds

An antioxidant compound is defined as one capable of inhibiting or minimizing oxidative degradation. In this context, phenolic compounds are the main antioxidants present in food. In products such as oils and fats, they are found mainly in the form of monophenols, such as tocopherols. On the other hand, in foods such as fruits, vegetables, teas, coffee and wine, they are more commonly found as water-soluble polyphenols (ROGINSKY; LISSI, 2005).

Polyphenols consist of secondary metabolites naturally present in plants and that play roles in energy production, electron transfer and metal absorption from the soil. Another function attributed to these compounds is the protection of cells against oxidative stress (KARPINSKA; SWISŁOCKA; LEWANDOWSKI, 2017). In this way, antioxidant compounds from the diet help in cellular defense, preventing oxidative damage to cellular components (SATO *et al*., 2011).

Coffee is a food considered a source of phenolic compounds in the diet, whose main representatives are chlorogenic acids. These acids consist of soluble polyols, which are formed by the esterification of caffeic and quinic acids, totaling 71 natural compounds (GEORGE; RAMALAKSHMI; RAO, 2008; KARPINSKA; SWISŁOCKA; LEWANDOWSKI, 2017).

Chlorogenic acids, according to their chemical identity, number and position of acyl residues, are named as caffeoylquinic acids (3-caffeoylquinic, 4-caffeoylquinic and 5-caffeoylquinic), dicaffeoylquinic acids (3,4-dicaffeoylquinic, 3,5- dicaffeoylquinic and 4,5-dicaffeoylquinic) feruloylquinic acids (3-feruloylquinic, 4-feruloylquinic and 5-feruloylquinic), p-coumaroylquinic acids (3-p-coumaroylquinic, 4-p-coumaroylquinic and 5-p-coumaroylquinic) and, finally, the mixed diesters of caffeoylferuloylquinic acids (JESZKA-SKOWRON; ZGOŁA-GRZESKOWIAK; GRZESKOWIAK, 2015). As reported by Farah *et al*. (2005), in green coffee beans, the main chlorogenic acid found is caffeoylquinic acid, followed by dicaffeoylquinic and feruloylquinic acids, which account for 80 and 76%, 15 and 18% and 5.2 and 6.2% of the total chlorogenic acids found in arabica and robusta coffees, respectively. In general, robusta coffee has 28% more chlorogenic acids compared to arabica coffee.

During the roasting process, the high temperature causes the breakdown of the carbon-carbon bonds of the chlorogenic acids, resulting in isomerization and degradation (FARAH *et*

al., 2005). Although these compounds undergo major changes during roasting, beverage antioxidant activity is ensured by the production of new compounds, such as melanoidins, with such activity (VIGNOLI *et al*., 2014).

As reported by Borsato *et al*. (2011), high notes regarding coffee aroma and flavor were obtained in samples that contained high concentrations of chlorogenic acids and sugars, so that the roasting conditions adopted were sufficient for the sugar degradation products to mask the acid and bitter flavors from the degradation of chlorogenic acids. However, these authors emphasize that, in the global evaluation of the beverage, samples with low chlorogenic acid content and high sugar concentrations were better evaluated.

Carlsen *et al*. (2010) evaluated the antioxidant activity of hundreds of food products consumed in different parts of the world. According to these authors, the antioxidant activity of the coffee beverage showed the greatest variation among all the analyzed beverages, with values between 0.89 mmol/100g and 16.33 mmol/100g being found. The latter value was obtained for double espresso coffee, which presented the highest value among all drinks. In addition, they found that filtered coffee has the same antioxidant capacity as red wine (2.5 mmol/100g).

2.1.3 Caffeine and trigonelline

Caffeine (1,3,7-trimethylxanthine) is a methylxanthine, belonging to the alkaloid class, being one of the bioactive compounds present in coffee. It has a stimulating effect on the nervous, muscular and cardiovascular systems, in addition to acting to increase cognitive performance and metabolism acceleration (BARTELLA *et al*., 2019; RAHIMI *et al*., 2018). However, some adverse effects can occur if caffeine consumption is excessive and include insomnia, anxiety, addiction and malabsorption of some nutrients (KUMAR *et al*., 2018). According to Yenisetti; Muralidhara (2016), caffeine is the most consumed psychoactive compound in the world.

This compound has a bitter taste and can be found in several commercialized products, such as instant coffee, espresso coffee, cappuccino, teas, energy drinks, soft drinks and cocoa-based products, in addition to certain medications. The caffeine content of these products varies considerably. However, espresso coffee has the highest contents, especially in relation to teas, soft drinks and energy drinks. It is believed that 80% of the world population consumes at least one product that contains caffeine daily (HECKMAN; WEIL; DE MEJIA, 2010; KUMAR *et al*., 2018).

Trigoneline is the second main alkaloid found in coffee. It is responsible for the formation of important compounds for the beverage flavor such as furans, pyrazines, pyridines

and pyrroles (CAPORASO *et al*., 2018). Consumption of 3.5 cups of coffee a day contributes up to one-third of an adult's minimum dietary requirement for nicotinic acid, a B-complex vitamin, a product of trigonelline demethylation during roasting. This vitamin is water soluble and is highly bioavailable in coffee compared to other sources. Regarding its biological effects, trigonelline and its derivatives have been related to antidiabetic, neuroprotective and antiproliferative activities (ANGELINO *et al*., 2018).

2.2 Spent coffee grounds (SCG)

Throughout the entire coffee production chain, several by-products are generated, whether they are related to the production of beans, such as husk and mucilage, or to the preparation of the beverage. Thus, as a result of the high demand for this product, which provides one of the most consumed and appreciated beverages in the world, it is essential from an environmental and economic point of view that its by-products are used (MUSSATTO *et al*., 2011a).

One of the main by-products generated is the SCG, which is the insoluble material obtained after contact between hot water and roasted and ground coffee beans for the production of the beverage (BALLESTEROS; TEIXEIRA; MUSSATTO, 2014; CRUZ *et al*., 2012; MUSSATTO *et al*., 2011b). It is estimated that around 6 million tons of SCG are produced per year in the world (GETACHEW; CHUN, 2017). The soluble coffee industry is the main producer of this by-product, concentrating about 50% of world production, the rest is produced domestically and in commercial establishments (CRUZ *et al*., 2012). For each kilo of soluble coffee produced, approximately two kilos of wet SCG are generated (MUSSATTO *et al*., 2011a).

SCG has received greater attention in recent years, as it is produced in large quantities and contains several interesting compounds. These compounds can be extracted and applied by various industrial segments, such as the food, pharmaceutical, cosmetic and chemical industries (BALLESTEROS *et al*., 2017b; SHANG *et al*., 2017). In addition, its use is desirable, as when discarded into the environment, the SCG becomes a source of environmental contamination. Some compounds, such as caffeine, phenolics and tannins, are responsible for the toxicity of this material (BALLESTEROS; TEIXEIRA; MUSSATTO, 2014; MUSSATTO *et al*., 2011a).

The main compounds found in SCG are polysaccharides, mainly cellulose and hemicellulose, which together account for about 50% of the dry matter. In addition, it has considerable amounts of lignin, insoluble dietary fiber, proteins, lipids, caffeine, low ash

contents and considerable amounts of bioactive compounds (BALLESTEROS; TEIXEIRA; MUSSATTO, 2014; SHANG *et al*., 2017).

Studies carried out in recent years have shown some potential uses for this by-product. Some proposed uses for SCG include use as a fertilizer (CERVERA-MATA *et al*., 2019), biofuel production (MARX *et al*., 2020), ion adsorbent (LE *et al*., 2019) and activated carbon production (PAGALAN JR *et al*., 2020). In addition, recent studies have demonstrated the potential of this material as a source of bioactives. Bravo *et al*. (2012) evaluated SCG from different beverage preparation methods and found that, although the amounts of bioactives were different between the methods, it was possible to extract considerable amounts of antioxidant compounds. López-Barrera *et al*. (2016) investigated the anti-inflammatory effect of SCG. These authors found that SCG has a high dietary fiber content, allowing its fermentation by the intestinal microbiota. In this process, the release of inflammatory mediators was reduced, demonstrating its ability to prevent inflammation and indicating the potential use of SCG in the food industry as a source of dietary fiber. Martinez-Saez *et al*. (2017) found in SCG, fiber, antioxidant compounds, essential amino acids and low glycemic index sugars. These authors evaluated the use of coffee grounds as an ingredient in bakery products, concluding that the final quality of the product was not affected by the incorporation of this ingredient.

The extraction of phenolic compounds and antioxidants from SCG has been studied as a promising way to obtain these important compounds for human health from a low-cost raw material, while adding value to this by-product (MUSSATTO *et al*., 2011b).

2.3 Extraction processes

Solvent extraction is a commonly used process for extracting bioactive compounds. In this process, the choice of the extracting solvent is a crucial step, as it has significant influence on several variables, such as the extraction yield and type of compounds extracted (SINGH *et al*., 2014).

The extraction processes can be used to provide extracts from various by-products. In these processes can be validated, for example, the effects of pressure, temperature, extraction time and type of solvent in the final quality of extracts obtained (SHANG *et al*., 2017). The optimization of these variables results in the best conditions for exploring the raw material, generating reliability, saving time and labor thus making the process attractive for large-scale applications (BALLESTEROS *et al*., 2017b).

Recent studies on the extraction of compounds from SCG have shown promising results. Xu *et al*. (2015) used subcritical water to extract phenolic compounds from SCG. Among the

extraction conditions tested, the optimum point was determined for the following conditions: temperature of 179 °C, extraction time of 36 min and 14.08g of SCG per liter of water, where it was possible to extract 88.34 mg GAE/g. Conde; Mussatto (2016) used hydrothermal pretreatment to recover phenolic compounds and flavonoids from SCG, which resulted in a phenolic extraction yield of 32.92 mg GAE/g and flavonoids equal to 8.29 mg QE/g. Bravo *et al*. (2013) evaluated different methods (soxhlet, solid-liquid and filter coffeemaker) and solvents (water, methanol and ethanol) for the extraction of phenolic compounds and antioxidants from SCG and concluded that the use of water together with the filter coffeemaker extraction method resulted in higher recovery of these compounds (13.94 mg GAE/g and 82.40 µmol Trolox/g). On the other hand, Al-Dhabi; Ponmurugan; Jeganathan (2017) evaluated the extraction yield of phenolic compounds using the ultrasound-assisted extraction process. Under the optimal conditions (244 W of ultrasonic power, temperature of 40 °C, time of 34 min and ratio of 1:17 g of SCG/mL of water) it was possible to obtain 36.25 mg GAE/g. These results are quite expressive when compared to other agro-industrial residues, such as grape pomace and carrot and apple peels, where levels lower than 15 mg GAE/g of dry sample were found (STYLIANOU *et al*., 2018). Shang *et al*. (2017) optimized the extraction of caffeine from SCG using high pressure and a mixture of water and ethanol. According to these authors, it was possible to recover from 3 to 9 mg of caffeine/g of SCG, for the ten different coffee cultivars used.

2.4 Microencapsulation

In recent years, the relationship between individuals and food has undergone significant changes. Thus, food now has the function not only of nourishing and providing energy, but also of improving health and promoting well-being. In this context, functional foods have received increasing attention and gained market space (YE; GEORGES; SELOMULYA, 2018). In addition, the increased interest on the part of consumers in acquiring healthier, nutritionally balanced foods that are free of artificial additives has led the food industry to seek alternative sources of bioactive compounds and antioxidants to be used (BRAVO *et al*., 2012).

Antioxidant compounds contribute to the prevention of chronic diseases related to oxidative stress such as diabetes, cancer, cardiovascular and neurodegenerative diseases. Oxidative stress appears when there is an imbalance between free radical production and antioxidant defenses. Thus, free radicals can damage macromolecules such as proteins, lipids and DNA, generating potential risks for the occurrence of various pathologies (CHOBOTOVA, 2009; PORRINI; RISO, 2000).

Factors such as environmental pollution and risk behaviors, such as smoking, can contribute to a tendency to increase the production of free radicals in the human body and, although there is an endogenous antioxidant production system, this may not be enough to eliminate these radicals. Thus, the consumption of exogenous antioxidants, such as polyphenols, is necessary (CAROCHO; MORALES; FERREIRA, 2018). However, antioxidants that are naturally present in foods alone may not be sufficient to prevent oxidative stress, and thus the popularity of antioxidant-added foods has grown (AGUIAR; ESTEVINHO; SANTOS, 2016).

Despite the beneficial effects of natural antioxidants, they are generally very prone to degradative processes, limiting their use in the food industry (BALLESTEROS *et al*., 2017a). Thus, the microencapsulation process can be an alternative to protect these compounds from degradation, allowing their incorporation into food matrices. Microencapsulation is a widespread technique used to protect bioactive compounds, consisting of involving these compounds in a polymeric matrix and creating a microparticle, in order to avoid or delay their contact with harmful factors, such as light, heat and oxygen (FUCHS *et al*., 2006; LOZANO-VAZQUEZ *et al*., 2015). It also has the advantages of improving the retention time of the bioactive compound in the food, allowing its controlled release, providing stability during processing and storage and masking undesirable flavors (BALLESTEROS *et al*., 2017a). Thus, microencapsulation enables the elaboration of food products with greater added value and highly stable and innovative functional products (ERATTE *et al*., 2018).

Microencapsulation can be performed for solid particles, liquid droplets, or even compounds in a gaseous state. The ingredient encapsulated within the microparticles is called the core, internal phase or filler material. The core can be formed from one or more ingredients and can consist of a crystalline material, an emulsion, a suspension of solids or a suspension of microparticles, for example. On the other hand, the material that coats these microparticles can be called a coating, wall material or membrane and can have one or more layers. The composition of the core and wall material as well as the microencapsulation method determine the final shape of the microparticle (GHARSALLAOUI *et al*., 2007). The size of the microcapsule is variable, ranging from submicrons to millimeters, depending on the technique used for the microencapsulation process (YE; GEORGES; SELOMULYA, 2018).

Considering that microcapsules carry active compounds of interest, it is important that they present some desirable functional properties such as encapsulation efficiency, storage stability and good release properties *in vitro* and *in vivo*, since one of the major challenges of

the technique is to ensure that the active compounds remain stable and are released into the human body at the proper time and place (YE; GEORGES; SELOMULYA, 2018).

Microencapsulation usually occurs through drying processes, given the liquid nature of extracts containing the bioactive compounds. Some common drying processes for microencapsulation are spray-drying, fluid bed and freeze-drying (AGUIAR; ESTEVINHO; SANTOS, 2016; GONÇALVES; ESTEVINHO; ROCHA, 2016). The type of drying and the coating material used are decisive for the retention capacity of the compound within the matrix. In this way, the proper choice of these variables ensure maximum incorporation and retention of the compound of interest (FERNANDES; BORGES; BOTREL, 2014; GONÇALVES; ESTEVINHO; ROCHA, 2016).

2.4.1 Wall materials

The choice of wall materials is a crucial step for the success of microencapsulation, as it is directly related to factors such as the efficiency of the process and stability of the microcapsules throughout the storage period (GHARSALLAOUI *et al*., 2007). Through the use of these agents, stabilization of the core material, controlled release, oxidative control, color, flavor and odor masking is promoted, in addition to reducing nutritional losses (ANAL; SINGH, 2007).

Generally, the wall materials most widely used for food use are carbohydrates (starch, modified starch, maltodextrins, dextran, chitosan, inulin), cellulose (carboxymethylcellulose, methylcellulose), gum (acacia, agar), lipids (wax, paraffin) and proteins (casein, gelatin, albumin). Each of these materials produces particles with specific properties (CHEN *et al*., 2019; ESTEVINHO *et al*., 2013).

According to Aguiar; Estevinho; Santos (2016) the material used for encapsulation must be able to form a cohesive film with the core material, provide stability, flexibility and strength, be inert to the active compound and allow controlled release of the encapsulated compound. In some applications, wall materials need to be chemically modified or are combined with other agents to provide better performance. In addition, characteristics such as low cost, non-toxicity and biodegradability are important for these materials (YE; GEORGES; SELOMULYA, 2018).

2.4.1.1 Proteins

Proteins are commonly used in microencapsulation processes, the most common being whey proteins and gelatins. Whey proteins have a globular structure and are soluble in milk. However, they become insoluble at their isoelectric point (KANDANSAMY; SOMASUNDARAM, 2012). These proteins are by-products obtained from cheese

manufacturing and have significant commercial potential, given their gelling, emulsification and amino acid profile properties (FLORES; SINGH; KONG, 2014).

The interest in the use of proteins in microencapsulation processes derives from their ability to bind to different active compounds or even trap them through the formation of structures such as emulsions and hydrogels (TAVARES *et al*., 2014). In addition, milk proteins are widely available, cheap, have good sensory properties, are natural and recognized as safe by regulatory agencies (LIVNEY, 2010).

Egg albumin has several important properties such as water solubility, biodegradability and emulsion-forming capacity, and can also be applied as an encapsulating agent (JIA *et al*., 2019). The solubility property of the protein has a direct effect on the release of the encapsulated material. Thus, the denaturation temperature of the proteins used in encapsulation can affect the solubility of the dried product. The denaturation temperature of egg albumin (60 °C) is slightly lower than that of casein-whey mixtures (70 °C) and whey proteins (95 °C) (TAN; ZHONG; LANGRISH, 2020). Kuhn; De Azevedo; Noreña (2020) evaluated the use of inulin, egg albumin and polydextrose in the encapsulation of Bougainvillea bract extract. According to these authors, all wall materials provided dried products with high antioxidant activity and good physical and rehydration properties.

2.4.1.2 Gum arabic

Gums have in common the property of imparting viscosity and/or thickening in aqueous suspensions. The degree to which this occurs depends on the type of gum and its concentration (AHMED; RAMASWAMY; NGADI, 2005). Various gums can be used for microencapsulation of compounds. However, the most used is gum arabic, also known as gum acacia. This gum has no smell and flavor and, therefore, does not interfere with the sensory characteristics of the product to which it is added. Furthermore, it is highly soluble in hot or cold water in concentrations of up to 50% by weight (KANDANSAMY; SOMASUNDARAM, 2012). However, issues related to cost have motivated studies for its partial or total replacement as an encapsulating agent (REZENDE; NOGUEIRA; NARAIN, 2018).

Chemically, gum arabic is a high molecular weight heteropolysaccharide consisting of D-galactose, L-arabinose, D-glucuronic acid, L-rhamnose and small amount of 4-O-methyl-D-glucuronic acid (AHMED; RAMASWAMY; NGADI, 2005).

A wide range of studies have employed gum arabic to microencapsulate different core materials through different microencapsulation techniques, including anthocyanins from saffron petals (JAFARI; MAHDAVI-KHAZAEI; HEMMATI-KAKHKI, 2016), bioactive

compounds from the pulp and acerola residue (REZENDE; NOGUEIRA; NARAIN, 2018), spent coffee grounds extract (ABRAHÃO *et al*., 2019; BALLESTEROS *et al*., 2017a) and blackberry extract (YAMASHITA *et al*., 2017), among others.

2.4.1.3 Maltodextrin

The designation dextrin is attributed to the product resulting from the hydrolysis of starch, which may present different values of equivalent dextroses. It is noteworthy that even dextrins, with identical values of equivalent dextroses, may have different characteristics depending on the production source (potato or corn, for example) and digestion method (SHISHIR *et al*., 2018).

Maltodextrin is a carbohydrate widely used in microencapsulation processes, and is found in the form of a white powder. This type of material has some properties that make its use interesting in this process, such as low viscosity and high solubility. However, due to poor interfacial properties, it may not guarantee good efficiency in microencapsulation. Thus, it is usually combined with other wall materials, in order to ensure greater protection of the encapsulated compound (EUN *et al*., 2020; GHARSALLAOUI *et al*., 2007). The mixture of maltodextrins with gums, proteins, alginate and other agents can improve the emulsification properties, increase the retention of bioactive compounds, decrease the oxygen permeability of the encapsulating wall and also promote a better controlled release profile of the encapsulated compound (SHISHIR *et al*., 2018).

