

Evaluation of Thermodynamic Properties and Antioxidant Activities of an Adsorbent-Bioactive Complex with Antioxidant Characteristics

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Jaboticaba peel powder (JPP) is a residue that contains phenolic compounds, such as anthocyanins and gallic acid. An adsorbent-bioactive complex (ABC) was synthesized using an extract rich in compounds with antioxidant properties obtained from JPP immobilized on microcrystalline cellulose from sweet sorghum bagasse. In this work, the result of thermal degradation of anthocyanins from JPP and ABC, activation energy (E_a), half-life time ($t_{1/2}$), decimal reduction time (D), temperature variation (Z), thermodynamic parameters (enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS)) and degradation of antioxidant activities were investigated. Anthocyanin degradation of 35, 60 and 85% was observed for JPP and 10, 30 and 65% for ABC at temperatures of 90-130 °C. E_a of JPP and ABC were 110 and 91 kJ mol⁻¹, respectively. ABC was able to increase from 143-690% the half-life time when compared to JPP. The Z parameter indicated that a greater temperature variation is necessary to degrade ABC anthocyanins (31 °C) when compared to JPP (25 °C). The thermodynamic parameters showed that the energy needed to be broken down to reach the transition state is higher for JPP than ABC, in addition ABC is closer to its thermodynamic equilibrium state. Thus, ABC can be used as an additive in pharmaceutical, cosmetics and food industries, maintaining bioactive and antioxidant properties.

Keywords: anthocyanins, antioxidant properties, degradation kinetics, thermodynamic analysis

Introduction

The growing consumer interest in functional foods has aroused the food industries in using natural pigments to manufacture food and beverages in order to mitigate the harmful effects that artificial pigments can cause.¹ In this sense, Future Market Insights (2023) estimates² that the global market value of natural food dyes will grow US\$ 1.6 billion in 10 years.

Anthocyanins are examples of flavonoids which are natural pigments that can be found in the tissues of plants, fruits, vegetables, grains and flowers.^{1,3} One of the problems

involving its use is its instability related to temperature, pH, light, oxygen, enzymes and relative humidity conditions.⁴ Thus, research related to new sources and strategies that optimize the stability of these natural dyes must be developed to meet the demand.

Ballesteros *et al.*⁵ have already encapsulated bioactive compounds from coffee grounds by freeze and spray-drying with different coating materials. Barbieri *et al.*⁶ analyzed the deep eutectic solvents to extract and stabilize phenolic compounds from rosemary (*Rosmarinus officinalis* L.). Arend *et al.*⁷ studied nanofiltration to recover and stabilize phenolic compounds from guava leaf extract. Gençdağ *et al.*⁸ stabilized anthocyanins using organic molecules and encapsulation techniques. De Souza Mesquita *et al.*⁹ did the combination of eutectic solvents

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and food grade silica in recovery and stabilization of anthocyanins from grape pomace and Tan *et al.*,¹⁰ used simultaneous encapsulation-copigmentation via protein-polysaccharide polyelectrolyte complexes to stabilize anthocyanins

Jaboticaba peel is a residue that contains a significant amount of bioactive compounds, especially anthocyanins. In addition, this residue also has other bioactive compounds such as tannins, flavonoids, depsides, volatiles, organic acids and tocopherols.¹¹ For this reason, jaboticaba peel has been studied for antiproliferative activity in tumor cell lines,¹² exerting anti-obesity effects in mice fed high fat content,¹³ used in the treatment of breast cancer¹⁴ and with a preventive effect on prostatic damage.¹⁵

Microcrystalline cellulose, the most abundant polymer on Earth, is a polysaccharide of linear polymeric chains of β -(1,4)-linked D-glucopyranosyl units. The cellulose surface is made up of hydroxyl groups, which can be functionalized.¹⁶ It presents itself as a possible raw material for food systems in film production. This polymer has good antimicrobial activity, can be used in packaging to prolong the shelf life of foods, is biodegradable and presents an ecological approach to sustainability.¹⁷⁻¹⁹

Aiming at stabilizing anthocyanins in a renewable, biodegradable material compatible with food matrices, it was proven in a previous work²⁰ that bioactive compounds can be immobilized on the surface of microcrystalline cellulose. The innovative character of this work is the study of the evaluation of the thermodynamic properties of a bioactive complex rich in phenolic compounds, with potential applications in industries due to its bioactive properties, among them, natural dyes.

Thus, the objective of this work was to submit the jaboticaba peel powder and the adsorbent-bioactive complex (anthocyanins adsorbed on microcrystalline cellulose) to thermal treatments, performing a comparative analysis of the degradation of the anthocyanins present in these materials using kinetic models applied to the thermal degradation. A comparative thermal study between the degradation of anthocyanins present both in jaboticaba peel powder (JPP) and in the adsorbent-bioactive complex (ABC) was carried out. Thus, this study was able to predict the activation energy (E_a), decimal reduction time (D), half-life time ($t_{1/2}$), temperature variation (Z), thermodynamic parameters (enthalpy change (ΔH), Gibbs free energy (ΔG) and entropy change (ΔS)) and degradation of activities antioxidants (ABTS (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid)), FRAP (ferric reducing antioxidant power) and DPPH (2,2-diphenyl-1-picrylhydrazyl)).

