Revista
Coleta Científica
ISSN: 2763-6496

COLETA SCIENTIFIC JOURNAL

Year IV, Vol. IV, n.8, Jul.-Dec ., 2020

ISSN: 2763-6496

DOI: https://doi.org/10.5281/zenodo.4716820

Submission date: 04/07/2020. Acceptance date: 12/20/2020.

THERMOGRAVIMETRIC ANALYSIS OF PEQUI OIL MICROPARTICLES (*CARYOCAR CORIACEUM* WITTM.) IN A POLYMERIC MATRIX OF ALGINATE AND CHITOSAN[1]

ANÁLISE TERMOGRAVIMÉTRICA DE MICROPARTÍCULAS DE ÓLEO DE PEQUI (CARYOCAR CORIACEUM WITTM.) EM MATRIZ POLIMÉRICA DE ALGINATO E QUITOSANA

Rachel Menezes Castelo
Orcid: https://orcid.org/0000-0002-4868-4371
Lattes: http://lattes.cnpq.br/5540142750028014
State University of Ceará, Fortaleza, Brazil
E-mail: rachel.menezes@aluno.uece.br

Luana Carvalho da Silva
Orcid: https://orcid.org/0000-0003-2921-8719
Lattes: http://lattes.cnpq.br/8459288295039709
State University of Ceará, Fortaleza, Brazil
E-mail: lu_luanacarvalho@hotmail.com

Joana de Barros Alexandre
Orcid: https://orcid.org/0000-0003-1059-3914
Lattes: http://lattes.cnpq.br/5267136809442425
State University of Ceará, Fortaleza, Brazil
E-mail: joaninha.alexandre10@gmail.com

Gabrielle Albuquerque Freire
Orcid: https://orcid.org/0000-0002-7730-0795
Lattes: http://lattes.cnpq.br/0459732020275664
State University of Ceará, Fortaleza, Brazil
E-mail: gabi.a.freire@hotmail.com

Tiago Linhares Cruz Tabosa Barroso
Orcid: https://orcid.org/0000-0002-0133-2969
Lattes: http://lattes.cnpq.br/9071332119203661
Federal University of Ceará, Fortaleza, Brazil
E-mail: tiagohogas@gmail.com

Roselayne Ferro Furtado
Orcid: https://orcid.org/0000-0003-4616-7888
Lattes: http://lattes.cnpq.br/4463527486987067
Embrapa Tropical Agroindustry, Fortaleza, Brazil
E-mail: roselayne.furtado@embrapa.br

[1]Article from the Annals of the I Symposium on Environment and Energy (I SiMAE) – Fortaleza, CE

Revista
Coleta Científica
ISSN: 2763-6496

COLETA SCIENTIFIC JOURNAL

Year IV, Vol. IV, n.8, Jul.-Dec ., 2020

ISSN: 2763-6496

DOI: https://doi.org/10.5281/zenodo.4716820

Submission date: 04/07/2020. Acceptance date: 12/20/2020.

ABSTRACT
Pequi oil has high level of antioxidant substances, phenolic compounds, vitamin A and E, substances that are sensitive to the presence of light and oxygen. In order to provide greater stability to these compounds, microencapsulation techniques have been applied. Microparticles have different characteristics depending on the matrix, the microencapsulation technique and the drying method used. Thermal stability of the resulting microparticles is always important for industrial applications. The objective of this work was to perform thermogravimetric analysis (TGA) of pequi oil microparticles (OP) with chitosan (QT) / alginate (AG) and alginate matrixes submitted to oven drying and freeze drying. The percentage weight loss was calculated over time. The QT/ AG/OP microcapsules showed a higher temperature and enthalpy of degradation than AG/OP, thus the electrolytic complexation of QT/AG resulted in better thermal stability. Regardless of the drying method applied, the QT/ AG/OP particles showed the first degradation peak at 375 ° C, thus this matrix was suitable for oil protection in terms of thermal resistance.

KEYWORDS: Encapsulation. Ionic Gelation. Thermal degradation.