2.4.2 Spray-drying

Spray-drying is the method most used by industry to perform microencapsulation of compounds. This method has several desirable characteristics, such as process simplicity, continuous flow operation, high product stability, flexibility, low cost, availability of equipment, ease of handling, transport and storage of dried particles. Due to all these characteristics, this method is widely used for large-scale encapsulation of compounds such as antibiotics, additives, vitamins and antioxidants from different sources (FANG; BHANDARI, 2012; FAZAELI *et al*., 2012; GHARSALLAOUI *et al*., 2007; PAINI *et al*., 2015; ROBERT *et al*., 2010).

In simple terms, spray-drying occurs in four steps, which include: the atomization of the liquid material, the drying of the liquid stream from a drying gas, the formation of particles and their subsequent collection (SCHAFROTH *et al*., 2012). In this process, the product to be atomized can be an emulsion, a suspension or a solution and the hot gas stream can be air (most commonly used) or even an inert gas. Due to the removal of water, the spray-dried product has

low moisture and water activity, ensuring greater microbiological stability and lower rates of chemical degradation (GHARSALLAOUI *et al*., 2007).

For spray-drying to be used as a microencapsulation process, some steps must be considered. Initially, a solution/emulsion must be prepared, that is, mixing the core material with the wall material, followed by a homogenization step. Subsequently, the particle atomization and dehydration step take place. The drying conditions applied in this step and the composition characteristics of the solution directly affect the retention of the encapsulated material (GHARSALLAOUI *et al*., 2007).

Several authors have used this drying technique to microencapsulate various compounds. Abrahão *et al*. (2019) performed the microencapsulation of bioactive compounds from spent coffee grounds by the spray-drying method and verified that the use of whey protein isolate was the most efficient encapsulating agent in preserving the antioxidant activity of the original extract. Tonon; Brabet; Hubinger (2010) used spray-drying to microencapsulate anthocyanins and antioxidant compounds from açai juice using maltodextrin, gum arabic and tapioca starch. According to these authors, maltodextrin provided the best results regarding the maintenance of anthocyanin content and antioxidant activity after 120 days of storage at different temperatures and water activities. Already Botrel *et al*. (2014) used spray-drying in the microencapsulation of fish oil and found that the use of maltodextrin or inulin together with the whey protein isolate provided a dried product with excellent physical qualities and good preservation of the core material.

2.4.3 Freeze-drying

Freeze-drying is a process that employs drying at low temperatures and is based on the sublimation process. Initially, the material to be dried is frozen and, later, placed in an environment with controlled temperature and low pressure for drying to occur. The freeze-drying process is able to preserve most of the raw material's initial properties, such as shape, appearance, flavor, color, texture and biological activity (CEBALLOS; GIRALDO; ORREGO, 2012). In this way, it is also an efficient method for the conservation of bioactive compounds.

Freeze-drying encompasses two main processes, which are freezing and drying. Initially, the temperature of the wet food is reduced and it is frozen, most often atmospheric pressure. The frozen material is placed in a container at reduced pressure, close to vacuum. Heat is supplied to this material, causing the frozen water to be sublimated into water vapor. About 90% of the water present in the material can be removed at this stage of the freeze-drying process. However, it is a slow step, which can take several days. Secondary drying can be

performed to remove unfrozen water molecules. At this stage, the temperature of the material is raised so that the water exits by desorption, which may or may not be conducted at reduced pressure, so that the product has a moisture content of around 1 to 4% (MAISNAM *et al*., 2017; SHUKLA, 2011).

Ballesteros *et al*. (2017) performed the microencapsulation of bioactive compounds by spray-drying and freeze-drying methods. According to these authors, the extracts contained phenolic compounds (350.28 mg GAE/100 mL), tocopherols (16.51 mg QE/100 mL- quercetin equivalent) and high total antioxidant activity (591.37 mg α-tocopherol/100 mL) mL). Gum arabic was shown to be harmful in the retention of phenolic compounds, flavonoids and antioxidant activity, with maltodextrin being more efficient in retaining these compounds. Furthermore, the freeze-drying method combined with maltodextrin provided the best results, retaining 62 and 73% of phenolic compounds and flavonoids, respectively, and preserving up to 86% of the antioxidant activity of the initial extract. Yamashita *et al*. (2017) performed microencapsulation by freeze-drying of anthocyanins from mulberry by-products and found that there was a high retention of these compounds, between 68 and 76%, indicating that this dried product could be used as a colorant by the food industry and also provide benefits to the health of the consumer. Elsebaie; Essa (2018) microencapsulated phenolic compounds from red onion skins using maltodextrin, isolated from soy protein, and a combination of these materials. The best result was obtained from the mixture of encapsulating agents, with an encapsulation efficiency of 94.3%. In addition, these authors applied the microparticles in a cake and found that the product had higher values for color, flavor, aroma, texture and general acceptability than that prepared by adding non-encapsulated polyphenolic extract.

2.4.4 Foam mat drying

Foam mat drying is a simple process compared to many other dried food production methods. It can be applied to a wide range of solid, semi-liquid or liquid food products, such as fruits and other vegetables, fruit juices, milk and dairy products, beverages and jams (ARAÚJO *et al*., 2020; HARDY; JIDEANI, 2017; MACEDO *et al*., 2021; PAULA *et al*., 2020; SANGAMITHRA *et al*., 2015).

In foam mat drying, initially, the wet material is transformed into a stable foam by adding stabilizing and or foaming agent (as proteins, gums and various emulsifiers, including glycerol monostearate, propylene glycerol monostearate, carboxymethylcellulose) and whipping (using blender, planetary mixer, or specially designed device). This procedure promotes the incorporation of air, forming bubbles in the food, producing a foam. The small

but numerous air bubbles formed increase the food contact area with the drying air, which favors heat and mass transfers, increasing the drying rate and reducing the total process time (HARDY; JIDEANI, 2017; MACEDO *et al*., 2021; SANGAMITHRA *et al*., 2015).

The ability of the foam mat process to reduce drying time reduces food exposure to hot air, contributing to the preservation of heat-sensitive compounds such as vitamin C, betalains and anthocyanins (RICHTER *et al*., 2021). These compounds perform several functions beneficial to the organism and therefore it is desirable that they be preserved. Other drying methods, such as freeze-drying and spray-drying, stand out for their ability to preserve bioactive compounds in foods. However, they are more expensive, more complex and slower processes (in the case of freeze-drying) than foam mat drying, which makes this method an interesting alternative for food drying (HARDY; JIDEANI, 2017; SANGAMITHRA *et al*., 2015).

Kanha; Regenstein; Laokuldilok (2020) performed the drying of black rice bran anthocyanin extracts by foam mat drying, spray-drying and freeze-drying and concluded that all methods presented powders with high anthocyanin content and high encapsulation efficiency (above 70%). Furthermore, the encapsulation efficiency obtained for foam mat drying at 70 and 80 °C was equal to that found for spray-drying and higher than that found for freeze-drying. Structurally, the powders obtained by foam mat were similar to freeze-drying powders, but larger in size.

3 General considerations

The optimization of biologically active compounds extraction processes has become an important strategy to make industrial processes increasingly sustainable and economical. The need for the proper use of raw materials and by-products that are still little explored encourages the development of research related to these materials. In this context, the by-products of the coffee production chain especially spent coffee grounds, have shown great potential for exploration and application in various industrial segments.

As a way to provide better stabilization of active compounds, microencapsulation processes have also shown promise. Thus, the use of different drying techniques and wall materials can bring new perspectives for the application of these extracts.

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SECOND SECTION

ARTICLE 1 - Optimization of extraction conditions of natural bioactive compounds from spent coffee grounds

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Abstract

In recent years, there has been a huge demand for the reduction of environmental contamination rates. In this context, the coffee industry deserves to be highlighted due to the large volumes of by-products generated during the coffee production chain, especially at the time of preparing the beverage, at which the spent coffee grounds (SCG) are generated. Thus, this study aimed to evaluate various solvents and methods of extraction of bioactive compounds from the SCG and optimize the process by response surface methodology. The extraction kinetics allowed to determine the optimal extraction time for phenolic compounds and was well represented by the Peleg model. The results indicated that the solvent and the extraction method had a significant effect on the extraction yield of the bioactive compounds evaluated. In general, the pure solvents had lower extraction yield compared to the ethanol/water mixture. Under optimized conditions it was possible to obtain 9.15 (mg GAE/g $SCG_{d.b.}$), 0.58 (mg QE/g $SCG_{d.b.}$), 255.55 (g $SCG_{d.b.}$/g DPPH) and 0.042 (mM Fe(II)/g $SCG_{d.b.}$) for TPC, flavonoids, antioxidant capacity (DPPH) and antioxidant capacity (FRAP), respectively. Therefore, the SCG proved a good source of bioactive compounds.

Keywords: SCG, Extraction kinetics, Phenolic compounds, Antioxidant capacity, Response surface methodology.

1 Introduction

The coffee industry is an extremely important sector for the global economy, generating jobs and income. However, like other segments of the industry, it generates waste that causes environmental, economic and social impacts. It is estimated that the coffee industry produces about 2 billion tons of by-products per year (Zabaniotou and Kamaterou, 2019). Thus, reusing coffee processing by-products, which are rich in organic compounds, has become a priority in several countries (Cruz et al., 2014).

Although these by-products were intended mainly for animal feed and use as fertilizers, some studies have suggested other more noble applications, which involve the extraction of antioxidants (Bravo et al., 2013; Monente et al., 2015; Mussatto et al., 2011a), pigment extraction from the coffee husk (Parra-Campos and Ordóñez-Santos, 2019), production of bio-oil and biodiesel (Chen et al., 2016; Kondamudi et al., 2008), use as adsorbent (González et al., 2013; Namane et al., 2005) and use in fermentative processes aimed at the production of different compounds (Cárdenas et al., 2019; Chala et al., 2019; Orozco et al., 2008). These studies demonstrate that there is a great potential for the use of by-products from the coffee production chain, and products with higher added value can be generated.

The coffee beverage is prepared not only by the large soluble coffee industries, but in the domestic sphere as well, in coffee shops and restaurants, generating large volumes of by-product called spent coffee grounds (SCG). According to Getachew and Chun (2017), the SCG is the main by-product of the coffee industry, generating around 6 million tons per year in the world. This by-product contains compounds such as polyphenols, lignin, hemicellulose, sugars, proteins, aliphatic acids, caffeine, trigonelline, melanoidins, oils, amino acids and minerals (McNutt and He, 2019; Xu et al., 2015; Zabaniotou and Kamaterou, 2019). Several studies have demonstrated the richness of SCG in antioxidant and bioactive compounds, such as caffeine and chlorogenic acids, which have already received several health claims attributed to coffee consumption (Bravo et al., 2012; Cruz et al., 2014). In addition, the extraction of phenolic compounds can be considered a viable and promising alternative to add value to SCG and, at the same time, promote the obtaining of this important ingredient from a low-cost raw material (Mussatto et al., 2011a).

In this way, several methods have been employed in the extraction of antioxidant and other bioactive compounds present in the SCG, including solid-liquid extraction with organic solvents, ultrasound-assisted extraction, extraction from supercritical fluids and high-pressure processes. In addition to the type of extraction used, other factors also make a significant

contribution to the efficiency of the process, such as the solid/solvent ratio, particle size, extraction time and temperature (Bravo et al., 2013; Mussatto et al., 2011a; Pinelo et al., 2007; Zabaniotou and Kamaterou, 2019). Given the above, the main purpose of this study was to evaluate the effect of different solvents, solid-liquid extraction methods, time and temperature to obtain bioactive compounds from coffee grounds, aiming to obtain a procedure with maximum extraction efficiency.

2 Material and methods

2.1 Raw material

Spent coffee grounds (SCG) from espresso coffee preparation from single origin coffee (*Coffea arabica*) were acquired from a local coffee shop. SCG were dried in an oven (Tecnal, TE-394/3-MP, Piracicaba, Brazil) at 60 °C, until constant weight. Subsequently, they were packed in laminated packages, sealed and stored.

2.2 Characterization of the raw material

The SCG were characterized in terms of moisture content, water activity (a_w), lipids, proteins, ash and color. Moisture of the samples was determined by gravimetric method at 105 °C (AOAC, 2005). The a_w was determined by direct reading in an electronic hygrometer (Aqualab, Series 3 TE, Washington, USA). Lipids were determined through soxhlet extraction using ethyl ether, protein content was determined by the Kjeldahl method and ash content was determined in a muffle at 550 °C (AOAC, 2005). Color was measured in a colorimeter (Konica Minolta, Spectrophotometer CM-5, Tokyo, Japan) and the results were expressed in terms of the coordinates a^*, b^*, L^*, chroma (C^*) and angle hue (°h).

2.3 Extraction procedures

Spent coffee extracts were prepared according to three different methods, in all cases, a solid-liquid ratio of 1:30 (w/v) and four different solvents were used: water (100%, specific mass of 1 g/mL, boiling point 100 °C), ethanol (99.5%, specific mass of 0.79 g/mL, boiling point 78 °C), acetone (99%, specific mass of 0.79 g/mL, boiling point 56 °C) and isopropanol (99%, specific mass of 0.79 g/mL, boiling point 82°C).

For the soxhlet extraction process (extraction 1), the samples were weighed and properly packed in cellulose cartridges. The samples and each of the solvents were then coupled in a

soxhlet type apparatus for a period of 3 hours. The temperatures used in each extraction process were determined according to the boiling temperature of each solvent.

For the evaluation of solid-liquid extraction at room temperature (extraction 2), the methodology proposed by Rufino et al. (2010), with some modifications was used. The samples were adequately weighed and 40 mL each of the solvents (water, ethanol acetone or isopropanol) were added separately. The system was homogenized and allowed to stand for 1 hour in the dark, followed by centrifugation at 2130g. The extraction solvent (40 mL) was again added to the residue of the first extraction, and the mixture remained at rest for another hour. Then, the extracts collected in each step were mixed and the volume completed to 100 mL with deionized water.

The third extraction method (extraction 3) consisted of mixing each of the solvents and the SCG in 250 mL Erlenmeyer, which were properly covered and kept in a shaking incubator (Marconi, MA 830/A, Piracicaba, Brazil) at 120 rpm and 65 °C for 90 min. The time was defined according to Mussatto et al. (2011a) and the temperature was determined based on the operational limits of the instrument. Subsequently, the contents of each Erlenmeyer were centrifuged (2130g/15 min) and the supernatant collected.

After each extraction, the extracts obtained were filtered in filter paper and stored (-20 °C) protected from light, until the analyzes were performed.

2.4 Extraction kinetics

Based on the best solvents and extraction method, determined in the previous step, a new extraction was performed. In this case, a kinetic curve for the extraction of phenolic compounds was constructed in order to determine the ideal extraction time. For the reactions, the solvent and the SCG were placed in 250 mL Erlenmeyer flasks, properly covered and kept for 24 hours in an incubator (Marconi, MA 830/A, Piracicaba, SP), with orbital shaking (120 rpm). To prepare the extraction kinetics curve, the conditions of ethanol concentration (50%) and temperature (47.5 °C) indicated by the central point of the Central Composite Rotatable Design (CCRD) were used (Table 2). In preparing the curve, 1 mL aliquots were removed at predetermined times until 12 hours of extraction were completed. After 24 hours, a new aliquot was removed. The content collected from each Erlenmeyer was centrifuged (2130g/15 min) and the volume of extract recovered after each extraction was quantified and used for calculations.

After analyzing the extraction curve and determining the optimal extraction time of the total phenolic compounds, the experiment was carried out for all points of the CCRD. At the

end of the extraction time, the total content of each Erlenmeyer was centrifuged, filtered on filter paper and stored (-20 °C) for the analysis.

2.5 Composition of extracts

The recovered extracts were evaluated for total phenolics content (TPC), total flavonoids (FLA), antioxidant activity (DPPH and FRAP methods) and browned compounds.

2.5.1 Total phenolics content (TPC)

TPC were determined according to the Folin-Ciocalteau method, with modifications (Bravo et al., 2012). Initially, the extracts (0.5 mL) were mixed with 2.5 mL of the reagent Folin-Ciocalteu (10%, v/v). After 4 min, 2 mL of sodium carbonate (4%, w/v) was added and the mixture was left to stand for 2 hours in the dark. The absorbance of the samples was read at 720 nm and a standard solution of gallic acid was used as a reference. The results were expressed in milligram gallic acid equivalent per dry weight of SCG (mg GAE/g $SCG_{d.b.}$).

2.5.2 Total flavonoids

To determine the flavonoid content of the extracts the methodology proposed by Mussatto et al. (2011a) was used, with some adaptations. To the extracts (0.6 mL) were added 1.8 mL of methanol, 0.12 mL of aluminum chloride (10%, w/v), 0.12 mL of potassium acetate (1 mol/L) and 3.4 mL of deionized water. The mixture was vortexed and kept in the dark for 30 min at room temperature. The absorbance was read at 415 nm and the total flavonoid content was expressed as milligrams of quercetin equivalent per dry weight of SCG (mg QE/g $SCG_{d.b.}$).

2.5.3 Antioxidant activity (DPPH)

The antioxidant activity was determined according to the DPPH method described by Rufino et al. (2010). A methanol solution (DPPH, 0.06 mM) was prepared immediately before use. Diluted extracts (0.1 mL) were added with 3.9 mL of this solution. Then, the reduction of the absorbance of the samples in 515 nm was verified every minute during the first 10 min and, later in intervals of 5 min until the stabilization. Thus, it was determined that the SCG extracts should react for 1 hour before reading the absorbance. The results were expressed as EC_{50} (g $SCG_{d.b.}$/g DPPH).

2.5.4 Antioxidant activity (FRAP)

The antioxidant activity of the extracts was also determined by the ferric reducing antioxidant power (FRAP). Initially, the FRAP reagent was prepared by mixing TPTZ, $FeCl_3$ and acetate buffer in a ratio of 1:1:10. Then, 2.7 of the FRAP was mixed with 90 µL of the extract and 270 µL of deionized water. After 30 min of reaction at 37 °C, the absorbance was read at 595 nm, using the FRAP reagent as blank (Rufino et al., 2010). The results were expressed as millimoles of ferrous equivalent per dry weight of SCG (mM Fe(II)/g $SCG_{d.b.}$).

2.5.5 Browned compounds

The methodology proposed by Bravo et al. (2013) with minor modifications was used. Briefly, 0.1 mL of each extract was properly diluted in deionized water to 4 mL. After 2 min, the absorbance of the samples was read at 420 nm.

2.6 Statistical analysis

A factorial scheme (3x4) was used to evaluate the effect of the extraction method and solvent on the content of TPC, flavonoids, antioxidant activity and browned compounds in the extracts. The data obtained were analyzed by analysis of variance (ANOVA) followed by the Tukey test, $p<0.05$. The desirability function proposed by Derringer & Suich (1980) was applied to assist in the determination of the best extraction method and solvent, in order to simultaneously maximize all responses.

The Peleg model was adjusted to the extraction kinetics data of phenolic compounds over time (Bucić-Kojić et al., 2007), according to Equation 1.

$$C(t) = C_0 + \frac{t}{k_1 + k_2 t} \quad (1)$$

where C(t) is the concentration of total phenolics at time t (mg GAE/$g_{d.b.}$), t is the extraction time in min, C_0 is the initial concentration of phenolics content at time t=0 (mg GAE/$g_{d.b.}$), k_1 is Peleg's rate constant (min $g_{d.b.}$/mg GAE) and K_2 is Peleg's capacity constant ($g_{d.b.}$/mg GAE).

Since C_0 in all experimental points was zero, Equation 1 was reorganized in the form presented by Equation 2.

$$C(t) = \frac{t}{k_1 + k_2 t} \quad (2)$$

The k_1 relates to extraction rate (B_0) at the very beginning ($t=t_0$), Equation 3.

$$B_0 = \frac{1}{k_1} \quad (3)$$

The k_2 is related to the equilibrium concentration (C_e) of the phenolic compounds in the extract, Equation 4:

$$C(t \to \infty) = C_e = \frac{1}{k_2} \quad (4)$$

The fit of the model was assessed using the coefficient of determination (R^2) and root mean squared deviation (RMSD), calculated according to Equation 5:

$$\text{RMSD} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\text{experimental} - \text{calculated})^2} \quad (5)$$

where n represents the number of experimental points.