Experimental

Obtaining powder and lyophilized extract from jaboticaba peel

Obtaining the powder and lyophilized extract of the jaboticaba peel was based on the methodology described in the previous work.²⁰ In this process, the peels were sanitized, washed and dried at a temperature of 55 °C until constant mass. The extract was produced in a ratio of 1:20 (m/v) from crushed bark and ethanol solution (50%) in an ultrasonic bath (UltraCleaner 800 A, supplier) under conditions of 25 kHz and 200 W, for 90 min. The material was then placed in a rotary evaporator so that the solvent was eliminated and subsequently lyophilized.

Microcrystalline cellulose (MCC) isolation

To obtain the MCC, the methodology of Morais *et al.*,²¹ and adapted by da Silva Neto *et al.*,²² was used. At this stage, a ratio of 1:4 (sorghum bagasse without extractives and distilled water) were placed in a heated bath at 80 °C. To the set, 2.5 g of sodium chlorite (NaClO_2) was added, with a purity of approximately 80%, and 3 mL of glacial acetic acid (CH_3COOH), with a purity $\geq 99.85\%$, was added every hour for 3 h. After that, the set was left for another 2 h in constant agitation.

Synthesis of the adsorbent-bioactive complex (ABC)

The ABC synthesis was based on the procedure presented by da Silva Neto *et al.*,²⁰ where the kinetic, equilibrium and thermodynamic conditions involved in its synthesis were studied. Thus, 8.0 g of lyophilized extract were weighed and dissolved in 500 mL of potassium chloride / hydrochloric acid (KCl / HCl) pH 2.5 buffer. This extract was then placed in Erlenmeyer flasks together with 5 g of microcrystalline cellulose and stirred for 60 min at a speed of 170 rpm at 25 °C. After this time, the sample was filtered and the solid fraction was dried at 45 °C for 5 h.

Determination of total anthocyanins (TA) and antioxidant activities content

The determination of the anthocyanin content was based on the procedure presented by Lee *et al.*²³ The antioxidant activities were evaluated by determining the iron ion reducing power (FRAP) according to the methodology described by Rufino *et al.*,²⁴ and evaluation of the ability to eliminate stable free radicals

(radical ABTS cation and radical DPPH) based on the methodologies developed by Rufino *et al.*,²⁵ and Silveira *et al.*,²⁶ respectively.

Heat treatments

This procedure was based on Verbeyst *et al.*²⁷ The treatments were carried out at three temperatures: 90, 110 and 130 °C. The samples were placed in Petri dishes and heated. Between 0 and 360 min, a portion of each sample was removed for analysis. Finally, the material was characterized for the antioxidant activities of anthocyanins, DPPH, ABTS and FRAP.

Study of thermal degradation of bioactive compounds using kinetic models

For modeling the degradation of bioactive compounds, first and second-order kinetic models were taken into account to see which best fit the experimental data.^{28,29} In a first-order reaction, the reaction rate depends only on the concentration of one of the reactants. Thus, considering an irreversible, monomolecular, first-order reaction at constant volume, the rate equation for this reaction can be given by equation 1:

$$-\frac{dC_A}{dt} = k_d C_A \quad (1)$$

where C_A is the concentration of bioactive compounds in a given time, in mg 100 g⁻¹; t is the time in min and k_d is the degradation kinetic constant in min⁻¹. With the initial condition that $C_A = C_{A0}$ at $t = 0$, it results in equation 2:

$$\frac{C_A}{C_{A0}} = e^{-k_d t} \quad (2)$$

where C_{A0} is the initial concentration of bioactive compounds, in mg 100 g⁻¹. Thus, with Statistica 7.0,³⁰ it was possible to calculate the value of the kinetic constant of thermal degradation.

In a second-order reaction, the reaction rate depends on the square of the reactant concentration. Thus, considering an irreversible, monomolecular, second-order reaction at constant volume, the rate equation for this reaction can be given by equation 3:

$$-\frac{dC_A}{dt} = k_{d2} C_A^2 \quad (3)$$

where k_{d2} is the second-order degradation kinetic constant

in 100 g⁻¹ mg min⁻¹. With the initial condition that $C_A = C_{A0}$ at $t = 0$, it results in equation 4:

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k_{d2} \times t \quad (4)$$

With equation 4 it is possible to calculate the half-life time, which is the time required for the initial concentration of the reagent to reduce to half of its value. Thus, for a second-order model, this time is calculated with the help of equation 5.

$$t_{1/2} = \frac{1}{C_{A0} k_{d2}} \quad (5)$$

The reaction rate constant can be related through the Arrhenius equation, equation 6:

$$k_{d2} = A \times e^{-E_d/RT} \quad (6)$$

where A is the frequency factor in min⁻¹; E_d is the activation energy of the degradation reaction in J mol⁻¹; T is the temperature in K and R is the gas constant in J mol⁻¹ K⁻¹. Applying the natural logarithm to equation 6, we get equation 7:

$$\ln k_{d2} = \ln A - \frac{E_d}{R} \times \left(\frac{1}{T} \right) \quad (7)$$

With the study of thermal degradation kinetics, it is usual to also calculate the time in which the 10 times reduction in the initial concentration of bioactive compounds occurs, this parameter is known as decimal reduction time (D), and for a second-order reaction this time was calculated from equation 8:

$$D = \frac{9}{k_{d2} C_{A0}} \quad (8)$$

There is also the Z parameter that indicates the temperature interval that provides a 10 times variation in the degradation rate, for the calculation of this parameter it is necessary to adjust the data to the model through linear regression analysis, according to equation 9.²⁹

$$\log(D) = -\frac{1}{Z} \times T + B \quad (9)$$

Thus, a plot of $\log(D)$ versus T (°C) provides the value of Z, which is given in °C, as well as the value of B, which is the linear coefficient of the line.

