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FULL PAPER

Kinetic of polyphenol losses during convection drying of cashew (*Anacardium occidentale L.*) apples

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Abstract

Lowering manufacturing costs and utilization of by-products are urgent requirements to improve the competitiveness of Vietnamese cashew nuts in the world market. Heat treatment strategies such as drying are common techniques to process waste sources into a food source. The degradation of polyphenol, vitamin C, and tannins in the process represent a major obstacle in maintaining the nutritional quality of cashew pulp as well as in de-acridization of raw materials. This work firstly attempted to determine the optimal convection drying conditions that gave the highest nutritional quality contents in cashew apples. Then, the polyphenol degradation kinetic of cashew apple material during the drying process was examined in zero-order and first-order kinetic models. The results suggested the best contents of polyphenol, vitamin C and tannin could be attained at the drying process at 55°C for 275 mins. In addition, the first-order kinetic model was used to describe the decomposition of polyphenols during the drying process and the equation to predict the residual polyphenol content in cashew apple was formed to optimize the process. Research parameters provide a database for the following processing processes in the production of cashew-derived food products.

1. Introduction

Cashew (*Anacardium occidentale* Linn.) is a nut tree native to Brazil-South America and has been cultivated worldwide for timber and fruits. The cashew nut contains nutrients that have been proven to be greatly beneficial for human health and could be easily processed into consumption-ready products, thus garnering growing consumer interest for diversified cashew-derived products in the global market.

The false fruit of cashew, commonly known as cashew apple, accounts for a large portion, around 85 to 90%, of the fruit but is often separated from cashew kernels and discarded after harvesting. Previous reports have indicated that the cashew apple is an easily digestible food that is rich in minerals and vitamins such as C, B1, B2, PP and carotene. In particular, the vitamin C content in the cashew apple is 5–6 times higher than that of lemon and around 7–8 times more than tangerines, pomelo, and many times more than bananas (MacLeod and de Troconis, 1982; Costa *et al.*, 2009; de Abreu *et al.*, 2013). However, the main drawback of the cashew apple is that the fruit contains an exceptionally large quantity of tannin, causing an acrid taste, tightening the palate of the apple when being processed into other products. This urges for the development of manufacturing processes that utilize the by-product cashew into other food products such as juices, wine, cashew vinegar and jam (Lavinas *et al.*, 2006).

Thermal technologies have been gaining currency recently due to their capability in altering the nutritional composition of various vegetables, fruits, and medicinal materials such as soursop jelly (Tran *et al.*, 2020), broccoli (Zhang and Hamauzu, 2004), asparagus (Sultana *et al.*, 2008), potato and carrot (Faller and Fialho, 2009) and *Condonopsis javanica* root (Pham *et*

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al., 2020). In addition, heat treatment is also able to change the materials morphologically, thus contributing to the extension of product shelf life and component preservation. However, since heating could bring about both beneficial and detrimental effects on the materials, it is essential to study the drying kinetics of desired materials to minimize nutrient loss and to determine optimal processing parameters for improving existing processing techniques. In this regard, numerous kinetic studies have been conducted on many food plant materials. Kyi *et al.* (2005) determined the reaction kinetics of polyphenol oxidation in cocoa beans during air drying at different temperatures and humidity. Results of process simulation revealed that the polyphenol oxidation rate was constant in different air conditions. The obtained activation energy of polyphenol oxidation reactions is in the range 27800-30312 $J.k^{-1}.mol^{-1}$. Reaction kinetics are consistent with the first-order hypothetical reaction. Teh *et al.* (2016) investigated the drying kinetics and polyphenol degradation during hot air drying and sun drying of cocoa beans. Polyphenol degradation kinetic results show that the process obeys the first order, this kinetic model is used to predict the decomposition process with the rate constant ranging from 0.011/h to 0.052/h. Reactions in food are usually assessed against zero-order and first-order kinetic models. Zero-order kinetics modelling refers to the Maillard (nonenzymatic browning) reaction, which implies that the concentration of the brown pigment products is negligible compared with the concentration of reactants present (Franzen *et al.*, 1990). The first-order kinetic models are evaluated based on polyphenol degradation and refer to the oxidation of polyphenols to o-Quinone, also described as the browning reaction (Tin *et al.*, 2005).

