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Impregnation of Açaí Residue Extracts in Silica-Aerogel

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ABSTRACT. Açaí (Euterpe Oleracea mart.) is a berry found in Amazon Rainforest, with a high content of polyphenols and flavonoids. This work studied the formulation of bioactive compounds extracted from E. Oleracea fruit, by impregnation in silica-aerogel. Three fruit fractions were studied: pulp, seeds and slurry, and two extracts were obtained from each fraction: an oil fraction obtained by Soxhlet extraction, and a polyphenolic-rich extract obtained by Pressurized Microwave Assisted Extraction. With pulp oil, impregnation yields of 58.6% were obtained by air drying, with surface area of 0.7687 m^2/g,. while with supercritical drying method, the impregnation yield decreased to 15.3%, with surface area of 823.4 m^2/g. This indicates a loss of oil by extraction during drying. With pulp extract, the best result was obtained using indirect wet impregnation and supercritical drying, with 16.4% of impregnation. By release assay, contents of 2.276 $mg/g_{(aerogel)}$ of polyphenols and 0.197 $mg/g_{(aerogel)}$ of anthocyanins were identified.

Key-words. Euterpe Oleracea Mart., Silica Aerogel, supercritical CO_2 dryer, microwave extraction, formulation of natural product.

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1. INTRODUCTION

Açaí is a black-purple berry obtained from *Euterpe Oleracea mart.* palm, typically found in Amazon Rainforest and strongly present in the diet of brazilians, especially in north and northeast regions. The name comes from the Tupian word *yasa'I* – fruit that cries – in a Brazilian Portuguese adaptation [1]. The interest in E. Oleracea fruit is related with its high content of anthocyanins, polyphenols, fatty acids and other bioactive compounds present in the fruit. Polyphenols and anthocyanins are secondary metabolites of plants with remarkable properties as antioxidant and/or natural dye activities. Some of these properties are their antioxidant, anti-inflammatory and antimicrobial functions [2].

The fruit provides health benefits, but it also causes environmental problems [3]. The açaí pulp consumption just in Pará, a Brazilian state, produces around 180 thousand ton of litter daily [4]. During the pulping process, pulp is separated from seeds (first fraction of residue), in a second step pulp is clarified by a filter where slurry (second fraction of residue), and finally it is characterized to certify that it is safe for consumption. When pulp batch is considered inappropriate for consumption, it is destined to residue in its totality (third fraction of residue).

According to literature, in the pulp of Euterpe Oleracea mart. berry some important compounds are present, such as anthocyanins (cyanidin 3-glucoside; 2, pelargonidin 3-glucoside) [5,6], flavonoids (orientin, homoorientin, vitexin, luteolin, chrysoeriol, quercetin, dihydrokaempferol, isovitexin, velutin, catequin, epicatechin, p-cumárico) [7,8], prothocyanidins, and some other interesting products (vanilic, ferulic, and gallic acid).[9] These compounds, present in natural pulp, are expected in different concentration in *açaí* slurry. In the seed prothocyanidins were basically the only

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polyphenol compounds identified, that have a high activity as anti-oxidants [10]. Moreover, each fraction has an oil content that can promote some impedance during the extraction of phenolic compounds if it is not previously removed. These oils also have commercial interest because of its high content of unsaturated fatty acids (oleic acid (60%), palmitic acid (22%), linoleic acid (12%), palmitoleic acid (6%)) and essential oil [11–13]. The oil also presents some phenol acids, such as vanillin acid, in the highest proportion. The main property of this pulp oil is the anti-inflammatory[11] and antidiarrheal effects[14]. However, polyphenols and anthocyanins are susceptible to early degradation under environmental condition [15–17]. An alternative to protect these compounds is to recover it in a polymeric matrix. The impregnation of bioactive substance into a polymeric matrix has been applied to protect and preserve it from oxygen free radical, UV-light exposition, and, on purpose to perform drugs controlled release or/and the improvement of its bioavailability [18].

On this purpose, aerogels has been shown as appropriate matrix to protect and release bioactive compounds [19–22]. The impregnation of active compounds is easily achieved because of the open porosity of aerogels and their large specific surface area, that allows to get a high load content during the impregnation of those substances [23–25]. Aerogels are obtained from wet-gels dried through a controlled drying process. Supercritical drying is a useful process for drying aerogels and avoiding the change of its porosity structure caused by the collapse of pores that can be caused by ambient drying. Moreover, silica aerogels are very versatile and have been studied and applied in many different fields such as aeronautics, biomedicine, construction, agriculture, among many others [26–30]. The effort on the studies of silica aerogel became from the interest on its intrinsic properties such as low thermic conductivity, high specific surface area, non-toxic and non-flammable character, and the facility on removing it from a medium [31].

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In cosmetic industry, a similar material as silica microspheres has been applied as a versatile ingredient due to its capacity to acts as anti-abrasive agent, anti-caking agent, opacifying agent, agent, free-flowing, gelling and thickening agent [32–34]. Because of these properties, silica contributes to the homogenous distribution of pigments in color cosmetics, even preventing the agglomeration of ingredients in the formulation, and fomenting the proper distribution and the long-lasting effect. Silica has been applied in many types of products, especially on skin care, oral care, hair care and dyes, make-up (powder, lipstick, lip gloss, among many others) and in antiperspirants [35–40]. Moreover, it is frequently used as an absorbent agent, due to its ability to absorb sweat, fats, and oil [36].

In addition, silica is used in the food industry as a food additive to increase the volume of a product without affecting its nutritional composition and as an antifoaming agent [34,41], and in pharmaceutical industry as drug delivery system and carrier [24,42]

On this way, the goal of this work is the use aerogel material for the protection of bioactive extracts obtained from E. Oleracea (açaí) residue, also to make possible the bioactive controlled release, and its application in a product.