Thermodynamic analysis of thermal degradation

In a thermal degradation analysis, the determination of some thermodynamic functions is necessary to better understand the phenomenon being studied. For a process of this nature, Mercali *et al.*,²⁸ proposed the use of equations to calculate the enthalpy change (ΔH), Gibbs free energy (ΔG) and entropy change (ΔS) and were calculated using equations 10, 11 and 12, respectively.

$$\Delta H = E_d - R \times T \quad (10)$$

$$\Delta G = -R \times T \times \ln \left(\frac{k_{d2} \times h}{k_B \times T} \right) \quad (11)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (12)$$

where: ΔH is the enthalpy change in J mol^{-1} ; ΔG is the change in Gibbs free energy in J mol^{-1} ; ΔS is the entropy change in $\text{J mol}^{-1} \text{K}^{-1}$; E_d is the activation energy of the degradation reaction in J mol^{-1} ; R is the ideal gas constant in $\text{J mol}^{-1} \text{K}^{-1}$; T is the temperature in K; k_{d2} is the thermal degradation constant in s^{-1} ; h is Planck's constant, with a value equal to $6.6262 \times 10^{-34} \text{ J s}$; k_B is the Boltzmann constant, with a value equal to $1.3806 \times 10^{-23} \text{ J K}^{-1}$.

Results and Discussion

Bioactive compounds and antioxidant activities

Table 1 presents the results obtained from the analysis of total phenolic compounds (TPC), total anthocyanins (TA) and determination of antioxidant activities (AA) by the iron reducing power (FRAP), inhibition of ABTS and DPPH radicals for jaboticaba peel powder (JPP), lyophilized extract (LE) and adsorbent complex-bioactives (ABC).

As shown in Table 1, JPP had a total phenolic compound content of $8536.6 \text{ mg GAE } 100 \text{ g}^{-1}$,

this value is higher than those reported by Rodrigues *et al.*,³¹ and Loubet Filho *et al.*,³² 2500 and $8820 \text{ mg GAE } 100 \text{ g}^{-1}$, respectively, for jaboticaba peel powder. The lyophilized extract showed TPC content ($28438.8 \text{ mg GAE } 100 \text{ g}^{-1}$) close to that reported by Pereira *et al.*,³³ ($27500.0 \text{ mg GAE } 100 \text{ g}^{-1}$). These differences may be associated with the different regions where jaboticaba was cultivated, as well as the extraction method used to quantify these compounds. With regard to the content of phenolic compounds present in the adsorbent-bioactive complex, a lower value was observed than those found for the peel as well as for the lyophilized extract, a similar behavior was observed by Alzate-Arbeláez *et al.*,⁴ when studying the adsorption of polyphenols from the Andean berry (*Vaccinium meridionale*) in nanocellulose from banana waste. The anthocyanin contents present in JPP and ABC, 67.80 and $21.7 \text{ mg } 100 \text{ g}^{-1}$, respectively, are higher than those reported by de Lima Marsiglia *et al.*,³⁴ for the alcoholic extract of jaboticaba peel.

Analyzing Table 1, it can be seen that the method of determining antioxidant activity by inhibition of the ABTS radical was the one that presented the highest values for JPP, LE and ABC; 1275, 5389 and $618 \text{ } \mu\text{mol TEAC g}^{-1}$, respectively, the inhibition by the DPPH radical was the one that presented the lowest values of antioxidant activities, approximately 775, 1434 and $211 \text{ } \mu\text{mol TEAC g}^{-1}$. Castañeda-Valbuena *et al.*,³⁵ when studying the antioxidant capacity of mango peel, observed lower values of DPPH ($249 \text{ } \mu\text{mol TEAC g}^{-1}$), ABTS ($1155 \text{ } \mu\text{mol TEAC g}^{-1}$) and FRAP ($100.89 \text{ } \mu\text{mol TEAC g}^{-1}$).

Thus, with the results of the bioactive components and antioxidant activities of the jaboticaba peel, the lyophilized extract and the complex it can be noted that these materials can be considered good sources of antioxidant compounds, and that they had a higher potential than some other fruits. Because it is an innovation, it was not possible to find data in the literature that could be used for comparative purposes of the adsorbent-bioactive complex.

