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Microcapsules of Blackberry Pomace (*Rubus fruticosus*): Light and Temperature Stability

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Blackberries are appreciated for its high nutritional value and important source of healthy compounds. Blackberries' pomace represents 20% of the total fruit, mainly composed by seeds and barks which contains a significant amount of phenolic compounds and anthocyanins. This study aimed to microencapsulate blackberries' pomace extract with maltodextrin using the spray dryer technique. Also the stability against light and temperature variations was evaluated during 36 days. There were two types of extraction, aqueous (CA) and hydroethanol (CE), which were encapsulated with maltodextrin DE 10 and submitted to spray drying. Subsequently the samples were evaluated against different conditions of temperature (4 and 25 ° C), presence and absence of light, analyzing parameters of color, phenolic compounds and anthocyanins. The results were analyzed using ANOVA and Tukey's test ($p<0.05$). The intensity of red color in the samples, represented by a*, decreased during storage. Analyzing phenolic compounds there was no significant difference in all samples, indicating that these compounds in both (CA and CE) extraction were not affected by variations of light and temperature. For anthocyanins, on temperature variation, no degradation was observed for CA. For CE losses represented less than 10 %. Analyzing the influence of light in anthocyanins degradation, the highest loss was observed in the presence of light (for both CA and CE), in the absence of light the CA sample was not degraded, and the CE lost about 8 %. Therefore microencapsulation with maltodextrin was effective for the protection of phenolic compounds and anthocyanins during the storage time studied, under the different proposed conditions (light and temperature), noting that CA extraction had better results. It can be concluded that the aqueous extraction was successful, helping to stabilize encapsulated samples of blackberry pomace over 36 days of storage.

1. Introduction

Blackberries (Rubus spp.) known as berries, which are small fruits with sweet taste and rounded format, are appreciated by consumers due to their high nutritional value and health benefits (Ferreira et al., 2009). This fruit is an important source of phenolic compounds, such as phenolic acids, tannins, elagitannins, flavonoids and anthocyanins (Ivanovic et al., 2014; Machado et al., 2015).
In fruit processing industries, about 20% of pomace is produced, basically composed of seeds and barks that still contain a large amount of phenolic compounds, such as anthocyanins (Ignat et al., 2011).
The extraction of antioxidants as phenolic compounds and anthocyanins is usually performed with the addition of organic solvents, with stirring or heating. Water extraction is a viable alternative for use in the food industry because it is a cheap and clean technology (Ivanovic et al., 2014; Reátegui et al., 2014).
Encapsulation provides a degree of stabilization for active compounds, since the wall material acts as a physical barrier to oxygen, light, and temperature, among other factors, avoiding deteriorating reactions (Madene et al., 2006).

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The most used materials for microencapsulation are maltodextrins, which are obtained by acid hydrolysis of various starches (corn, potato, or others). In general, they have high water solubility, low viscosity, smooth taste and colorless solutions are widely used in the food industry (Gibbs et al., 1999; Saenz et al., 2009).
In this context, the present study aimed to microencapsulate by spray dryer the extracts (aqueous and hydroalcoholic) of blackberry pomace, evaluating the stability against light and temperature variations.

2. Material and Methods

Blackberry pomace (Rubus fruticosus) was locally purchased from a producer in the city of Paraibuna, SP-BR. Maltodextrin (DE10) was supplied by Cargil® (Campinas-SP). The reagents were of analytical grade.

2.1. Production of extracts and microcapsules by spray drying

An experimental design (central composite design) with eleven experiments in the total was applied, the response surface methodology was used to evaluate the temperature and time influence in anthocyanin extraction.
Two extracts from blackberry pomace were prepared: aqueous and hydroethanolic extract. The aqueous extract was obtained from the dilution of blackberry pomace in distilled water (500 mg / mL) and mechanically stirred at 60 ° C for 45 minutes, according to response surface. The hydroethanolic extract was obtained by diluting the pomace (500 mg / mL) in ethyl alcohol 80 % (v / v), under mechanical stirring for 48 hours, filtration and rotoevaporation at 65 ° C until total solvent evaporation (Shirahigue et al., 2011).
Maltodextrin (DE 10) was added directly to the filtrates, in a ratio of 1 : 1 (w/w), using mechanical agitation (Ferrari et al., 2012). The aqueous and hydroethanolic extracts mixed with maltodextrin (CA and CE, respectively) were dried in a Buchi B-191 mini spray dryer, the inlet air temperature was 170 ° C and outlet 105 ° C; Atomization pressure: 4 bar; Average drying air flow: 3.5 m^3 / h; Average feed flow: 0.5 L / h (Valduga et al., 2008). After drying the powders were placed in plastic containers and stored under different temperature and light conditions for stability evaluation.