The response surface methodology (RSM) was used to optimize the extraction. A Central Composite Rotatable Design (CCRD) was used to evaluate the effects of ethanol concentration and temperature on the recovery of TPC, flavonoids, antioxidant activity (DPPH and FRAP) and browned compounds. Quadratic models were adjusted to the experimental data and non-significant parameters were removed. The level of significance used was 5% ($p<0.05$). The statistical significance of the model coefficients was determined by Student's t-test. The evaluation of the fit of the models was made by the coefficient of determination (R^2). The desirability function proposed by Derringer and Suich (1980) was applied to choose the best extraction condition and new experiments were carried out to validate the optimal condition.

All analyzes of the extracts were performed in triplicate and all statistical analyzes were performed using Statistica software (Statsoft, Tulsa, USA).

3 Results and discussion

3.1 SCG characterization

Table 1 shows the composition of the SCG. As noted, after drying, SCG showed low moisture and a_w values, contributing to its preservation. The high content of lipids found in SCG (12.09 g/100g) is expected and reflects the low efficiency in extracting lipids for the coffee beverage, which are retained in the insoluble material (Cruz et al., 2012). This value is in agreement with that found by Cruz et al. (2012) and Passos and Coimbra (2013) which was in the range of 9.3 to 16.2 and 12.95 g/100g, respectively. With regard to protein content, values

reported in the literature are 12.8 to 16.9 (Cruz et al., 2012),14.39 (Somnuk et al., 2017) and 13.6 g/100g (Mussatto et al., 2011b), being close to the value found in this study (14.2 g/100g). The protein content is higher in SCG in relation to coffee beans due to the leaching of compounds during the preparation of the beverage, increasing the concentration of the compounds not extracted (Mussatto et al., 2011b).

Table 1 - Chemical characterization of SCG

Chemical composition	Value
Moisture ($g/100g_{d.b.}$)	7.23±0.62
a_w	0.206±0.008
Lipids ($g/100g_{d.b.}$)	12.09±0.22
Proteins ($g/100g_{d.b.}$)	14.2±1.55
Ashes ($g/100g_{d.b.}$)	1.76±0.01
L^*	27.04±0.16
a^*	5.82±0.03
b^*	7.65±0.08
C^*	9.61±0.08
°h	52.73±0.14

Results are expressed as mean±SD (n = 3).

The ash content (1.76 g/100g) can be considered an indicator of the mineral content present in the sample. As found by Cruz et al. (2012) and Mussatto et al. (2011b), the ash content in SCG was 0.82 to 3.52 and 1.6 g/100g, respectively, with potassium being the main mineral element found.

3.2 Effect of solvent and extraction method

Extraction processes using different solvents are often used to obtain bioactive compounds from natural sources. This is a process in which a certain solid matrix has its extracted compounds of interest from a liquid solvent. Some of the most used solvents in the extraction of phenolic and antioxidant compounds in food matrices are water, acetone, ethanol and methanol (Ballesteros et al., 2017; Bravo et al., 2013; Musa et al., 2011). These solvents have different polarities and, therefore, influence differently in obtaining the compounds of interest. On the other hand, the choice of the technique used for extraction will depend on factors such as the simplicity and convenience of the method (Musa et al., 2011).

The values of TPC, flavonoids, antioxidant activity and browned compounds are shown in Fig. 1. According to the statistical analysis, there was a significant influence of both factors (method and solvent) on the results obtained. In addition, the interaction between these factors was significant. As seen in Fig. 1, for all methods used, the best results were obtained when water was used as an extraction agent, resulting in the best yields of TPC, flavonoids and antioxidant activity. Using water, there was no significant difference between the results of extraction methods 1 and 3 (except for browned compounds), which are higher than the values obtained from extraction method 2. The browned compounds, in turn, were better extracted by water and ethanol, both by the extraction method 3.

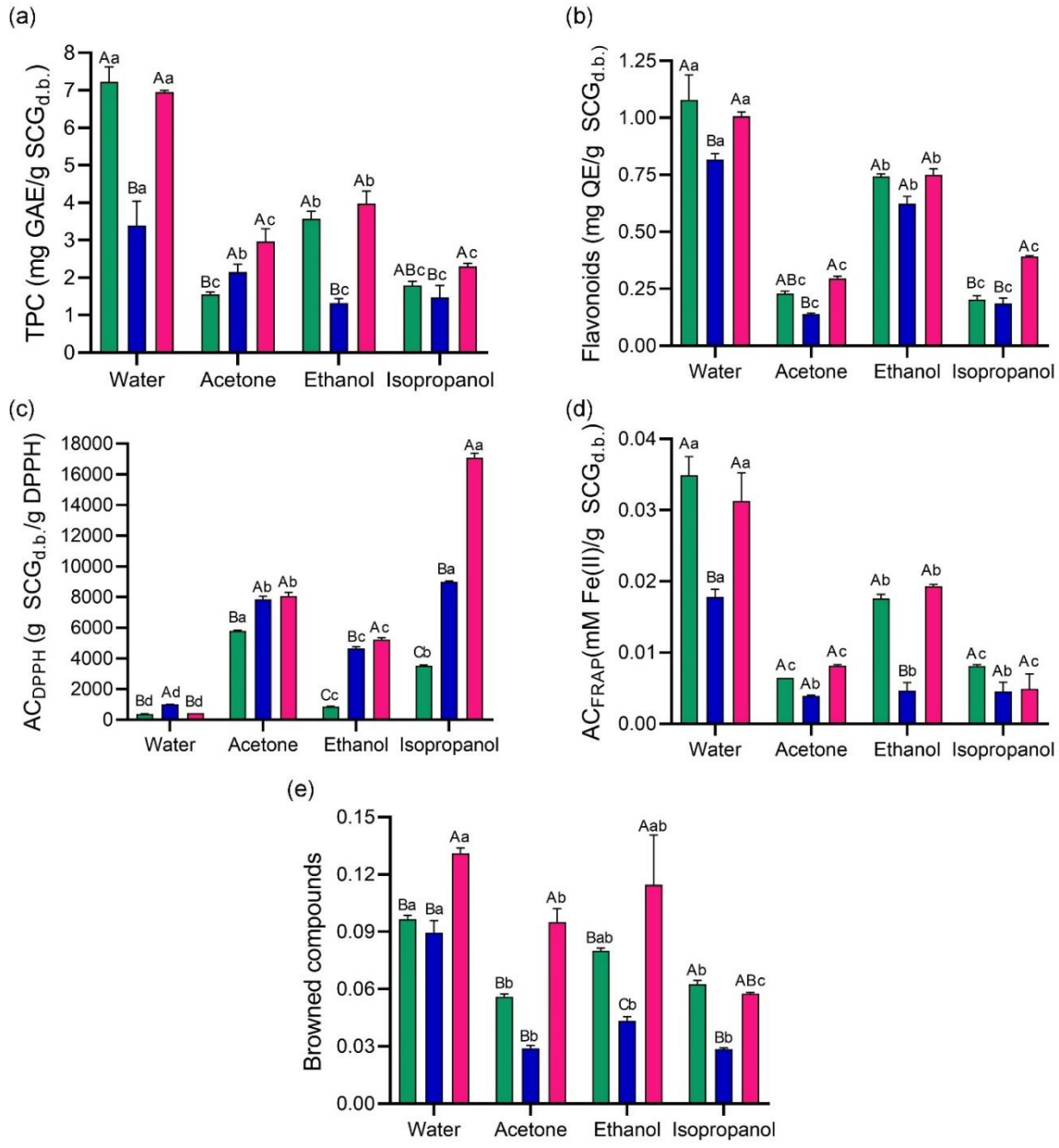

Figure 1 – Composition of the extracts using different solvents and extraction methods. (a) TPC: total phenolics content, (b) flavonoids, (c) AC: antioxidant capacity by DPPH, (d) AC: antioxidant capacity by FRAP, and (e) browned compounds. Green, blue and pink bars represent extraction methods 1, 2 and 3, respectively.

The values are shown as means±SD (n=3). The same uppercase letter indicates no significant difference between extraction methods. The same lower case letter indicates that there is no significant difference among the solvents.

Although extraction method 1 presents higher temperatures, which could result in higher yields, method 3, which is a turbulent method due to the presence of agitation, favors the processes of mass transfer and greater intraparticle diffusion (Gerke et al., 2018). This may have contributed to similar extraction results between these two methods.

As in this study, when evaluating different solvents for the extraction of phenolic and antioxidant compounds, Bravo et al. (2013) concluded that water was the most suitable solvent due to the high extraction yields presented. Pettinato et al. (2019) found that pure water and pure methanol resulted in the same amounts of phenolics extracted, while pure alcohol showed lower extraction yield. On the other hand, the mixture of water and ethanol provided the highest yield, showing that the composition of the solvent is extremely related to its efficiency in extracting the compounds of interest. Furthermore, because they are solvents considered safe and environmentally friendly, water and ethanol become very interesting for the extraction of bioactive compounds (Pettinato et al., 2019).

The global desirability values are shown in Fig. 2. According to these results, it can be seen that method 3 was the most efficient for the extraction of bioactive substances and that water followed by ethanol were the best solvents. Thus, the extraction method 3, together with water and ethanol were chosen for the next step of this study.

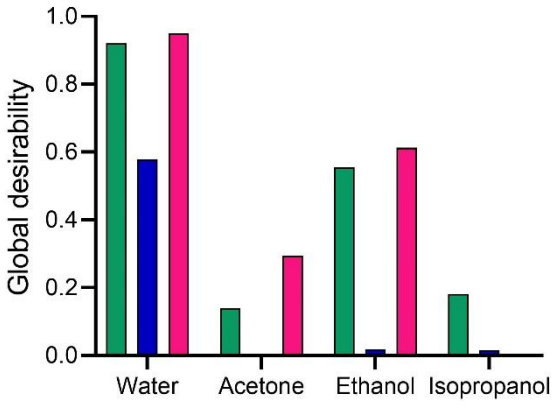

Figure 2 – Global desirability values for each response variable. Green, blue and pink bars represent extraction methods 1, 2 and 3, respectively.

3.3 Extraction kinetics of total phenolic compounds

The extraction kinetics of phenolic compounds using the ethanol:water mixture (50% solution of ethanol) as a solvent and 47.5 °C is shown in Fig. 3a. It can be seen that the extracted TPC content increases exponentially with the extraction time up to a maximum value of 9.19 mg mg GAE/g $SCG_{d.b.}$. As reported by Jokic et al. (2010) it appears that at the beginning of the process there was a high rate of extraction and, subsequently, the amount of phenolics extracted decreased and tended to equilibrium. The substantial increase of compounds in the extracts during the first min of the process is a common event to be observed and may be related to the extraction of compounds located superficially in the intact particles or inside particles that present some kind of fissures, enabling contact between solvent and extractable compounds (Oreopoulou et al., 2020). Subsequently, the intraparticle diffusion mechanism starts to control the process, which reduces the yield (Gerke et al., 2018). According to our results, 95% of the total phenolic compounds extracted after 24 hours were obtained in the first 90 min of extraction, with a low increase in the phenolic content after that period.

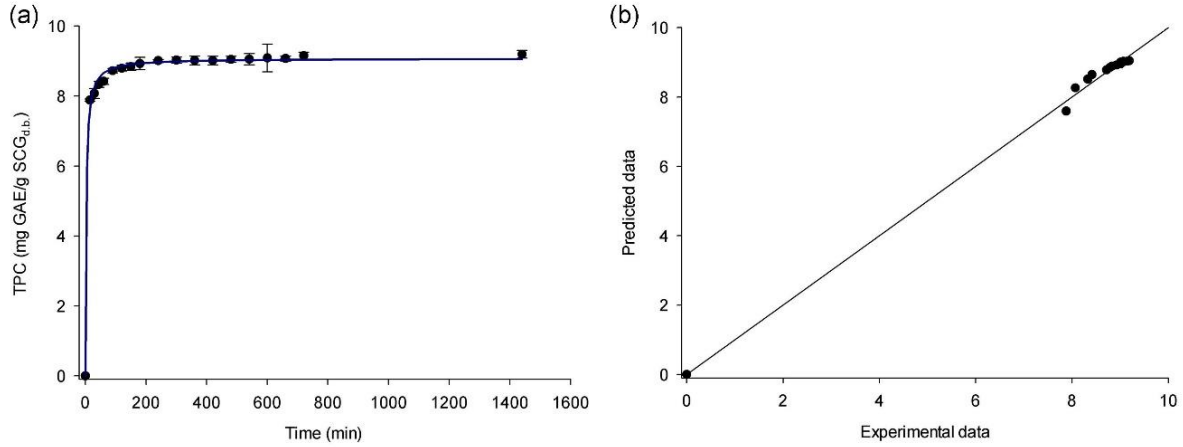

Figure 3 – Extraction kinetics of TPC using 50% aqueous ethanol solution and temperature of 47.5 °C. The line represents the adjusted Peleg model (a) and Correlation between experimental and predicted values by the Peleg model (b).

The Peleg model was adjusted to the extraction data over time and showed a high value of the coefficient of determination (R^2=0.996) and a low error value (RMSD=0.1181), indicating good agreement between the values predicted by the model and those obtained experimentally (Fig. 3b) and demonstrating its suitability to represent the process of extracting TPC from SCG. In fact, the extraction curves can be described very well by adjusting the Peleg model, as they present behavior similar to that of moisture sorption curves (Bucić-Kojić et al.,

2007). Pettinato et al. (2019) also reported a good fit of the Peleg model to describe the extraction kinetics of phenolic compounds from SCG.

The values of the k_1 e k_2 constants in the Peleg model were 0.321 (min $g_{d.b.}$/mg GAE) and 0.110 ($g_{d.b.}$/mg GAE), respectively and were used to calculate B_0 and C_e. The value of k_1 is related to B_0 and indicates the initial extraction rate. The B_0 value found was 3.119 (mg GAE/min g $SCG_{d.b.}$). On the other hand, k_2 is related to the equilibrium concentration (C_e), which presented a value of 9.060 (mg GAE/g $SCG_{d.b.}$).

3.4 Extraction with ethanol/water

In this step, the extractions were performed with different ethanol concentrations (0 a 100% solution of ethanol) and temperature ranging from 30 to 65 °C. The time was fixed at 90 min, according to the result of the extraction kinetics. Table 2 shows the real and coded values of these variables and the content of TPC, flavonoids, antioxidant capacity and browned compounds obtained in the extracts after each treatment. Variables such as temperature and solvent concentration are extremely related to the rate of extraction of bioactive compounds from a solid matrix (Mussatto et al., 2011a). Therefore, these variables were studied aiming at the maximum extraction of these compounds.

As shown in Table 2, the results ranged from 3.77 to 9.36 mg GAE/g $SCG_{d.b.}$), 0.38 to 0.66 (mg QE/g $SCG_{d.b.}$), 292.05 to 1004.01 (μmol Trolox/g $SCG_{d.b.}$), 0.006 to 0.037(mM Fe(II)/g $SCG_{d.b.}$) and 0.094 to 0.139 for TPC, flavonoids, DPPH, FRAP and browned compounds, respectively. It is also observed that, according to the extent to which the extraction conditions were modified, there were variations in the bioactives content, indicating that these variables have an effect during the extraction process. The surfaces that represent each response variable are shown in Fig. 4. In this Figure, it can be seen that there is a region common to the center and tending to maximum temperature, in which all responses are tending to a maximum concentration, except for DPPH, in which this region represents the lowest values, as expected for the highest antioxidant activity.

Table 2 – Levels of independent variables (ethanol concentration and temperature) according to the Central Composite Rotatable Design (CCRD) and experimental results of TPC, flavonoids, antioxidant capacity (DPPH and FRAP) and browned compounds of the extracts

Assay	Ethanol concentration (%)	T (°C)	TPC (mg EAG/g $SCG_{d.b.}$)	FLA (mg QE/g $SCG_{d.b.}$)	AC_{DPPH} (g $SCG_{d.b.}$/g DPPH)	AC_{FRAP} (mM Fe(II)/ g $SCG_{d.b}$)	Browned compounds
1	14.64 (-1)	35.13 (-1)	8.24±0.18	0.44±0.01	367.48±8.62	0.031±0.000	0.097±0.002
2	14.64 (-1)	59.87 (1)	8.61±0.00	0.52±0.01	293.08±1.01	0.033±0.001	0.114±0.001
3	85.36 (1)	35.13 (-1)	6.2±0.22	0.42±0.01	684.08±7.42	0.023±0.000	0.104±0.003
4	85.36 (1)	59.87 (1)	7.26±0.01	0.49±0.02	578.64±0.30	0.027±0.000	0.112±0.001
5	50 (0)	65 (+α)	9.36±0.14	0.66±0.01	298.01±0.59	0.037±0.002	0.139±0.001
6	100 (+α)	47.5 (0)	3.77±0.03	0.38±0.01	1004.01±1.06	0.006±0.000	0.094±0.001
7	50 (0)	30 (-α)	9.02±0.13	0.46±0	326.98±16.69	0.033±0.001	0.116±0.001
8	0 (-α)	47.5 (0)	7.55±0.17	0.43±0.01	631.86±6.77	0.022±0.002	0.096±0.001
9	50 (0)	47.5 (0)	9.02±0.03	0.54±0.01	300.6±8.00	0.035±0.001	0.129±0.001
10	50 (0)	47.5 (0)	9.08±0.06	0.55±0.00	309.59±12.10	0.036±0.002	0.134±0.001
11	50 (0)	47.5 (0)	9.26±0.14	0.53±0.01	292.05±9.19	0.037±0.001	0.131±0.001

TPC: total phenolics content; FLA: flavonoids; AC: antioxidant capacity

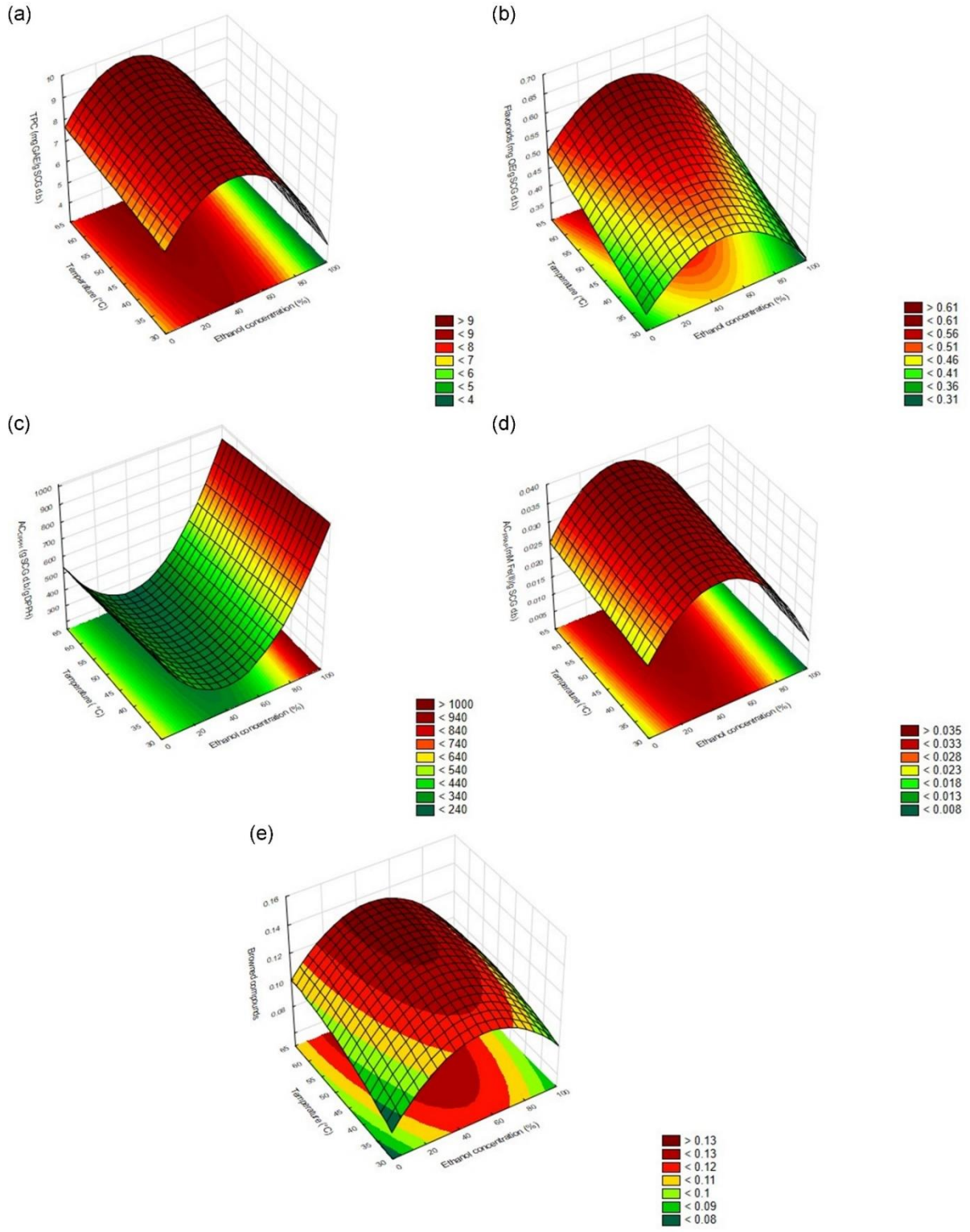

Figure 4 – Three-dimensional plots for (a) TPC: total phenolics content, (b) flavonoids, (c) AC: antioxidant capacity by DPPH, (d) AC: antioxidant capacity by FRAP, and (e) browned compounds as a function of input variables (ethanol concentration and temperature).