Table 1. Total phenolic compounds, total anthocyanins and antioxidant activities of jaboticaba peel powder, lyophilized extract and adsorbent complex-bioactives

Sample	Analyses				
	TPC / (mg GAE 100 g ⁻¹)	TA / (mg 100 g ⁻¹)	FRA / ($\mu\text{mol TEAC g}^{-1}$)	ABTS / ($\mu\text{mol TEAC g}^{-1}$)	DPPH / ($\mu\text{mol TEAC g}^{-1}$)
JPP	8536.6 ± 209.3	67.80 ± 1.0	961.7 ± 19.8	1275.0 ± 100.5	774.3 ± 32.2
LE	28438.8 ± 788.5	211.7 ± 7.4	2384.1 ± 43.1	5388.9 ± 834.13	1434.4 ± 139.9
ABC	3564.7 ± 137.5	21.7 ± 0.3	355.4 ± 0.6	618.4 ± 71.9	211.3 ± 5.7

JPP: jaboticaba peel powder; LE: lyophilized extract; ABC: adsorbent complex-bioactives; TPC: total phenolic compounds; TA: total anthocyanins; TEAC: trolox equivalent antioxidant capacity; GAE: gallic acid equivalent; ABTS: 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid); FRAP: ferric reducing antioxidant power; DPPH: 2,2-diphenyl-1-picrylhydrazyl.

Thermal stability kinetics of total anthocyanins from JPP and ABC

In this study, the thermal stability kinetics of anthocyanins in jacobite peel powder and in the complex synthesized via adsorption were investigated after thermal treatments at temperatures of 90, 110 and 130 °C, varying the heating time from 0 to 360 min. Figures 1a-1c show the results obtained for the ratio between anthocyanin concentrations before and after heat treatment.

Analyzing Figures 1a-1c, it is observed that the thermal degradation rates of anthocyanins are greater as there is an increase in temperature for JPP and ABC. Upon reaching kinetic equilibrium, the percentage of anthocyanin degradation was 35, 60 and 85% for JPP and 10, 30 and 65% for ABC at temperatures of 90, 110 and 130 °C, respectively. In this context, it is evident that the complex synthesized via adsorption increased (20-30%) the stability of anthocyanins present in it, even when subjected to high temperatures.

Application of kinetic models in the thermal degradation of anthocyanins

The first- and second-order kinetic models were applied to the experimental data obtained, however, the second-

order model was the one that best fitted the data based on the coefficients of determination (R^2) of the model that ranged from 0.872 to 0.991, and the sum of squared residues were less than 0.02, as shown in Table 2. With the aid of this model, the kinetic degradation constants (k_d) were calculated for each temperature studied, as well as the half-life time for JPP and ABC, as shown in Table 2.

Within the temperature range studied (90-130 °C) it was observed that the kinetic constants of degradation increased with increasing temperature, showing that the degradation of these compounds occurred more quickly. Regarding the half-life times, it is observed that they are inversely proportional to the temperature, and when comparing the values for the two materials, it is observed that the adsorbent-bioactive complex was able to increase (143-690%) the half-life time of anthocyanins present in the complex.

Determination of the activation energy of the thermal degradation of anthocyanins

The degradation energy was calculated by correlating the inverse of the temperatures with the logarithm of the kinetic constants of thermal degradation for each studied condition. Applying a linear regression and using the Arrhenius equation, the frequency factor (A) and the

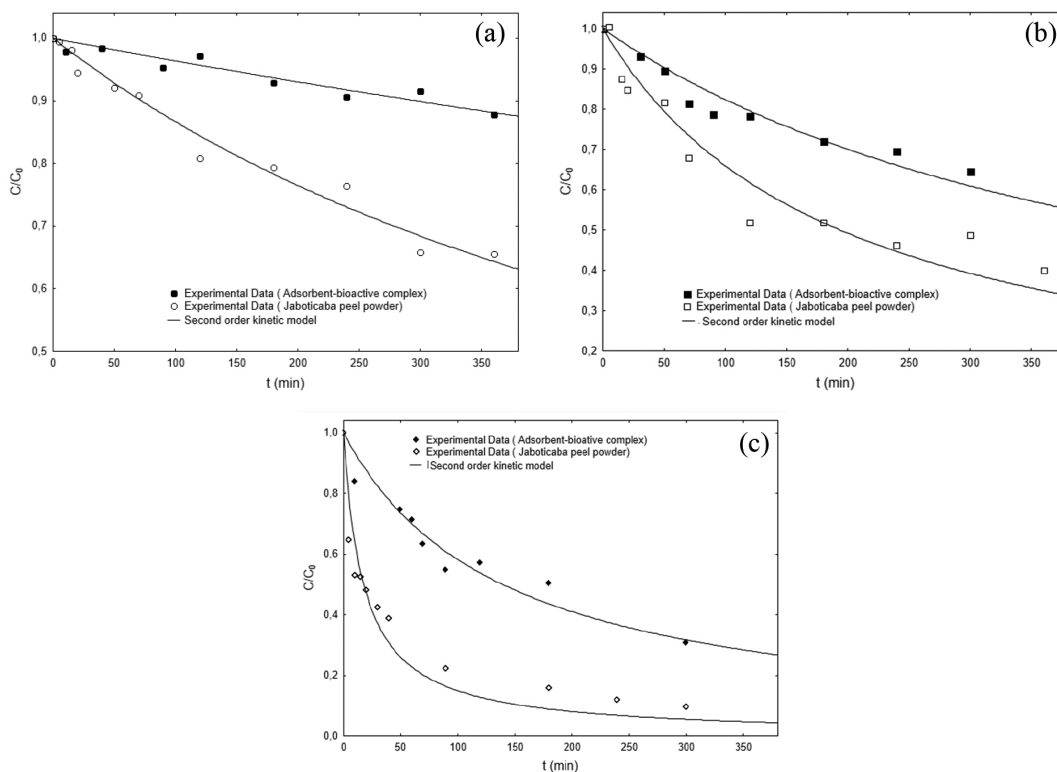


Figure 1. Degradation of anthocyanins in jacobite peel powder (JPP) and adsorbent complex-bioactives (ABC) during heating at 90 °C (a), 110 °C (b) and 130 °C (c).