Given the highlighted role of polyphenols in food products and the urgent need to valorize cashew materials in food applications, we thereby attempted to investigate the polyphenol degradation kinetic of cashew apple material during the drying process. We first subject the materials to convection drying in a lab-scale instrument to optimize the drying parameters with respect to various quality indicators of cashew apple (i.e., vitamin C, tannin, and polyphenol contents). Subsequently, the degradation polyphenols in zero-order and first-order kinetic were modelled. The results are expected to aid in improvements in cashew drying processes and contribute to food waste reduction.

2. Materials and methods

2.1 Plant materials

Cashew apples after being selected and harvested in Binh Phuoc province, Vietnam (Coordinates 11°45′N 106°55′E, March 2020) were transported to the laboratory. The experimental cashew fruit has a uniform red-yellow colour (about 8 weeks from the time the fruit begins to form), succulent, smooth skin, sour, sweet, acrid, and characteristic aroma. Only fruits that are non-damaged and unspoiled were used. The time from harvesting to processing does not exceed 24 hours under normal conditions (32°C).

The experiment was conducted at the experimental area NTT Institute of High Technology, Nguyen Tat Thanh University, campus 331 Highway 1A, An Phu Dong Ward, District 12, HCMC, Vietnam.

2.2 Drying equipment

The drying instrument was an oven with hot airflow with a maximum temperature of 70°C directly contacted with the material surface. A support blower was employed to blow out moisture at 60 Hz frequency. The oven was designed with flexible adjustment and equipped with an auto heat sensor and 12 drying trays (40×30 cm) with a mesh hole of 1 cm in diameter (Figure 1).

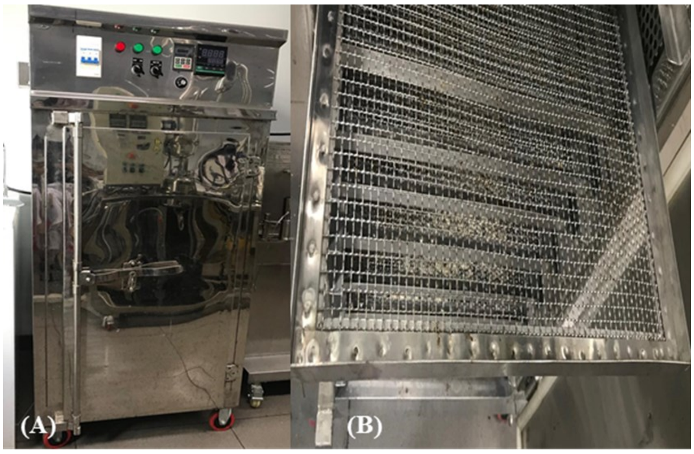

Figure 1. Convection oven (A), and drying tray (B).

2.3 Cashew apple processing

Cashew fruit, after being harvested, is separated from seeds and the cashew apples were classified. Damaged fruit is removed and used raw materials had an average height of 2 cm and fruit diameter of 1 cm with light yellow colour and tight skin. The apples were washed with salt solution (concentration 1% w/v) and then sliced vertically with a slice thickness of 1-1.5mm to prepare for the drying process (Figure 2). The drying process parameters were set according to the experimental layout such as size (cut vertically and horizontally), temperature (50-65°C) and drying time. Cashew slices are spread on the drying tray (hole size of 1 cm), dried to constant weight according to each experiment and then assessed for nutritional qualities afterwards.

