HISTORY OF MANUSCRIPT PUBLICATION

JOURNAL OF FUNCTIONAL FOOD AND NUTRACEUTICAL (SINTA 3)

Title:

Drying and Degradation Kinetics of the Physicochemical Characteristics of Parijoto Fruit (Medinilla speciosa) with Calcium Chloride Pre-Treatment

Authors:

Novita I. Putri, Jelle Van Audenhove, Clare Kyomugasho, Ann Van Loey, Marc Hendrickx

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3. Author Response
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6. Accepted Confirmation
7. Final Article

I. Submission to JFFN

Outlook

[jffn] Submission Acknowledgement - Manuscript 165

From Dr. Maria D.P.T. Gunawan Puteri <no-reply@sgu.ac.id>
Date Sat 13/07/2024 20:48
To Novita Ika Putri <novitaika@unika.ac.id>

Dear Novita Ika Putri,

Your manuscript entitled "DRYING AND DEGRADATION KINETICS OF THE PHYSICOCHEMICAL CHARACTERISTICS OF PARIJOTO FRUIT (MEDINILLA SPECIOSA) WITH CALCIUM CHLORIDE PRE-TREATMENT" has been successfully submitted online and is presently being given full consideration for publication in Journal of Functional Food and Nutraceutical

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Please mention the above manuscript ID in all future correspondence or when calling the office for questions.
You can also view the status of your manuscript at any time by checking your Author Center after logging in to: https://journal.sgu.ac.id/jffn/index.php/jffn/authorDashboard/submission/165

Thank you for submitting your manuscript to Journal of Functional Food and Nutraceutical.

Dr. Maria D.P.T. Gunawan Puteri

Editorial Office Journal of Functional Food and Nutraceutical (JFFN)

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Website: **https://journal.sgu.ac.id/jffn**

II. Submissions Needing Revision

Notifications

[jffn] Editor Decision

2024-09-02 06:19 AM

Dear Novita Ika Putri, Bernardus David Lai, Gelbert Jethro Sanyoto, Victoria Kristina Ananingsih,

Your manuscript has been assessed by our reviewers. They have raised a number of points which we believe would improve the manuscript and may allow a revised version to be published in JFFN. We have reached a decision regarding your submission to Journal of Functional Food and Nutraceutical, "DRYING AND DEGRADATION KINETICS OF THE PHYSICOCHEMICAL CHARACTERISTICS OF PARIJOTO FRUIT (MEDINILLA SPECIOSA) WITH CALCIUM CHLORIDE PRE-TREATMENT".

Our decision is: **Revisions Required**

You can make revisions and answers of each reviewer comment in a separate paper. You can agree or disagree with what a reviewer comments and please make highlight by colour text in the manuscript. Once the revised manuscript is prepared including the author responses form, you can upload it and submit it through our system.

Download author responses form:
https://drive.google.com/file/d/1k22zBVUIPPQ112UaqYoRD3aus2w9FDqb/view?usp=sharing

Please send back the article within **5 (five) working days** time after you receive this email through our journal system.

If you do not have your username and password for the journal's web site, you can use this **link** to reset your password (which will then be emailed to you along with your username).

Once again, thank you for submitting your manuscript to JFFN and I look forward to receiving your revision.

Best regards,
Della Rahmawati
Department of Food Technology, Faculty of Life Sciences & Technology, Swiss German University, Tangerang, 15143, Indonesia

III. Author Response

Dear Editor and Reviewers,

We would like to thank you for the comments and inputs on our manuscript. We highly appreciate the remarks and suggestions which we believe will improve the quality of this manuscript.

Each comment has been carefully considered and the manuscript has been revised accordingly. Please find below our reply for the comments from the reviewers. Authors' responses can be found under the comment written in red. Changes made in the paper will be indicated by the Track Changes function in Ms. Word. Comments given in the word file of the manuscript are replied in the word file. The comments from Reviewer B (written in pdf file) has been added to the word file as well.

We did not find a template for Author response form. We also did not find any requirement or template on how to submit the revised manuscript. Therefore, we are hoping that this Ms. Word file is sufficient. Please let us know if a certain format needs to be followed.

We would like to thank you for reconsidering our manuscript and we are looking forward to your response.

Yours sincerely,

On behalf of all authors

Dr. Novita Ika Putri, MS

Reviewer A:
Recommendation: Accept Submission

Insight aspirations

National

Originality of work

High

Originality of work (comment)

Mengangkat Pangan lokal "parijoto" mengandung antioksidan alami sebagai pangan fungsional.

The meaning of contribution to the advancement of science

Very Obvious

The meaning of contribution to the advancement of science (comments)

kinetika kerusakan komponen aktif selama proses pengeringan "parojoto" penting dalam pengembangannya sebagai pangan fungsional

Analysis and synthesis

Sufficient

Analysis and synthesis (comment) 08998904545

Telah dijelaskan mekanisme stabilitas dan degradasi antioksidannya dengan baik, kecuali warna.
Namun model kinetika yang digunakan belum dicantumkan.
Kajian ini juga perlu merekomendasikan suhu pengeringan yang optimal untuk "parijoto" berdasarkan parameter yang dianalisis.
File naskah terlampir.

Author's response :

- All the kinetic models used have been described in the methodology section. Degradation kinetic using the first order kinetic is described in Equation 4. The drying kinetic models are described in Table 1.
- Optimum drying temperature has been explained in the discussion, conclusion and abstract section.

Conclusion

Sufficient

Conclusion (comment)

suhu pengeringan yang optimal untuk "parijoto" dan model kinetika perlu ditambahkan

Authors' response :

- Optimum drying temperature has been explained in the discussion, conclusion and abstract section.

Effectiveness of article titles

Straightforward and informative

Effectiveness of article titles (comment)

-

Abstract

Abstracts are not clear and concise

Authors' response :

- Abstract has been modified to hopefully become clearer and more concise

Abstract (comment)

suhu pengeringan yang optimal untuk "parijoto" dan model kinetika perlu ditambahkan.

Authors' response :

- Optimum drying temperature has been explained in the discussion, conclusion and abstract section.

Keywords

The keywords are existed, consistent and reflect important concepts in the article

Keywords (comment)

-

Use of supporting instruments (tables, graphs, images)

Less informative or less complementary

Use of supporting instruments (tables, graphs, images) (comment)

Terkait keterangan Tabel dan Gambar dapat dilihat pada file naskah terlampir.