Table 2. Values of kinetic constants of thermal degradation (k_d) and half-life ($t_{1/2}$) for the second-order model

Sample	Parameter			
Temperature / °C	$k_d \times 10^{-2} / (100 \text{ g mg}^{-1} \text{ min}^{-1})$	$t_{1/2} / \text{min}$	R^2	SSE
JPP				
90	0.0019	660	0.872	0.0103
110	0.0065	193	0.911	0.0209
130	0.0712	18	0.991	0.0056
ABC				
90	0.0025	2620	0.908	0.0012
110	0.0147	468	0.924	0.0082
130	0.0495	139	0.940	0.0196

JPP: jaboticaba peel powder; ABC: adsorbent complex-bioactives; k_d : kinetic constants of thermal degradation; $t_{1/2}$: half-life; R^2 : coefficient of determination; SSE: sum of squared errors.

activation energy of the degradation reaction (E_d) were obtained, which were 25 and 110 kJ mol^{-1} and, 20 and 91 kJ mol^{-1} for JPP and ABC, respectively. Analyzing the degradation activation energy values, it is noted that a lower value was found for ABC, indicating that the anthocyanins present in the ABC are stabilized when compared to the JPP.

A value close to that found in the present work for the energy of degradation was reported by Jiménez *et al.*,³⁶ when determining the degradation reaction of anthocyanins in blackberry juice extract, for a temperature range of 100 to 140 °C, which was 94.0 kJ mol^{-1} , and higher than that reported by Qiu *et al.*,³⁷ when studying the degradation of anthocyanins in dried purple potato slices in the temperature range of 50-80 °C, which was 72.18 kJ mol^{-1} .

Determination of D and Z parameters

Applying the data of the degradation constants and the initial concentrations of anthocyanins in JPP and ABC, it was possible to obtain the decimal reduction times (D) for each evaluated temperature, as well as the parameter (Z) according to Table 3.

Table 3. Experimental values of the decimal reduction time (D) and parameter Z for JPP and ABC at the evaluated temperatures

Temperature / K	D / min	Z / °C
JPP		
363.15	5727	25
383.15	1674	
403.15	153	
ABC		
363.15	23560	31
383.15	4007	
403.15	1190	

JPP: jaboticaba peel powder; ABC: adsorbent complex-bioactives.

Analyzing the data obtained in Table 3, it appears that the time required for a 10 times reduction in the initial concentration of bioactive compounds in the extract to occur is greater at lower temperatures. It was also verified that the temperature interval that causes a 10 times variation in the degradation rate (Z) was equal to 25 °C for the JPP and 31 °C for ABC. Therefore, in the analysis of one more parameter, it is proved that the fact that these bioactive compounds are adsorbed on microcrystalline cellulose, makes them more resistant to thermal degradation.

Thermodynamic parameters (ΔH , ΔS and ΔG) of the thermal degradation of anthocyanins

With the values of the degradation constants and energy of degradation calculated for each heat treatment, it was possible to calculate the variations in enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) of the degradation processes. The results obtained in the thermodynamic analysis are shown in Table 4.

Table 4. Thermodynamic functions for the degradation of anthocyanins from JPP and ABC

Thermodynamic function	Temperature / K		
	363.15	383.15	403.15
JPP			
$\Delta H / (\text{kJ mol}^{-1})$	106.53	106.37	106.20
$\Delta G / (\text{kJ mol}^{-1})$	134.72	138.39	137.76
$\Delta S / (\text{J mol}^{-1} \text{ K}^{-1})$	-77.61	-83.58	-78.28
ABC			
$\Delta H / (\text{kJ mol}^{-1})$	88.04	87.88	87.71
$\Delta G / (\text{kJ mol}^{-1})$	133.89	135.79	138.98
$\Delta S / (\text{J mol}^{-1} \text{ K}^{-1})$	-126.24	-125.05	-127.17

JPP: jaboticaba peel powder; ABC: adsorbent complex-bioactives; ΔH : enthalpy; ΔG : Gibbs free energy; ΔS : entropy.

For both materials, the positive enthalpy value implies an endothermic degradation process, since a greater degradation of anthocyanins was observed with increasing temperature. Regarding the Gibbs free energy variation for the degradation of anthocyanins, the positive sign of this thermodynamic function implies a non-spontaneous reaction process, thus, for the three temperatures under study, the degradation reactions were non-spontaneous, that for the degradation reaction to occur, it will be necessary to add energy. With the entropy variation value, it is concluded that the degradation process suggests that there is a more organized transition state of the molecules when compared to the beginning of the reaction.