Treatment 5, which consists of a 50% ethanol concentration and the highest extraction temperature (65 °C), stood out for the high values of all evaluated variables. On the other hand,

treatment 6, which has the highest ethanol concentration, showed low recovery for all compounds (Table 2). In general, it can be seen that there is a region where the combination of water and ethanol results in higher yields for these compounds, thus, it is verified that ethanol contributes to the process up to a certain concentration level. In addition, higher temperatures helped to improve the process. With the increase in temperature, an increase in the extraction of compounds from the solid matrix is expected due to the increased diffusivity of the solute (Oreopoulou et al., 2020). Also, when the process temperature is increased, there is possibly a rupture of the cell wall of the material and greater leaching of the solute into the medium, in addition to reducing the viscosity of the solvent, resulting in higher extraction (Gerke et al., 2018).

These results are in agreement with those reported by other studies that concluded that the combination of water and alcohols may be more efficient in the extraction of bioactive compounds when compared to the extraction using only pure water, as reported for mashua tubers (Chirinos et al., 2007), black and mate tea (Turkmen et al., 2006) and spent coffee grounds (Bravo et al., 2013; Mussatto et al., 2011a). Jokic et al. (2010) also found that the amount of phenolics extracted was higher in a 50% ethanol concentration compared to higher concentrations (60, 70 and 80%) and also in relation to pure water.

Bravo et al. (2013) found a lower value of antioxidant activity for ethanol extracts when compared to pure water or water/ethanol extracts. According to these authors, alcohol can interfere negatively in the extraction of antioxidant compounds due to the precipitation of high molecular weight melanoidins, preventing the extraction of these compounds and the phenolics linked to them. On the other hand, water helps in the extraction of low molecular weight melanoidins that have higher phenolic compounds associated with their nucleus, contributing to the increased antioxidant activity of the extracts. Similarly, Budryn et al. (2009) also concluded that melanoidins and chlorogenic acids have higher solubility when in an aqueous medium compared to ethanol. Melanoidins are brown colored compounds produced during coffee roasting by the Maillard reaction and have antioxidant activity. According to Bravo et al. (2012) the melanoidin index in SCG extracts is up to 5 times lower compared to coffee beverage.

The values of TPC reported in this study were lower than those reported by Bravo et al. (2013), but are close to those found by Angeloni et al. (2019) and Abrahão et al. (2019) who report values of 9.72 and 7.57 mg GAE/g SCG for phenolics in SCG extracts obtained from espresso technique. The differences found may be related to several factors such as the type of coffee used, arabica or robusta, roasting level and extraction method (Bravo et al., 2012). The

beverage production method has a major impact on the recovery of compounds of interest. Generally, it is found that the espresso has a lower recovery rate when compared to other methods. Even so, the phenolic compounds extracted by this method can be applied by the food and pharmaceutical industries, either to develop new products or to increase the nutritional value and stability of existing products (Angeloni et al., 2019; Bravo et al., 2012).

The values of the adjusted model parameters for each response variable as a function of ethanol concentration and temperature are shown in Table 3. The determination coefficients (R^2) of these models ranged from 0.94 to 0.97, indicating high agreement between the values obtained experimentally and those estimated by the models. The high R^2 value indicates the good adequacy of the models for all response variables, within the range of values studied. In these models, non-significant terms ($p>0.05$) were removed.

Table 3 – Coefficients of the regression models adjusted to the experimental data and respective values of the coefficients of determination (R^2)

Parameters	TPC	FLA	AC_{DPPH}	AC_{FRAP}	Browned compounds
β_0	6.39175	0.21830	676.7963	0.016960	0.004788
β_1	0.10607	0.00533	-15.36691	0.000677	-
β_{11}	-0.00137	-0.00006	0.19356	-0.000008	-0.000016
β_2	0.01930	0.00426	-2.23063	0.000118	0.002818
β_{22}	-	-	-	-	-0.000021
β_{12}	-	-	-	-	-0.000005
R^2	0.97	0.94	0.96	0.94	0.97

TPC: Total phenolics content, FLA: Flavonoids, AC: Antioxidant capacity.

Fig. 5 shows the Pareto graphs for all response variables. As noted, the variables ethanol concentration (X_1) and temperature (X_2) had a significant effect ($p<0.05$) for all responses evaluated. Furthermore, linear (L) and quadratic (Q) terms, as well as the interaction between variables (Fig. 5e) were significant. According to these results, ethanol concentration was the variable with the greatest influence on the recovery of all compounds under study (Fig. 5a to 5e). The mixture between water and other solvents has been shown to be more efficient for the recovery of several compounds. Madhava Naidu et al. (2008) found that the highest proportion of water in the water/isopropanol mixtures resulted in the highest content of chlorogenic acid and phenolic compounds in green coffee extracts and Pavlović et al. (2013) found higher TPC values as the ethanol concentration was reduced, with the maximum value found for the lowest concentration (20%).

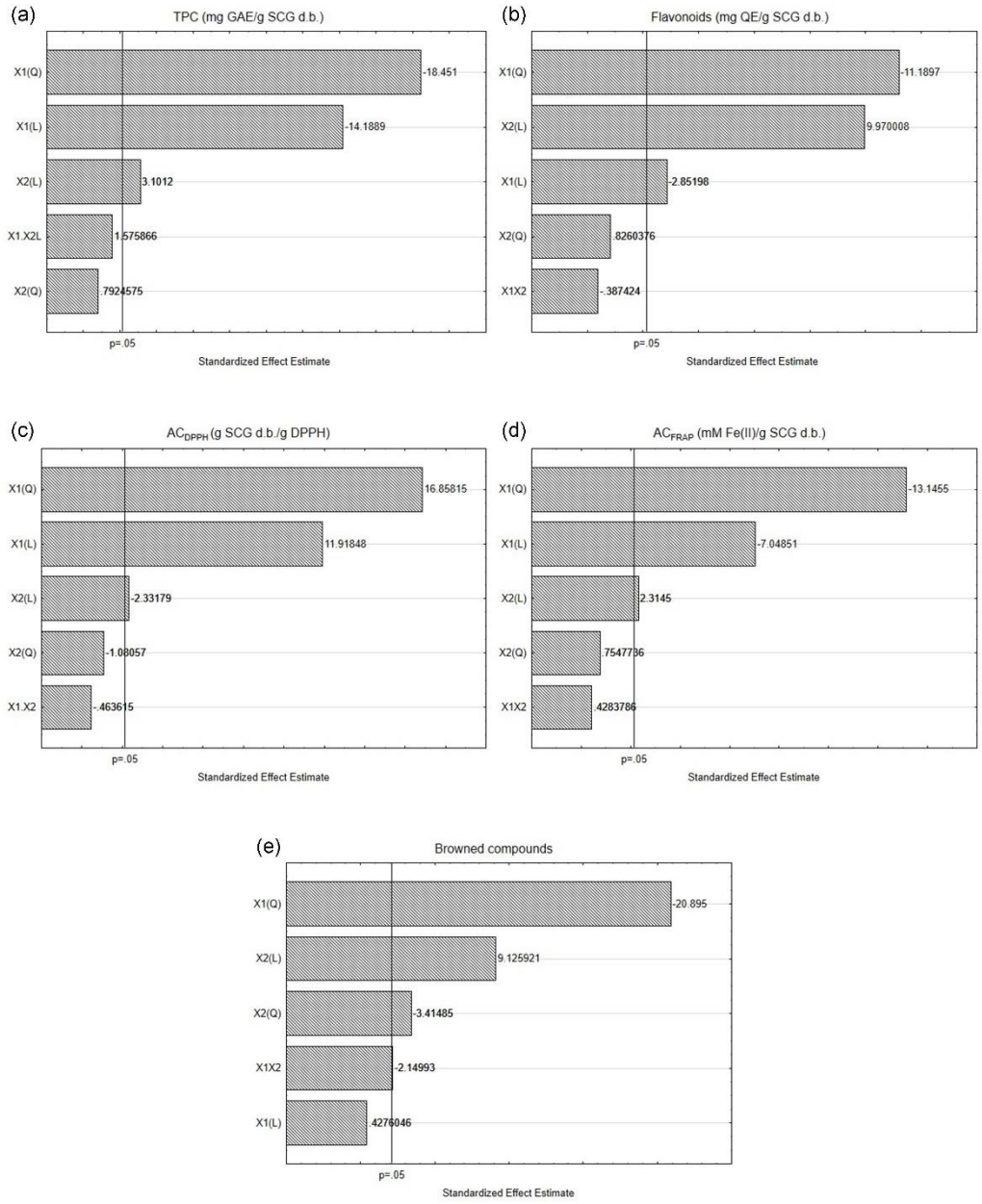

Figure 5 – Pareto graphs showing the effects of the ethanol concentration (X_1) and temperature (X_2) variables and their interaction (X_1X_2) on the response variables: (a) TPC: total phenolics content, (b) flavonoids, (c) AC: antioxidant capacity by DPPH, (d) AC: antioxidant capacity by FRAP, and (e) browned compounds. L and Q represent linear and quadratic effects, respectively.

In order to determine an ideal condition for the extraction of these compounds, the desirability function was applied, resulting in the surface shown in Fig. 6. This figure shows the region where the levels of TPC, flavonoids and antioxidant compounds are maximized, simultaneously.

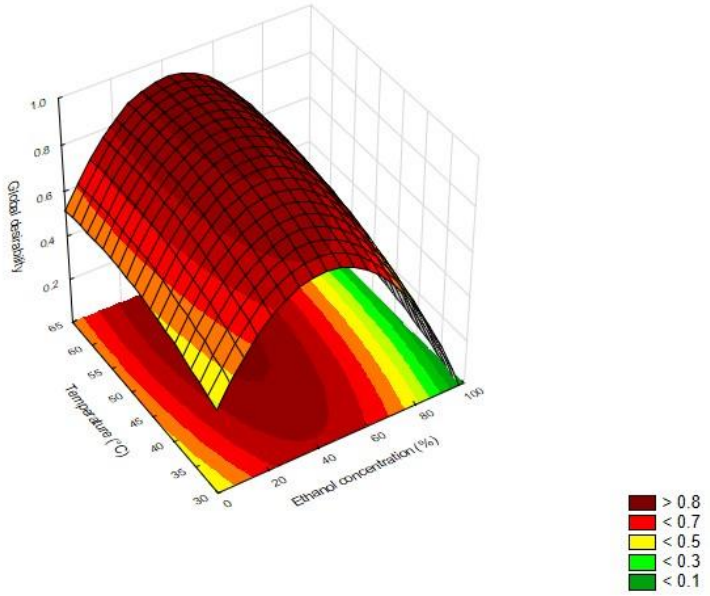

Figure 6 – Three-dimensional surface indicating the region of maximum extraction of SCG bioactive compounds.

The ideal ethanol concentration was 45% and the temperature was 63.3 °C. Under these conditions the predicted values for TPC, flavonoids, antioxidant capacity (DPPH) and antioxidant capacity (FRAP), were 9.61 (mg GAE/g $SCG_{d.b.}$), 0.61 (mg QE/g $SCG_{d.b}$), 236.16 (g $SCG_{d.b}$/g DPPH) and 0.038 (mM Fe(II)/g $SCG_{d.b.}$), respectively. Thus, a new validation experiment using the optimal condition indicated above was performed, resulting in average values of 9.15 (mg GAE/g $SCG_{d.b.}$), 0.58 (mg QE/g $SCG_{d.b}$), 255.55 (g $SCG_{d.b}$/g DPPH) and 0.042 (mM Fe(II)/g $SCG_{d.b.}$) for TPC, flavonoids, antioxidant capacity (DPPH) and antioxidant capacity (FRAP), respectively indicating the proximity between the estimated and experimental values.

4 Conclusion

The results obtained in this study showed that SCG has several bioactive compounds that can be recovered for later application, increasing the sustainability of the coffee production chain. However, the recovery efficiency of these compounds is strongly influenced by the solvent and extraction method applied. The independent variable ethanol concentration in a concentration equal to or less than 50% showed the best extraction results compared to pure solvents. In addition, it was evident that the composition of the solvent has an even stronger effect than the temperature in relation to the recovery of bioactives from SCG. According to

the optimal conditions established in this study, the concentration of ethanol should be 45% and the temperature 63.3 °C to obtain the best yield of the compounds evaluated.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

Acknowledgement

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ARTICLE 2 - Valorization of spent coffee grounds: Encapsulation of bioactive compounds by foam mat drying by mixture design approach and comparison with spray- and freeze-drying methods

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(Elaborated in accordance to Powder Technology - preliminary version)

Abstract

The spent coffee grounds extracts have several bioactive compounds that can be recovered for later application. However, due to the sensitivity to degradative processes, microencapsulating these compounds can be a good strategy. Thus, in the present study, drying by foam mat, spray- and freeze-drying were proposed to microencapsulate bioactive compounds extracted from espresso coffee grounds. For this, albumin, maltodextrin and gum arabic were used as wall materials, with the optimal proportion, 4, 6 and 10% of each of these materials defined according to the mixture design. The foams produced were dried in a tunnel dryer at different temperatures and air velocities. The product dried by foam mat, spray- and freeze-drying was characterized in terms of moisture, water activity, bulk density, solubility, hygroscopicity, wettability, color, phenolic compounds and antioxidants. For all drying methods, dried products with good physico-chemical properties and high levels of phenolic and antioxidant compounds were obtained. The encapsulation efficiency of each method was calculated and compared. The encapsulation efficiency values were between 66.46 and 88.01%. The bioactive content and the encapsulation efficiency of the foam mat were lower when compared to the other methods.

Keywords: Spent espresso coffee; drying methods; wall material; microencapsulation; encapsulation efficiency.

1 Introduction

Coffee is a raw material produced all over the world and, together with the high volume produced, large quantities of by-products are also generated [1]. One of the main by-products is spent coffee grounds (SCG), obtained after preparing the beverage. According to Stylianou et al. [2] espresso coffee grounds are the main by-product generated by coffee shops around the world. The composition of this by-product can be of interest for several applications and its use can also contribute to the reduction of environmental contamination, caused by inadequate disposal [1]. In addition, consumers are increasingly concerned with health-related issues, which puts pressure on the food industry to be in constant search for natural compounds that have some biological activity [3].

Recent studies have demonstrated the richness of bioactive compounds in SCG, as reported by Bravo et al. [4] who found that SCG extracts have a high antioxidant capacity and antigenotoxic effects and by Ramalakshmi et al. [5] who demonstrated that SCGs have anti-tumor and anti-allergenic activity. Ballesteros et al. [6] reported a significant amount of phenolic and antioxidant compounds in SCG extracts, especially flavonoids and chlorogenic acids, indicating SCG as a possible and promising source of these compounds.

In general, bioactive compounds are very sensitive and can undergo degradation. As such, protecting them from external agents such as light, moisture and oxygen is necessary. A commonly used method for this purpose is microencapsulation [6,7]. Microencapsulation consists of a technique in which a liquid, solid, or gaseous material is trapped within small particles, covered by an encapsulating material. A physical barrier is thus created protecting the encapsulated compounds from external factors [8]. Thus, microencapsulation makes it possible to better maintain active compounds during food production and storage processes [9].

Spray- and freeze-drying are commonly used to encapsulate various compounds. However, these are processes that demand expensive equipment and operating conditions [10]. With this in mind, the study of new drying processes can be of great interest. In this context, foam mat drying is a promising alternative. This drying method consists of the transformation of the liquid food into a stable foam through the addition of agents that assist in the formation and stabilization of the foam. Some interesting features of foam mat drying include shorter drying time, low cost, easy execution, good preservation of heat-sensitive compounds, preservation of volatiles and good rehydration properties of the dried product. In addition, although it can be applied as an isolated method, foam mat drying can also be combined with other methods, such as freeze-drying [11].

Although several studies have evaluated the use of industrial wastes and other sources for the extraction and encapsulation of bioactive compounds, these studies used methods other than foam mat drying for encapsulation, such as complex coacervation [12], double emulsion [13], extrusion [14], spray-drying [15,16] e and freeze-drying [17]. Furthermore, no reports have yet been found in the literature on the use of foam mat drying to encapsulate SCG compounds. Thus, this work aimed to determine the optimal combination of wall materials (albumin, maltodextrin and gum arabic) for the production of a stable foam from SCG extracts and to evaluate the effect of drying conditions (temperature and air velocity) on the physical-chemical properties of powders produced. In addition, the foam mat dried product was compared to the product obtained by traditional drying, spray and freeze-drying processes.

2 Material and methods

2.1 Spent Coffee Grounds (SCG) and chemicals

The SCG were kindly donated by a local coffee shop, in Lavras, Brazil. The SCG were previously dried in an oven with air circulation (Tecnal, TE-394/3-MP, Piracicaba, Brazil) at a temperature of 60 °C, until constant weight (moisture<8%).

Maltodextrin with dextrose equivalent (DE) 10 was purchased from Maltogil. Egg albumin was purchased from Naturovos. Gum arabic was purchased from Synth. 2,2-diphenyl-1-picrylhydrazyl (DPPH radical), Gallic acid, Trolox (6-hydroxy-2,5,7,8-tetramethyl chroman-2-carboxylic acid), Folin–Ciocalteau reagent were purchased from Sigma-Aldrich.

2.2 Extract preparation

The aqueous extracts of SCG were prepared using a solid-liquid ratio 1:30 (w/v). SCG and deionized water were placed in a 250 mL covered Erlenmeyer and kept in an incubator with shaking (Marconi, MA 830/A, Piracicaba, SP) at 120 rpm and 63 °C for 90 min. Subsequently, the mixture was centrifuged (2130g/15 min) and filtered on filter paper to eliminate suspended particles. The extract was stored in an amber bottle, under refrigeration (8 °C), until drying process.

2.3 Foam preparation

The wall materials (albumin, maltodextrin and gum arabic) were added to the SCG extracts, according to the mixture design shown in Table 1. The concentration of the wall material was fixed at 20% (w/w) in relation to the final solution. The mixture was stirred

vigorously in a homogenizer (Ultra-Turrax IKA T18 basic, Wilmington, EUA) for 5 min at 5000 rpm. To obtain the foam, this solution was added in a planetary mixer (Arno, BPA, São Paulo, Brazil) and kept under agitation at maximum velocity for 20 min [18].

2.4 Foaming properties

The foams produced were evaluated for stability, density and overrun properties, according to methodologies proposed by Kanha et al. [10]. Porosity was assessed according to Macedo et al. [19].