Authors response :

- Additional information on the caption of table and graph has been added in the revised manuscript

Use of terms and language

Good terms and language

Use of terms and language (comment)

-

General comments

Kajian yang menarik untuk dikembangkan sebagai data dasar pengembangan pangan fungsional dari "parijoto"

Reviewer B:
Recommendation: Revisions Required

Insight aspirations

Local

Originality of work

Enough

Originality of work (comment)

The meaning of contribution to the advancement of science

Very Obvious

The meaning of contribution to the advancement of science (comments)

Prolonging the anthocyanin activities of Parijoto fruit allows the fruit to be used as a functional ingredient.

Authors' response :

- Thank you very much for the input. It has been added to the discussion section of the manuscript.

Analysis and synthesis

Good

Analysis and synthesis (comment)

The author provided sufficient data and analysis. Some statistical terms need to be explained further. Additionally, some conclusions need to consider the results of statistical analysis.

Authors' response :

- The physical meaning of the coefficient obtained from the modelling has been explained further. Most of the conclusions were drawn from the model fitting process, more specifically by comparing the coefficient obtained, which could be considered as statistical analysis. The authors feel that solid conclusions could be drawn about the physical meaning of these coefficients for the drying process of *parijoto* fruits since many studies have shown the validity of these coefficients to describe the kinetics of drying and degradation.

Conclusion

Good

Conclusion (comment)

Effectiveness of article titles

Straightforward and informative

Effectiveness of article titles (comment)

Abstract

Clear and concise abstract

Abstract (comment)

Keywords

The keywords are existed, consistent and reflect important concepts in the article

Keywords (comment)

Use of supporting instruments (tables, graphs, images)

Less informative or less complementary

Use of supporting instruments (tables, graphs, images) (comment)

Most of the figures and tables are clear. More explanation is required about the colour analysis method and results.

Authors' response :

- Colour analysis method has been modified to be clearer.
- More interpretation of the colour analysis has been added to the discussion section.

Use of terms and language

Good terms and language

Use of terms and language (comment)

Overall, the manuscript is easy to read and uses proper English. Be careful with some typos, use of articles (a, an, the) and formatting (e.g. subscript).

Authors' response :

- Misspelling, formatting mistakes and improper use of articles has been minimized.

General comments

The paper explains the effect of CaCl2 pretreatment on the degradation of antioxidant activities and anthocyanin content of Paritojo fruit dried at different temperatures (60, 70, and 80 C). The author has shown the results in sequential order, and has clearly explained the possible mechanism of CaCl2 in preserving anthocyanin and assisting the drying process However, there are some notes:
1) The equipment used (Heto PowerDry LL1500) was a freeze dryer. Please explain how you dried the fruits at 60, 70, and 80 C.
2) Please make Figure 4-6 (L,a,b results) clearer
3) Other notes in the file

Authors' response :

1). We apologize for the confusion. The cabinet drier used is Binder ED 115. The manuscript has been revised. Thank you for the correction

2). In order to make Figure 4-6 clearer, the graph is separated into 2, based on the pre-treatment.

3) Other notes have been addressed

IV. Revised Manuscript A

Drying and Degradation Kinetics of the Physicochemical Characteristics of Parijoto Fruit (*Medinilla speciosa*) with Calcium Chloride Pre-Treatment

ABSTRACT

Parijoto (*Medinilla speciosa*) is an Indonesian local plant with high levels of bioactive compounds crucial in improving overall health. However, these bioactive compounds are susceptible to high temperatures from prolonged heating processes and environmental factors such as oxygen, light, and pH. Therefore, a significant decline in the *parijoto* fruit quality may occur during drying, which prompts a need for a solution to prevent damage to the bioactive compounds in the fruits. As a food additive, calcium chloride ($CaCl_2$) can help maintain cell wall strength and prevent damage from enzymatic, mechanical, and microbial activities in food products. The study aimed to investigate the impact of soaking with $CaCl_2$ (10 min) and drying temperatures (60, 70, and 80ºC) for 8 hours on physicochemical characteristics such as antioxidant activity, total anthocyanin content, and colour. The moisture ratio, colour intensity, antioxidant activity and total anthocyanin content at hourly intervals during drying were measured. The results indicated that soaking in $CaCl_2$ can lead to osmotic dehydration, accelerating the drying rates and preserving the anthocyanin content. The kinetics of the degradation of anthocyanins and antioxidant activity were established, as well as the drying kinetic model for *parijoto* fruits. The Page model was found to be the most relevant and suitable drying kinetics model based on the drying design in this study compared to the other two models.

Keywords: *Parijoto* fruit; Degradation kinetic, Drying kinetic, Calcium chloride

Kinetika Pengeringan dan Degradasi Karakteristik Fisikokimiawi Pada Buah Parijoto (Medinilla speciosa) dengan Pra-Perlakuan Kaslium Klorida

ABSTRAK

Parijoto (*Medinilla speciosa*) adalah tanaman lokal Indonesia yang mengandung senyawa bioaktif tinggi yang penting untuk meningkatkan kesehatan secara keseluruhan. Namun, senyawa bioaktif ini rentan terhadap suhu tinggi dari proses pemanasan yang panjang dan faktor lingkungan seperti oksigen, cahaya, dan pH. Oleh karena itu, penurunan kualitas buah parijoto yang signifikan dapat terjadi selama pengeringan, sehingga diperlukan solusi untuk mencegah kerusakan pada senyawa bioaktif di buah tersebut. Sebagai bahan tambahan makanan, kalsium klorida ($CaCl_2$) dapat membantu menjaga kekuatan dinding sel dan mencegah kerusakan akibat aktivitas enzimatik dan mikroba pada produk pangan. Penelitian ini bertujuan untuk menginvestigasi dampak perendaman dengan $CaCl_2$ (10 menit) dan suhu pengeringan (60, 70, dan 80ºC) selama 8 jam terhadap karakteristik fisiko-kimia seperti aktivitas antioksidan, total kandungan antosianin, dan warna. Perbandingan rasio kadar air, intensitas warna, aktivitas antioksidan, dan kandungan total antosianin diuji setiap jam selama proses pengeringan. Hasil penelitian menunjukkan bahwa perendaman dalam $CaCl_2$ dapat menyebabkan dehidrasi osmotic sehingga mempercepat laju pengeringan, dan menjaga kandungan antosianin. Pada studi ini, dilakukan pula pemodelan kinetika degradasi antosianin dan aktivitas antioksidan, serta model kinetika pengeringan untuk

Commented [A1]: Pada suhu pengeringan mana yang optimal untuk mengeringkan parijoto, berdasarkan karakteristik fisikokiminya?

buah parijoto. Model Page terbukti menjadi model kinetika pengeringan yang paling relevan dan sesuai berdasarkan desain pengeringan dalam studi ini.