When comparing with the thermodynamic functions obtained for the degradation of anthocyanins from JPP and ABC, it is observed that for both materials the process is endothermic and non-spontaneous, however, lower enthalpy values for the anthocyanins of the complex, imply that the energy needed to be broken down to reach the transition state is higher. For the Gibbs free energy variation similar values were observed, however, for the entropy variation smaller values were found for the complex, this implies the material is closer to its state of thermodynamic equilibrium, that is, it is little reactive and consequently there is an increase in the time required to form the activated complex.³⁸

Effect of heat treatment on the degradation of anthocyanins, total phenolic compounds and antioxidant activities (ABTS, FRAP and DPPH)

Figures 2a-2e present a comparative analysis of the degradation percentage for the total anthocyanin content, total phenolic compounds and antioxidant activities by the inhibition of DPPH and ABTS radicals and by the reducing power of iron (FRAP) for bark powder and adsorbent complex before and after heat treatment (360 min).

Analyzing Figure 2a, which shows the percentage of thermal degradation of anthocyanins present in JPP and ABC, it is observed that for the three temperatures studied, ABC was able to reduce the degradation of these compounds. At a temperature of 130 °C, JPP had a degradation of approximately 26%, while ABC had a value below 1%. For the degradation of the total phenolic compounds, the biggest difference happened at the temperature of 90 °C where the JPP had a degradation of approximately 13% and the ABC 2%. With regard to antioxidant activities, at a temperature of 130 °C, the DPPH radical suffered a degradation of 22% for JPP, while for ABC it was approximately 1.3%. The ABTS radical showed the greatest percentage difference at the temperature of

90 °C where JPP lost about 33% of its antioxidant activity and ABC only 16%. Analyzing the loss of antioxidant activity in relation to the iron reducing power (FRAP), the JPP presented the smallest degradation differences when comparing the two materials, however, at the temperature of 90 °C the JPP had a degradation of 10% and the ABC 7%.

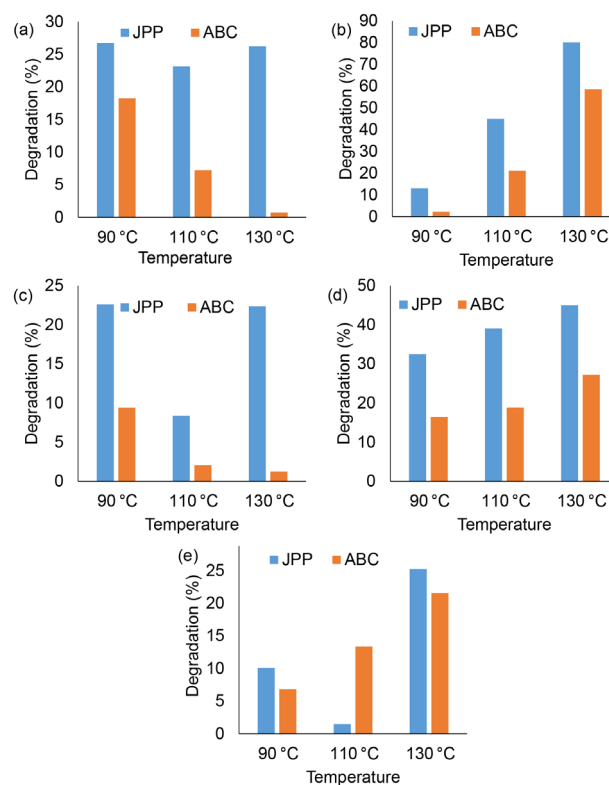


Figure 2. Degradation behavior of total anthocyanins (a), total phenolic compounds (b), and antioxidant activities by inhibition of DPPH (2,2-diphenyl-1-picrylhydrazyl) (c), ABTS (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid)) (d), FRAP (ferric reducing antioxidant power) (e), in jaboticaba peel powder (JPP) and adsorbent complex-bioactives (ABC).

Therefore, it can be seen that the jaboticaba peel is a rich source of bioactive compounds, and according to Nascimento *et al.*³⁹ diets enriched with this residue have a greater antioxidant capacity and tests carried out on mice that fed jaboticaba peel daily did not show symptoms of colitis or cancer, in addition to preventing the formation of tumors. Consequently, immobilizing these compounds in a matrix such as microcrystalline cellulose increases their usefulness so that even when exposed to adverse conditions they do not lose their usefulness and antioxidant functions in the human body.

Conclusions

In the thermal processing, it was verified with the kinetic study that the anthocyanins present in the

jaboticaba peel powder (JPP) and in the adsorbent-bioactive complex (ABC) were degraded showing kinetic constants of degradation increasing with the temperature.

Comparing the half-life times, it was verified that using microcrystalline cellulose as an adsorbent of bioactive compounds, the half-life time of anthocyanins increased by 297, 143 and 690% with the thermal treatments carried out at temperatures of 90, 110 and 130 °C, the same occurred for the decimal reduction time, comparing with the JPP. The Z parameter indicated that for the degradation time of the anthocyanins of the complex to undergo a decimal reduction, it will be necessary to increase the processing temperature by 31 °C, a value higher than that found for the jaboticaba peel, which was around 25 °C. With the thermodynamic analysis of the anthocyanin degradation process, it can be stated that it is an endothermic and non-spontaneous process.