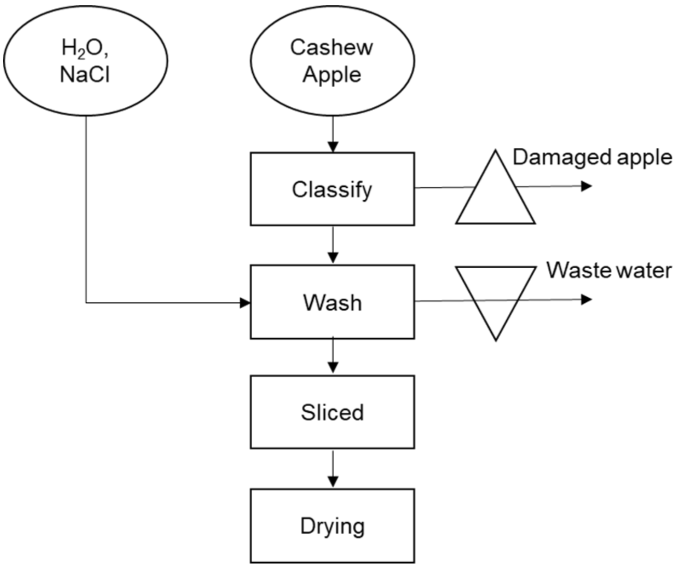

Figure 2. Cashew apple drying process

2.4 Moisture content

Moisture content was determined by drying to constant weight. First, 0.5 g of the sample was dried at 105°C for about 50 mins. Then the sample was weighed again after cooling. The moisture content was determined as follows.

$$W(\%) = \frac{M_1 - M_2}{M_1} \times 100$$

Where M_1 = mass of sample before drying, g and M_2 = mass of sample after drying, g,

2.5 Determination of ascorbic acicid

The ascorbic acid content was determined according to the method of AOAC 967.21 which was previously described by Puwastien *et al.* (2011) and Dao *et al.* (2021). The principle of the method bases on the oxidation of ascorbic acid into dehydroascorbic acid and colourless lenco derivatives using 2,6 dichlorophenolindophenol (DCPIP). When the excess DCPIP (one excess drop in blue) reacts with the lenco derivative, the colour of the solution turns pink. First, 1 g of the sample was ground and extracted using distilled water. The extracted solution was added with distilled water to 100 mL. Then, 10 mL of the solution was added with 1 mL HCl 0.04 N in a flask. The flask was then titrated with 2, 6-dichlorophenolindophenol (DCPIP) until the solution changes into a pink colour that lasts for 30 s. The standard solution was prepared by titrating 1 mL HCl in 10 mL of standard solution (pure L-ascorbic acid and distilled water 1:10 w/v) using DCPIP.

Total Ascorbic Acid content (TAA) by dry material is calculated as follows:

$$TAA\left(\frac{mg}{g}\,dry\,material\right) = \frac{\{(V_1 - 0.05) \times V_2 \times 10 \times m_1 \times df\} \times m_2}{10 \times m_2 \times (V_3 - 0.05) \times m_3}$$

Where V_1 = the average DCPIP volume of the sample, mL, V_2 = the volume of the container of the extracted sample, mL, m_1 = the standard mass of ascorbic acid, g, df = the sample dilution factor, V_3 = the DCPIP volume of ascorbic acid standard, mL and m_3 = the sample mass according to the dry concentration, g

2.6 Determination of tannin content

The tannin content was determined by the Lowenthal method which was previously described by Dao *et al.* (2021). First, cashew apples were pressed at room temperature (30°C) to afford the extract. Then, 10 mL of the extract was transferred into a 250 mL flask, followed by the addition of 1 mL of indigo-carmine indicator and 100 mL of distilled water. The flask was titrated using $KMnO_4$ 0.1N until the colour of the flask changes to yellow.

2.7 Total polyphenol content

The total polyphenol content was determined according to the Folin – Ciocalteu colourimetric principle described previously (Zorić *et al.*, 2014; Tran *et al.*, 2020). First, five similar cashew apples were pureed and then 1g of the sample was taken for triple extraction. The extract was then filtered using Whatman No.1 filter paper, followed by the addition of water to 100 mL. Then 1 mL of extract was taken and added with 1 mL of Folin-Ciocalteu solution. After 5 mins, 1 mL of 20% Na_2CO_3 was added and mixed well with the solution. The solution was incubated in the dark for 1 hr and then spectrometrically measured at a wavelength of 765 nm. The total polyphenol content was expressed as mg gallic acid/g dry mass.

Total polyphenol content (TPC) by dry material is calculated as follows:

$$TPC\left(\frac{mg}{g}\,dry\,material\right) = \frac{V_1 \times df \times C_1 \times 0.1 \times V_2}{V_3 \times (100 - h)}$$

Where V_1 = the volume of the cuvet, mL, V_2 = the volume of the container of the extracted sample, mL, V_3 = extract volume of fresh sample, mL, C_1 = polyphenol concentration measured from UV-vis, µg/mL and h = the moisture in the sample, %

2.8 Polyphenol degradation kinetics

The use of different kinetic models is also widely used to predict the nutrient changes of fruits and vegetables during the drying process. The kinetics of nutrient changes in fruits and vegetables are commonly found in terms of the zero-order and first-order reaction, as follows:

The zero-order kinetic model:

$$\frac{-dC_A}{dt} = k$$

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The first-order kinetic model:

$$\frac{-dC_A}{dt} = k.C_A$$

Where C_A = nutrient concentration A at any moment t, and k = reaction rate constant

2.9 Data analysis

Each analytical experiment was repeated 3 times. Data were processed by Microsoft Excel software to calculate total polyphenol content for each different drying mode. The data is kinetically processed using Origin 9 software. The software is also used to plot the correlation of process parameters.