To determine the stability of the foam, a glass cylinder was used, which was filled with foam (V_i) and left to stand for 1h at a controlled temperature (BOD at 30 °C). The reduction in foam volume (V_f) over time was used in the stability calculation, according to Equation 1.

$$\text{Stability (\%)} = \frac{\text{Vf}}{\text{Vi}} \times 100 \quad (1)$$

To determine the density (ρ), the foams were placed in a 100 mL glass cylinder. The density was determined according to Equation 2.

$$\rho\ (\text{g/mL}) = \frac{\text{m}}{\text{V}} \quad (2)$$

The overrun was calculated based on the mass of extract (M_i) and foam (M_f) both placed in a 100 mL glass cylinder. The overrun was calculated according to Equation 3.

$$\text{Overrun (\%)} = \frac{\text{Mi}-\text{Mf}}{\text{Mf}} \times 100 \quad (3)$$

When calculating porosity, foam density (ρ_{foam}) and extract density ($\rho_{extract}$), were considered, according to Equation 4.

$$\text{Porosity} = 1 - \frac{\rho\text{foam}}{\rho\text{extract}} \quad (4)$$

2.5 Foam mat drying, spray- and freeze-drying

The foams used in the drying step were produced after determining the optimum condition for the elaboration of the foam. For drying, the foams were evenly distributed on a circular stainless steel drying surface (16x1.5 cm) coupled to a tunnel dryer (Eco Engenharia Educacional, MD018 model, Brazil). Drying was interrupted when the samples reached 5% moisture and the dried product was removed with the aid of a spatula. The dryings were carried

out at air temperatures of 50, 60, and 70 °C and air velocity of 1 and 2 m/s, totaling six treatments. The mass of the samples was recorded during drying and drying kinetics curves were drawn up.

In both dryings, spray- and freeze-drying, the mixture of wall materials (according to the optimal proportion defined for the foam) and the extract was initially vigorously stirred in a homogenizer (Ultra-Turrax IKA T18 basic, Wilmington, USA) for 5 min at 5000 rpm. In spray-drying, a spray-dryer (Yamato Scientific Co. Ltd, ADL311S) was used at an inlet air temperature of 160±1 °C, outlet air temperature 60±1 °C, feed flow rate of 2 mL/min and air pressure of 0.1 MPa.

For freeze-drying, the foams produced according to the established optimum condition were carefully placed in a beaker (250 mL) to a height of 2 cm and the beakers were taken to freeze at -20 °C/48 hours in a freezer. Nonfoamed extract (extract just stirred with the wall materials) in the same thickness was also used. After freezing, the samples were inserted into a freeze dryer (FreeZone 2.5, Labconco, USA) with a condenser temperature of −50 °C and a pressure of 0.010 mBar for 72 hours. Upon completion of the sublimation process, the temperature was gradually raised to 25 °C.

The powders resulting from drying were stored in sealed laminated packaging and kept at -20 °C until the analyzes were carried out.

2.6 Physicochemical properties of the dried product

2.6.1 Moisture and water activity (a_w)

The moisture was determined by the gravimetric method. The samples were dried under vacuum at 70 °C, until constant weight. The weight of the sample before and after drying was used to calculate the moisture.

The a_w was measured by direct reading on an electronic hygrometer (Aqualab, 3-TE model, Decagon Devices, Inc., Pullman, WA, USA), at 25 °C.

2.6.2 Bulk density

To determine the bulk density, 5 g of the powders (m) were placed in a 10 mL graduated cylinder, followed by a light tap to level the sample [20]. The volume was measured (v) and the density was calculated, according to Equation 5.

$$\rho\ (g/mL) = \frac{m}{v} \quad (5)$$

2.6.3 Solubility

The methodology proposed by Kanha et al. [10] with minor modifications was used. Briefly, 1 g of sample was weighed and mixed with 10 mL of distilled water. The mixture was subjected to magnetic stirring for 30 min followed by centrifugation at 2260 g/15 min. The supernatant was collected in petri dishes and dried in an oven at 105 °C until constant weight. Subsequently, the plates were weighed to determine the dry solids.

2.6.4 Hygroscopicity

To evaluate the product hygroscopicity, 0.5 g of the powders were placed in petri dishes inserted in a desiccator containing a saturated solution of NaCl (75%). The samples were kept in a BOD incubator (SPLABOR, SP-500, São Paulo, Brazil) at 20 °C for 7 days. After this period, the samples were weighed to assess water absorption [21].

2.6.5 Wettability

The wettability was determined according to Jinapong et al. [22]. For this, 100 mL of distilled water at 25 °C was placed in a 250 mL beaker and 0.1 g of sample was poured into the water through a funnel. The funnel was placed in a burette to maintain a distance of 10 cm between the bottom of the funnel and the surface of the water. The time for all powder particles penetrated in the water was recorded and used to compare the wettability of samples.

2.6.6 Color

A colorimeter (Konica Minolta, Spectrophotometer CM-5, Tokyo, Japan) was used to obtain the colorimetric parameters evaluated in the powders.

2.6.7 Efficiency of encapsulation

To determine the efficiency of encapsulation, powders were evaluated for phenolic compounds content and total antioxidant activity (DPPH and FRAP). The extracts for these determinations were prepared as described by Dadi et al. [23], with minor modifications. Initially, 1 mL of water was added to 100 mg of weighed microparticles and the mixture was vortexed vigorously for approximately 2 min. Subsequently, 9 mL of ethanol was added and the mixture was again stirred to obtain a homogeneous system, followed by centrifugation at 2260 g/15 min and filtration through Whatman filter paper. To determine the bioactive

compounds, present only on the surface of the microparticles 100 mg of sample were used added to 10 mL of ethanol. This mixture was vortexed for about 10 seconds followed by centrifugation (2260g/15 min). The supernatant was collected and filtered. The encapsulation efficiency (EE) was obtained from the two extracts, calculated according to Equation 6.

$$\text{EE}\ (\%) = \frac{\text{Total value} - \text{Surface value}}{\text{Total Value}} \times 100 \quad (6)$$

2.6.7.1 Determination of total phenolic content (TPC)

The Folin-Ciocalteu method was used to determine the content of total phenolic compounds [24]. Briefly, 0.5 mL of the diluted extracts were mixed with 2.5 mL of the Folin-Ciocalteu reagent (10%) and 2 mL of sodium carbonate (7.5%) and vortexed. After 2 hours of reaction at room temperature, the absorbance was read at 720 nm on a spectrophotometer. A standard curve of gallic acid was constructed and the results were expressed as mg gallic acid equivalent per gram of microparticles dry matter (mg GAE/g).

2.6.7.2 Antioxidant activity (DPPH assay)

The methodology described by Rufino et al. [25] was used. Briefly, 0.1 mL of the properly diluted extract was mixed with 3.9 mL of DPPH methanol solution (0.06 mM). The mixture was stirred and kept in the dark for 1 hour for the reaction. The absorbance reading was performed at 515 nm and the results were expressed as g of microparticles dry matter per g of DPPH (g/g DPPH).

2.6.7.3 Antioxidant activity (FRAP assay)

This assay was performed according to the methodology proposed by Rufino et al. [25]. Initially, 90 µL of the extract, 270 µL of distilled water and 2.7 mL of the FRAP reagent were added to the test tube (consisting of TPTZ, $FeCl_3$ and acetate buffer). The mixture was vortexed and kept at 37 °C in a water bath for 30 min, protected from light. The absorbance reading was performed at 595 nm. A standard curve with known concentrations of Fe (II) was constructed and the results were expressed as mM Fe_2SO_4 per gram of microparticles dry matter (mM Fe_2SO_4/g).

2.6.8 Extract characterization

The extracts were characterized in relation to the content of phenolic compounds and antioxidant activity (DPPH and FRAP), according to methodologies already described in the previous topics.

2.6.9 Experimental design and statistical analyses

The simplex centroid design was used to evaluate the effect of the mixture of the albumin (X1), maltodextrin (X2), and gum arabic (X3) on the foaming properties (stability, density, overrun and porosity) and the physical-chemical characteristics of the dried product. As determined in preliminary tests, to guarantee the formation of foam in all treatments, the minimum value of each component in the mixture would be restricted to 4%, so that $4 \leq X_1 \leq 12$, $4 \leq X_2 \leq 12$ and $4 \leq X_3 \leq 12$ and the sum of X1, X2, X3 is 20%. All formulations, with their respective coded and real values, are presented in Table 1. Cubic models were adjusted to the experimental data of stability, density, overrun and porosity. Analysis of variance was used to assess the statistical significance of each response variable. The best models to represent each parameter were chosen after the removal of non-significant terms.

The desirability function described by Derringer and Suich [26] was used to assist in determining the ideal foam formulation, that is, the point of maximum stability, overrun and porosity and minimum density. The individual desirability values (d_i) were calculated for each response variable, according to Equations 7 and 8.

$$d_i \begin{cases} 1, \text{if } \hat{y}_i \leq T_i \\ \left(\frac{U_i - \hat{y}_i}{U_i - T_i}\right), \text{if } T_i < \hat{y}_i < U_i \\ 0, \text{if } \hat{y}_i > U_i \end{cases} \quad (7)$$

$$d_i \begin{cases} 0, \text{if } \hat{y}_i \leq L_i \\ \left(\frac{\hat{y}_i - L_i}{T_i - L_i}\right), \text{if } L_i < \hat{y}_i < T_i \\ 1, \text{if } \hat{y}_i > T_i \end{cases} \quad (8)$$

Where $\hat{y}_i$ is the response estimated by the model. T_i is the optimal value; U_i is the maximum value for the responses that are desired to be minimum; L_i is the minimum value for the responses that are desired to be maximum.

To calculate the overall desirability (D) was used the Equation 9.

$$D = \sqrt[N]{\left(\prod_{i=1}^{N} d_i\right)} \quad (9)$$

Where N represents the number of individual desirabilities.

The dryings were carried out according to a completely randomized design. The drying experiments in foam mat were performed as a full factorial design (3x2). The differences between drying treatments were assessed using ANOVA followed by the Tukey test, at the level of $p<0.05$.

All analyzes were performed in triplicate and the Statistica software (Statsoft, Tulsa, USA) was used for statistical analysis, model adjustment, graphing and parameter optimization.

3 Results and discussion

3.1 Foam properties and model fitting

The foaming properties showed average values of 60.83-97.25%, 0.20-0.42 g/mL, 133.51-388.47% and 57.07-79.49% for stability, density, overrun and porosity, respectively (Table 1).

Table 1 – Experimental design used for the mixture of albumin, maltodextrin and gum arabic and experimental results for the properties of foam

Treatments	Actual and coded values (in parentheses), %			Foam parameters			
	X1 (Albumin)	X2 (Maltodextrin)	X3 (Gum arabic)	Stability (%)	Density (g/mL)	Overrun (%)	Porosity (%)
1	12(100)	4(0)	4(0)	94.34±0.03	0.20±0.01	387.07±13.16	79.46±0.56
2	4(0)	12(100)	4(0)	60.83±0.26	0.42±0.03	133.51±16.30	57.07±3.00
3	4(0)	4(0)	12(100)	95.19±0.87	0.22±0.00	343.41±7.76	77.44±0.4
4	8(50)	8(50)	4(0)	84.65±1.96	0.31±0.02	216.2±21.47	68.3±2.15
5	4(0)	8(50)	8(50)	96.68±0.3	0.21±0.00	388.47±5.66	79.19±0.25
6	8(50)	4(0)	8(50)	86.15±0.00	0.29±0.01	237.81±12.69	70.38±1.11
7	9.33(67)	5.33(17)	5.33(17)	91.72±1.33	0.26±0.03	282.18±12.51	73.67±2.93
8	5.33(17)	9.33(67)	5.33(17)	81.6±0.24	0.31±0.00	222.17±0.17	68.96±0.02
9	5.33(17)	5.33(17)	9.33(67)	97.25±0.00	0.20±0.00	370.03±0.77	79.49±0.30
10	6.67(33)	6.67(33)	6.67(33)	93.69±0.90	0.24±0.01	307.86±12.43	75.47±0.75
11	6.67(33)	6.67(33)	6.67(33)	92.03±0.46	0.26±0.01	279.56±16.16	73.63±1.12
12	6.67(33)	6.67(33)	6.67(33)	92.61±1.15	0.26±0.02	282.22±27.16	73.77±1.86

Values are expressed as the average of triplicate±standard deviation (n=3).

Fig. 1 shows the response surfaces for all properties evaluated in the foams. The adjusted models were significant ($p<0.05$) for all properties evaluated. The high values of R^2 (Table 2) indicated the good adequacy of the models to represent the relationship between the dependent variables (response variables) and the independent variables (X1, X2 and X3).

High values of stability were observed between the maltodextrin/gum arabic vertices (Fig. 1a), which refer to binary mixtures of pseudocomponents X2 and X3, in mixtures of about 25% of X2 and 75% of X3. However, the higher albumin concentration together with the lower maltodextrin and gum arabic concentrations also resulted in good foam properties. The addition of maltodextrin and gum arabic tended to produce lower values of density, higher overrun and porosity (Fig. 1b, 1c and 1d). Moreover, the linear terms and the interaction between maltodextrin and gum arabic were significant (Table 2) and had a synergistic effect on stability, overrun and porosity, demonstrating that the use of this mixture increases the value of these properties.

Table 2 – Predicted coded equations by the special cubic model for experimental data of foam parameters and coefficient of determination (R^2)

Foam parameters	Models	R^2
Stability (%)	$y = 94.47X_1 + 60.29X_2 + 95.66X_3 + 27.46\,X_1X_2 - 33.27X_1X_3 + 74.57X_2X_3 + 46.56X_1X_2X_3$	0.99
Density (g/mL)	$y = 0.20X_1 + 0.43X_2 + 0.22X_3 + 0.29X_1X_3 - 0.54X_2X_3$	0.95
Overrun (%)	$y = 383.81X_1 + 123.96X_2 + 353.15X_3 - 158.99\,X_1X_2 - 453.82X_1X_3 + 611.36X_2X_3$	0.93
Porosity (%)	$y = 79.42X_1 + 56.98X_2 + 77.87X_3 - 28.17X_1X_3 + 51.75X_2X_3$	0.95

X1: albumin; X2: maltodextrin; X3: gum arabic.

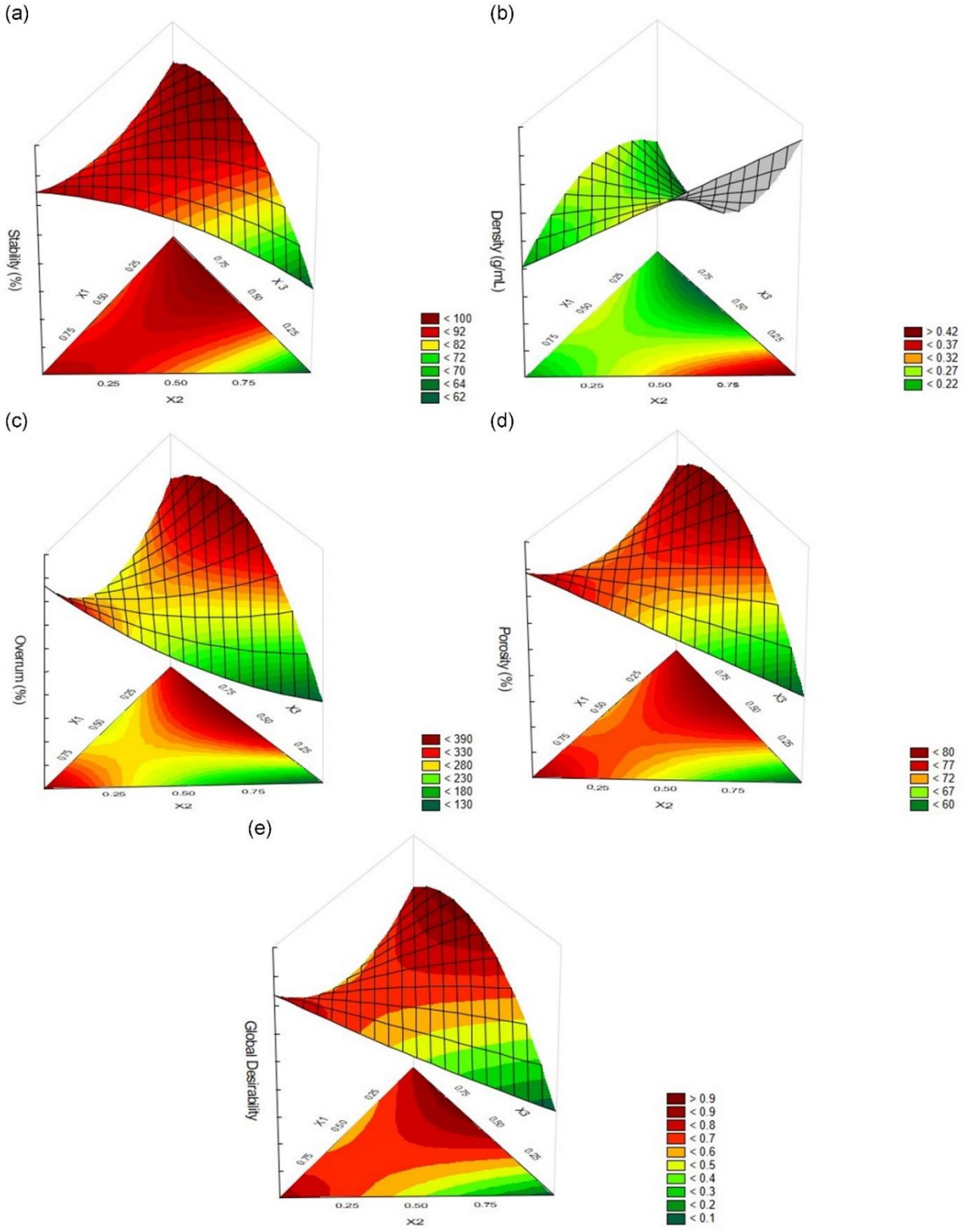

Figure 1 – Surface plots for the effects of albumin (X1), maltodextrin (X2) and gum arabic (X3) on the foaming properties: stability (a), density (b), overrun (c) and porosity (d) and surface plot obtained for the optimization of foam properties (e).

Gum arabic can contribute to the increase in viscosity of the medium [27]. Thus, the increase in viscosity may have contributed to the greater stability of the foam due to less

mobility of the liquid phase and of the gases trapped in its structure [11]. Moreover, as in the present study, Sramek et al. [28] also used albumin in low concentration as a foaming agent and found that the addition of maltodextrin was beneficial for thickening and increased foam stability. The foam stability is a key factor for the success of drying. Generally, additives are employed to provide stability and aid in foaming. Stabilizing agents, such as polymers, help prevent coalescence from occurring. Furthermore, proteins, such as those in eggs, are often used as foaming agents and work by reducing surface tension [11].

The lowest density values observed are linked to the highest volume expansion values (Table 1). Lower density values are desirable as they favor a larger surface area for drying, resulting in a faster and more efficient process [29]. The foams with densities between 0.1 and 0.6 g/mL are usually suitable for the drying process. In addition, generally at density values below 0.5 g/mL, foams can be considered stable [30].

3.1.1 Optimization and validation

The optimization of the proportion of each wall material in the mixture was used to guarantee the production of foam with desirable characteristics for drying. The properties of stability, density, overrun and porosity were used in the optimization. The desirability function had a maximum global value of 0.99 and indicated that the ideal values of X1, X2 and X3 were 4, 6 and 10%, respectively (Fig. 1e). Under these conditions, the predicted values were 100%, 0.17 g/mL, 410% and 82% for stability, density, overrun and porosity, respectively. Thus, according to the ideal conditions indicated, a new validation experiment was carried out to compare the predicted and experimental values. Under the optimized conditions, the values obtained for each parameter were, respectively, 98%, 0.19 g/mL, 407% and 80% for the properties of stability, density, overrun and porosity. These values are very close to those estimated by the model and confirm their good suitability.

Finally, foams produced according to the optimal formulation were developed for the stage of convective drying at different temperatures and air velocities. In addition, the ideal amounts of X1, X2 and X3 were used for spray- and freeze-drying process.

3.2 Foam mat drying

Foams with an initial moisture content of around 80% were continuously dried to a final moisture content of 5%. The drying curves at different temperatures and air velocities are shown in Fig. 2a. The times required to reach the final moisture content ranged from 200 to 450 min.

The shortest drying time was observed for the highest temperature (Fig. 2b). This fact occurs due to the higher drying rates observed due to the greater temperature difference between the air and the foam [31].