The adsorbent-bioactive complex reduced the thermal degradation of anthocyanins and total phenolic compounds (TPC) for the three evaluated temperatures, with a percentage reduction of 65% of anthocyanin degradation at the temperature of 90 °C. The complex synthesized in the present work reduced degradation by approximately 58% of DPPH radicals, 52% of ABTS radicals and 31.8% of iron reduction (FRAP) at temperatures of 90, 110 and 90 °C, respectively.

References

- Nabi, B. G.; Mukhtar, K.; Ahmed, W.; Manzoor, M. F.; Ranjha, M. M. A. N.; Kieliszek, M.; Bhat, Z. F.; Aadil, R. M.; *Food Biosci.* **2023**, *52*, 102403. [Crossref]
- Future Market Insights, <https://www.futuremarketinsights.com/reports/global-natural-food-colours-market>, accessed in January 2024.
- Banerjee, S.; Singh, R.; Singh, V.; *Environ. Technol. Innovation* **2023**, *29*, 102977. [Crossref]
- Alzate-Arbeláez, A. F.; Dorta, E.; López-Alarcón, C.; Cortés, F. B.; Rojano, B. A.; *Food Chem.* **2019**, *294*, 503. [Crossref]
- Ballesteros, L. F.; Ramirez, M. J.; Orrego, C. E.; Teixeira, J. A.; Mussatto, S. I.; *Food Chem.* **2017**, *237*, 623. [Crossref]
- Barbieri, J. B.; Goltz, C.; Cavalheiro, F. B.; Toci, A. T.; Igarashi-Mafra, L.; Mafra, M. R.; *Ind. Crops Prod.* **2020**, *144*, 112049. [Crossref]
- Arend, G. D.; Soares, L. S.; Camelo-Silva, C.; Sanches, M. A. R.; Penha, F. M.; Díaz-De-Cerio, E.; Verardo, V.; Prudencio, E. S.; Segura-Carretero, A.; Tischer, B.; Cunha Petrus, J. C.; Verruck, S.; Rezzadori, K.; *Food Biosci.* **2022**, *50*, 101997. [Crossref]
- Gençdağ, E.; Özdemir, E. E.; Demirci, K.; Görgüç, A.; Yılmaz, F. M.; *Curr. Plant Biol.* **2022**, *29*, 100238. [Crossref]
- de Souza Mesquita, L. M.; Sosa, F. H. B.; Contieri, L. S.; Marques, P. R.; Viganó, J.; Coutinho, J. A. P.; Dias, A. C. R. V.; Ventura, S. P. M.; Rostagno, M. A.; *Food Chem.* **2023**, *406*, 135093. [Crossref]
- Tan, C.; Sun, Y.; Yao, X.; Zhu, Y.; Jafari, S. M.; Sun, B.; Wang, J.; *Food Chem.* **2023**, *416*, 135732. [Crossref]
- Albuquerque, B. R.; Pereira, C.; Calhelha, R. C.; Alves, M. J.; Abreu, R. M. V.; Barros, L.; Oliveira, M. B. P. P.; Ferreira, I. C. F. R.; *Food Chem.* **2020**, *309*, 125735. [Crossref]
- Paludo, M. C.; de Oliveira, S. B. P.; de Oliveira, L. F.; Colombo, R. C.; Gómez-Alonso, S.; Hermosín-Gutiérrez, I.; Prata, R.; Lima, A. F.; Teixeira Filho, J.; Ballus, C. A.; Godoy, H. T.; *Curr. Plant Biol.* **2022**, *29*, 100233. [Crossref]
- Trindade, P. L.; Martins, F. F.; Soares, E. R.; Bernardes, E. M.; Vardiero, F.; Resende, A. C.; Souza-Mello, V.; Daleprane, J. B.; *J. Funct. Foods* **2022**, *97*, 105238. [Crossref]
- da Silva-Maia, J. K.; Nagalingam, A.; Cazarin, C. B. B.; Maróstica Junior, M. R.; Sharma, D.; *Food Chem.: Mol. Sci.* **2023**, *6*, 100167. [Crossref]
- Longo, M. B.; Lamas, C. A.; Rossetto, I. U.; Nogueira-Lima, E.; Collares-Busatto, C. B.; Maróstica Junior, M. R.; Quitete, V. H. A. C.; *Braz. Arch. Biol. Technol.* **2023**, *66*, 1. [Crossref]
- Zhang, Y.; Zhang, Y.; Xu, W.; Wu, H.; Shao, Y.; Han, X.; Zhou, M.; Gu, P.; Li, Z.; *Colloid Interface Sci. Commun.* **2023**, *53*, 100707. [Crossref]
- Debnath, B.; Duarah, P.; Haldar, D.; Purkait, M. K.; *Food Packag. Shelf Life* **2022**, *34*, 100937. [Crossref]
- Bangar, S. P.; Esua, O. J.; Nickhil, C.; Whiteside, W. S.; *Food Packag. Shelf Life* **2023**, *36*, 101048. [Crossref]
- Ren, H.; Xu, Z.; Gao, M.; Xing, X.; Ling, Z.; Pan, L.; Tian, Y.; Zheng, Y.; Fan, W.; Yang, W.; *Int. J. Biol. Macromol.* **2023**, *227*, 827. [Crossref]
- da Silva Neto, J. M.; Oliveira, L. S. C.; de Gusmão, R. P.; Lima, F. S.; Maia, C. E.; *Chem. Eng. Res. Des.* **2023**, *193*, 245. [Crossref]
- Morais, J. P. S.; Rosa, M. F.; Marconcini, J. M.; *Procedimentos para Análise Lignocelulósica*, 1st ed.; Embrapa Algodão: Campina Grande, Brasil, 2010. [Link] accessed in July 2024
- da Silva Neto, J. M.; Oliveira, L. S. C.; da Silva, F. L. H.; Tabosa, J. N.; Pacheco, J. G. A.; da Silva, M. J. V.; *BioResources* **2019**, *14*, 3534. [Crossref]
- Lee, J.; Durst, R. W.; Wrolstad, R. E.; *J. AOAC Int.* **2005**, *88*, 1269. [Crossref]
- Rufino, M. S. M.; Alves, R. E.; de Brito, E. S.; de Morais, S. M.; Sampaio, C. G.; Pérez-Jiménez; Calixto, S.; *Comunicado Técnico 125 - Metodologia Científica: Determinação da Atividade Antioxidante Total em Frutas pelo Método de Redução do Ferro (FRAP)*, 1st ed.; Embrapa Agroindústria Tropical: Fortaleza, Brasil, 2006. [Link] accessed in July 2024
- Rufino, M. S. M.; Alves, R. E.; de Brito, E. S.; de Morais, S. M.; Sampaio, C. G.; Pérez-Jiménez; Calixto, S.; *Comunicado*