Wet-impregnation method (directly and indirectly) was applied to introduce the bioactive compounds on the silica aerogel pores. Supercritical CO_2 drying was chosen as a dry method to keep-hold the mesoporous structure present on the wet-gel[18]. Conventional soxhlet was chosen as conventional technique for the oil extraction. Pressurized Microwave-Assisted Extraction (PMAE) was applied as intensification pre-treatment on the polyphenol extraction.

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2. Material and Methods

2.1. Preparation of aerogel monoliths

Silica gels were prepared using tetramethyl ortosilicate (TMOS) as precursor. TMOS and methanol were mixed in a safe recipient where ammonium hydroxide-water was added droplet by droplet. Then, 1 mL of solution was transferred to cylindrical moulds and covered with a film for the proper gelification. The process of gelification is fast, and in a few minutes alcohol-gels are ready to start the ageing process, for which they are kept submerged in solvent during 7 days in order to strengthen its structure, washing them with new solvent every 24 hours in order to remove any trace of unreacted water. (*molar ratio:* 1 TMOS : 3 MeOH : 4 H_2O : $5x10^{-3}$ NH_4OH) [43].

2.2. Açaí residue extract

2.2.1. Preparation of matrix for extraction

Matrix preparation is specific for each fraction of residue: first fraction (seeds) has an average diameter size of 1.2 cm, and it had to be milled to a size of 5mm (knife-mill Retsch SM100) and then dried in an oven during 48 h at 45ºC. Second and third fractions (slurry and pulp, respectively) were frozen at -80ºC and then lyophilized (Telstar LyoQuest) during 72 h.

2.2.2. Oil extraction

A known mass of each fraction was placed in an extraction thimble and placed at a Soxhlet apparatus, wherein hexane was applied as solvent to remove the oil content in

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each fraction, for 8 h, with 5 cycles of Soxhlet reflux per hour. After extraction, hexane was evaporated under vacuum. Known initial and final mass used in the process make possible to determine the percentage of oil content in each fraction.

2.2.3. Polyphenol extraction

Maceration and Pressurized Microwave Assisted Extraction (PMAE) were applied as extraction technique and as pre-treatment for extraction, respectively. Ethanol/Water (1:1) was used as solvent for the extraction, and citric acid as pH regulator. Extracts were characterized in terms of extraction yield, total polyphenols content (TPC), total Anthocyanins contents (TAC), and antioxidant activity by oxygen radical absorbance capacity (ORAC). HPLC was used to determine the extract composition. Hydro-ethanol extracts were purified using Dioxan HB20 activated by methanol (1% HCl). Hexane extracts were purified using a vacuum drier.

2.3. Wet impregnation

2.3.1. Indirect wet impregnation

After ageing process, alcohol-gels were transferred to different recipients containing the impregnation solutions of each extract fraction, keeping them there for 72 hours, during which the solution was replaced every 24h. Moreover, ethanol and methanol were tested as impregnation solvent, and oil extract from the pulp by hexane was compared with an oil sample extracted from the pulp by supercritical carbon dioxide.

2.3.2. Direct wet impregnation

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Extract obtained was added directly during sol-gel preparation, adding it to the solvent employed during the process.

2.4. CO_2 supercritical drying

The drying process was described in detail in previous works [45, 46]. Briefly, drying process took place in a closed circuit, including a buffer of CO_2, the chamber where monoliths were charged and a pump for CO_2 recycling. Initially, the chamber is isolated from the rest of system and then charged with pure solvent, keeping monoliths submerged in the solvent to avoid damages in their structure. In a second step, the buffer is loaded with CO_2, that is compressed at 120 bar and heated at 42ºC. When these conditions are achieved, the chamber is opened and CO_2 starts to flow through the system thanks to a pump. Supercritical CO_2 recycling is maintained during 1h, thus reaching saturation of CO_2 by the solvent. Then, the chamber is again isolated, CO_2 from the buffer is released in order to introduce fresh CO_2 into the system. Operating in this way, 3 cycles were performed in order to obtain completely dried silica aerogels. With this procedure, at the same time that silica are dried, as the impregnated compound is not soluble in CO_2, it is precipitated in the pores of the aerogel by an antisolvent process[44].

2.5. Aerogels characterization

2.5.1. Physicochemical Analysis

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Aerogels were subjected to milling and degassing at vacuum. The specific surface area and average pore diameter were then determined by adsorption of N_2 at -196ºC, and calculated by BET (Brunauer, Emmett, Teller) method. Average pore volume was characterized by desorption curve of N_2 (BJH method). Chemical bond-structures were analysed by FTIR (Bruker Platino-ATR). Thermo-stability and impregnation yield were determined by Thermogravimetric (TGA) analysis.

2.5.2. Analytic active substances

The total content of polyphenols in the impregnation solutions were quantified in order to obtain the amount of free active substances. It was characterized in terms of total polyphenols content (TPC) and total Anthocyanins contents (TAC). HPLC is used to determine the extract composition.

2.5.2.1. Total polyphenols content (TPC)

For TPC analysis a capped test tube was used, in which 40 µL of the extract, 3 mL of ultrapure water and 200 µL of folin-ciocalteau reagent were added. It was also necessary to prepare a control sample using 40 µL of extraction solvent, 3 mL of ultrapure water and 200 µL of folin-ciocalteau reagent. Tubes were closed and homogenized at 40°C for 5 minutes. After this period, 600 µL of Na_2CO_3 (20% v/v) solution was added, tubes were vigorously stirred, and kept in hot-water-bath at 40°C for 30 minutes. At the end the samples were analyzed by spectrophotometry (λ= 765nm). The TPC concentration is given in Gallic acid equivalent per 100 g of dry material.