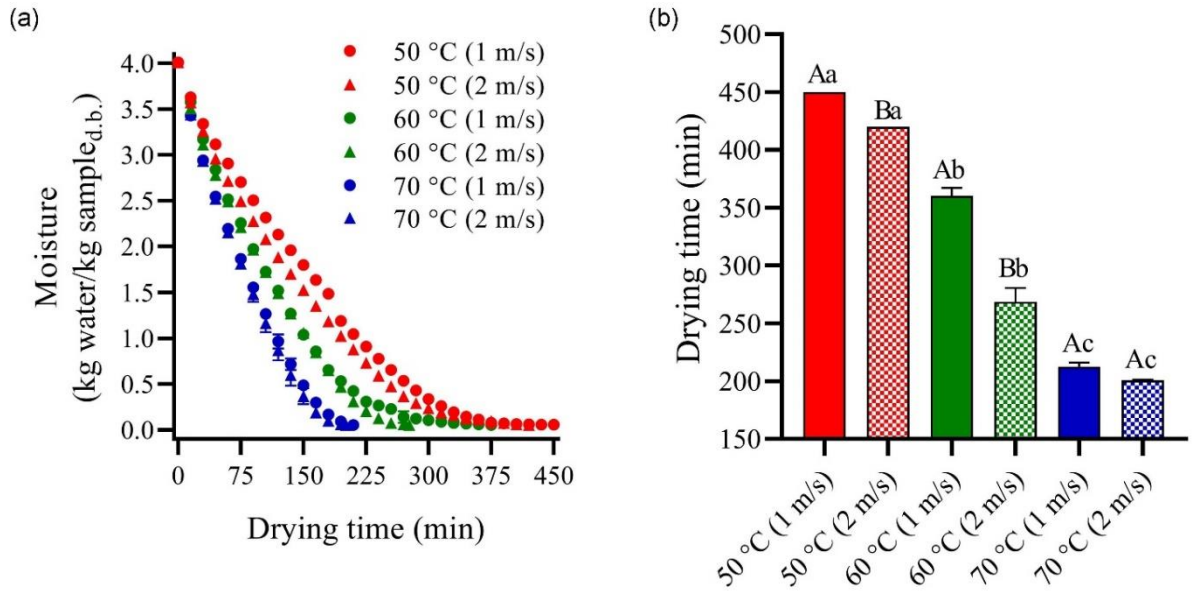

Figure 2 – Drying curves (a) and drying time (b) at different temperatures and air velocities used in foam mat drying.

The values are shown as means±SD (n=3). The same uppercase letter indicates no significant difference between air velocities. The same lower case letter indicates that there is no significant difference among the temperatures.

Air velocity also significantly affected the drying time. The increase in air velocity resulted in a shorter drying time for temperatures of 50 and 60 °C. However, there was no significant difference ($p>0.05$) for drying carried out at 70 °C (Fig. 2b). A longer drying occurred at the lowest temperature (50 °C) and lowest air velocity (1 m/s). A similar result was obtained by Vega-Gálvez et al. [32] who verified a shorter drying time for a higher temperature and a higher air velocity. The effects caused by changes in the velocity of the drying air are diverse and are related to aspects such as the effective diffusivity of moisture, drying rate, solubility of the dried product, bioactive content and color changes [32–34].

3.3 Effect of drying on the properties of powders

3.3.1 Moisture and water activity (a_w)

The moisture content of powdered products affects their stability as well as their reconstitution properties [10]. In general, the powders obtained by all drying methods showed low moisture content, less than 6%. No significant differences were observed ($p>0.05$) between

the moisture content of the powders obtained by foam mat, their values being superior to the other methods (Fig. 3a). The lowest moisture values were obtained for foam mat freeze-drying (FMFD) and freeze-drying methods (FD) (Fig. 3a). The moisture presented by the spray-drying (SD) method is closely related to the process conditions applied to this drying. In general, the wall material used has little effect on the moisture content of spray dried products, on the other hand, operational conditions strongly influence this property [35].

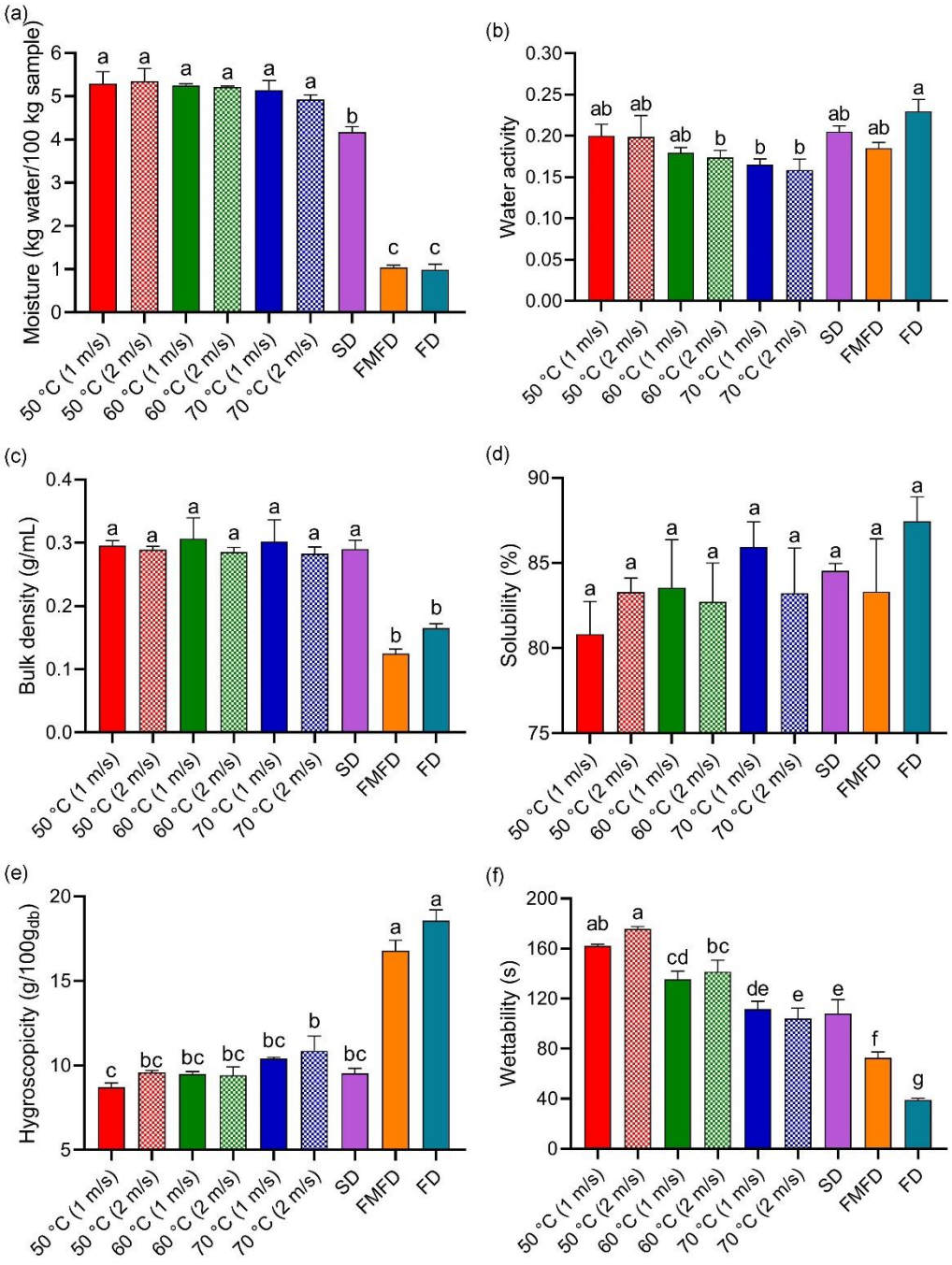

Figure 3 – Values of moisture content (a), water activity (b), bulk density (c), solubility (d) hygroscopicity (e) and wettability (f) of the dried particles by foam mat drying, spray-drying (SD), foam mat freeze-drying (FMFD) and freeze-drying (FD). Bars with the same letters indicate no significant differences ($p>0.05$).

In relation to a_w, the dried product presented low values of this parameter, below 0.30, demonstrating its good stability for all drying methods (Fig. 3b). According to Darniadi et al. [36] powder products with a water activity below 0.40 have low microbial growth and biochemical reaction rates. The FD treatment showed higher a_w when compared to the foam mat method at 60 °C (2 m/s) and the highest temperature (70 °C) for both air velocities. Although some statistical differences were observed, the range of variation of a_w between the methods was very small (0.16 - 0.23). According to Pinto et al. [30], low values of moisture and water activity provide higher stability to the product due to reduced chemical and enzymatic reactions and reduced growth of microorganisms. In addition, less adhesiveness and better rehydration properties are expected for these products.

3.3.2 Bulk density, solubility, hygroscopicity and wettability

Bulk density is an important property of powdered products and is related to several factors, including rehydration properties, packaging, transportation, marketing and product appearance. The size and moisture of the dried product are determinants for the density [37]. As seen in Fig. 3c, there was no significant difference ($p>0.05$) between the densities obtained for the FMFD and FD treatments. However, these were lower than the densities presented for foam mat and SD. A similar result was reported by Darniadi et al. [36] who found a lower density for the dried product by FMFD compared to SD. The apparent density values presented by the SD and FD methods are close to those found by Dadi et al. [23] for particles containing bioactive compounds of moringa extract obtained by spray- and freeze-drying. Moreover, as in this study, the authors also found lower values for the apparent density of the particles obtained by freeze-drying.

The solubility and wettability properties are linked to the reconstitution characteristics of the powdered product [27]. As seen in Fig. 3d, all powders showed good solubility and there was no significant difference ($p> 0.05$) among the solubilities of the powders obtained by different drying methods, which presented an average value of 80.23%. These results are in agreement with the report by Darniadi et al. [36] who also did not observe any significant difference in the solubility of the blueberry juice powder obtained by FMFD and SD. The fact

that there is no difference between treatments may be related to the high water solubility of the materials used as encapsulants (proteins and carbohydrates) and also of the core material. This behavior was also observed by Botrel et al. [35] when evaluating the solubility of oils encapsulated by spray-drying using maltodextrin, inulin and whey protein isolate as wall materials.

Hygroscopicity represents the ability of dried products to absorb water [23]. Therefore, it is a property that interferes with the stability of the product. It can be observed that the highest hygroscopicity was obtained for the treatments that presented the lowest moisture content, being the FMFD and FD (Fig. 3e). Kanha et al. [10] observed that the product obtained by foam mat drying showed greater hygroscopicity as the temperature of the drying air was increased, reducing the moisture content of the powder. However, in the present study, this effect was not observed due to the similarity among the moisture content of the foam mat powders. The hygroscopicity values of the present study are lower than 11.9-19.7, 45.3 and 33.8 g/100g reported by Kanha et al. [10] for foam mat drying, spray- and freeze-drying, respectively. However, it is worth mentioning that hygroscopicity depends not only on the drying method but also on the wall material used, as observed by Dadi et al. [23].

The shorter wettability was observed for the FD method, followed by FMFD (Fig. 3f). In addition, it is observed that the wettability time of the particles obtained by drying in a foam mat at the highest temperature (70 °C) did not differ from the wettability time of the SD method.

3.3.3 Colorimetric parameters

Color is an important attribute related to the appearance of a product. The main chromatic attributes are luminosity (L^*), hue (°h) and chroma (C^*). The hue is related to the perception of a certain color, while the chroma indicates the purity of the color [38]. According to Fig. 4a, the parameter L^* was significantly affected ($p<0.05$) by the drying method employed. It is also observed that the lowest L^* values were obtained for the foam mat drying method, indicating that this treatment resulted in darker samples. On the other hand, the SD treatment, followed by FMFD and FD presented the highest values of this parameter. These results are in agreement with those reported by Kanha et al. [10] who reported that there was no significant difference among the values of L^* for drying in a foam mat at different temperatures (60, 70 and 80 °C) and that these were lower than those found for spray- and freeze-drying methods. The lowest chroma value (C^*) was obtained for the SD method (Fig. 4b). On the other hand, FD showed a higher C^* when compared to all the foam mat drying, indicating higher color intensity for these samples. According to Ramallo and Mascheroni [38], the values of °h are

between 0 and 270, being 0 (pure red), 90 (pure yellow), 180 (pure green) and 270 (pure blue). The lowest value of °h was found for FD. The highest values were observed for drying in foam mat at 50 °C and SD, which did not differ statistically ($p>0.05$) (Fig. 4c). For all treatments the values were near the yellow color.

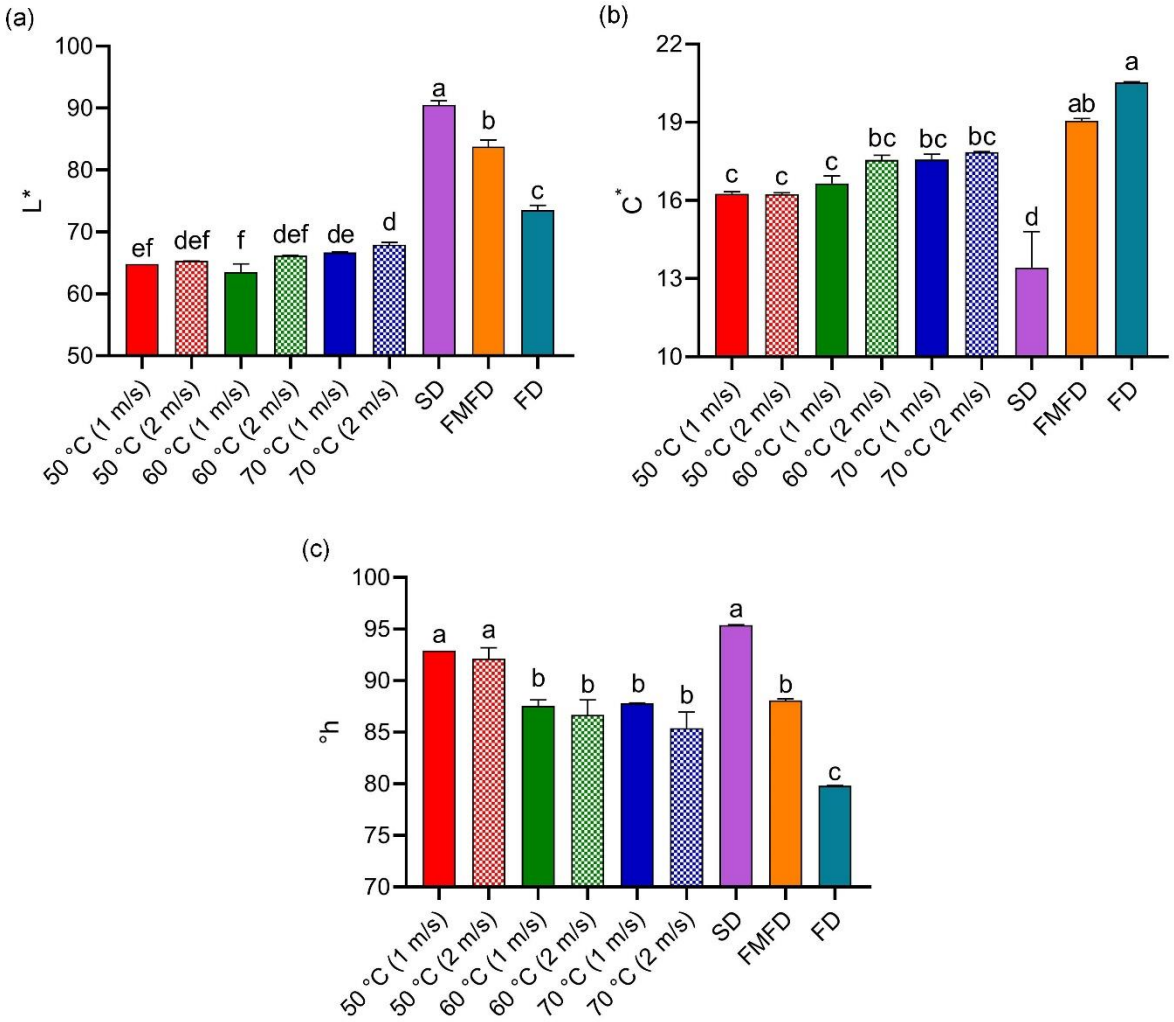

Figure 4 – Colorimetric parameters, L^* (a), C^* (b) and hue angle (°h) of the dried particles obtained by foam mat drying, spray-drying (SD), foam mat freeze-drying (FMFD) and freeze-drying (FD). Bars with the same letters indicate no significant differences ($p>0.05$).

3.4 Encapsulation efficiency

Efficiency is an important parameter to be evaluated in microencapsulation processes, regardless of the method or the compound to be encapsulated [39]. Thus, this parameter for different drying methods was calculated and compared. The content of phenolic compounds and antioxidant activity in the extracts showed an average value of 7.27 mg GAE/g, 389.32 g/g

DPPH and 0.037 mM Fe_2SO_4/g for total phenolic compounds and antioxidant activity by DPPH and FRAP methods, respectively. The percentage of these compounds retained in the matrix is shown in Table 3. The values obtained for the encapsulation efficiency were between 66.46-81.70, 79.47-86.14, 80.34-85.92 and 79.90-88.01% for foam mat drying, SD, FMFD and FD, respectively. In general, all drying methods showed high levels of bioactive substances inside the microparticles compared to the content of these compounds on the surface (data not shown), which is highly desirable. Drying in a foam mat satisfactorily preserved the bioactive compounds of the spent coffee grounds extract and showed high efficiency values. However, it can be seen that particles obtained by the SD, FMFD and FD methods had a higher bioactive content compared to the dried particles obtained by foam mat, and higher encapsulation efficiency. On the other hand, Kanha et al. [10] found equal values of encapsulation efficiency in anthocyanin powders for foam mat and spray-drying, being higher than those of freeze-drying. As seen in Table 3, no significant differences ($p>0.05$) were observed between the levels of bioactive and encapsulation efficiency for the SD and FMFD methods.

Table 3 – Content of total bioactive compounds and encapsulation efficiency for the different drying methods used in the encapsulation of spent coffee grounds extract

Samples	TPC (mg GAE/g)	DPPH (g/g DPPH)	FRAP (mM Fe_2SO_4/g)	Encapsulation efficiency (%, TPC)	Encapsulation efficiency (%, DPPH)	Encapsulation efficiency (%, FRAP)
Foam mat drying (50 - 1m/s)	5.82 ± 0.02^{d}	4670.42 ± 15.70^{a}	0.0248 ± 0.0007^{cd}	71.44 ± 1.52^{de}	78.37 ± 0.99^{d}	66.49 ± 1.31^{b}
Foam mat drying (50 - 2m/s)	5.92 ± 0.01^{c}	4618.58 ± 24.46^{a}	0.0272 ± 0.0010^{bc}	69.27 ± 0.52^{e}	79.02 ± 0.69^{cd}	68.12 ± 1.26^{b}
Foam mat drying (60 - 1m/s)	5.79 ± 0.06^{d}	4565.91 ± 58.47^{ab}	0.0226 ± 0.0014^{d}	75.43 ± 0.88^{c}	79.41 ± 0.36^{cd}	66.46 ± 2.57^{b}
Foam mat drying (60 - 2m/s)	5.77 ± 0.24^{d}	4552.41 ± 12.50^{ab}	0.0258 ± 0.0012^{bd}	74.40 ± 0.52^{cd}	78.25 ± 0.25^{d}	69.07 ± 0.29^{b}
Foam mat drying (70 - 1m/s)	5.87 ± 0.00^{d}	4486.35 ± 12.05^{b}	0.0239 ± 0.0003^{d}	80.36 ± 0.86^{b}	78.60 ± 0.37^{cd}	67.79 ± 4.11^{b}
Foam mat drying (70 - 2m/s)	5.79 ± 0.02^{d}	4498.22 ± 11.18^{b}	0.0238 ± 0.0005^{d}	81.70 ± 0.98^{b}	80.10 ± 0.11^{bcd}	69.59 ± 1.25^{b}
Spray-drying (SD)	6.67 ± 0.09^{a}	4045.87 ± 30.20^{d}	0.0291 ± 0.0007^{b}	86.14 ± 0.32^{a}	82.81 ± 0.02^{a}	79.47 ± 0.59^{a}
Foam mat freeze-drying (FMFD)	6.52 ± 0.10^{ab}	3994.33 ± 16.40^{d}	0.0287 ± 0.0002^{b}	85.92 ± 1.50^{a}	81.68 ± 0.29^{ab}	80.34 ± 1.70^{a}
Freeze-drying (FD)	6.25 ± 0.05^{b}	4173.23 ± 46.52^{c}	0.0334 ± 0.0008^{a}	88.01 ± 0.28^{a}	80.33 ± 0.54^{bc}	79.90 ± 0.12^{a}

Values are expressed as mean±standard deviation (n=3). Averages in the same column and followed by same superscript letter do not differ from each other ($p>0.05$).