Kata kunci: Buah parijoto; Kinetika degradasi, Kinetika pengeringan, Kalsium klorida

Commented [A2]: Kinetika degradasi antosianin dan aktivitas antioksidan berdasarkan nilai k dan Ea. Perlu ditampilkan datanya dalam abstrak, demikian pula dengan ordo reaksinya?

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INTRODUCTION

Parijoto (*Medinilla speciosa*) is a local Indonesian plant that grows, often uncultivated, in Kudus, Central Java. *Parijoto* is currently often cultivated as a decorative plant. However, the fruit of *parijoto* contains a high number of bioactive compounds such as ascorbic acid, carotenoids, flavonoids, vitamin E, flavonol glycoside and phenolic compounds which may act as antioxidants (Angriani, 2019). Antioxidant compounds play an essential role in the health of the body, as they can protect the body from oxidative damage, inhibit oxidative stress, reduce inflammation, and boost the immune system (Haerani et al., 2018).

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Previous research has shown that anthocyanin compound in *parijoto* fruit can be used as a natural blue colorant (Priska et al., 2018). Anthocyanin can also act as antioxidant, anti-cancer, anti-diabetics, and anti-inflammation (Basri, 2021; Tan et al., 2021). However, the bioactive compounds in the *parijoto* fruit are very vulnerable to damage, especially the anthocyanin compound and the antioxidant components such as flavonoids and phenolics (Wachidah, 2013). The damage to such compounds can be caused by high-temperature processes and environmental conditions such as oxygen, light, and pH (Feng et al., 2015). Drying, on the other hand, is a standard preservation method because it can increase the storage life and facilitate the distribution, supply, and ease-of-use. Therefore, it is necessary to prevent the damage of bioactive compounds due to the drying temperature of the *parijoto* fruit, e.g by pre-treatments.

Using organic acid solutions (citric acid, acetic acid) and salt solutions (Na^{+}, Ca^{2+}) with specific concentrations as a pre-drying treatment can retain bioactive compounds in food materials. Calcium chloride ($CaCl_2$) is a salt classified as a food additive. According to a study by Guo et al. (2023), the lifespan of lychee fruit increased because $CaCl_2$ increased the strength of the cell wall and prevented the activity of polyphenol oxidase (PPO) enzymes and microbes. Looking at the potential of *parijoto* fruit as a novel health-promoting food ingredient, this study aims to firstly examine the effect of $CaCl_2$ and temperature in the drying process of *parijoto* fruit. Secondly, this study also aims to establish the drying and degradation kinetics, which will be useful in developing *parijoto* fruit products that are shelf-stable with optimum bioactive compound activities.

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MATERIALS AND METHOD

~~2.1.~~ Materials

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Fresh *parijoto* fruits were obtained from Kudus, Central Java. Other materials used in this study are $CaCl_2$ (E. Merck, Germany), KCl (E. Merck, Germany), CH_3COONa (E. Merck, Germany), 2-diphenyl-1-picrylhydrazyl (Sigma Aldrich, USA), and methanol 99.98% (E. Merck, Germany). All the chemicals used are of analytical grade unless specified.

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~~**2.2. Methods**~~

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~~2.2.1.~~ *Parijoto* fruit preparation and pre-treatment

Parijoto fruits were separated from the branch, sorted and then washed under a running tap water. Half of the cleaned *parijoto* fruits were submerged in $CaCl_2$ 2% solution for 10 min. (sample code: Ca) while the other half were not submerged as a control (sample code: K).

~~2.2.2.~~ Drying process

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Drying was done using a dryer cabinet HetoPowerDry LL1500. *Parijoto* fruits were placed on a tray and were spread evenly. The control and pre-treated samples were dried at 60, 70, and 80ºC for 8 hours. During the drying process, the mass of the *parijoto* fruits was weighed every 1 hour. After drying, the samples were grinded with mortar and pestle for further chemical analysis of the antioxidant activity and total anthocyanin.

~~2.2.3.~~ Ultrasound-assisted methanol extraction for chemical analysis

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Five grams of the grinded dried *parijoto* fruit was suspended in 50 ml methanol. The mixture was subjected to ultrasound in a sonication bath (BioBase, China) at frequency 40 kHz for 30 min and then was let to sit for another 1 h. The mixture was filtered and the filtrate were diluted into 100 ml using methanol. The extract was stored until further analysis for anthocyanin and antioxidant activity analysis.

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~~2.2.4.~~ Total anthocyanin analysis

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Anthocyanin analysis was done using pH differential method described in Turmanidze et al. (2016). The methanol extract obtained was further diluted 2x using methanol. Two milliliters of the diluted samples were mixed with 2 ml of KCl buffer solution pH 1 and CH_3COONa buffer solution pH 4.5. The mixture was incubated in a dark room for 15 min. The absorbance of the

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mixture was measured using UV-Vis spectrophotometer (UV1280, Shimadzu, Japan) at wavelength 520 and 700 nm. Total anthocyanin in the extract were measured using the equations below:

$$A = (A_{520} - A_{700})_{pH\,1} - (A_{520} - A_{700})_{pH\,4.5} \quad (1)$$

$$Total\ Anthocyanin\ (\text{mg/L}) = \frac{A \times MW \times DF \times 1000}{\varepsilon \times L} \quad (2)$$

where A is the absorbance value at different wavelength, MW is the molecular weight of cyanidine-3-glucoside (449.2 g/mol), DF is the dilution factor (20), ε is the molar absorptivity of cyanidine-3-glucoside (26900 L/mol.cm) and L is the cuvet width (1 cm).