2.5.2.2. Total Anthocyanins contents (TAC)

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The TAC analyzes were performed with the aid of a spectrophotometer. Samples were diluted (1:4) in a potassium hydroxide buffer (0.025M KCl) at pH 1.0 and buffered with acetate trihydrate buffer ($CH_3CO_2Na.3H_2O$ 0.4M) at pH 4.5. Samples were diluted in both buffers solution, at pH 1.0 and 4.5, and each solution was measured at 520 nm and 700 nm. The concentration of anthocyanins in each sample is given in g of cyanidin equivalent per 100 g of dry material.

2.6. Release

The impregnated aerogels were subjected to a release test in order to quantify the amount of impregnated polyphenols. In addition, the anthocyanins were quantified for the aerogels impregnated with the extract of the pulp. The release test consisted of subjecting a known mass of impregnated aerogel to the microwave assisted extraction process at 1.5 bar using a known volume of solvent (Ethanol / Water 50% v / v acidified, pH = 3), for 20 seconds. Subsequently, the calculation of the total polyphenol content (TPC) expressed in mg $GAe/g_{aerogel}$ and total anthocyanins in mg $AC/g_{aerogel}$ is performed, using the Folin-Ciocalteu method (section 2.5.2.1) and the pH-differential method (section 2.5.2.2), respectively.

3. Results and Discussion

3.1. Aerogels

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According to IUPAC distribution, the adsorption-desorption N_2 curve of the blank material (plotted on the Fig. 1) performs a hysteresis type IV [45] and isotherm H_1, typical found for materials with very narrow pores, open or closed cylinders, and uniform size and distribution. The pure silica aerogel is a mesoporous material according to its pores size distribution. Moreover, this distribution is homogenous presenting an average value of 11 nm. The supplied pore data refers to the adsorption isotherm to avoid the pore blocking effect that occurred during the N_2 desorption due to the capillary condensation that blocks the pores and interferes with the correct determination of the texture parameters [46].

(Fig. 1)

However, the type of impregnation (direct or indirect) and the drying method can interfere in the structure, as well as in its specific surface area, average pore volume, and, average pore diameter, as discussed in the following sections.

3.2. Wet impregnation: preliminary assay

Initially, wet impregnation was performed by indirect impregnation process and with low content of oil obtained from the three different residual fractions, in order to determine which was the best solvent for impregnation: methanol or ethanol. Table 1 show a small decrease of specific surface area after impregnation of the aerogels, taking pure silica as reference, that might indicate that oil content has filled some pores. Also,

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taking this value as evaluation parameter, it is possible to conclude that ethanol works better as solvent for impregnation than methanol. Probably, this is related with low solubility of this oil in methanol by visual inspection of the aerogels, it was not observed any substantial change in colour or opacity.

(Table 1)

The oil obtained from slurry and from seed were impregnated following the best result obtained from pulp-oil. As it can be seen in Table 1, pore volume showed a lower reduction when it was impregnated with these oils than when it was impregnated with pulp oil, suggesting a lower impregnation yield, which may be related to differences in the composition of the three oil fractions.

The impregnated oil percentage in each fraction of residue was determined by soxhlet extraction, using the initial and final mass employed in the soxhlet process to calculate it. Results show that aerogels impregnated with seeds oil have 7.5±0.1%, with slurry oil have 6.8±0.9% and with dry-pulp have 42.0±1.8% of oil content.

3.2. Wet impregnation:

The type of impregnation (direct or indirect) and the drying method can interfere in the structure, as well as in its specific surface area, average pore volume, and, average pore diameter. These data were recovered and summarized in table 2.

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(Table 2)

3.2.1. Wet impregnation: oil extract

The first fact to point out is the differences in the size of monoliths dried by air and by supercritical. Monoliths formed were split into two groups to evaluate the effects of drying method under aerogel structure and its loaded compounds. Air drying induced pore collapsing and as result monoliths are much smaller than molds (Fig. 3(A-II). In the other hand, monoliths dried by supercritical kept the shape and size of the mold (Fig. 3(A-I).

The visual analysis is the first parameter to determine how successful the impregnation was. Taking the color intensity as a parameter is possible to determine that indirect impregnation (Fig. 3(C-I & C-II) worked better than direct impregnation (Fig. 2(B-I & B-II).

In addition, the pore diameter of those gels obtained from SC CO_2 drying (table 2) and direct impregnation method (13.4 nm) are bigger than that of gels impregnated with the indirect method (10.9 nm). This is because the direct addition of extract in aerogels increased the gelification time interfering in the pore formation. Moreover, it was observed that using this method, the monoliths slowly expelled the oil, previous added, during the maturation processes.

Related to the efficiency of the drying process, an important difference was observed on the color intensity between those samples obtained from SC CO_2 drying (Fig. 3(B-I & C-I)) and by natural air drying (Fig. 3(B-II & C-II)). A possible reason for this fact is the partial extraction of oil by SC CO_2, a disadvantage of SC CO_2 drying process that is further discussed in section 3.4.

(Fig. 2)

3.2.2. Wet impregnation: polyphenolic extract

Anthocyanins present in the pulp polyphenolic extract are responsible for the purple color observed in the monoliths impregnated with this extract. Thus, the color can also work as a parameter to infer if the impregnation happened or not. In this way, it is possible to see in Fig. 3B the difference produced by indirect impregnation, taking as comparative Fig. 3A, a blank. Results presented on Table 2 also show the difference on their pore size, the difference between pores size and pore volume on blank material, 11.0 nm and 3.1cm^3/g, and on impregnated silica aerogel, 9.1 nm and 1.8 cm^3/g. These results indicate that the polyphenols are really occupying these pores or bigger pours was occupied first (low impedance on this occupation).