RESUMO
Óleo de pequi apresenta em sua constituição altos teores de substâncias antioxidantes, compostos fenólicos, vitamina A e E, substâncias essas sensíveis a presença de luz e oxigênio. A fim de proporcionar maior estabilidade a esses compostos, as técnicas de microencapsulação vêm sendo aplicadas. Micropartículas apresentam diferentes características a depender da matriz, da técnica de microencapsulação e do método de secagem utilizados. Estabilidade térmica das micropartículas resultantes é sempre importante para aplicações a nível industrial. O objetivo desse trabalho foi realizar análise termogravimétrica (TGA) de micropartículas de óleo de pequi (OP) com matrizes de quitosana (QT)/ alginato (AG) e de alginato submetidas as secagens em estufa e por liofilização. A perda de massa percentual foi calculada em relação ao tempo. As microcápsulas de QT/AG/OP apresentaram maior temperatura e entalpia de degradação do que AG/OP, podendo inferir assim que a complexação eletrolítica de QT/AG resultou em melhor estabilidade térmica. Independentemente do método de secagem aplicado, as partículas de QT/AG/OP apresentaram o primeiro pico de degradação em 375 °C, sendo esta matriz de polissacarídeo adequada para a proteção do óleo em termos de resistência térmica.

PALAVRAS-CHAVE: *Encapsulamento. Gelificação iônica. Degradação Térmica.*

INTRODUCTION

The pequi tree (*Caryocar coriaceum* Wittm) is a tree species native to the Brazilian Cerrado belonging to the Caryocaraceae family (ASCARI; TAKAHASHI; BOAVENTURA, 2013). The species is considered of high economic importance, since there are several ways of using it, serving the food, medicinal and cosmetic sectors

Revista
Coleta Científica
ISSN: 2763-6496

COLETA SCIENTIFIC JOURNAL

Year IV, Vol. IV, n.8, Jul.-Dec ., 2020

ISSN: 2763-6496

DOI: https://doi.org/10.5281/zenodo.4716820

Submission date: 04/07/2020. Acceptance date: 12/20/2020.

(EMERENCIANDO, 2017). The pequi pulp oil consists mainly of palmitic (35.17%) and oleic (55.87%) fatty acids, with a total of 37.97% saturated and 61.35% unsaturated, with 0.68 % not identified (DE LIMA *et al* ., 2007). These characteristics related to unsaturated fatty acids are very important, since the consumption of unsaturated fatty acids has been reported to be beneficial to health (ASCHERIO *et al* ., 1996). Pequi oil due to its chemical composition has gained prominence in scientific research, and encapsulation may favor the preservation of the characteristics of the bioactive compounds present for a longer time.

Ionic gelling is a microencapsulation method that has the advantage of employing mild conditions, since it does not use high temperatures, vigorous agitation or organic solvents, being suitable for the encapsulation of substances that would degrade under such conditions (COLAK *et al* ., 2016). Sodium alginate is a polysaccharide extracted from brown algae or bacteria widely used in ionic gelation studies. It is composed of residues of β -D -mannuronic acid (M) joined by type bonds (1→4) and residues of its epimer, α-L- guluronic acid (G), in various proportions. These residues are arranged in the form of blocks of mannuronic (M) or guluronic (G) acids, linked so that the sequence of these residues in the molecule is alternated (HELGERUD *et al* ., 2012). Chitosan is an amino polysaccharide, derived from the deacetylation process of chitin (DAMIAN *et al* ., 2005) .

polyelectrolytic complex between chitosan and alginate, allows that several properties of both polymers are maintained, such compounds present even greater stability to variations in pH and greater efficiency in the controlled release of active principles (YAN *et al* ., 2000). Chitosan is used to reinforce the microparticle in order to favor the encapsulation of the active agent (RIBEIRO et *al* ., 2005) and prevent the rapid erosion of the alginate gel (TØNNESEN AND KARLSEN, 2002). Another important factor is that alginate has a tendency to acquire pores in its structure, thus, the formation of a chitosan membrane on the surface of the microparticle tends to decrease the rate of release of the substance present in its interior (BHATTARAI *et al* ., 2011).

Several drying methods can be used in order to favor the storage of microparticles obtained by ionic gelation . Drying is the process in which a heat source is applied under controlled conditions to remove volatile substance (not exclusively water) present in the material using the evaporation process, producing solid products (MONTEIRO; AZEREDO, 2012). The main objective for drying a food or product is to extend the shelf life and protection, so the absence of water in the material inhibits microbial growth and enzymatic activity.

Thermogravimetric analysis (TGA) is used to investigate processes related to thermal stability and decomposition, dehydration and oxidation, measuring the mass variations of a sample as a function of temperature and time during heating (TENGKU-ROZAINA, BIRCH, 2019; XIAO *et al* ., 2014), being a way to assess the thermal resistance of encapsulated particles. The objective of this study was to perform a thermogravimetric analysis of pequi oil microparticles, produced by ionic gelation , in alginate polymer matrix and electrolytic complexation with chitosan, subjected to two drying methods: oven drying and lyophilization.