~~2.2.5.~~ **Antioxidant activity analysis**

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Antioxidant activity was measured using the method described in Ahmed et al. (2015). The methanol extract was diluted into 1500 ppm using methanol. Afterwards, 0.3 ml of the diluted sample were reacted with 9 ml of DPPH solution (Merck, Germany) in the dark room for 30 min. Blank solution were prepared using 0.3 ml methanol and 9 ml DPPH solution. After 30 min, the absorbance of the sample (Asample) and blank solution (Ablank) was measured using UV-Vis spectrophotometer (UV1280, Shimadzu, Japan) at 517 nm. The antioxidant activity is calculated using the equation below.

$$Antioxidant\ activity\ (\%) = \left[\frac{(A_{blank} - A_{sample})}{A_{blank}}\right] \times 100 \quad (3)$$

~~2.2.6.~~ Degradation kinetics

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The degradation kinetic of the total anthocyanin content and antioxidant activity was fitted into the first order kinetic equation (eq. 4). The degradation kinetic coefficient (k) was obtained from the regression of the experimental data (Fogler, 2006 in Peron et al., 2017).

$$\ln(C_t) = \ln(C_0) - kt \quad (4)$$

C_t = Concentration of total anthocyanin or Antioxidant activity at time *t*
C_0 = Initial concentration of total anthocyanin or Antioxidant activity
k = degradation kinetics coefficient
t = time (h)

Furthermore, half-life time (t1/2), the time in which the component's degradation reached half of its initial value, was calculated using eq. 6 below (Peron et al., 2017).

$$t_{1/2} = Ln\left(\frac{0.5}{k}\right) \quad (6)$$

$t_{1/2}$ = half-life time
k = degradation kinetic coefficient

~~2.2.7.~~ **Drying kinetics**

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Water content analysis was done using gravimetric method, which 2.5 g sampele was dried in a porcelain dish at 100°C. Water content analysis was carried out throughout the drying process and the drying kinetic model was done through the moisture ratio (MR) calculation in eq 7 below.

$$MR = \frac{M_t}{M_0} \qquad (7)$$

M_t = moisture content (d.b) at time t
M_0 = initial moisture content (d.b)

The MR data obtained will be used to determine the drying kinetic based on the three types of semi-empirical models (Turan & Firatligil, 2019), which can be seen in Table 1. Mathematical modelling was done using nonlinear regression. Increasing R2 values and increasing RMSE values are factors in determining the relevant kinetic drying model (Vardin & Yilmaz, 2018). RMSE determination was done following eq 8.

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$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(MR_{exp.i} - MR_{pre.i}\right)^2\right]^{\frac{1}{2}} \qquad (8)$$

N = number of observations
$MR_{exp.i}$ = MR experimental
$MR_{pre.i}$ = MR prediction

Table 1. Drying kinetic models

Model	Equation
Lewis	$MR = \exp(-kt)$
Henderson & Pabis	$MR = a \cdot \exp(-kt)$
Page	$MR = \exp(-kt^n)$

~~2.2.8.~~ **Effective moisture diffusivity**

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Effective moisture diffusivity coefficient (D_{eff}) describes the effectiveness of water diffusion processes in a drying process (Chen et al., 2016). The D_{eff} was calculated based on the value of k (slope) of the linear regression of eq. 9 below.

$$\ln(MR) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}}{r^2}\right)(t) \qquad (9)$$

$$k = -\frac{\pi^2 D_{eff}}{r^2} \quad (10)$$

MR = *moisture ratio*
r = material's radius
t = time

Activation energy (E_a) is the minimum energy needed to start the reaction (Syah et al., 2020). The value of E_a of the moisture diffusion process was obtained through a regression of eq 11 below.

$$D_{eff} = D_0 \, . \, e^{\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)} \quad (11)$$

T = temperature (K)
R = ideal gas constant (8.314 J mol^{-1} K^{-1})
D_0 = exponential equation constant

~~2.2.9.~~ Color intensity

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Color intensity measurement was done through digital imaging analysis. The digital images of the *parijoto* fruits during drying was captured using a smartphone (Infinix Note 11 Pro, Infinix Mobile, China). The digital images of *parijoto* fruit were taken every hour during drying inside a modified mini photo studio box. Color intensity measurements of the digital images based on L*, a*, and b* colors are conducted using the eyedropper tool in Adobe Photoshop CS3 software (Adobe, USA). Measurements were taken three times at different points.

~~2.2.10.~~ Data analysis

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Data analysis and model fitting were carried out using Microsoft Excel and SPSS statistical software analysis v.23. Analysis of variance was carried out to measure statistically significant difference at α 0.5.

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RESULTS AND DISCUSSION

~~1.1.~~ Antioxidant activity

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Figure 1 shows the antioxidant activity of the *parijoto* fruit before and after drying. The $CaCl_2$ submersion pre-treatment did not significantly influence the antioxidant activity of *parijoto* fruit, while higher drying temperature significantly decrease the antioxidant activity of *parijoto* fruits.

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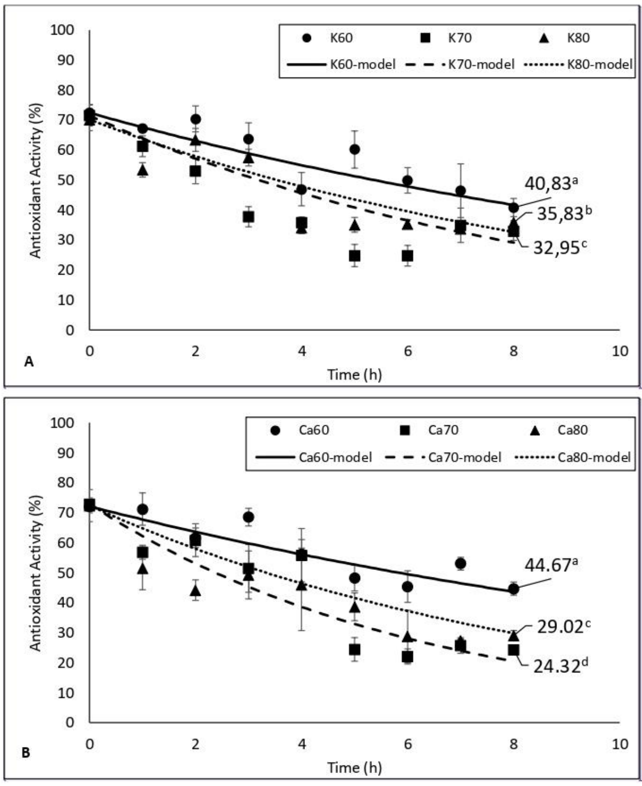

Figure 1. Antioxidant activity of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B)

High temperatures can damage antioxidant compounds in materials, leading to decreased antioxidant activity (Hwang & Do Thi, 2014). According to research by Aloo et al. (2022), $CaCl_2$ soaking treatment can maintain the ascorbic acid content and antioxidant compounds in bell

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K60, K70 dam K80 menunjukkan apa?
K60-Model, dst menunjukkan apa?

Angka 40,83 dst menunjukkan apa? huruf yang dibelakangnya menunjukkan apa?

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C60, C70 dam C80 menunjukkan apa?
C60-Model, dst menunjukkan apa?