3. Results and discussion

3.1 The influence of the size of raw materials on the quality of the dried cashew apple

Size of raw material is the factor affecting the drying process, as well as the retention of polyphenol, vitamin C and tannin content in cashew apple. Experiment results on the above factors with respect to material size are presented in Figure 3. The results showed that there were significant changes in polyphenol, vitamin C and tannin content when the material size was changed during the drying process. Dried horizontally cut cashews apple retained 7.33% of polyphenols whereas the figure for the vertically cut cashew apple was 41.73%. As for vitamin C content, the retention ratio for horizontally cut and vertically cut apple was 12.09% and 20.04%, respectively. Regarding tannin content, vertically cut apples showed a higher retention rate of 61.92%, higher than that of horizontally cut samples, at 43.57%. This might be explained by the fact that the large size reduces the surface contact area between the material, thereby reducing the efficiency of the extraction process. In addition, cashews cut vertically during the process exhibited better permeability and better nutritional retention. Therefore, the vertical cut size was selected for the next experiment arrangement.

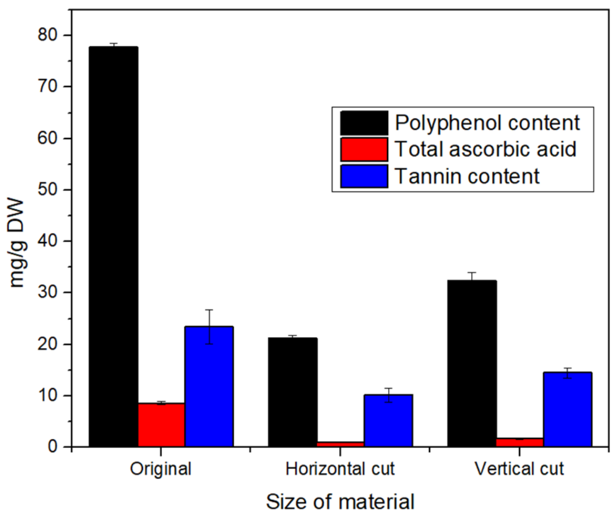

Figure 2. Cashew apple drying process

3.2 The influence of temperature and drying time on the quality of the dried cashew apple

Temperature and time are the two main factors that influence the process efficiency, cost, and quality of the product. The impact of other drying processes on the content of polyphenol compounds, vitamin C and tannin are shown in Figure 4. In the range of 50-65°C elevated drying temperature was found to be associated with a quicker drying process. However, the content of polyphenols, vitamin C, and tannin was largely lost. These compounds are easily oxidized when subjected to prolonged and high heat. The moisture and nutritional content of the sample also decreased due to the escape of water into the environment under exposure to hot air flows.

When increasing the drying time to 360 mins (at 50°C), the retention ratio was 35% for total polyphenols, 4% for vitamin C, 46% for the tannin content. The different effects of the drying methods on the loss or retention of phenolic substances in cashew slices can be attributed to the different stability of the different phenolic compounds against the drying conditions. However, there is a significant loss of vitamin C, Vitamin C loss during heat processing has been reported by El-Ishaq and Obirinakem (2015) and Johnson *et al.* (2013). Oxidation of ascorbic acid under high-temperature conditions and the depletion of ascorbic acid due to its use in the protection of polyphenol oxidation are major causes of vitamin C depletion (Toor and Savage, 2006).

Based on the variation of the compounds over time from Figure 4, it is found that a temperature of 55°C for 275 mins is the minimum time required (<10% humidity) and maximum retention of compounds Total polyphenols, vitamin C and tannins will simultaneously reduce the drying time of the process as well as reduce process energy costs.