- Técnico 128 - Metodologia Científica: Determinação da Atividade Antioxidante Total em Frutas pela Captura do Radical Livre ABTS⁺*, 1st ed.; Embrapa Agroindústria Tropical: Fortaleza, Brasil, 2007. [Link] accessed in July 2024
26. Silveira, A. C.; Kassuia, Y. S.; Domahovski, R. C.; Lazzarotto, M.; *Comunicado Técnico 421 - Método de DPPH Adaptado: Uma Ferramenta para Analisar Atividade Antioxidante de Polpa de Frutos da Erva-Mate de Forma Rápida e Reprodutível*, 1st ed.; Embrapa Florestas: Colombo, Brasil, 2018. [Link] accessed in July 2024
27. Verbeyst, L.; Crombruggen, K.; Van der Plancken, I.; Hendrickx, M.; Van Loey, A.; *J. Food Eng.* **2011**, *105*, 513. [Crossref]
28. Mercali, G. D.; Jaeschke, D. P.; Tessaro, I. C.; Marczak, L. D. F.; *Food Chem.* **2013**, *136*, 853. [Crossref]
29. Mercali, G. D.; Gurak, P. D.; Schmitz, F.; Marczak, L. D. F.; *Food Chem.* **2015**, *171*, 200. [Crossref]
30. *Statistica*, version 7.0; StatSoft Inc., Tulsa, OK, USA, 2008.
31. Rodrigues, M. A. V.; Bertolo, M. R. V.; Marangon, C. A.; Martins, V. C. A.; Plepis, A. M. G.; *Int. J. Biol. Macromol.* **2020**, *160*, 769. [Crossref]
32. Loubet Filho, P. S.; Baseggio, A. M.; Vuolo, M. M.; Reguengo, L. M.; Telles Biasoto, A. C.; Correa, L. C.; Bogusz Jr., S. B.; Cagnon, V. H. A.; Cazarin, C. B. B.; Maróstica Jr., M. R.; *Curr. Res. Food Sci.* **2022**, *5*, 382. [Crossref]
33. Pereira, L. D.; Ascheri, D. P. R.; Bastos, S. M. C.; Ascheri, J. L. R.; Santos, S. C.; *Cienc. Agrotecnol.* **2018**, *42*, 431. [Crossref]
34. de Lima Marsiglia, W. I. M.; Oliveira, L. S. C.; Almeida, R. L. J.; Santos, N. C.; da Silva Neto, J. M.; Santiago, A. M.; de Melo, B. C. A.; da Silva, F. L. H.; *J. Indian Chem. Soc.* **2023**, *100*, 100995. [Crossref]
35. Castañeda-Valbuena, D.; Ayora-Talavera, T.; Luján-Hidalgo, C.; Álvarez-Gutiérrez, P.; Martínez-Galero, N.; Meza-Gordillo, R.; *Food Bioprod. Process.* **2021**, *127*, 212. [Crossref]
36. Jiménez, N.; Bassama, J.; Bohuon, P.; *J. Food Eng.* **2020**, *279*, 109951. [Crossref]
37. Qiu, G.; Wang, D.; Song, X.; Deng, Y.; Zhao, Y.; *Food Res. Int.* **2018**, *105*, 121. [Crossref]
38. Georgieva, V.; Zvezdova, D.; Vlaev, L.; *Chem. Cent. J.* **2012**, *6*, 81. [Crossref]
39. Nascimento, R. P.; Rizzato, J. S.; Polezi, G.; Moya, A. M. T. M.; Silva, M. F.; Machado, A. P. F.; Franchi Jr., G. C.; Borguini, R. G. B.; Santiago, M. C. P. A.; Paiotti, A. P. R.; Pereira, J. A.; Martinez, C. A. R.; Maróstica Jr., M. R.; *Food Biosci.* **2023**, *53*, 102578. [Crossref]

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