Angka 44,67 dst menunjukkan apa? huruf yang dibelakangnya menunjukkan apa?

peppers after 16 days of storage at room temperature. Similar findings can be observed in this study for *parijoto* fruits dried at 60ºC treatment, which shows higher results in the soaked fruit than the control. Calcium ions in $CaCl_2$ can form calcium pectate cross-links with pectin molecules in food materials. This can enhance mechanical properties in *parijoto* fruit, thereby preserving intracellular antioxidant compounds. Goutam et al. (2010) in Aloo et al. (2022) also mentioned that calcium ions could decrease oxidative enzyme activity, thus maintaining antioxidant activity stability against oxidative degradation in *parijoto* fruit. However, the positive effect of the $CaCl_2$ soaking was not observed for drying at 70 and 80ºC, indicating that the high temperature's destructive effect affects the antioxidant activity more than the protection of the $CaCl_2$ pre-treatment.

~~1.2.~~ **Total anthocyanin content**

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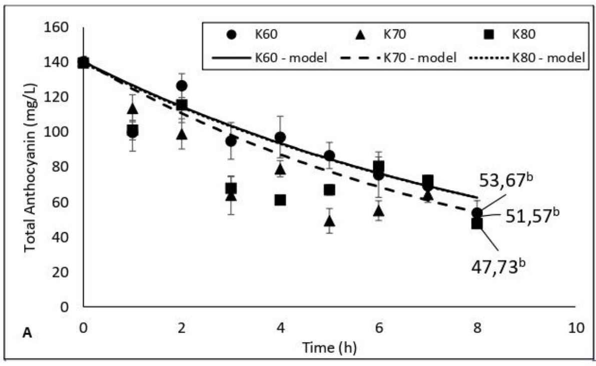
Figure 2 shows the total anthocyanin content of the dried *parijoto* fruits. Drying caused *parijoto* fruits to lose its anthocyanin content significantly. However, the results show that $CaCl_2$ pre-treatment significantly preserve the anthocyanin content of *parijoto* fruits. On the other hand, the drying temperature did not significantly affect the anthocyanin content of the fruit.



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K60, K70 dam K80 menunjukkan apa?
K60-Model, dst menunjukkan apa?

Angka 53,67 dst menunjukkan apa? huruf yang dibelakangnya menunjukkan apa?

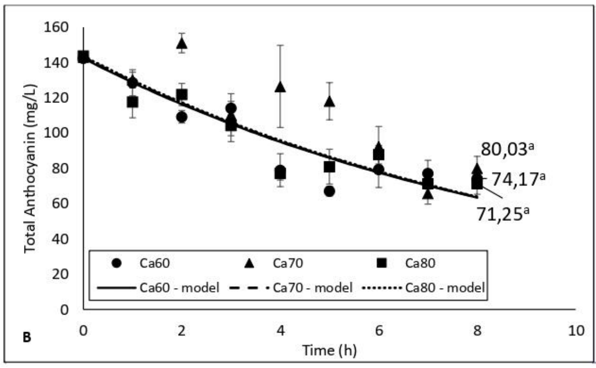

Figure 2. Total anthocyanin content of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B)

Research by Feng et al. (2022) showed that the utilization of $CaCl_2$ solution can preserve the phenolic compounds and stability of antioxidant compounds in luffa (*Luffa cylindrica*). Calcium pectate cross-links may form during the $CaCl_2$ pre-treatment and they can strengthen the interaction between pectin and anthocyanin (Lin et al., 2016) which may protect the anthocyanin content from the heat treatment during drying. Furthermore, the formation of calcium pectate cross-links enhances the integrity of the cell and prevents cellular damage which encourage of enzymatic browning in food materials due to the release of the polyphenol oxidase (PPO). Since anthocyanins are natural compounds in *parijoto* fruit belonging to the phenolic group, damage to anthocyanin compounds from the PPO activity can be prevented. This could explain the higher total anthocyanin content in $CaCl_2$-soaked samples compared to the control.

~~1.3.~~ **Degradation kinetic coefficient of antioxidant activity and total anthocyanin content**

The values of k, $t_{1/2}$ and E_a obtained from the first order kinetic regression from the antioxidant activity and total anthocyanin content during drying are presented in Table 2. These values are useful in describing the properties degradation kinetics during drying and to compare the susceptibility of the properties to heat degradation. Higher k value indicates faster degradation

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C60, C70 dam C80 menunjukkan apa?
C60-Model, dst menunjukkan apa?

Angka 80,03 dst menunjjukkan apa? huruf yang dibelakangnya menunjukkan apa?

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and thus, a more susceptible material. On the other hand, higher $t_{1/2}$ showed a slower and more difficult degradation, which indicate a more stable material (Peron et al., 2017).

The results of the antioxidant activity analysis show that the degradation rate constant (k) increases with higher drying temperatures. This indicates a faster decline in antioxidant activity with increasing drying temperature, affecting the time for antioxidant activity to reach half its initial value ($t_{1/2}$). Thus, it can be concluded that the antioxidant activity of *parijoto* fruits is very vulnerable to increase in temperature during drying.

On the contrary, the k value of the total anthocyanin degradation kinetic remained the same with higher drying temperature. This indicate that the temperature difference in this study did not affect the kinetics of the anthocyanin degradation. Interestingly, $CaCl_2$ treatment caused significant reduction in the k value and increase in the $t_{1/2}$ value. This may be due to calcium pectate interactions with anthocyanins as previously discussed (Lin et al., 2016), which can slow down anthocyanin degradation. However, the $CaCl_2$ submersion did not slow down the degradation of antioxidant activity of *parijoto* fruits during drying.

Table 2. Values of k and $t_{1/2}$

Parameter	Pre-treatment	Temp (ºC)	k (h^{-1})	$t_{1/2}$ (h)
Antioxidant activity	Control	60	0.0691	10.03
		70	0.1121	6.18
		80	0.0955	7.26
	$CaCl_2$	60	0.0628	11.04
		70	0.1590	4.36
		80	0.1109	6.25
Total anthocyanin content	Control	60	0.1012	6.85
		70	0.1193	5.81
		80	0.1006	6.89
	$CaCl_2$	60	0.0885	7.83
		70	0.0882	7.86
		80	0.0869	7.98

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~~1.4.~~ Moisture diffusion properties of *parijoto* fruits during drying

The values of D_{eff} and E_a of *parijoto* fruits dried with different conditions are presented at Table 3. Higher value of D_{eff} indicates that moisture could diffuse out of the fruit tissue more effectively during drying (Chen *et al.*, 2016). On the other hand, higher E_a indicates that more energy is required to start moisture diffusion out of the tissue.