3.3 Polyphenol degradation kinetics

Kinetic modelling was carried out to determine the mechanism and predict the degradation level of polyphenols at any given drying temperature and time. The kinetic was presented at 4 different temperature levels ranging from 50 to 65°C. Total polyphenol content was determined after 15 mins of drying corresponding to each drying mode. Experimental data on the decomposition of polyphenols were fitted to the zero- and first-order models. The nonlinear form of equations 2-3 with the drying time was used to verify the kinetic models and proposed polyphenol degradation mechanism (Figures 5-6).

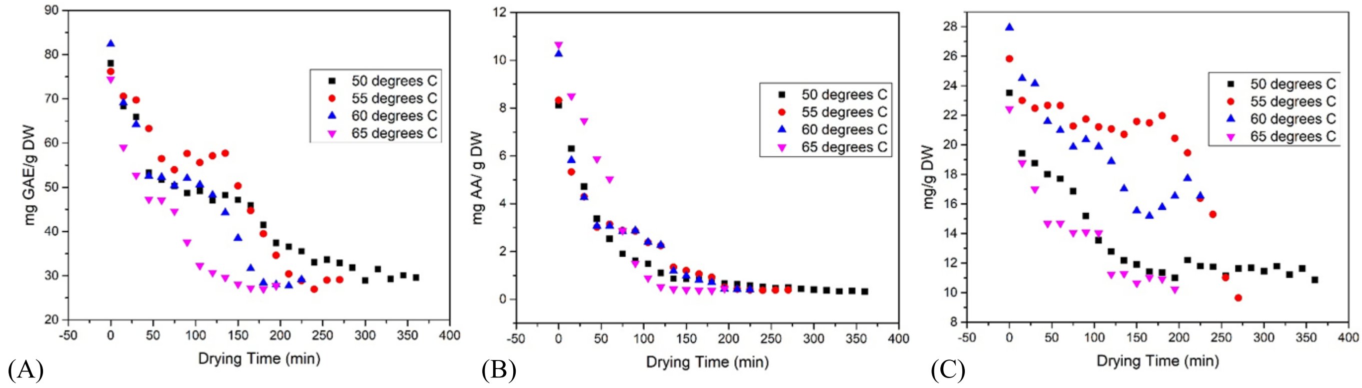

Figure 4. Diagram showing the changes in total polyphenol (A), vitamin C (B), tannin (C) content under different drying conditions.

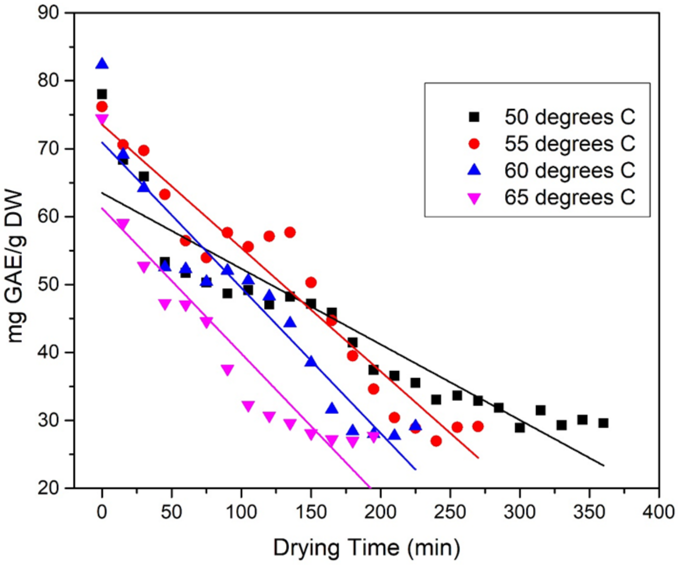

Figure 5. The zero-order kinetic model of total polyphenols at different drying temperatures