The color was more intense on those gels obtained from direct impregnation (Fig. 3(C-II)). On this specific case, the strongest color is related with the impossibility of aging process deriving from the direct impregnation did not allow the monoliths gelification, even after several hours. Reason for why this batch was just air-drying and had no maturation time. As results, this batch changed its type of porosity, as indicated by results in Table 2, becoming a microporous material with pore size of 0.3nm, and volume of pore of 0.04cm3/g. The shape obtained is also unusual, due to the air-drying happening inside the mold, and thus, the contraction of monoliths resulting from pore collapsing happened only on horizontal direction. The gelification problem is also related with the change of reagents ratio.

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(Fig. 3)

It is also possible to highlight the structural modification promoted by the impregnation and the dry process on the silica aerogel as mesoporous material. The shape of N_2 adsorption isotherms is affected by size and geometry of porous material. In this way it is possible to classify the material according its isotherm. The impregnated material, obtained by SC CO_2 Drying shows the same type of isotherm that was observed in pure silica, H_1. However its curve is more pronounced, denoting a smaller pores size. This result is related with pores occupation by polyphenols.

(Fig. 4)

3.3. Thermo-stability of materials

The thermostability of pure silica aerogel (support material) and the impregnated material can be analyzed by the temperature of onset in a thermogravimetric analysis. The polyphenolic extracts of seed and slurry can be considered stable until 140ºC and 170 ºC, respectively. Pulp extract has no thermo-stability observed. This is because cyanidin, the main anthocyanin present in Açaí extract had been reported as thermostable only below 30ºC[17]. The pulp oil shows thermostability until 315ºC, that may be caused by the extraction process, as when the oil is recovered in rotavapor it loses its volatile fraction.

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The same result was observed with the oil obtained from the other fractions. The fixed oil mass is represented by 42% in dry mass of pulp fraction, 3.5% of seed fraction, and 1.2% of slurry fraction.

The silica support is thermostable until 380ºC, and it is basically inert until this temperature, There is a significant mass loss at 560ºC, around 10%, and a secondary loss at 760ºC with a small mass loss of 4%. Thus, the total mass loss is14%.

In addition, the pulp phenolic extract has it thermostability improved when it was impregnated in the support, achieving a maximum thermostability of 270°C when indirect impregnation method was applied. A similar improvement was observed when seed polyphenolic extract was impregnated at the same condition, 275°C. In opposition, under the same conditions, the thermo-stability of oil extract impregnated decreased to 235°

3.4. Impregnation yield and release assay

3.4.1. Oil Extract

Total mass impregnated can be given by the difference between the residual mass in an impregnated sample and the residual mass in the blank. Following this, the total impregnated mass is given in percentage in table 3.

(Table 3)

According the results in table 3, direct impregnation, which had slow gelification, had smallest impregnation yield when compared to indirect impregnation. During the release assay those aerogels impregnated by direct method had a low release concentration of

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polyphenols even having a highest concentration of oil impregnated. It is attributed to low gelification of monoliths. Another fact that also contributed here was that during the maturation step oil was slowly expelled out of the pores

With the indirect impregnation method, an increase the oil concentration during the impregnation produced a higher impregnated yield. This is related to the high capacity of silica to absorb oil. In addition, samples dried by air and by supercritical fluids show a high difference in impregnation yield. This may be caused by the type of deposition of oil extract inside the pores. The polyphenols in the oil extract have hydroxyl groups which can perform bonds with the Si-O structure of the aerogel, while fatty acids are usually linked in a triglycerides groups, which difficult performing a strong bond. Despite of the loss produced by drying process, removing part of content impregnated, the release assay shown that the amount of polyphenols released was proportional to the initial concentration and it was not affected by the SC drying.

According to TGA analysis, the maximum yield of impregnation, 58.6%, was attained when indirect impregnation and air drying were applied. In the same batch, those monoliths dried by SC drying had an impregnation yield around 15%. On the other hand, the air drying method affect the porous structure, resulting in the pores collapsing.

3.4.2. Polyphenol extract

According to TGA data presented in Table 4, the maximum impregnation yield was 16.4% attained with indirect impregnation and SC drying method. Increasing the concentration of initial solution did not affect the impregnation yield but decreased the impediment of bioactive substances in occupying the pores resulting in a color change,

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as observed in Fig. 5. Moreover, the release assay can confirm it by the increase of polyphenols and anthocyanins released.

Monoliths obtained with direct impregnation could not gelify properly and then were dried just by air and with no maturation time. This process change the structure of material converting it in a microporous material. The impregnation yield was not affected by this event but it did affect the capacity of aerogels release the impregnated content.

The impregnation of mesoporous silica aerogel allowed to increase the thermostability of extract from 30ºC to 270ºC, with indirect method. A similar thermostability was observed with both drying processes. Though it was observed, in the same batch, a slight tendency of higher values in those samples produced by supercritical fluid drying, with a variation of ±10ºC in onset temperature. However, impregnation method was significant. Those samples produced with direct method present substantially smaller thermostability than those impregnated with indirect method: 270ºC and 195ºC, respectively. This is related to water present in the sol-gel process. In this process it is first produced a hydro-gel, and during the maturation time water –OH groups are replaced by the alcohol –OH groups, becoming alcohol-gel. Herein these samples, directly impregnated, had not gelified properly, making impossible the maturation step and the properly attain of alcohol-gel. It may interfere in the linking between Si-O and polyphenol, reducing the thermo-stability.

(Table 4)

(Fig. 5)

3.5. FTIR Analysis

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In the analysis of pure extract, it is observed a large band between 3200-3400 cm^{-1} related to stretching of –OH polymeric chains. At 1650 cm^{-1} there is a peak related to C=C from the aromatic chain. Moreover, there was observed a weak signal at 1440cm^{-1}, attributed to the deformation of C-H, and at the range of 1000-1100 cm^{-1}, corresponding to C-O bonding stress from phenol[47,48]. These bands are characteristic of polyphenols from extract. In addition some authors had related them with anthocyanins [49,50]. Moreover two more weak peaks were observed: a stretching vibration related to the linear $C-H_2$ at 2896 cm^{-1} and at 2976 cm^{-1}.