With higher drying temperatures, a higher diffusion coefficient could be achieved. $CaCl_2$ submersion as pre-treatment also significantly increased the diffusion coefficient and lowered the activation energy. This indicates that moisture more easily escaped from the tissue and cells of *parijoto* fruits. Thus, a more efficient and faster drying occurred for *parijoto* fruits dried with pre-treatment and at higher temperatures. The results correlate well with the drying kinetics in Figure 3, discussed below. The presence of salts such as $CaCl_2$ could induce osmotic dehydration in fruit cells (Udomkun et al., 2014). Osmotic dehydration occurred due to the difference in the osmotic pressure between the materials and the salt solutions used to submerge them. Osmotic dehydration can only partially remove water from the materials and usually uses a pre-treatment as the materials require further processing to be shelf-stable (Berk, 2018).

Table 3. *Effective Moisture Diffusivity* and Activation Energy

Pre-treatment	Temp (°C)	D_{eff} (m^2s^{-1})	E_a (kJ/mol)
Control	60	3.27×10^{-3}	35.53
	70	6.91×10^{-3}	
	80	6.71×10^{-3}	
$CaCl_2$	60	4.49×10^{-3}	29.48
	70	9.00×10^{-3}	
	80	8.13×10^{-3}	

~~1.5.~~ Drying kinetics of *parijoto* fruits

The change in the moisture ratio during drying for all the different treatments is shown in Figure 3. Based on the drying kinetics, a moisture ratio plateau (which indicate no further moisture reduction) was already reached at approximately 7 hours and 4 hours for 70 and 80°C, respectively, with a final moisture ratio of about 0.05 for the control sample and about 0.02 for pre-treated samples. On the other hand, *parijoto* fruits dried at 60°C, both with or without pre-treatment, did not reach the same level of moisture ratio after 8 hours. *Parijoto* fruits with $CaCl_2$ submersion reached a lower final moisture ratio than the control samples at all temperature levels, indicating

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a more effective drying due to the pre-treatment before drying. As discussed, $CaCl_2$ pre-treatment caused osmotic dehydration, significantly increasing moisture diffusivity out of *parijoto* fruits (Table 3).

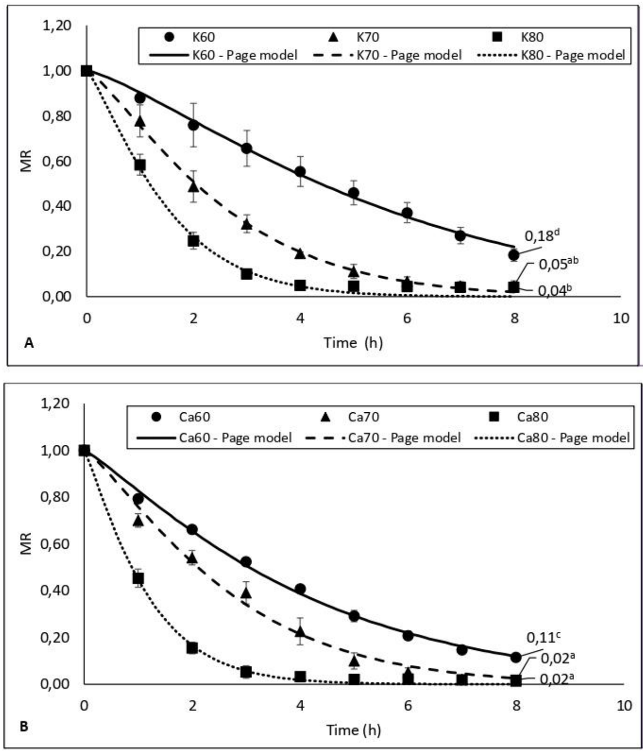

Figure 3. Moisture ratio of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B)

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MR singkatan dari apa?
K60, K70 dam K80 menunjukkan apa?
K60-page Model, dst menunjukkan apa?

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Ca60, Ca70 dam Ca80 menunjukkan apa?
Ca60-page Model, dst menunjukkan apa?

Angka 0,11 dst menunjjukkan apa? huruf yang dibelakangnya menunjukkan apa?

Three models were fitted into the drying kinetics, i.e. Lewis, Henderson & Pabis and Page model. The coefficients obtained from the model fitting are presented at Table 3. Based on the R^2 and RSME values, Page model best describe the drying kinetics of *parijoto* fruits using cabiner dryer. Similar model has been used to describe the drying of gilaburu berries (Dönmez & Kadakal, 2024) and aryl of pomegranate (Vardin & Yilmaz, 2018). The value of k increased significantly with higher temperature and with $CaCl_2$ submersion pre-treatment, which indicate faster drying.

Table 4. Coefficients of drying kinetics with different models

Pre-treatment	Suhu (°C)	Model	k	n	a	R^2	RMSE
Control	60	Lewis	0.165			0.947	0.099
		Henderson & Pabis	0.174		1.041	0.952	0.119
		Page	0.103	1.292		**0.966**	**0.019**
	70	Lewis	0.379			0.977	0.143
		Henderson & Pabis	0.394		1.045	0.980	0.143
		Page	0.281	1.266		**0.988**	**0.015**
	80	Lewis	0.648			0.986	0.195
		Henderson & Pabis	0.657		1.016	0.986	0.185
		Page	0.566	1.229		**0.989**	**0.027**
$CaCl_2$	60	Lewis	0.239			0.989	0.112
		Henderson & Pabis	0.246		1.023	0.990	0.117
		Page	0.189	1.163		**0.995**	**0.016**
	70	Lewis	0.369			0.974	0.141
		Henderson & Pabis	0.377		1.027	0.975	0.133
		Page	0.275	1.242		**0.984**	**0.032**
	80	Lewis	0.857			0.994	0.223
		Henderson & Pabis	0.864		1.006	0.994	0.210
		Page	0.802	1.158		**0.995**	**0.014**

~~1.6.~~ Color changes of *parijoto* fruits during drying

Digital image analysis was carried out to the *parijoto* fruits during drying. The visual representations of the color change are shown in Table 5. The results of the analysis (L*, a* and b* values) are shown in Figure 4-6. Heat from the drying immediately caused a change in the color profile of *parijoto* fruits from initially dark purple to reddish color. Slight increase of the L* values were observed after drying and a significant increase of the a* value was observed which indicates the increased intensity of the red color after drying. On the other hand, the value of b* changed from negative to positive, which indicate a change of color hue from dominant blue to yellow after drying.