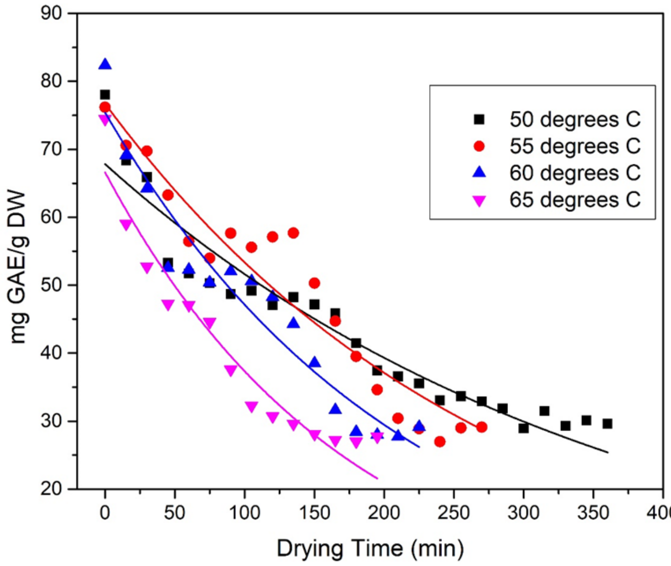

Figure 6. The first order kinetic model of total polyphenols at different drying temperatures.

Experimental results indicated that the polyphenol degradation was in accordance with the first order kinetic with the correlation coefficient R^2 varying from 0.9122 to 0.9035 depending on the temperature level. Low oscillation and a high mean of all R^2 values suggest that the data obtained from the experiment is compatible with the first-order model shown in Figure 6.

The first model of polyphenol degradation reaction has the following form:

$$\frac{-dC_A}{dt} = k.C_A$$

$$C_t = C_0 \times e^{-k\times t} \quad C_t = C_0 \times e^{-k\times t}$$

Figure 6 depicts the first-order reaction estimated with experimental data. Corresponding to each model at a specific drying condition, one first-order polyphenol decomposition constant and on descriptive coefficient could be inferred. These results are summarized and presented in Table 1.

The phenolic compound is known as an antioxidant and is susceptible to decomposition under light and temperature conditions. Therefore, heat is one of the factors that directly affect the decomposition of phenolic compounds. As in the study where blanching conditions were investigated with respect to total polyphenol content in carrots (Gonçalves *et al.*, 2010), it is revealed that when blanching temperature increases, polyphenol content total saw a sharp reduction. On the other hand, another study investigating the pasteurization and sterilization process of pineapple juice by Zheng and Lu (2011) also showed similar results that the pasteurization temperature increased, along with an increase in storage time caused reduction in the total polyphenol content.

Table 1 shows the different degradation coefficients of total polyphenols in different temperature levels. When the temperature changes from 50 to 65°C, the decomposition of polyphenols increases, evidenced by the higher k at 0.0057 (min^{-1}). The cause of the decomposition of polyphenols could be attributable to a greater escape rate of moisture when the drying temperature is high, leading to aggravated nutrient and total polyphenol loss. The phenomenon in which the reaction rate constant was increased is consistent with the results of Lien (2014) reporting that drying of germinated soybeans at 40, 50 and 60°C corresponded

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with a rising reaction rate constant from 0.048 to 0.104 h^{-1}. Alean *et al.* (2016) also showed that the polyphenol content of dried cocoa beans decreased when the drying temperature increased from 40 to 60°C. Similarly, Vega-Gálvez *et al.* (2012) reported that rising drying temperature from 40 to 80°C caused polyphenols of apple materials to decrease.

Table 1. Total polyphenol degradation kinetic parameters.

Model	Drying temperature (°C)	k_1 (min^{-1})	C_0	R^2
Zero-order	50	0.1114	63.477	0.86416
	55	0.1816	73.550	0.93020
	60	0.2139	70.922	0.90032
	65	0.2136	61.228	0.84770
First-order	50	0.0027	67.827	0.91852
	55	0.0036	76.721	0.91220
	60	0.0047	75.405	0.92596
	65	0.0057	66.597	0.93050

Increased heat production in the product increases total polyphenol degradation. The results showed that the total polyphenol content lost 26% after 45 mins of heating, suggesting a high level of decomposition of polyphenols. The prediction equation for the remaining polyphenol content in the raw material is shown as follows:

$$\frac{C_t}{C_0} = e^{-0.0036t}$$

Where C_t = polyphenol content at any time t, C_0 = Initial concentration of total polyphenols contained in cashew apple and t = time for drying.

4. Conclusion

The results of this study show that the drying condition at 55 °C for 275 mins maintained the maximum nutritional content. The first-order kinetic model was consistent with the experimental data from the drying process of total polyphenols. In addition, the study also determined a model to predict the content of total polyphenol remaining during the drying process of the cashew apple.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

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