2.2. Microcapsule stability to light and temperature

The samples were evaluated during 36 days for temperatures of 4 and 25 ° C (CA 4 °, CA 25 °, CE 4 °, CE 25 °), Light and No Light (CA L, CA N. L, CE L and CE N. L) at 25°C using two fluorescent lamps of 20W and a dark chamber. Color, total phenolic compounds and total monomeric anthocyanins were evaluated. The capsule disintegration was performed using water, agitation and centrifugation at 4000 rpm for10 min (Díaz et al., 2015).
The determination of total phenolic compounds (TPC) was performed using Folin-Ciocalteu reagent. The results were expressed in μg gallic acid equivalent (GAE).mg $^{-1}$ product (Pierpoint, 2004; Singleton and Rossi, 1965).
The total monomeric anthocyanins (TMA) content was measured using the differential pH method (Lee et al., 2005) according equation (1) and (2) with results expressed in μg cyanidin-3-glucoside.mg $^{-1}$.

$$AT = (ABS\ 520nm - ABS\ 700nm)pH\ 1{,}0 - (ABS\ 520nm - ABS\ 700nm)pH\ 4{,}5 \quad (1)$$

$$Total\ monomeric\ anthocyanins\ (TMA) = \frac{(AT\ x\ MW\ x\ Df x 10^3)}{\varepsilon\ x\ \lambda} \quad (2)$$

Where: MW = 449.2 g/mol (molar mass of cyanidin-3-glucoside); Df = dilution factor; 10^3 = conversion factor from g to mg; ε = 26900L/mol (molar absorptivity of cyanidin-3-glucoside); λ = 1 cm (optical path length of the cuvette).
The color was evaluated using a Minolta® CR400 portable colorimeter, using the CIEL*a *b* system, and the hue (H) angle and chromaticity (C) was calculated using equations (3) and (4), respectively.

$$H(°) = tan^{-1}\ \frac{b^*}{a^*} \quad (3)$$

$$C = \sqrt{(a^*)^2 + (b^*)^2} \quad (4)$$

The total loss percentage for anthocyanins and phenolic compounds during the storage period was calculated by the ratio between the concentration at the last storage day (d36), and the initial concentration (d0) (Souza et al., 2014).
The analyzes were performed in triplicate and evaluated by Anova and Tukey test ($p < 0.05$) using the statistical program Sisvar 5.6.

3. Results and discussion

Evaluating the color (L, a *, b *, H ° and C) it was observed (Figure 1) that for the luminosity (L), CA 4 ° C and CE 4 ° C had lower losses when compared to the CA and CE at the temperature of 25 ° C, the same pattern was observed in a *, b * and H °. The samples in the absence of light presented the greater loss of color in all parameters.

