ABSTRACT – This work focuses on the kinetic modeling development and estimation of its parameters of blackberry pulps anthocyanin degradation. Experimental data on the isothermal pulp processing are presented at four different temperatures. With this, temperature influence on the anthocyanin degradation was evaluated. A first-order kinetic model was perfectly fitted to the experimental data. The reaction rate constant at each temperature was then determined and adjusted to the Arrhenius equation. The activation energy value was 52.3 kJ mol$^{-1}$, suggesting a strong temperature dependence on the reaction system.

1. INTRODUCTION

Some fruits that have the delicacy and nutritional potential recommended by nutrition experts are red fruits, especially blackberries. The functional properties are important today for the health benefits, and blackberry has high nutritional quality, as they are rich in vitamin C, A, and complex B, fiber, folic acid, contain around 85% water and 10% carbohydrates (Lila, 2004). In addition, they are a source of functional compounds, such as ellagic acid and anthocyanins (Silva et al., 2016). The color of blackberries is due to the presence of anthocyanins, which give the bright red, blue and purple colors to several fruits and vegetables (Summen and Erge, 2014). Eleven anthocyanins in raspberries have been identified (Mullen et al., 2002). Cyanidin-3-sophoroside and cyanidin-3-glucoside are the major anthocyanins found in raspberries (De Ancos et al., 2000).

The demand for natural food colorants is increasing due to concerns over the safety of synthetic food colorants (Jackman et al., 1987; Li et al., 2013). There is a growing interest in using phenolic compounds as natural food colorants, especially anthocyanins (Li et al., 2013; Verbeyst et al., 2011; Wang and Xu, 2007). However, low stability values during processing and storage have hindered the application of anthocyanin colorants. Chemical structure, pH, temperature, light, oxygen, enzyme, co-pigment, metallic ions, sulfur dioxide, and ascorbic acid can affect the stability of anthocyanins (Li et al., 2013).

To analyze the degradation of these components during industrial processing, it is necessary to use mathematical models with experimental validity (Vieira et al., 2015). For this, the kinetic parameters associated with the degradation reaction must be available, which are the activation energy and the frequency factor that is associated with the effect of temperature on the system.
Therefore, the purpose of this paper is to provide details of the determination of all kinetic parameters associated with the degradation of anthocyanins in blackberry pulps. Thus, this work will be a basis for future research related to the industrial processing and shelf-life.

2. MATERIALS AND METHODS

Blackberries were obtained from the region of the south of Minas Gerais – Brazil, and it was squeezed to form a considerable amount of juice immediately before heating. Heating was made in four different experimental temperatures, and in each one there was collected a small sample, in a determined period of time, in order to quantify the total content of anthocyanin by UV-Vis spectroscopy using the pH differential method proposed by Lee et al. (2005). Figure 1 provides an illustrative diagram to summarize the materials and method used in this present research.

A first-order model (Equation 1) was considered based on literature works dealing with bio compounds degradation kinetics, such as ascorbic acid and total anthocyanin (Silva et al., 2016; Vieira et al., 2015).

\[ C_A = C_{A0}e^{-kt} \]  

(1)

Where \( C_A \) expresses the total anthocyanins concentration (\( \text{mg} \ \text{L}^{-1} \)) at any time \( t \), \( C_{A0} \) is the initial concentration of anthocyanins, and \( k \) is the degradation rate constant that depends on temperature according the Arrhenius law (Equation 2).

\[ k = k_0e^{-E_a/RT} \]  

(2)

with \( k_0 \) as the pre-exponential factor (\( \text{h}^{-1} \)), \( E_a \) as the activation energy (\( \text{J} \ \text{mol}^{-1} \)), and \( R \) as the gas constant (8.314 J \( \text{mol}^{-1} \ \text{K}^{-1} \)). All kinetic parameters were estimated using the EXCEL® exponential adjustment for the first-order model considered in this work. The model reproducibility was confirmed by a visual inspection of the parity and residual plot.

3. RESULTS AND DISCUSSION

Figure 2 (A) shows an exponential evolution of \( C_A \) for the experimental data, and also the exponential first-order kinetics adjustment, suggesting this model can be used to represent the process by simulation. The anthocyanin contents of blackberry pulp decreased from increasing heating temperature and time. This finding was in agreement with those reported in previous
studies with another kind of fruits (Summen and Erge, 2014).

![Figure 2](image1.png)

**Figure 2** – (A) First-order kinetics of anthocyanin thermal degradation in blackberry pulp at four different temperatures, ♦ (60 ºC), ■ (70 ºC), ▲ (80 ºC) and × (90 ºC): experimental points of anthocyanin concentration (mg L⁻¹) as a function of time expressed in minutes and the adjusted exponential models as continuous lines. (B) kinetic rate constant as a function of temperature inverse with the Arrhenius’ exponential adjustment.

It is well-known that anthocyanin degradation is due to enzymatic reactions, non-enzymatic oxidation reactions and condensation reactions with other compounds such as ascorbic acid. Anthocyanins enzymatic degradation could be present because pasteurization step was not applied previously. In the non-enzymatic oxidation reactions, oxygen can either react with anthocyanins through a direct oxidative mechanism and/or it can oxidize other compounds which can react with anthocyanins and form colorless compounds (Buvé et al., 2018). The results of this present work do not provide sufficient information to be conclusive on the type of pathway that contributed to most of the anthocyanin degradation. However, considering the high degradation achieved, it is possible that both mechanisms are influencing together.

Figure 2 (B) provides the kinetic rate constant as a function of the inverse of temperature in order to identify the Arrhenius’ parameters (k₀) and activation energy (Eₐ). Using the EXCEL® exponential adjustment, its possible to obtain the Arrhenius’ parameters: k₀ = 3.05×10⁵ min⁻¹ and Eₐ = 52.3 kJ mol⁻¹, with a determination coefficient (R²) equals 0.9872. High activation energy implies that anthocyanins are more susceptible to degradation by exposure to elevated temperatures. The activation energy for the degradation of anthocyanins during heating at 60-90 ºC was reported as 21.6 kJ mol⁻¹ for wild strawberry (Özşen and Erge, 2012), 68 kJ mol⁻¹ for acerola pulp (Silva et al., 2016). Therefore, our finds are in agreement with what has been reported in the literature. Factors that could contribute to the wide distribution of kinetic parameters include of course intrinsic characteristics of the product such as variety and maturity, pH, and probably dissolved oxygen levels (Dhuique-Mayer et al., 2007).

**4. CONCLUSION**

The aim of this work was to find the kinetic parameters for anthocyanin thermal degradation in blackberry juice. Experimental data were fitted in a first-order kinetic model. The activation energy obtained was 52.3 kJ mol⁻¹, suggesting a strong temperature dependency. High
processing temperatures can damage anthocyanin in a long time. Considering that processing such as pasteurization of juice and pulp has a short time, it is possible to conclude by analyzing the model and experiments that this component does not suffer high degradation. Therefore, time is the most important variable to quantify degradation. In addition, in the near future, it would be interesting to carry out acceptability tests to determine shelf-life of blackberry juice. This will allow the integration of sensory and analytical data, becoming the next step of a science-based approach to shelf-life estimation being related to the process kinetic parameters.

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