Revista
Coleta Científica
ISSN: 2763-6496

COLETA SCIENTIFIC JOURNAL

Year IV, Vol. IV, n.8, Jul.-Dec ., 2020

ISSN: 2763-6496

DOI: https://doi.org/10.5281/zenodo.4716820

Submission date: 04/07/2020. Acceptance date: 12/20/2020.

MATERIALS AND METHODS

Material

In this work, the following material was used: medium viscosity sodium alginate salt from Dinâmica®, with a purity of 90%, low molecular weight chitosan (75-85% deacetylation) from Sigma- Aldrich , calcium chloride of Dynamics, Span 80 and Tween 80 Surfactants (Chemical Dynamics).

The pequi (*C. coriaceum*) was purchased directly from producers in Barbalha-CE, and the oil was extracted from the fruit pulp at the Laboratory of Agroindustrial Processes (EMBRAPA) using the cold extraction method according to Lima *et al* . (2019). The pulp was submitted to a temperature ≤ 45ºC in an industrial stove and centrifuged at 4500 rpm for 15 min to separate the oil, and stored in glass vials at 5ºC.

Formation of microparticles

For the preparation of the emulsion to be microencapsulated with pequi oil and sodium alginate, 1.2% (m/v) alginate was prepared in distilled water (100 mL) and left under stirring for 24 h at room temperature (25 °C).). Tween 80 (0.55%) was added to the alginate solution and homogenized in Ultra-Turrax ® (T-25 digital, IKA®), being stirred at 12,000 rpm for 2 min. Sodium alginate solution was mixed with pequi oil (2 g) and surfactant Span 80 (0.45%). At the end, the emulsion was homogenized in Ultra-Turrax ®, being stirred at 12,000 rpm for 5 min. The emulsion was dropped into a solution of calcium chloride 1.3% (m/v) and chitosan 1.2% (m/v). In the treatment for the formation of microparticles with alginate matrix, only 1.3% (m/v) calcium chloride solution was used. For the formation of particles by ionic gelation, the extrusion technique was used, using the Encapsulator equipment Büchi B-395 (Büchi , Essen, Germany). A drip nozzle with a diameter of 120 µm, frequency of 120 Hz, voltage of 300 v and 80% agitation was used. At the end, the spheres were submitted to drying: a) in a heating oven at 50 ºC for 2h30 min and b) dried in a lyophilizer (CHRIST, model 1-8 LSCbasic) after previous freezing in an ultrafreezer .

Thermal analysis

For the thermal characterization of pequi oil microparticles by thermogravimetric analysis (TGA), the STA 6000 equipment (PerkinElmer) was used. Approximately 10 mg of the samples were weighed and investigated in the temperature ranges from 25 to 750 °C with a heating rate of 10 °C/min and nitrogen gas flow rate of 20 mL /min.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA) is a technique in which changes in the mass of a sample are measured as a function of time and temperature, as it is subjected to a controlled temperature program in a controlled atmosphere (CAI *et al* ., 2018).). However, TGA alone is not sufficient to interpret the weight loss of the sample. Thus, derived thermogravimetry (DTG) is used because, when we apply the derivation operations to raw thermograms, it provides an improvement in the information contained in the thermogram (RAMBO *et al* ., 2015). Figure 1 shows the DTG curves for pequi oil (OP), Alginate microparticles (AG), Chitosan microparticles, Alginate and

Revista
Coleta Científica
ISSN: 2763-6496

COLETA SCIENTIFIC JOURNAL

Year IV, Vol. IV, n.8, Jul.-Dec ., 2020

ISSN: 2763-6496

DOI: https://doi.org/10.5281/zenodo.4716820

Submission date: 04/07/2020. Acceptance date: 12/20/2020.

pequi oil (QT/AG/OP) and AG/OP microparticles, observing the influence of drying method (oven and lyophilization) on thermal degradation.