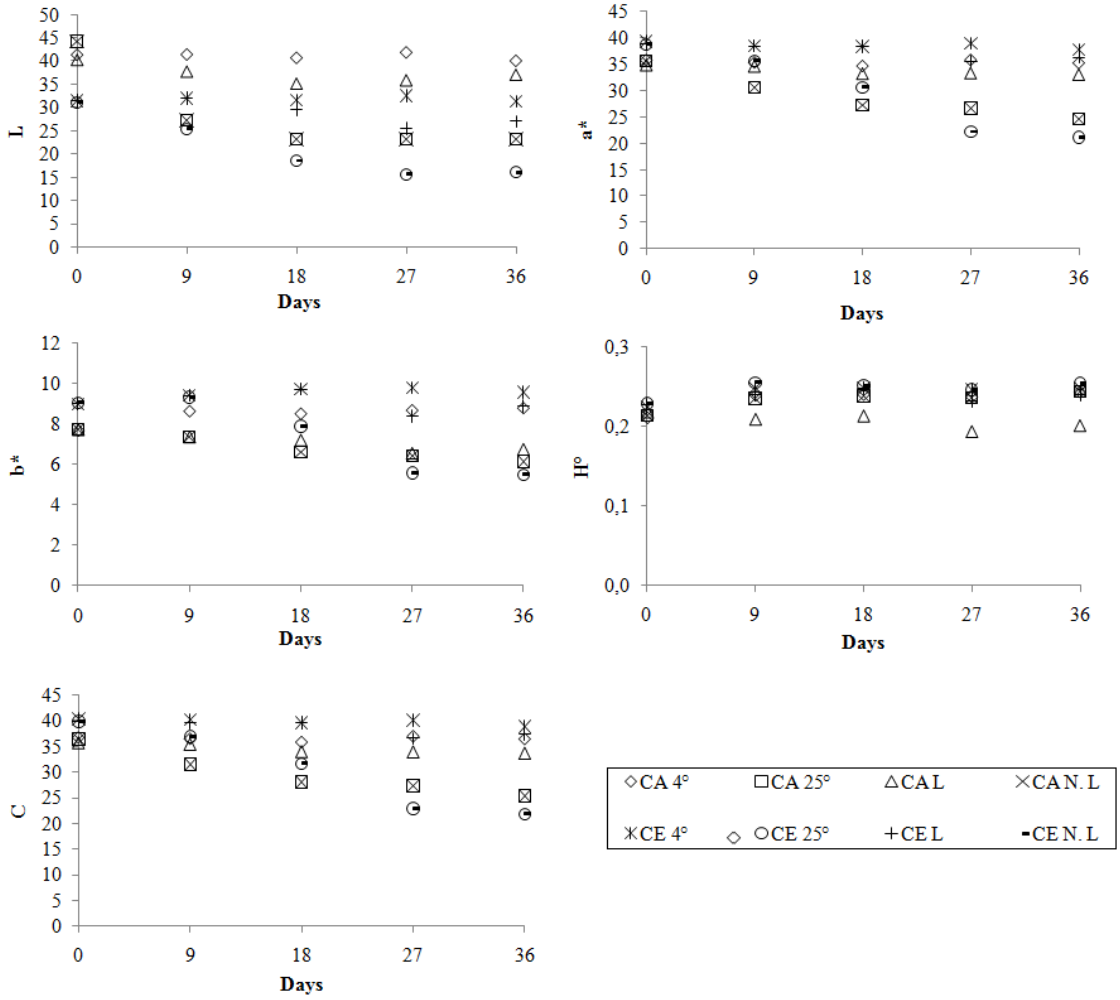

*Figure 1. Color parameters (L, a *, b *, H ° and C) of microcapsule solutions under light and temperature conditions. L = Light; N.L = No Light. L*= luminosity; a*= variations between green (-) and red (+); b*= variations between blue (-) and yellow (+); C= chromaticity; H= hue angle. CA= microcapsule aqueous; CE= microcapsule* hydroethanolic.

Regarding the parameter a *, 4 ° C temperature kept the values constant, indicating greater red intensity in the samples and better stability in this condition. CA 4 ° C had a loss of 1.53 % compared to 47.69 % in CA 25 ° C. In CE 4 ° C the loss was 4.21 % and 44.96 % in CE 25 ° C.

Another study observed the same pattern in a * and b * color parameters compared to higher temperatures for anthocyanins, where encapsulation with arabic gum protected the samples from heating (Guan and Zhong, 2015).

The decrease of red (a *) may be related to anthocyanins, due to the loss of the flavilium cation and hydrolysis of a double bond in the C-ring of the anthocyanin molecule (Goto and Kondo, 1991). In addition, glucose or sucrose from anthocyanins can be degraded during heat treatments producing glycol that reduces red Intensity (Brouillard and Delaporte, 1977).

Regarding the phenolic compounds (Table 1) there was an increase of 32.28 % in CA 4 ° C, whereas CA 25 ° C, with light and without light, showed no significant difference between 1 and 36 days of storage. It was also observed that TPC were not influenced in CE under the different light and temperature conditions.

Table 1. Total phenolic compounds and total monomeric anthocyanins in 36 days of storage