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$CaCl_2$ pre-treatment seems to have insignificant impact on the color of *parijoto* fruits after drying. The change of the color from purple to reddish color due to drying may be caused by the increase in the acidity level of the fruits, due to the change of the proportion after moisture removal. Anthocyanin color changed at different acidity level, in which it becomes redder at acidic environment.

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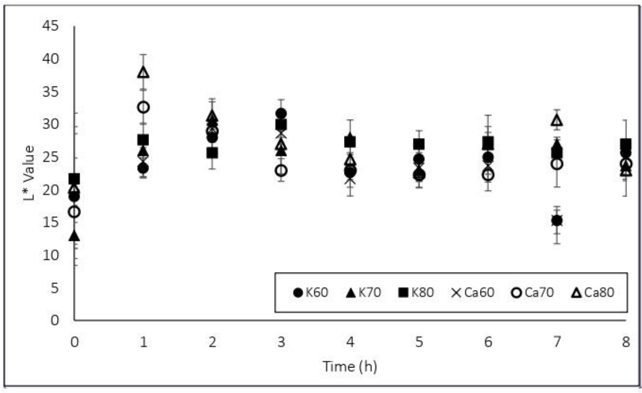

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Figure 4. L* values from the digital image analysis of the *parijoto* fruits during drying with different condition

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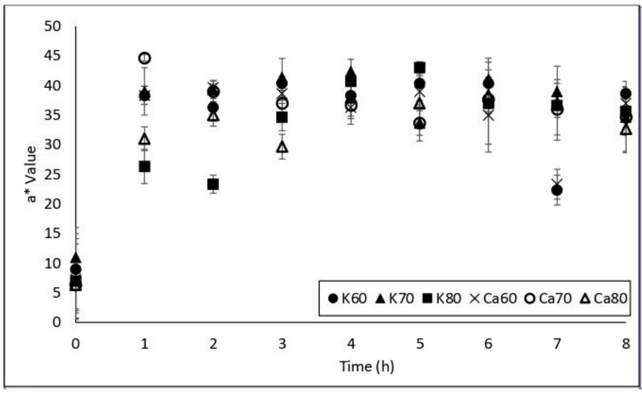

Figure 5. a* values from the digital image analysis of the *parijoto* fruits during drying with different condition

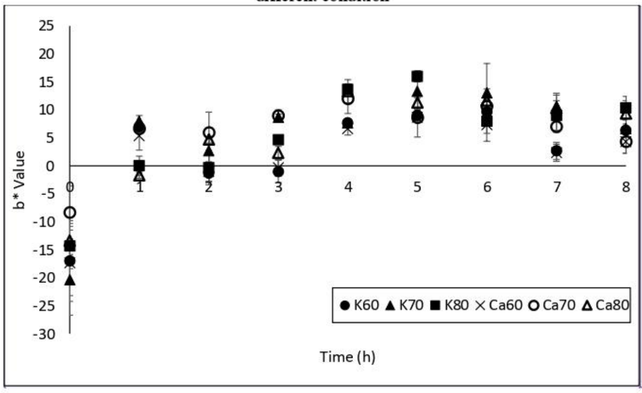

Figure 6. b* values from the digital image analysis of the *parijoto* fruits during drying with different condition

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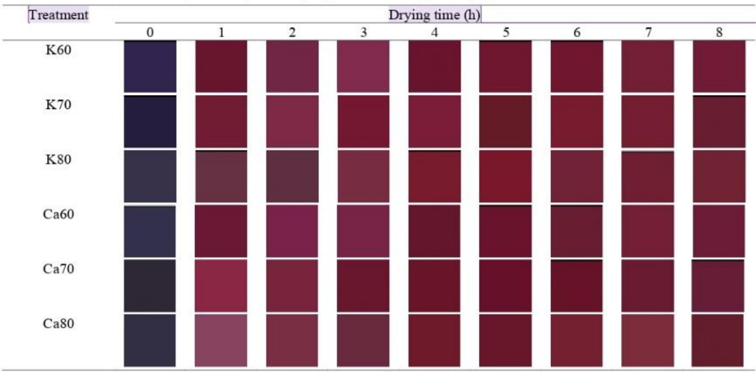
Table 5. Digital color profile of *parijoto* fruits throughout drying with different treatments



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CONCLUSIONS

Drying of *parijoto* fruit at 60-80ºC may cause significant reduction on its antioxidant activity and total anthocyanin content. The antioxidant activity of *parijoto* fruits is especially susceptible to an increase in temperature during drying. However, with $CaCl_2$ submersion as pre-drying treatment, the degradation of anthocyanin content can be reduced. $CaCl_2$ submersion and higher drying temperature can also increase the drying rate of *parijoto* fruit, which make it possible to dry at a shorter time to prevent further degradation of the anthocyanin content. Higher drying rate correlates to a higher effective diffusion coefficient and the drying kinetics of *parijoto* fruits can best be described by the Page model.

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Commented [A35]: Tampilkan persamaan kinetika dari model Page yang mendeskripsikan kinetika pengeringan buah parijoto hasil penelitian ini.

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V. Revised Manuscript B

Drying and Degradation Kinetics of the Physicochemical Characteristics of Parijoto Fruit (*Medinilla speciosa*) with Calcium Chloride Pre-Treatment

ABSTRACT

Parijoto (*Medinilla speciosa*) is an Indonesian local plant with high levels of bioactive compounds crucial in improving overall health. However, these bioactive compounds are susceptible to high temperatures from prolonged heating processes and environmental factors such as oxygen, light, and pH. Therefore, a significant decline in the *parijoto* fruit quality may occur during drying, which prompts a need for a solution to prevent damage to the bioactive compounds in the fruits. As a food additive, calcium chloride ($CaCl_2$) can help maintain cell wall strength and prevent damage from enzymatic, mechanical, and microbial activities in food products. The study aimed to investigate the impact of soaking with $CaCl_2$ (10 min) and drying temperatures (60, 70, and 80ºC) for 8 hours on physicochemical characteristics such as antioxidant activity, total anthocyanin content, and colour. The moisture ratio, colour intensity, antioxidant activity and total anthocyanin content at hourly intervals during drying were measured. The results indicated that soaking in $CaCl_2$ can lead to osmotic dehydration, accelerating the drying rates and preserving the anthocyanin content. The kinetics of the degradation of anthocyanins and antioxidant activity were established, as well as the drying kinetic model for *parijoto* fruits. The Page model was found to be the most relevant and suitable drying kinetics model based on the drying design in this study compared to the other two models.