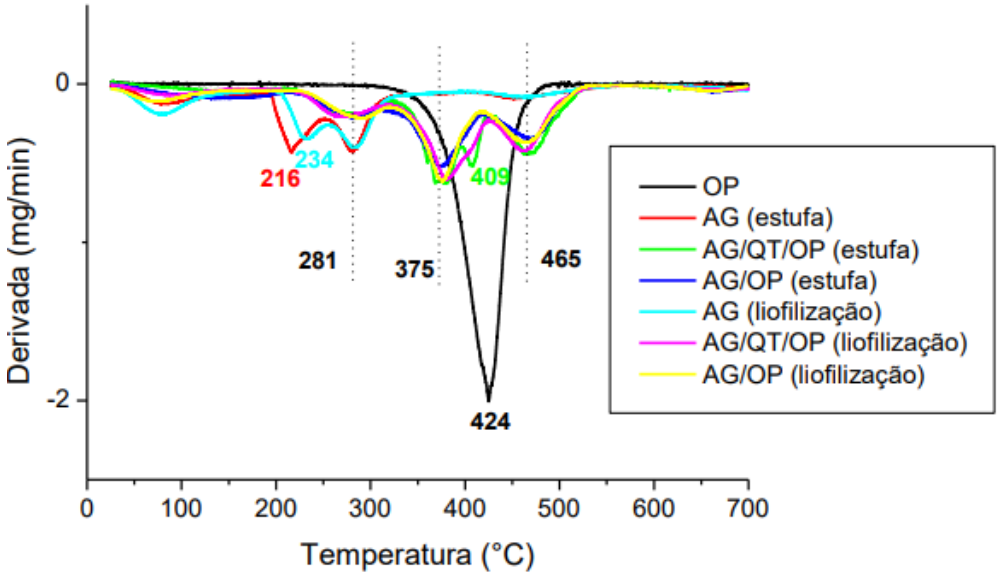

Figure 1 – Thermogravimetric analysis of pequi oil microparticles.

The OP had its degradation at approximately 424 ºC. All microparticles showed an initial degradation event at approximately 100 ºC, referring to water loss (Da Silva; De Paula; Feitosa, 2007). AG (greenhouse) and AG (lyophilization) particles showed a second polymeric degradation event at approximately 215 ºC. The AG/QT/OP microparticles, regardless of the drying method applied, showed the second degradation peak at 375 °C, indicating better stability due to the affinity of the electrostatic interactions of the polymers (CHANG *et al* ., 2016). The AG/OP microparticles were also not influenced by the thermal degradation in terms of the drying method, with similar events starting at 281 ºC.

In Alouh 's studies *et al* . (2019) alginate/chitosan hybrid microparticles exhibited four stages of thermal degradation. The first occurred in the range of 25 to 240 °C corresponding to water molecules trapped in the network (GOPALAKANNAN *et al* ., 2016). The second and third peak observed between 240 and 370°C occurred due to the decomposition of the biopolymers . The last stage of thermal degradation of the granules took place between 370 and 525 °C. Popa *et al* . (2008) found that the chitosan/alginate complex modifies the degradation mechanism of the resulting particles, introducing new events compared to the crude polymers. These results corroborate with those found in this work.

CONCLUSIONS

The pequi oil microparticles obtained by ionic gelation in a polymer matrix of alginate and chitosan showed better thermal stability results, regardless of the drying method. Results like these are important when looking for a commercial application in

Revista
Coleta Científica
ISSN: 2763-6496

COLETA SCIENTIFIC JOURNAL

Year IV, Vol. IV, n.8, Jul.-Dec ., 2020

ISSN: 2763-6496

DOI: https://doi.org/10.5281/zenodo.4716820

Submission date: 04/07/2020. Acceptance date: 12/20/2020.

the food area, and it is necessary to define the best condition for drying the particles based on temperature and enthalpy of degradation.

REFERENCES

ABLOUH, EH; HANANI, Z.; ELADLANI, N. *et al.* Chitosan microspheres/sodium alginate hybrid beads: an efficient green adsorbent for heavy metals removal from aqueous solutions. **Sustain Environ Res** *,* v. 29 **,** no. 5, p. 1-11, 2019.

ASCARI, J.; TAKAHASHI, JA; BOAVENTURA, MAD The phytochemistry and biological aspects of Caryocaraceae family. **Brazilian Journal of Medicinal Plants** , v. 15, no. 2, p. 293–308, 2013.

ASCHERIO, A. *et al* . Dietary fat and risk of coronary heart disease in men: Cohort follow up study in the United States. **British Medical Journal** , v. 313, no. 7049, p. 84–90, 1996.

BHATTARAI, RS; DHANDAPANI, NV; SHRESTHA, A. Drug delivery using alginate and chitosan beads: An Overview. **Chronicles of Young Scientists** , vol. 2, p. 192 – 196, 2011.