Pure Silica Aerogel (Fig. 6- III) has a weak band at 3500-3400 cm^{-1}, that is related to stretching of –OH that can be related to residual water or alcohol. In the low part of spectra it is possible to observe some peaks at 1084 cm^{-1}, 812 cm^{-1} and 458 cm^{-1} related to Si-O-Si stretching, bending and vibration, respectively [51]. Finally, at 971 cm^{-1} there is a stretching band vibration of Si-O in terminal groups[52].

All those peaks present in the FTIR of pure extract were identified in the impregnated material in a different intensity, excluding those under 1300 cm^{-1}, covered by silica signal. This is another evidence of impregnation happen and compounds present in the extract were succesfully incorporated into aerogels pores.

(Fig. 6)

In the FTIR spectra of oil extract (Fig. 7-IV), it is observed a small peak between 3200-3400 cm^{-1} related to stretching of –OH groups present in polyphenols. Its intensity is smaller than was observed for polyphenolic extract because it is not the main

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component in oil. On graphic 6-II, it overlaps with a peak near to 3470 cm^{-1} produced by excess of water in this sample, consequence of the drying method employed.

Moreover it was possible to observe in the extract a peak nearly to 3000 cm^{-1} related to alkene groups stretching vibration (C=C-H) attributed to unsaturated fatty acids. In this same area there is a strong peak at 2935 cm^{-1} related to –CH vibration in alkane. At 1750 cm^{-1} there is an intense peak related to the carbonyl starching of phenolic acids. At 1448 cm^{-1}, there is a peak related to starching of -CH=CH- present in aromatic chain. At 1162 cm^{-1} a peak related to C-O vibration and at 728 cm^{-1} a peak attributed to C-H deformation, both related to carboxylic acid [53]. All these peaks confirm the presence of saturated and unsaturated fatty acids. Also it can be highlightedthe presence of phenolic acid such as vanillic acid [11]. In addition, there is no difference between IR spectra resulting from pulp oil and seed oil analysis, they present the same main composition.

The peak attributed to stretching of C=O, present in phenolic acids, is present in both impregnated material (Fig. 7(II& III)), pointing the impregnation happened. At the spectra of sample air-drying (Fig. 7-II) we can observe that fatty acids were also successfully impregnated at silica pores (peak at 1750 cm^{-1}). In another hand, peaks related to fatty acids, such as 3000 cm^{-1} (C=O), 2935 cm^{-1} (O-H), 1448 cm^{-1} (-CH=CH-), and, 1370 cm^{-1} (C-H), are not present in the impregnated material after sc-drying; confirming it was lost during the SC-drying. At Graphic 6 silica band hides those peaks low to 1300 cm^{-1}, referent to phenolic acids.

(Fig. 7)

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3.6. Seed extracts indirectly impregnated

Seed oil and polyphenolic extract were impregnated following the best impregnation methods observed for pulp extracts.

Seed phenolic extract also presents a color prevenient from tannins, that gave a light pink tone to aerogels impregnated. In the same way of other extracts, the color can be pointed as an indicative of a successful impregnation. The maximal yield was achieved by indirect impregnation method and SC-drying, 29.3 wt%, applying a solution of 825.2 mg Age/L. In the release assay was possible to release 5.639 mg GAe/g $_{aerogel}$.

Oil extracted from seed has a low content of phenolic compounds responsible for pigments. For this reason, impregnated gels do not show an intense color. The maximum yield obtained was 29.3 wt% by indirect method, while by SC-drying the yield was 6 wt%.

Functional groups observed in seed extracts are equivalent to those observed in pulp extracts, producing similar FTIR spectra. Both seed extracts were successfully impregnated in gels, as expected from the results of pulp impregnation. Seed oil was removed during the SC-drying process.

4. Conclusions

In this work the impregnation of extracts obtained from the residue of Açaí (E. Oleracea mart.) has been investigated using different extraction fractions. The study was

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performed employing oil obtained by hexane solvent extraction and polyphenolic extract obtained by PMAE and purified by resin to eliminate the water of extraction and some eventual sugar present on it. Direct and indirect wet impregnation methods were tested. Each batch was divided in two parts to study the influence of the drying process (supercritical drying and air-drying) under monoliths structure and its loaded material.

Supercritical drying was successfully applied for the impregnation of polyphenolic extract maintaining the pore size of the aerogels, and eliminating residual solvent. When air drying was applied, the mesoporous structure of the aerogels was lost, obtaining a microporous material. However the supercritical drying process promoted the loss of loaded oil content because of its affinity by some compounds of oil content such as fatty acids, although polyphenols present in the oil were not lost.

TGA analysis was used to evaluate the impregnation yield (wt%). For oil extract the maximum wt% was 58.6% when indirect impregnation and air drying were applied and it decreased to 15% using SC drying, which indicates the extraction of components during SC drying. The maximum impregnation yield for polyphenolic extract was achieved with indirect impregnation and SC drying method, 16.4%; increasing the concentration of extract did not imply in a higher impregnation yield. Although the total impregnation yield was not affected by the increasing of concentration of oil during the impregnation, the Total phenolic content (TPC) and total anthocyanins content (TAC) analysis demonstrated higher concentrations of these compounds increased when the oil concentration was increased, thus indicating a selective impregnation of these active compounds that also results in a more intense purple color of impregnated aerogels.

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The release assay results corroborate that the best method of impregnation is the indirect, because a high amount of active substance was impregnated using this method even when part of oil loaded was loss during drying. For polyphenolic extract, to increase the concentration of extract indicate a lower impediment of the polyphenols and anthocyanins in occupying the pores. These results also confirm the low affinity of polyphenols for CO_2-SC

From the FTIR analyses, it is appreciated that the active substances from the extracts were impregnated inside the aerogels. Furthermore, it can be deduced that the water contained in the alcohol-gels is not effectively removed by the wet-direct impregnation method.