	TPC (µg GAE.mg $^{-1}$ product)					
	d $_0$	d $_9$	d $_{18}$	d $_{27}$	d $_{36}$	%loss*
CA 4 °	23.13^{bB} ±1.11	23.60^{bC} ±0.07	23.29^{bC} ±1.04	18.29^{cC} ±0.39	30.60^{aB} ±1.51	+32.28
CA 25 ° C	25.64^{abB} ±0.62	22.38^{cC} ±0.20	24.53^{bC} ±0.12	19.86^{dB} ±0.43	26.67^{aC} ±1.11	+3.99
CA L	25.84^{aB} ±1.82	23.53^{aC} ±0.47	25.31^{aC} ±0.63	19.01^{bBC} ±0.37	25.13^{aC} ±0.13	2.75
CA N.L	25.64^{ab} ±0.62	22.38^{cC} ±0.20	24.53^{bC} ±0.12	19.86^{dB} ±0.43	26.67^{aC} ±1.11	+3.99
CE 4 °	37.78^{aA} ±0.54	38.00^{aAB} ±1.74	34.04^{bAB} ±0.77	28.82^{cA} ±0.50	38.58^{aA} ±0.68	+2.12
CE 25 ° C	38.18^{aA} ±1.37	39.56^{aA} ±1.01	32.44^{bB} ±1.01	28.42^{cA} ±0.50	38.40^{aA} ±0.35	+0.58
CE L	39.42^{aA} ±0.50	35.91^{bB} ±1.61	36.04^{bA} ±1.21	29.60^{cA} ±0.35	38.22^{abA} ±0.81	3.04
CE N.L	38.18^{aA} ±1.37	39.56^{aA} ±1.01	32.44^{bB} ±1.01	28.42^{cA} ±0.50	38.40^{aA} ±0.35	+0.58
	TMA (µg cyanidin-3-glucoside.mg $^{-1}$)					
	d $_0$	d $_9$	d $_{18}$	d $_{27}$	d $_{36}$	%loss*
CA 4 °	1.18^{abB} ±0.02	0.98^{dC} ±0.02	1.12^{bcC} ±0.03	1.07^{cCD} ±0.02	1.22^{aD} ±0.03	+3.78
CA 25 ° C	1.19^{aB} ±0.04	0.84^{bD} ±0.04	1.02^{abD} ±0.03	1.21^{aC} ±0.21	1.05^{abE} ±0.03	11.16
CA L	1.13^{aB} ±0.05	0.78^{cD} ±0.02	0.99^{bD} ±0.01	0.83^{cD} ±0.03	0.79^{cF} ±0.02	30.04
CA N. L	1.19^{aB} ±0.04	0.84^{bD} ±0.04	1.02^{abD} ±0.03	1.21^{aC} ±0.21	1.05^{abE} ±0.03	11.16
CE 4 °	2.48^{abA} ±0.02	2.18^{dA} ±0.03	2.49^{aA} ±0.03	2.39^{bcA} ±0.06	2.38^{cdA} ±0.02	4.04
CE 25 ° C	2.46^{aA} ±0.02	2.18^{cA} ±0.03	2.20^{bcB} ±0.03	2.19^{bcAB} ±0.04	2.26^{bB} ±0.01	8.22
CE L	2.53^{aA} ±0.02	1.77^{dB} ±0.01	2.22^{bB} ±0.01	2.04^{cB} ±0.02	1.71^{dC} ±0.08	32.45
CE N. L	2.46^{aA} ±0.02	2.18^{cA} ±0.03	2.20^{bcB} ±0.03	2.19^{bcAB} ±0.04	2.26^{bB} ±0.01	8.22

Average followed by the same lowercase letter in the row and upper case in the column did not differ by Tukey's test ($P < 0.05$). d = days; L = Light; N.L = No Light; * Positive signs indicate increase. CA= microcapsule aqueous; CE= microcapsule hydroethanolic. TPC= total phenolic compounds; TMA= total monomerica anthocyanins.

Anthocyanins (Table 1) did not show degradation in CA 4 ° C and CA 25 ° C between 1 and 36 days of storage. In CE 4 ° C there was a loss of 4.04 % and 8.22 % in CE 25 ° C.

Another study observed a direct proportional relationship between the hydrolysis and the increased temperature, resulting in a lower stability of anthocyanins. The lower temperatures studied (- 20 ° C and 5 ° C) reduced the degradation of anthocyanins in extracts of Jamelao (Eugenia jambolana) throughout the storage (Sharma et al., 2016).

Light influenced the degradation of TMA, with a reduction of 30.04 % in CA Light. In CA No Light there was no loss. In the CE Light sample the degradation was greater 32.45 % as compared to 8.22 % in CE No Light. As previously studied (Weber et al., 2017) the samples stored in the dark presented greater stability, thus, the temperature had only a slightly accelerating effect on the anthocyanin degradation.

The limiting factor for the use of anthocyanins as a substitute for synthetic dyes is their low stability against factors such as light and temperature (Lopes et al., 2007). In general, it was observed that microencapsulation acts as a shield when the temperature is the variable in relation to color, and when light is the variable in relation to anthocyanins, thus minimizing degradation of samples under 4 ° C and no light.

Regarding the temperature at 25°C the loss was not great 11.26% in CA and 8.22% in CE. However, the microencapsulation can be used to storage in food industry at 25°C (ambient temperature). In relation to presence or absence of light, its indicated a packaging with materials which do not penetrate light.

4. Conclusions

Microencapsulation with maltodextrin was efficient for the protection of phenolic compounds and anthocyanins during the studied storage period and the different conditions proposed. This process can be used for technical applications in parallel with the re-propose of industrial waste, the use of this pomace is promising, since it has important antioxidant compounds, which when encapsulated may have technological applications by the food industry. Finally, is important to highlight that the light influency was more pronounced by light presence than temperature, the losses of bioactive compounds was higher in presence of light. The extraction with water, microcapsule CA was the only one that did not present anthocyanin loss in the temperature of 4 º C, indicating its potential since this type of aqueous extraction is low cost and ecofriendly (does not use organic solvents). In general, higher stability was observed in microcapsules with aquous extraction, stored at 4 ° C and without light, being the best stability condition for microcapsules of blackberry pomace. In the other hand, the microcapsules can be used for food industry for a variety of products, with food packaging without light penetration and storage at ambient temperature.

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