The encapsulation method, core/wall material ratio and chemical properties of the encapsulated compound are some of the factors that can affect the efficiency of the encapsulation [23]. According to Ballesteros et al. [6], the drying process directly affects the encapsulation efficiency of bioactive compounds extracted from coffee grounds, since the drying employed can alter the particle morphology. Thus, freeze-drying can result in a lower surface area/volume ratio when compared to spray-drying and, consequently, can protect more compounds located closer to the surface. Dadi et al. [23] observed that the use of maltodextrin and high methoxyl pectin mixture resulted in higher efficiency in the encapsulation of phenolic and flavonoid compounds when compared to the use of pure maltodextrin. In addition, they obtained higher efficiency results when using spray-drying, when compared to freeze-drying. On the other hand, Ballesteros et al. [6] concluded that maltodextrin and freeze-drying were more efficient for the retention of bioactives when compared to the spray-drying technique and the use of gum arabic as an encapsulating agent.

4 Conclusion

Foams with favorable drying properties were obtained from the combination of albumin, maltodextrin and gum arabic. The ideal proportion of each agent in the mixture has been established, being 4, 6 and 10%, respectively. After drying, it was found that the method used significantly affected the physical-chemical properties and the efficiency of encapsulation. Freeze-dried products had lower moisture content, bulk density and wettability time compared to foam mat and spray-drying methods. However, the solubility of the powders did not differ for the different methods. Foam mat drying demonstrated good encapsulation efficiency results. However, when compared to spray- and freeze-drying, drying in a foam mat showed higher loss of the bioactive compounds evaluated, as well as lower efficiency. Although foam mat drying has performed slightly less than traditional microencapsulation methods, it is worth mentioning that this method has, as one of its main advantages, the simplicity of execution. Thus, in future work, we encourage the use of this technique together with other agents to assess improvements in relation to the quality of the products obtained.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

Acknowledgement

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ARTICLE 3 - Encapsulation of phenolic compounds and antioxidants from spent coffee grounds: physicochemical characterization of spray-dried and freeze-dried products

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(Elaborated in accordance to LWT - Food Science and Technology - preliminary version)

Abstract

Spent coffee grounds (SCG) are a by-product that causes environmental impacts worldwide. Thus, consciously reusing the SCG is an eminent need. This work aimed to encapsulate phenolic compounds and antioxidants obtained from SCG extracts through spray- and freeze-drying techniques, using different isolated and combined wall materials. The dried powders produced were evaluated for moisture content, water activity, bulk density, hygroscopicity, color, content of phenolic compounds and antioxidants and the results were compared. The results showed that all evaluated treatments resulted in a powdered product with low values of bulk density, moisture and water activity, especially for freeze-drying. The freeze-dried product also showed greater hygroscopicity. Regarding the content of phenolic compounds and antioxidants, both drying methods showed high levels of these compounds in the dried product and good encapsulation efficiency, reaching 83.43%. In most cases, spray-drying and freeze-drying did not differ statistically ($p>0.05$) in relation to bioactive compounds content and encapsulation efficiency. In relation to wall materials, albumin showed the worst performance in the retention of bioactive compounds. On the other hand, pure gum arabic and combined with maltodextrin led to better preservation of these compounds.

Keywords: By-products, spent coffee grounds, powder quality, wall materials, antioxidant activity.

1 Introduction

Coffee is produced and consumed in different regions of the world. On the world stage, Brazil stands out as the largest producer of this food. In Brazil, each inhabitant consumes 4.79 kg of roasted coffee per year, which places the country in the second position in the world ranking of coffee consumption. This consumption has increased since the 90s, reaching the level of 21.2 million bags of 60 kg in the year 2020 (ABIC, 2021).

The coffee beverage is the result of a long production chain with several stages from planting to final preparation. All these steps end up generating residues, divided into processing residues which represent more than 50% of the fruit mass, and residues related to the preparation of the beverage. Part of the coffee produced worldwide is destined for the soluble coffee industries and the rest is used in homes, restaurants, and coffee shops (Cruz et al., 2012; Ramalakshmi, Rao, Takano-Ishikawa, & Goto, 2009).

For the production of the beverage, it is necessary to extract compounds from the coffee powder with hot water or steam. After this process, spent coffee grounds (SCG) are generated, which are usually improperly discarded (Zuorro & Lavecchia, 2012). However, SCG can be considered an alternative source of several compounds with biological activity, such as antioxidants and caffeine. In addition, they have in their constitution organic compounds such as cellulose, fatty acids and lignin that can also be recovered. Thus, the sustainable use of SCG becomes an alternative for obtaining products with greater added value and reducing problems of environmental contamination (Angeloni et al., 2019).

The phenolic compounds and antioxidants can be extracted in appreciable amounts from the SCG for further application (Cruz et al., 2012; Mussatto, Ballesteros, Martins, & Teixeira, 2011). The insertion of antioxidant compounds in food matrices undergoing some type of processing is a common practice and, although synthetic antioxidants have good stability and lower cost, issues related to their safety have aroused interest in their replacement by natural antioxidants, which have good properties with respect to safety, toxicity and tolerance level (Ranic et al., 2014). However, due to sensitivity to external factors such as light, the presence of oxygen and moisture, it may be necessary to encapsulate these compounds, making them more stable and safer as food ingredients (Ballesteros, Ramirez, Orrego, Teixeira, & Mussatto, 2017).

Several microencapsulation processes can be applied, the spray-drying is one of the most used and efficient methods. This technique consists of a process in which a liquid material is dispersed in a drying medium to produce a powdered material (Schafroth, Arpagaus, Jadhav,

Makne, & Douroumis, 2012). The wall materials used in this process have a direct effect on the quality and stability of the dried product (Carmo et al., 2018). Some important properties for choosing these agents are solubility, molecular weight, glass transition temperature, diffusivity and cost (Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007). On the other hand, freeze-drying is a widely used technique due to the good preservation of heat-sensitive compounds (Ceballos, Giraldo, & Orrego, 2012). According to Ballesteros et al. (2017) the choice of drying technique and wall material directly influences the preservation capacity of the encapsulated compounds.

Microencapsulation processes applied to SCG extracts have been little explored. Therefore, this study aimed to carry out the encapsulation of coffee grounds extracts using the combination of different wall materials (albumin, maltodextrin and gum arabic) and drying methods (spray-drying and freeze-drying) in order to verify the effect of these factors in the physicochemical properties and in the encapsulation efficiency of bioactive compounds from the powder particles.

2 Material and methods

2.1 Materials

Spent coffee grounds (SCG) were donated by a local coffee shop (Cafezal, Lavras, MG, Brazil). The SCG were oven dried at 60 °C until constant weight. Subsequently, they were stored in properly sealed plastic containers until extraction. Egg albumin was purchased from Naturovos. Maltodextrin (DE 10) was purchased from Maltogil. Gum arabic was purchased from Synth.

2.2 Extraction of bioactive compounds

SCG extracts were prepared from a mixture of SCG and water in a 1:30 (w/v) ratio. The mixture was added to a 250 mL Erlenmeyer, properly capped and left under stirring (120 rpm, 63 °C) in an incubator (Marconi, MA 830/A, Piracicaba, SP) for 90 min, as defined in preliminary tests. At the end of the extraction period, the extract was collected, centrifuged and filtered on filter paper, followed by storage in an amber flask under refrigeration until drying was performed.

2.3 Spray-drying and freeze-drying encapsulations

SCG extracts were encapsulated using albumin, maltodextrin and gum arabic as wall materials. The amount of wall material used was set at 20% (total weight basis). Seven tests were performed: 100% albumin, 100% maltodextrin, 100% gum arabic, a mixture of albumin and maltodextrin (1:1), a mixture of albumin and gum arabic (1:1), a mixture of gum arabic and maltodextrin (1:1) and a mixture of albumin, maltodextrin and gum arabic (1:1:1). After mixing the wall and extract materials, the solution was vigorously stirred at 5000 rpm for 5 min (Ultra-Turrax IKA T18 basic, Wilmington, EUA) and this homogeneous solution was used for drying.

For spray-drying, a lab scale spray-dryer (Yamato Scientific Co. Ltd, ADL311S) with an inlet temperature of 160±1 °C and an outlet temperature of 60±1 °C was used. The feed flow rate used was 2 mL/min and air pressure of 0.1 MPa.

For freeze-drying, the mixed solutions were previously added in beakers at a height of 2 cm and frozen in a freezer at -20 °C/48 hours. Subsequently, the frozen samples were placed in a freeze-dryer (FreeZone 2.5, Labconco, USA) under the following conditions: condenser temperature of −50 °C and pressure of 0.010 mbar, for 72 hours, at room temperature (18 °C). The dried encapsulated product was collected, crushed using a pestle and stored in a sealed aluminum package maintained in a desiccator containing silica, until the analysis was carried out.

2.4 Properties of encapsulated powders

2.4.1 Moisture content and water activity (a_w)

The moisture content of the particles was determined gravimetrically by the drying method in an oven at 105 °C, until constant weight (AOAC, 2000).

To determine the a_w, an electronic hygrometer was used (Aqualab, 3-TE model, Decagon Devices, Inc., Pullman, WA, USA), at 25 °C.

2.4.2 Bulk density

The bulk density of the particles was determined based on the mass/volume ratio occupied by the dried powders. A known sample mass was inserted into a 10 mL graduated cylinder and the surface was gently smoothed by tapping. The volume occupied by the sample was then measured and used in the bulk density calculations (Chinta et al., 2009).

2.4.3 Solubility

The solubility assessment was performed according to the method proposed by Botrel, Borges, Fernandes, & Carmo (2014) with minor modifications. Briefly, 2.5 g of the powders were weighed and added to 20 mL of deionized water. The solution was stirred vigorously for 2 min and the homogenized material was placed in test tubes and centrifuged at 2260g for 15 min. The supernatant was collected and placed in petri dishes and placed in an oven at 110 °C for drying to constant weight. The results were expressed in %.

2.4.4 Hygroscopicity

Hygroscopicity was determined according to the method described by Sun-Waterhouse & Waterhouse (2015). Briefly, 1g of powder was placed in petri dishes and placed in a desiccator containing saturated NaCl solution (75% relative humidity) for a period of seven days at 20 °C. After this period, the samples were weighed again and the hygroscopicity was expressed as g of water absorbed per 100g of powder.

2.4.5 Color measurement

The colorimetric parameters of the particles were determined in a colorimeter (Konica Minolta, Spectrophotometer CM-5, Tokyo, Japan) using D65 illuminant and 10° observation angle. The equipment was previously calibrated. The samples were placed in petri dishes and placed above the light source to obtain the readings of the parameters L^* (lightness), a^* (redness/greenness), b^* (yellowness/blueness), C^* (chroma) and hue angle (°h).

2.4.6 Encapsulation efficiency

To determine the encapsulation efficiency (EE) of dried powders produced by spray-drying and freeze-drying methods, the methodology described by Dadi, Emire, Hagos, & Eun (2020) was used. Initially, extracts were prepared to quantify the content of total phenolic compounds and total antioxidant activity. For this, 100 mg of the dried powders were mixed with 1 mL of deionized water and the mixture was vortexed. Afterwards, 9 mL of ethanol were added and the mixture was again stirred for another 5 min, followed by filtration and storage of the extract. The extracts for determining these compounds on the surface of the microparticles were produced from 100 mg of dried powder added to 10 mL of ethanol. The mixture was vortexed for 10 seconds, followed by centrifugation and extract filtration. In both extracts, the EE was calculated according to Equation 1.

$$\text{EE}\ (\%) = \frac{\text{Total value} - \text{Surface value}}{\text{Total Value}} \times 100 \quad (1)$$

2.4.7 Total phenolic content (TPC)

The content of total phenolic compounds was determined according to Folin-Ciocalteu assay (Singleton & Rossi, 1965). For the determinations, 2.5 mL of the Folin-Ciocalteu reagent (10%) was added to 0.5 mL of the extract followed by the addition of 2 mL of sodium carbonate (7.5%). The mixture was vortexed and left to stand in the dark for 2 hours. After the reaction time, the absorbance reading of the samples was performed at 720 nm in a spectrophotometer (Biospectro, SP-220). A curve with known concentrations of gallic acid was used as a standard and the results were expressed as mg gallic acid equivalent per gram of powder dry matter (mg GAE/g).

2.4.8 Antioxidant activity (DPPH)

To determine the total antioxidant activity by DPPH assay, the methodology proposed by Rufino et al. (2010) was used. 0.1 mL of the extract was added to 3.9 mL of a DPPH (0.06 mM) methanolic solution. The mixture was vortexed and allowed to stand in a dark environment at room temperature for 1 hour. Subsequently, the reading of the absorbance at a wavelength of 515 nm was performed. The result was expressed as g of powder dry matter per g of DPPH (g powder/g DPPH).

2.4.9 Antioxidant activity (FRAP)

The FRAP assay was performed according to Rufino et al. (2010). 90 µL of extract, 270 µL of distilled water and 2.7 mL of FRAP reagent were mixed (TPTZ, $FeCl_3$ and acetate buffer), in this order. Subsequently, this mixture was vortexed and placed in a water bath (37 °C) for 30 min in a dark environment. After the reaction time, the absorbance reading of the samples at 595 nm was performed. A standard Fe(II) curve was used and the results were expressed as mM Fe_2SO_4 per gram of powder dry matter (mM Fe_2SO_4/g).

2.5 Statistical analysis

All analyzes were performed in triplicate and results are expressed as mean±standard deviation. Analysis of variance (ANOVA) was used to evaluate the results, followed by the Tukey test, at the level of $p<0.05$. In Principal Component Analysis (PCA), the data were organized in an a x b matrix (where a represents the number of samples and b the number of

variables) and the data were autoscaled. The software Statistica (Statsoft, Tulsa, USA) was used.

3 Results and discussion

3.1 Physicochemical properties of powders

The values determined for moisture, a_w, bulk density, solubility and hygroscopicity of the powders are shown in Table 1. It was found that these properties were significantly influenced by the drying method and wall material used.

Moisture is a key factor in establishing the shelf life of a dried product, since high moisture content can favor particle agglomeration processes and microorganism growth, resulting in physical, chemical changes and global food acceptance (Goyal et al., 2015). According to our results, the use of all wall materials associated to the microencapsulation process resulted in dried powders with low moisture content (less than 4%) for both drying methods (Table 1). The moisture content of spray-dried powders was between 3.37 and 3.93% and there was no significant difference ($p<0.05$) between treatments 1 to 7. Botrel, de Barros Fernandes, Borges, & Yoshida (2014) also found no significant difference in the moisture content of particles obtained by spray-drying using different wall materials. On the other hand, lower moisture content was obtained for the freeze-drying samples, with values between 1.05 and 1.96% and only treatment 12 had lower moisture compared to treatment 9 ($p>0.05$). The moisture values found are in agreement with those reported by Fang & Bhandari (2011) who evaluated bayberry drying by spray-drying, obtaining a dried product with 4.04% moisture and Sanchez, Baeza, Galmarini, Zamora, & Chirife (2013) who encapsulated red wine by freeze-drying finding a moisture value of 1.53%.

Regarding a_w values, it was observed that there was a difference ($p<0.05$) between the drying methods. Spray-drying produced particles with the highest a_w value, ranging between 0.22 and 0.28 (Table 1), with the lowest values found for treatments 1 and 5, which were statistically equal ($p>0.05$). Freeze-drying resulted in lower values for this parameter, with values between 0.15 and 0.20. Treatments 8, 12 and 14 resulted in the highest a_w values, being statistically equal to each other ($p>0.05$). Rezende, Nogueira, & Narain (2018) reported a_w values ranging from 0.07 to 0.26 for spray-drying and freeze-drying when using gum arabic and maltodextrin as wall materials. In addition, as in the present study, these authors also found higher a_w values in spray-dried particles.

Bulk density is a physical property of particles that can affect product stability and flowability (Goyal et al., 2015). The drying method used resulted in significant differences ($p<0.05$) in the bulk density values of the particles (Table 1). The spray-dried powder had higher bulk density values, between 0.28 and 0.37 g/mL. The highest values were found for treatments 5 and 7, which were statistically equal ($p>0.05$). These values are close to those reported by Tonon, Brabet, & Hubinger (2010) for spray-dried açaí juice using maltodextrin (0.39 g/cm^3) and gum arabic (0.37 g/cm^3). The bulk density values of the freeze-dried powder ranged from 0.21 to 0.24 g/mL. In this case, only treatment 11 had a higher value when compared to treatment 14. Dadi et al. (2020) also found higher bulk density for the dried product obtained by spray-drying. According to these authors, the irregular morphology resulting from freeze-drying can result in empty spaces among the particles, increasing their volume and consequently reducing the bulk density.

Table 1 – Physicochemical properties of the SCG extract encapsulated with albumin, maltodextrin and gum arabic by spray-drying and freeze-drying

Drying	Treatments		Moisture (%)	a_w	Bulk density (g/mL)	Solubility (%)	Hygroscopicity (%)
SD	1	A	3.69 ± 0.18^{Aa}	0.24 ± 0.00^{Ab}	0.29 ± 0.00^{Ac}	79.40 ± 1.66^{Ab}	13.27 ± 0.42^{Ba}
	2	M	3.38 ± 0.22^{Aa}	0.28 ± 0.01^{Aa}	0.34 ± 0.01^{Ab}	90.39 ± 0.46^{Aa}	12.08 ± 0.33^{Aab}
	3	GA	3.85 ± 0.23^{Aa}	0.26 ± 0.00^{Aa}	0.28 ± 0.00^{Ac}	82.31 ± 0.22^{Bb}	8.42 ± 0.20^{Bd}
	4	A+M	3.40 ± 0.29^{Aa}	0.27 ± 0.00^{Aa}	0.28 ± 0.01^{Ac}	80.04 ± 0.27^{Ab}	8.28 ± 0.11^{Bd}
	5	A+GA	3.37 ± 0.44^{Aa}	0.22 ± 0.00^{Ab}	0.37 ± 0.00^{Aa}	79.09 ± 1.30^{Ab}	11.41 ± 0.35^{Babc}
	6	GA+M	3.91 ± 0.23^{Aa}	0.27 ± 0.01^{Aa}	0.30 ± 0.01^{Ac}	83.44 ± 0.92^{Bb}	8.73 ± 0.41^{Bcd}
	7	A+M+GA	3.93 ± 0.06^{Aa}	0.27 ± 0.01^{Aa}	0.37 ± 0.00^{Aa}	82.03 ± 2.07^{Ab}	9.63 ± 0.82^{Bbcd}
FD	8	A	1.60 ± 0.01^{Bab}	0.20 ± 0.01^{Ba}	0.22 ± 0.01^{Bab}	80.27 ± 2.62^{Ac}	20.40 ± 0.01^{Aa}
	9	M	1.96 ± 0.08^{Ba}	0.16 ± 0.01^{Bc}	0.24 ± 0.01^{Bab}	90.49 ± 1.25^{Aa}	13.66 ± 0.34^{Ad}
	10	GA	1.85 ± 0.32^{Bab}	0.17 ± 0.01^{Bbc}	0.22 ± 0.01^{Bab}	85.74 ± 1.48^{Aab}	16.74 ± 1.48^{Abc}
	11	A+M	1.56 ± 0.09^{Bab}	0.16 ± 0.00^{Bbc}	0.24 ± 0.01^{Ba}	74.50 ± 2.85^{Bd}	15.17 ± 0.45^{Acd}
	12	A+GA	1.05 ± 0.02^{Bb}	0.19 ± 0.00^{Ba}	0.22 ± 0.00^{Bab}	70.60 ± 0.82^{Bd}	19.30 ± 1.96^{Aab}
	13	GA+M	1.19 ± 0.26^{Bab}	0.15 ± 0.01^{Bc}	0.24 ± 0.00^{Bab}	90.71 ± 0.34^{Aa}	16.63 ± 1.00^{Abc}
	14	A+M+GA	1.80 ± 0.12^{Bab}	0.18 ± 0.01^{Bab}	0.21 ± 0.01^{Bb}	83.83 ± 1.74^{Abc}	17.66 ± 0.84^{Aabc}

Values are expressed as mean±standard deviation. The same uppercase superscript letter indicates no significant difference between drying methods. The same lower case superscript letter indicates that there is no significant difference among the wall materials for each drying method ($p<0.05$). SD= Spray-drying, FD = Freeze-drying, A= albumin, M= maltodextrin, GA = Gum arabic.