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References

[1] Açaí in Dicionário infopédia da Língua Portuguesa, (2018).

[2] O. V. Zillich, U. Schweiggert-Weisz, P. Eisner, M. Kerscher, Polyphenols as active ingredients for cosmetic products, 2015. doi:10.1111/ics.12218.

[3] D. de L. Gonçalves, D. do S.B. Brasil, Problemas ambientais e sustentabilidade nas várzeas da Amazônia Tocantina: um estudo no Projeto de Assentamento Agroextrativista São João Batista II, Abaetetuba, Estado do Pará, Brasil, Revista Pan-Amazônica Saúde. 7 (2016) 89–99. doi:10.5123/S2176-62232016000400011.

https://doi.org/10.1016/j.supflu.2018.12.004

[4] V.S. Bezerra, O. Freitas-Silva, L.F. Damasceno, Açaí: produção de frutos, mercado e consumo, Resumos. (2016).

[5] D. Del Pozo-Insfran, C.H. Brenes, S.T. Talcott, Phytochemical Composition and Pigment Stability of Açai (Euterpe oleracea Mart.), Journal of Agricultural and Food Chemistry 52 (2004) 1539–1545. doi:10.1021/jf035189n.

[6] A.G. Schauss, X. Wu, R.L. Prior, B. Ou, D. Patel, D. Huang, J.P. Kababick, Phytochemical and nutrient composition of the freeze-dried amazonian palm berry, Euterpe oleraceae Mart. (Acai), Journal of Agricultural and Food Chemistry. 54 (2006) 8598–8603. doi:10.1021/jf060976g.

[7] J. Kang, Z. Li, T. Wu, G.S. Jensen, A.G. Schauss, X. Wu, Anti-oxidant capacities of flavonoid compounds isolated from acai pulp (Euterpe oleracea Mart.), Food Chemistry. 122 (2010) 610–617. doi:10.1016/j.foodchem.2010.03.020.

[8] J. Kang, C. Xie, Z. Li, S. Nagarajan, A.G. Schauss, T. Wu, X. Wu, Flavonoids from acai (Euterpe oleracea Mart.) pulp and their antioxidant and anti-inflammatory activities, Food Chemistry. 128 (2011) 152–157. doi:10.1016/j.foodchem.2011.03.011.

[9] L.A. Pacheco, Chemical characterization, bioactive properties, and pigment stability of polyphenolics in acai (Euterpe Oleracea Mart.), Vasa. (2009).

[10] L. Barros, R.C. Calhelha, M.J.R.P. Queiroz, C. Santos-Buelga, E.A. Santos, W.C.B. Regis, I.C.F.R. Ferreira, The powerful in vitro bioactivity of Euterpe oleracea Mart. seeds and related phenolic compounds, Industrial Crops and Products. (2015). doi:10.1016/j.indcrop.2015.05.086.

[11] H.A.S. Favacho, Caracterização Fitoquímica E Avaliação Da Atividade Anti-Inflamatória E Antinociceptiva Do Óleo Fixo De Euterpe Oleracea Mart., (2009) 79.

[12] C. Lubrano, J.R. Robin, A. Khaiat, Composition en acides gras, stérols et tocophérols d'huiles de pulpe de fruits de six espèces de palmiers de Guyane, Oléagineux. (1994).

[13] H. ROGEZ, Açaí: Preparo, Composição e Melhoramento da Conservação., Belém, Brazil: EDUFPA. (2000) 313.

[14] M.J. Plotkin, M.J. Balick, Medicinal uses of South American palms, Journal of Ethnopharmacology. (1984). doi:10.1016/0378-8741(84)90001-1.

[15] K. Sólyom, R. Solá, M.J. Cocero, R.B. Mato, Thermal degradation of grape marc polyphenols, Food Chemistry. (2014). doi:10.1016/j.foodchem.2014.03.021.

[16] J. Alean, F. Chejne, B. Rojano, Degradation of polyphenols during the cocoa drying process, Journal of Food Engineering. (2016). doi:10.1016/j.jfoodeng.2016.05.026.

[17] D. Wang, Y. Ma, C. Zhang, X. Zhao, Thermal characterization of the anthocyanins from black soybean (Glycine max L.) exposed to thermogravimetry, LWT - Journal of Food Science and Technology. (2014). doi:10.1016/j.lwt.2013.10.007.

[18] A.N. Mustapa, A. Martin, L.M. Sanz-Moral, M. Rueda, M.J. Cocero, Impregnation

https://doi.org/10.1016/j.supflu.2018.12.004

of medicinal plant phytochemical compounds into silica and alginate aerogels, The Journal of Supercritical Fluids. (2016). doi:10.1016/j.supflu.2016.06.002.

[19] C. Barbé, J. Bartlett, L. Kong, K. Finnie, H.Q. Lin, M. Larkin, S. Calleja, A. Bush, G. Calleja, Silica particles: A novel drug-delivery system, Advanced Materials. (2004). doi:10.1002/adma.200400771.

[20] I.I. Slowing, J.L. Vivero-Escoto, C.-W. Wu, V.S.-Y. Lin, Mesoporous silica nanoparticles as controlled release drug delivery and gene transfection carriers, Advanced Drug Delivery Reviews. Rev. (2008). doi:http://dx.doi.org/10.1016/j.addr.2008.03.012.

[21] I.I. Slowing, B.G. Trewyn, S. Giri, V.S.-Y. Lin, Mesoporous Silica Nanoparticles for Drug Delivery and Biosensing Applications, Advanced Functional Materials. (2007). doi:10.1002/adfm.200601191.