CAI J. *et al* . Processing thermogravimetric analysis data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis: Case study of corn stalk. **Renewable and Sustainable Enerdy Reviews** , v. 82, p. 2705-2715, 2018

COLAK, N. *et al* . Bog bilberry phenolics, antioxidant capacity and nutrient profile. **Food Chemistry** , v. 201, p. 339–349, 2016.

DA SILVA, DA; DE PAULA, RCM; FEITOSA, JPA Graft copolymerisation of acrylamide onto cashew gum. **European polymer Journal** , v. 43, p. 2620–2629, 2007.

DAMIAN, C. *et al* . CHITOSAN: A POLYSACCHARIDE AMINO WITH FUNCTIONAL CHARACTERISTICS. **feed _ Nutri ,** v. 16, p. 195–205, 2005.

DE AZEREDO, HM C.. **Food stability fundamentals** . 2nd ed. Brasília, DF: Embrapa, 2012.

DE LIMA, A. *et al* . Chemical composition and bioactive compounds present in the pulp and almond of pequi (*Caryocar brasiliense* Camb .). **Brazilian Journal of Fruticulture** , v. 29, no. 3, p. 695–698, 2007.

EMERGENCY, NMJ 53f. **Evaluation of the antibacterial activity of artisanally extracted pequi oil (Caryocar sp.).** TCC (Graduation in Nutrition), Federal University of Pernambuco, 2017.

Revista Coleta Científica
ISSN: 2763-6496

COLETA SCIENTIFIC JOURNAL

Year IV, Vol. IV, n.8, Jul.-Dec ., 2020

ISSN: 2763-6496

DOI: https://doi.org/10.5281/zenodo.4716820

Submission date: 04/07/2020. Acceptance date: 12/20/2020.

GOPALAKANNAN, V.; VISWANATHAN, N. One pot synthesis of metal ion anchored alginate-gelatin binary biocomposite for efficient Cr(VI) removal. **Int J Biol Macromol** . v.83, p. 450–459, 2016.

HELGERUD, T.; GASEROD, O.; FJAEREIDE, T.; ANDERSEN, OP; LARSEN, CK **Food Stabilizers , Thickeners and Gelling Agents** , A. Imeson , Ed., p. 50–71, 2012.

LIMA, AC, BARROS, MES, SOUZA, ACR DE, ARAÚJO, Í. M. DA S., MAGALHÃES, HCR, & PACHECO, GM (2019). Obtaining Pequi Pulp Oil by Physical Separation Using Centrifugation. **Embrapa Technical Communication** 254, 6.

POPA, MI; LISA, G.; AELENEI, N. Thermogravimetric characterization of chitosan / alginate microparticles loaded with different drugs . **polymer Bulletin** , v. 61, p. 481–490, 2008.

OLIVEIRA, EF; PAULA, HCB; PAULA, RCM Alginate / cashew gum nanoparticles for essential oil encapsulation . **Colloids and Surfaces B: Biointerfaces** , v. 113, p. 146-151, 2014.

RAMBO, MKD *et al* . Study of thermogravimetric analysis of different lignocellulosic biomasses using principal component analysis. **Science and Nature** , v. 37 no. 3, p. 862-868, 2015.

RIBEIRO, AJ; SILVA, C.; FERREIRA, D.; VEIGA, F. Chitosan-reinforced alginate microspheres obtained through the emulsification / internal gelation technique . **European Journal of Pharmaceutical Science** , v. 25, p. 31-40, 2005.

TENGKU-ROZAINA, TM; BIRCH, EJ; Thermal Analysis for Lipid Decomposition by DSC and TGA. **Encyclopedia of food chemistry** , v.2, 345-352, 2019.

TØNNESEN, HH; and KARLSEN, J. Alginate in Drug Delivery Systems. **Drug Development and Industrial Pharmacy** , vol. 28(6), p. 621–630, 2002.

XIAO, Z.; LIU, W.; ZHU, G.; ZHOU, R.; NIU, Y. Production and characterization of multinuclear microcapsules encapsulating lavender oil by complex coacervation. **Flavor and Fragrance Journal,** v.29, 166-172, 2014.

YAN, X.; KHOR, E.; LIM, LY PEC films prepared from Chitosan-Alginate coacervates. **chemical & pharmaceutical bulletin** , v. 48, no. 7, p. 941–946, 2000.