As observed in Table 1, there was a significant difference ($p>0.05$) between the solubility values of the particles. In general, the particles showed good solubility and some treatments showed equal solubility values for both drying methods. Compared to freeze-drying, solubility for spray-dried powders was found to be lower when gum arabic and a gum arabic/maltodextrin mixture were used. On the other hand, the use of a mixture of albumin/maltodextrin and albumin/gum arabic resulted in lower solubility values for the freeze-dried product. The addition of albumin reduced the solubility of the freeze-dried product when compared to the use of pure maltodextrin and gum arabic. According to Cortés-Rojas, Souza, & Oliveira (2015) the solubility is strongly influenced by the particle size and also by the feed composition. Thus, the wall material used in drying can change the solubility of the particles. For spray-drying, it was observed that treatment 2 had the highest solubility. As for freeze-drying, treatments 9, 10 and 13 that contained maltodextrin and gum arabic had the highest solubilities, probably due to the high solubility of these wall materials.

The ability of a product to absorb water is known as hygroscopicity, which is a property that directly affects the stability of the product (Dadi et al., 2020). In general, all freeze-drying treatments resulted in more hygroscopic powders when compared to spray-drying, except for treatment 2 (pure maltodextrin) which did not differ from freeze-drying (Table 1). The difference in the hygroscopicity of the samples may be related to as weel, the molecular weight of the wall material used. Moreover, dried powders with lower moisture content can absorb more water, with hygroscopicity being inversely proportional to the moisture content of the sample (Akhavan Mahdavi, Jafari, Assadpoor, & Dehnad, 2016).

3.2 Color

The characteristic color of the products is directly linked to the ingredients present during their preparation (Goyal et al., 2015). The powders obtained for all treatments can be seen in Fig. 1.

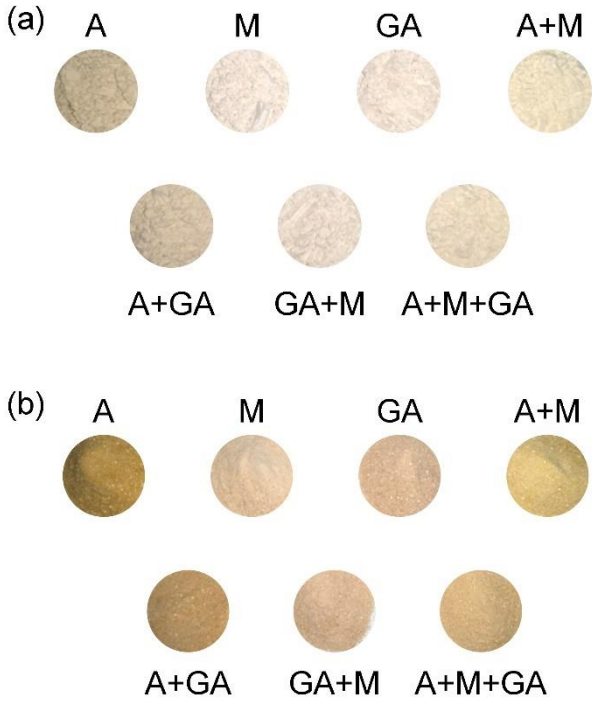

Figure 1 – Product obtained after spray-drying (a) and freeze-drying (b) using different wall materials.

As observed in Table 2, the lowest values of the L^* parameter were obtained for the freeze-dried extract. It can also be observed that the use of pure maltodextrin (treatments 2 and 9) resulted in lighter samples (higher L^* value) for both drying methods. Kuhn, de Azevedo, & Noreña (2020) also observed that spray-dried samples had higher L^* when compared to freeze-drying treatments, this effect being attributed to color changes resulting from the high temperature of the spray-dryer. For the parameter a^* it was observed that the samples dried by freeze-drying were all located in the first quadrant ($+a^*$) demonstrating a red color trend. On the other hand, samples that contained albumin and were spray-dried (treatments 1, 4, 5 and 7) had negative a^* values, indicating a trend of green coloration. Regardless of the drying method, all samples had a positive b^* value, indicating a yellow color. The highest values of the b^* parameter was obtained for the freeze-dried samples, highlighting treatment 11. This treatment also had the highest value of the C^* parameter. Parameter C^* indicates color purity (Rezende et al., 2018). The °h values were between 85.99-98.81 and 78.19-89.04 for spray- and freeze-dried samples, respectively, confirming the trend of the samples towards a yellow hue (90°).

Table 2 – Color parameters (L^*, a^*, b^*, C^* and $^\circ h$) of the SCG extract encapsulated with albumin, maltodextrin and gum arabic by spray-drying and freeze-drying

Drying		Treatments	L^*	a^*	b^*	C^*	$^\circ h$
SD	1	A	85.05 ± 0.07^{Ag}	-2.05 ± 0.07^{Be}	23.12 ± 0.01^{Ba}	23.22 ± 0.01^{Ba}	95.18 ± 0.01^{Ac}
	2	M	92.62 ± 0.01^{Aa}	0.36 ± 0.01^{Bc}	9.36 ± 0.01^{Bg}	9.36 ± 0.01^{Bg}	87.77 ± 0.01^{Ae}
	3	GA	88.84 ± 0.02^{Af}	0.77 ± 0.01^{Ba}	11.18 ± 0.01^{Be}	11.21 ± 0.01^{Be}	85.99 ± 0.02^{Ag}
	4	A+M	89.82 ± 0.03^{Ac}	-3.28 ± 0.01^{Bg}	21.21 ± 0.01^{Bb}	21.48 ± 0.01^{Bb}	98.81 ± 0.01^{Aa}
	5	A+GA	89.26 ± 0.01^{Ae}	-1.06 ± 0.01^{Bd}	15.52 ± 0.01^{Bd}	15.54 ± 0.01^{Bd}	93.93 ± 0.01^{Ad}
	6	GA+M	90.65 ± 0.01^{Ab}	0.60 ± 0.01^{Bb}	10.97 ± 0.01^{Bf}	10.98 ± 0.01^{Bf}	86.78 ± 0.01^{Af}
	7	A+M+GA	89.36 ± 0.01^{Ad}	-2.48 ± 0.01^{Bf}	17.97 ± 0.00^{Bc}	18.14 ± 0.01^{Bc}	97.86 ± 0.01^{Ab}
FD	8	A	72.83 ± 0.03^{Bc}	1.81 ± 0.01^{Ae}	28.45 ± 0.01^{Ab}	28.51 ± 0.01^{Ab}	86.32 ± 0.03^{Bb}
	9	M	79.81 ± 0.11^{Ba}	3.49 ± 0.05^{Ab}	19.38 ± 0.03^{Ae}	19.72 ± 0.01^{Ae}	79.72 ± 0.01^{Be}
	10	GA	71.51 ± 0.11^{Bd}	3.48 ± 0.01^{Ab}	16.60 ± 0.08^{Ag}	17.01 ± 0.01^{Ag}	78.19 ± 0.01^{Bf}
	11	A+M	74.96 ± 0.04^{Bb}	0.47 ± 0.05^{Af}	29.03 ± 0.04^{Aa}	29.07 ± 0.01^{Aa}	89.04 ± 0.03^{Ba}
	12	A+GA	71.19 ± 0.08^{Bd}	2.60 ± 0.01^{Ac}	21.85 ± 0.04^{Ad}	21.98 ± 0.01^{Ad}	83.18 ± 0.01^{Bd}
	13	GA+M	74.64 ± 0.20^{Bb}	3.92 ± 0.03^{Aa}	18.89 ± 0.02^{Af}	19.33 ± 0.04^{Af}	78.22 ± 0.01^{Bf}
	14	A+M+GA	72.78 ± 0.28^{Bc}	1.99 ± 0.01^{Ad}	22.51 ± 0.02^{Ac}	22.62 ± 0.01^{Ac}	84.91 ± 0.01^{Bc}

Values are expressed as mean±standard deviation. The same uppercase superscript letter indicates no significant difference between drying methods. The same lower case superscript letter indicates that there is no significant difference among the wall materials for each drying method ($p<0.05$). SD= Spray-drying, FD = Freeze-drying, A= albumin, M= maltodextrin, GA = Gum arabic.

3.3 Bioactive compounds and encapsulation efficiency

Table 3 shows the contents of total phenolic compounds (TPC) and total antioxidant activity (DPPH and FRAP), as well as the encapsulation efficiency for the dried product obtained by spray-drying and freeze-drying from different wall materials. It was verified that the wall material and the drying method significantly affected the evaluated responses.

The TPC value in the dried particles ranged from 3.09 to 6.83 mg EAG/$g_{d.b.}$, with no significant difference ($p>0.05$) being observed between the TPC content of the dried product obtained by both drying methods, except for treatment 8, in which the freeze-dried powder resulted in a lower TPC value compared to treatment 1. Among the wall materials tested, GA stood out for having the highest TPC for spray-drying and freeze-drying.

The analysis of the antioxidant activity (AA) was performed according to the DPPH and FRAP methods, showing values from 2034.55 a 7664.86 g $powder_{d.b.}$/g DPPH and 0.015 to 0.076 mM $Fe_2SO_4/g_{d.b.}$, respectively. The DPPH assay indicated that the highest value was obtained for treatment 1, which reflects a lower antioxidant activity of the sample. With the exception of treatment 9, all samples obtained by freeze-drying exhibited greater antioxidant activity when compared to spray-drying (Table 3). Among the wall materials, it was observed that the highest antioxidant activity was conferred by the use of gum arabic and by the mixture of gum arabic and maltodextrin. On the other hand, the worst results were obtained by using pure albumin for both drying methods. Akhavan Mahdavi et al. (2016) also concluded that the mixture of gum arabic and maltodextrin promoted better preservation of anthocyanin contents in the dried product. According to Tonon et al. (2010), the high solubility of maltodextrin and gum arabic may favor the microencapsulation process of bioactive compounds and antioxidants, when compared to less soluble materials. Regarding the FRAP assay, no significant differences ($p>0.05$) were observed between the antioxidant activity of spray-dried and freeze-dried samples. However, similarly to the DPPH method, it was found that the highest antioxidant activities were obtained with the use of gum arabic, for both drying methods. It is noteworthy that some differences between the results obtained by different methods of determination of antioxidant activity may occur and that they are due to the fact that each method has a specific specificity and site of action (Rezende et al., 2018).

Table 3 – Content of total phenolic compounds, total antioxidant activity and percentage of encapsulated compounds of the SCG extract encapsulated with albumin, maltodextrin and gum arabic by spray-drying and freeze-drying

Drying		Treatments	TPC (mg GAE/$g_{d.b.}$)	AA DPPH (g $powder_{d.b.}$/g DPPH)	AA FRAP (mM $Fe_2SO_4/g_{d.b.}$)	EE (TPC, %)	EE (DPPH, %)	EE (FRAP, %)
SD	1	A	3.85 ± 0.14^{Ad}	7664.86 ± 49.30^{Aa}	0.015 ± 0.001^{Ae}	52.00 ± 1.95^{Bd}	59.08 ± 0.93^{Ad}	59.66 ± 1.30^{Af}
	2	M	5.46 ± 0.10^{Ab}	2531.51 ± 44.56^{Bd}	0.038 ± 0.001^{Abc}	73.15 ± 1.36^{Ab}	65.29 ± 1.47^{Ac}	72.99 ± 0.67^{Abc}
	3	GA	6.83 ± 0.08^{Aa}	2245.60 ± 64.49^{Ae}	0.068 ± 0.002^{Aa}	83.43 ± 0.97^{Aa}	82.15 ± 1.10^{Aa}	79.80 ± 1.11^{Aa}
	4	A+M	4.41 ± 0.09^{Acd}	5740.07 ± 56.67^{Ab}	0.020 ± 0.000^{Ad}	61.24 ± 1.21^{Ac}	60.65 ± 0.14^{Ad}	63.78 ± 0.37^{Ae}
	5	A+GA	4.44 ± 0.10^{Acd}	5736.73 ± 51.94^{Ab}	0.020 ± 0.000^{Ad}	67.52 ± 1.57^{Abc}	61.79 ± 0.79^{Acd}	68.48 ± 0.28^{Ad}
	6	GA+M	4.99 ± 0.07^{Abc}	2231.17 ± 44.08^{Ae}	0.052 ± 0.000^{Ab}	76.04 ± 0.34^{Aab}	74.89 ± 0.36^{Ab}	76.49 ± 0.24^{Aab}
	7	A+M+GA	4.66 ± 0.04^{Ac}	4515.01 ± 21.23^{Ac}	0.023 ± 0.001^{Acd}	70.76 ± 0.55^{Ab}	63.57 ± 0.63^{Acd}	70.50 ± 1.74^{Acd}
FD	8	A	3.09 ± 0.07^{Be}	5418.01 ± 25.47^{Ba}	0.017 ± 0.002^{Ad}	64.84 ± 1.50^{Ac}	54.17 ± 1.44^{Be}	55.53 ± 0.24^{Bd}
	9	M	4.98 ± 0.01^{Abc}	3574.72 ± 21.61^{Ac}	0.028 ± 0.001^{Ac}	70.31 ± 0.08^{Abc}	69.24 ± 1.41^{Abc}	72.21 ± 0.98^{Ab}
	10	GA	6.29 ± 0.04^{Aa}	2055.57 ± 7.88^{Bd}	0.076 ± 0.013^{Aa}	79.54 ± 0.55^{Aa}	76.99 ± 0.90^{Ba}	76.05 ± 0.48^{Aa}
	11	A+M	4.30 ± 0.13^{Acd}	5314.61 ± 20.66^{Ba}	0.019 ± 0.002^{Ac}	69.72 ± 2.06^{Abc}	61.65 ± 2.26^{Ad}	63.09 ± 0.54^{Ac}
	12	A+GA	4.31 ± 0.15^{Acd}	4235.66 ± 50.43^{Bb}	0.024 ± 0.001^{Ac}	65.04 ± 2.34^{Ac}	61.70 ± 0.49^{Ad}	66.67 ± 0.72^{Ac}
	13	GA+M	5.06 ± 0.20^{Ab}	2034.55 ± 48.86^{Bd}	0.050 ± 0.006^{Ab}	75.15 ± 3.04^{Aab}	71.93 ± 0.80^{Ab}	73.86 ± 1.00^{Aab}
	14	A+M+GA	4.84 ± 0.58^{Abd}	3567.55 ± 24.82^{Bc}	0.021 ± 0.002^{Ac}	68.74 ± 8.26^{Abc}	66.05 ± 1.27^{Acd}	65.56 ± 1.36^{Bc}

Values are expressed as mean±standard deviation. The same uppercase superscript letter indicates no significant difference between drying methods. The same lower case superscript letter indicates that there is no significant difference among the wall materials for each drying method ($p<0.05$). TPC= Total phenolic compounds; AA= Antioxidant activity, SD= Spray-drying, FD = Freeze-drying, A= albumin, M= maltodextrin, GA = Gum arabic.

Encapsulation efficiency (EE) values ranged from 52.00 to 83.43%, 54.17 to 82.15% and 54.53 to 80.81% for TPC, antioxidant activity by DPPH and antioxidant activity by FRAP, respectively. In general, for both drying methods, it was found that the highest EE values for TPC and AA were obtained using pure gum arabic or combined with maltodextrin. On the other hand, the use of pure albumin or combined with other wall materials reduced the encapsulation efficiency of these compounds. When evaluating the EE of phenolic compounds and flavonoids obtained from SCG, Ballesteros et al. (2017) concluded that the use of pure maltodextrin, together with the freeze-drying technique, provided the best efficiency results. These authors also found that the mixture of gum arabic and maltodextrin had a deleterious effect on the antioxidant activity of the dried product, which did not occur in the present study. The EE values of the present study are within the range of values found by other authors when using spray-drying and freeze-drying. Rezende et al. (2018) reported values of 17.25-69.75% for encapsulation efficiency of acerola bioactive compounds, using gum arabic and maltodextrin as wall materials. Saikia, Mahnot, & Mahanta (2015) found EE values of phenolic compounds from Averrhoa carambola pomace ranging from 66.99-97.22% using maltodextrin as a wall material. Ballesteros et al. (2017) report EE values between 62 and 73% for SCG phenolic compounds and flavonoids using maltodextrin.

Some factors related to drying processes can result in loss of bioactive compounds and impair encapsulation efficiency. Among these factors the concentration of the wall material, cracks on the microparticle surface due to the high temperatures used in the spray-dryer and the formation of pores for the sublimation of water during freeze-drying can be cited (Rezende et al., 2018).

3.4 Principal Component Analysis (PCA)

PCA analysis was applied for exploratory data analysis, seeking to verify differences between samples. The score and loading graphs for the first two main components (PC1 and PC2) are shown in Fig. 2a and Fig. 2b, respectively. As noted, PC1 explained 43.79% and PC2 explained 39.26% of the total data variance. Thus, 83% of the total variance was explained by these two main components. The score plot (Fig. 2a) indicated a clear separation between the two sample groups. The spray-drying samples had a tendency to be located on the positive side of PC1, while the samples obtained by freeze-drying were distributed almost entirely on the negative side of this PC, demonstrating that there are differences in the composition of the powders obtained by these processes. An evaluation of the loadings was also performed and the variables related to discrimination among treatments can be seen in Fig. 2b. Bulk density,

solubility, moisture, a_w, $^{\circ}h$, L^*, FRAP and TPC were all allocated on the positive side of PC1. The highest values of these parameters were found for samples obtained by spray-drying. Treatments 2, 3 and 6 stood out for the highest values of TPC and FRAP. On the other hand, treatment 1 differed from the others by the high DPPH value. The parameters hygroscopicity, C^*, b^* and a^* were distributed on the negative side of PC1, with the highest values of these variables attributed to freeze-dried powders.

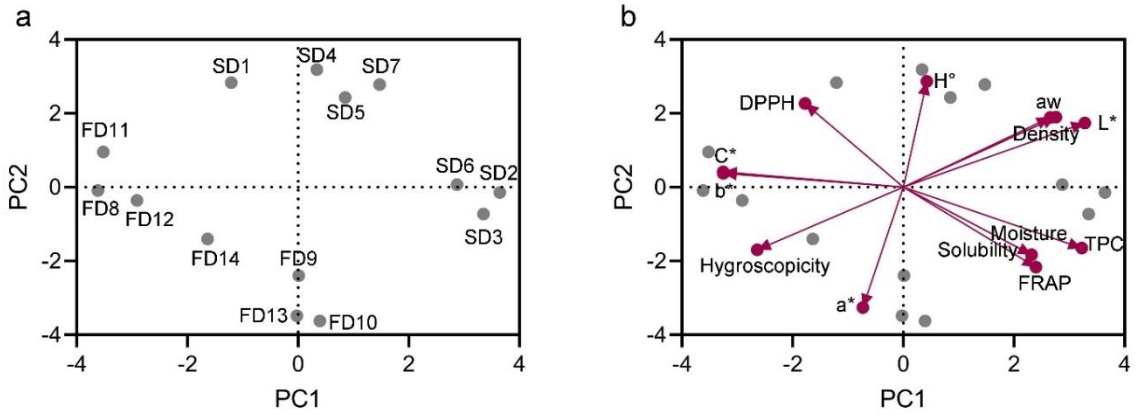

Figure 2 – PCA score plot and (a) and scores and loadings graph (b) generated with data of the moisture, a_w, bulk density, solubility, hygroscopicity, color parameters, TPC, DPPH and FRAP.

4 Conclusions

This study demonstrated that SCG can be used as a source of easily extractable bioactive compounds and that these compounds can be encapsulated in order to ensure their greater preservation for use in the food industry. Both drying techniques used resulted in a dried product with low moisture values, a_w, good rehydration properties and high content of bioactive compounds. In addition, the type of drying and wall material used resulted in a dried product with distinct properties, which allows its application in foods that are also different. Gum arabic and the mixture of gum arabic and maltodextrin showed better performance in maintaining the content of phenolic compounds and antioxidants of SCG extracts. In all tests, the encapsulation efficiency was above 50%, reaching a maximum value of 83.43%.

Declaration of interest

The authors declare that there are no conflicts of interest.

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