[22] P. Yang, S. Gai, J. Lin, Functionalized mesoporous silica materials for controlled drug delivery, Chemical Society Reviews. (2012). doi:10.1039/c2cs15308d.

[23] M. Alnaief, S. Antonyuk, C.M. Hentzschel, C.S. Leopold, S. Heinrich, I. Smirnova, A novel process for coating of silica aerogel microspheres for controlled drug release applications, Microporous Mesoporous Mater. 160 (2012) 167–173. doi:10.1016/j.micromeso.2012.02.009.

[24] I. Smirnova, S. Suttiruengwong, W. Arlt, Feasibility study of hydrophilic and hydrophobic silica aerogels as drug delivery systems, Journal of Non-Crystalline Solids. 350 (2004) 54–60. doi:10.1016/j.jnoncrysol.2004.06.031.

[25] C.A. García-González, M. Alnaief, I. Smirnova, Polysaccharide-based aerogels—Promising biodegradable carriers for drug delivery systems, Carbohydrate Polymers. 86 (2011) 1425–1438. doi:10.1016/j.carbpol.2011.06.066.

[26] J. Ge, M. Li, Q. Zhang, C.Z. Yang, P.H. Wooley, X. Chen, S.Y. Yang, Silica aerogel improves the biocompatibility in a poly-ε-caprolactone composite used as a tissue engineering scaffold, International Journal of Polymer Science. (2013). doi:10.1155/2013/402859.

[27] I. Lázár, H.F. Bereczki, S. Mano, L. Daróczi, G. Deak, I. Fábián, Z. Csernátony, Synthesis and study of new functionalized silica aerogel poly(methyl methacrylate) composites for biomedical use, Polymer Composites. (2015). doi:10.1002/pc.22949.

[28] P.J. Reséndiz-Hernández, D.A.C. Hernández, J.M. Nonell, J.C.E. Bocardod, Bioactive and biocompatible silica/pseudowollastonite aerogels, Science and Technology of Advanced Materials. 96 (2014) 21–26. doi:10.4028/www.scientific.net/AST.96.21.

[29] E. Cuce, P.M. Cuce, C.J. Wood, S.B. Riffat, Toward aerogel based thermal superinsulation in buildings: A comprehensive review, Renewable and Sustainable Energy Reviews. (2014). doi:10.1016/j.rser.2014.03.017.

[30] AERSUS, La tecnología del futuro para el aislamiento térmico en el espacio, CORDIS Eur. Serv. Inf. Comunitario Sobre Investig. y Desarro. (2016).

https://doi.org/10.1016/j.supflu.2018.12.004

[31] J.L. Gurav, I.-K. Jung, H.-H. Park, E.S. Kang, D.Y. Nadargi, Silica Aerogel: Synthesis and Applications, Journal of Nanomaterials. 2010 (2010) 1–11. doi:10.1155/2010/409310.

[32] Evonik, Silica - Technical DataSheet, Univers. Sel. Source Cosmet. Ingredients. (2017). https://cosmetics.specialchem.com/selectors?q=silica (accessed July 14, 2018).

[33] PPG ind., Silica Products, (n.d.).

[34] M.G. and S.D. Md Zulphakar Ali, A Review - Effects of Food additives and Preservatives on Man, World Journal of Pharmaceutical Sciences. 4 (2018) 89–103.

[35] L. Fageon, R. Lorant, Cosmetic composition comprising a superabsorbent polymer and silica aerogel particles, WO2013087926A1, 2011.

[36] S. Khenniche, G. Plos, Cosmetic composition of hydrophobic silica aerogel particles and a polymer comprising a sugar unit, US20150190319A1, 2012.

[37] P. Pierre, E. Lheureux, Matt-effect composition comprising hydrophobic aerogel particles and silica particles, WO2013190104A2, 2012.

[38] C. Bebot, V. Masse, A.-S. Gras, Cosmetic composition comprising an aequeous dispersion of hydrophobic silica aerogel particles and a particular alcohol, US20150320663A1, 2012.

[39] R. Lorant, A subject matter of the present invention is a composition for topical application comprising hydrophobic silica aerogel particles and at least one emulsifying silicone elastomer. Another subject matter of the invention is a method for the cosmetic treatm, US9445985B2, 2012.

[40] S.R. Robertson, R.J. Edmundson, Novel mascara composition having very small particles, US5053221A, 1989.

[41] L.A. Rauner, Method for reducing or preventing foam in liquid mediums, 1966.

[42] U.S. Government, Code of federal regulations: Food and Drugs, the office of the federal register national archives and records administration, Washington, 1998.

[43] L.M. Sanz-Moral, M. Rueda, A. Nieto, Z. Novak, Ž. Knez, Á. Martín, Gradual hydrophobic surface functionalization of dry silica aerogels by reaction with silane precursors dissolved in supercritical carbon dioxide, Journal of Supercritical Fluids (2013). doi:10.1016/j.supflu.2013.09.010.

[44] M. Rueda, L.M. Sanz-Moral, A. Nieto-Márquez, P. Longone, F. Mattea, Á. Martín, Production of silica aerogel microparticles loaded with ammonia borane by batch and semicontinuous supercritical drying techniques, Journal of Supercritical Fluids (2014). doi:10.1016/j.supflu.2014.06.012.

[45] T. Sing , K.S.W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure and Applied Chemistry. 57 (1985) 603–619.

https://doi.org/10.1016/j.supflu.2018.12.004

[46] S.P. Rigby, R.S. Fletcher, Experimental Evidence for Pore Blocking as the Mechanism for Nitrogen Sorption Hysteresis in a Mesoporous Material, Journal of Physical Chemistry B. (2004). doi:10.1021/jp031253s.

[47] F. R. Callejas, Tablas de Espectroscopía Infrarroja, Dep. Física y Química, UNAM. (n.d.).

[48] C. A. M. GARCÍA, Identificacíon de flavonoides con actividades antioxidantes presentes en Alchornea coelophylla (Euphorbiaceae), Univ. Tecnológica Pereira, Fac. Tecnol. Esc. QUÍMICA. (2014).

[49] J.K. Ahmed, Effect of Chlorophyll and Anthocyanin on the Secondary Bonds of Poly Vinyl Chloride (PVC), International Journal of Materials Science and Applications. 4 (2015) 21. doi:10.11648/j.ijmsa.s.2015040201.15.

[50] Â.A. Teixeira-Neto, A.L. Shiguihara, C.M.S. Izumi, M.A. Bizeto, F. Leroux, M.L.A. Temperini, V.R.L. Constantino, A hybrid material assembled by anthocyanins from aaí fruit intercalated between niobium lamellar oxide, Dalt. Trans. (2009) 4136–4145. doi:10.1039/b820610d.

[51] Y. Özbakir, Z. Ulker, C. Erkey, Monolithic composites of silica aerogel with poly(methyl vinyl ether) and the effect of polymer on supercritical drying, Journal of Supercritical Fluids. (2014). doi:10.1016/j.supflu.2015.04.001.

[52] S. Aspromonte, A. Sastre, A. Boix, M.J. Cocero, E. Alonso, Optimization and modelling of the supercritical CO2 deposition of CoxOy nanoparticles in MCM41, Journal of Supercritical Fluids. (2016). doi:10.1016/j.supflu.2015.11.026.

[53] R.J. Meilunas, J.G. Bentsen, A. Steinberg, Analysis of Aged Paint Binders by FTIR Spectroscopy, Studies in Conservation. (1990). doi:10.2307/1506280.

https://doi.org/10.1016/j.supflu.2018.12.004

Figure captions

Fig. 1 - Isothermal of pure silica and pore volume distribution

Fig. 2 – Dry monoliths of silica gel impregnated with oil extract from pulp: (A) blank, (B) direct process, and, (C) indirect process; dried by: (I) supercritical CO_2, and (II) air.

Fig. 3 – Dry monoliths of silica gel impregnated by extract from pulp by ethanol/water: (A) blank, (B) direct process, and, (C) indirect process; dried by: (I) supercritical CO_2, and (II) air.

Fig. 4 - Isothermal and pore volume distribution of silica aerogel impregnated with polyphenolic pulp dried by (I) supercritical CO_2, and (II) air.

Fig. 5 – Dry monoliths of silica gel impregnated by extract from pulp by ethanol/water: (I) Low concentration, and (II) high concentration.

Fig. 6 – FTIR spectra of (I) pulp extract, (II) silica aerogel impregnated by pulp extract, and (III) pure silica aerogel.

Fig. 7 - FTIR spectra of (I) pure silica aerogel, (II) silica aerogel impregnated by Pulp Oil, dried by air, (III) silica aerogel impregnated by Pulp Oil, dried by SC and (IV) pure silica aerogel.

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Tables and table captions

Table 1 – Textural properties of aerogels.

Extract	Fraction	Solvent	Specific Surface area (m2/g)	Average pore volume (cm3/g)	Average pore diameter (nm)
Blank	-	-	910	3.0	11.0
Oil	Pulp	Methanol	817	2.7	10.9
Oil	Slurry	Ethanol	835	2.8	11.2
Oil	Seed	Ethanol	859	2.9	11.0

Table 2 – Textural properties of aerogels impregnated by extracts obtained from the different fractions of Açaí residue.

Extract	Fraction	Impregnation process	Dry Process	Specific Surface area (m2/g)	Average pore volume (cm3/g)	Average pore diameter (nm)
Blank		-	SC	910	3.04	11.0
Blank		-	Air			
Oil	Pulp	Direct	SC	892	2.98	13.4
Oil	Pulp	Indirect	SC	848	2.89	10.9
Oil	Pulp	Indirect	SC	823	2.78	11.0
Oil	Seed	Indirect	SC	847	2.54	12.4
Polyphenolic	Pulp	Direct	SC	-	-	-
Polyphenolic	Pulp	Direct	Air	595	0.04	0.3
Polyphenolic	Pulp	Indirect	SC	856	1.80	9.1
Polyphenolic	Pulp	Indirect	air	830	0.26	3.6
Polyphenolic	Pulp	Indirect	SC	873	1.60	8.2
Polyphenolic	Seed	Indirect	SC	739	2.43	10.0

Direct= wet impregnation by Direct method; Indirect = wet impregnation by Indirect method.

Table 3 –Impregnation yield and total polyphenol content released.

Extract impregnated	Impregnation method	Dry process	Wt%	Polyphenols release (mg GAe/$g_{aerogel}$)
Pulp Oil*	Direct	SC	9.1	0.229
		Air	13.5	
Pulp Oil**	Indirect	SC	12.9	0.120
		Air	37.5	
Pulp Oil***	indirect	SC	15.3	0.317
		Air	58.6	0.191

3.7g/L,7.0 g/L,***700g/L*
(GAe = Gallic Acid equivalent)

Table 4 – Impregnation yield of polyphenolic extract and total polyphenol and anthocyanin content released.

Impregnation method	Dry process	Wt %	Initial concentration		Released concentration	
			Polyphenols (mg GAe/L)	Anthocyanins (mg AC/L)	Polyphenols (mg GAe/$g_{Aerogel}$)	Anthocyanins (mg AC/ $g_{Aerogel}$)
direct	*Air*	*11.0*	-	-	*0.708*	*0.034*
Indirect	*SC*	*16.4*	*527.4*	*24.3*	*1.391*	*0.042*
Indirect	*SC*	*16.4*	*1547.8*	*72.1*	*2.276*	*0.197*

SC= Supercritical; GAe = Gallic Acid equivalent; AC=Anthocyanin Content