Keywords: *Parijoto* fruit; Degradation kinetic, Drying kinetic, Calcium chloride

Kinetika Pengeringan dan Degradasi Karakteristik Fisikokimiawi Pada Buah Parijoto (Medinilla speciosa) dengan Pra-Perlakuan Kaslium Klorida

ABSTRAK

Parijoto (*Medinilla speciosa*) adalah tanaman lokal Indonesia yang mengandung senyawa bioaktif tinggi yang penting untuk meningkatkan kesehatan secara keseluruhan. Namun, senyawa bioaktif ini rentan terhadap suhu tinggi dari proses pemanasan yang panjang dan faktor lingkungan seperti oksigen, cahaya, dan pH. Oleh karena itu, penurunan kualitas buah parijoto yang signifikan dapat terjadi selama pengeringan, sehingga diperlukan solusi untuk mencegah kerusakan pada senyawa bioaktif di buah tersebut. Sebagai bahan tambahan makanan, kalsium klorida ($CaCl_2$) dapat membantu menjaga kekuatan dinding sel dan mencegah kerusakan akibat aktivitas enzimatik dan mikroba pada produk pangan. Penelitian ini bertujuan untuk menginvestigasi dampak perendaman dengan $CaCl_2$ (10 menit) dan suhu pengeringan (60, 70, dan 80ºC) selama 8 jam terhadap karakteristik fisiko-kimia seperti aktivitas antioksidan, total kandungan antosianin, dan warna. Perbandingan rasio kadar air, intensitas warna, aktivitas antioksidan, dan kandungan total antosianin diuji setiap jam selama proses pengeringan. Hasil penelitian menunjukkan bahwa perendaman dalam $CaCl_2$ dapat menyebabkan dehidrasi osmotic sehingga mempercepat laju pengeringan, dan menjaga kandungan antosianin. Pada studi ini, dilakukan pula pemodelan kinetika degradasi antosianin dan aktivitas antioksidan, serta model kinetika pengeringan untuk

buah parijoto. Model Page terbukti menjadi model kinetika pengeringan yang paling relevan dan sesuai berdasarkan desain pengeringan dalam studi ini.
Kata kunci: Buah parijoto; Kinetika degradasi, Kinetika pengeringan, Kalsium klorida

INTRODUCTION

Parijoto (*Medinilla speciosa*) is a local Indonesian plant that grows, often uncultivated, in Kudus, Central Java. *Parijoto* is currently often cultivated as a decorative plant. However, the fruit of *parijoto* contains a high number of bioactive compounds such as ascorbic acid, carotenoids, flavonoids, vitamin E, flavonol glycoside and phenolic compounds which may act as antioxidants (Angriani, 2019). Antioxidant compounds play an essential role in the health of the body, as they can protect the body from oxidative damage, inhibit oxidative stress, reduce inflammation, and boost the immune system (Haerani, et al., 2018).

Previous research has shown that anthocyanin compound in *parijoto* fruit can be used as a natural blue colorant (Priska et al., 2018). Anthocyanin can also act as antioxidant, anti-cancer, anti-diabetics, and anti-inflammation (Basri, 2021; Tan et al., 2021). However, the bioactive compounds in the *parijoto* fruit are very vulnerable to damage, especially the anthocyanin compound and the antioxidant components such as flavonoids and phenolics (Wachidah, 2013). The damage to such compounds can be caused by high-temperature processes and environmental conditions such as oxygen, light, and pH (Feng et al., 2015). Drying, on the other hand, is a standard preservation method because it can increase the storage life and facilitate the distribution, supply, and ease-of-use. Therefore, it is necessary to prevent the damage of bioactive compounds due to the drying temperature of the *parijoto* fruit, e.g by pre-treatments.

Using organic acid solutions (citric acid, acetic acid) and salt solutions (Na^+, Ca^{2+}) with specific concentrations as a pre-drying treatment can retain bioactive compounds in food materials. Calcium chloride ($CaCl_2$) is a salt classified as a food additive. According to a study by Guo et al. (2023), the lifespan of lychee fruit increased because $CaCl_2$ increased the strength of the cell wall and prevented the activity of polyphenol oxidase (PPO) enzymes and microbes. Looking at the potential of *parijoto* fruit as a novel health-promoting food ingredient, this study aims to firstly examine the effect of $CaCl_2$ and temperature in the drying process of *parijoto* fruit. Secondly, this study also aims to establish the drying and degradation kinetics, which will be useful in developing *parijoto* fruit products that are shelf-stable with optimum bioactive compound activities.

MATERIALS AND METHOD

2.1. Materials

Fresh *parijoto* fruits were obtained from Kudus, Central Java. Other materials used in this study are $CaCl_2$ (E. Merck, Germany), KCl (E. Merck, Germany), CH_3COONa (E. Merck, Germany), 2-diphenyl-1-picrylhydrazyl (Sigma Aldrich, USA), and methanol 99.98% (E. Merck, Germany). All the chemicals used are of analytical grade unless specified.

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2.2. Methods

2.2.1. *Parijoto* fruit preparation and pre-treatment

Parijoto fruits were separated from the branch, sorted and then washed under a running tap water. Half of the cleaned *parijoto* fruits were submerged in $CaCl_2$ 2% solution for 10 min. (sample code : Ca) while the other half were not submerged as a control (sample code : K).

2.2.2. Drying process

Drying was done using a dryer cabinet HetoPowerDry LL1500 . *Parijoto* fruits were placed on a tray and were spread evenly. The control and pre-treated samples were dried at 60, 70, and 80ºC for 8 hours. During the drying process, the mass of the *parijoto* fruits was weighed every 1 hour. After drying, the samples were grinded with mortar and pestle for further chemical analysis of the antioxidant activity and total anthocyanin.

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2.2.3. Ultrasound-assisted methanol extraction for chemical analysis

Five grams of the grinded dried *parijoto* fruit was suspended in 50 ml methanol. The mixture was subjected to ultrasound in a sonication bath (BioBase, China) at frequency 40 kHz for 30 min and then was let to sit for another 1 h. The mixture was filtered and the filtrate were diluted into 100 ml using methanol. The extract was stored until further analysis for anthocyanin and antioxidant activity analysis.

2.2.4. Total anthocyanin analysis

Anthocyanin analysis was done using pH differential method described in Turmanidze et al. (2016). The methanol extract obtained was further diluted 2x using methanol. Two milliliters of the diluted samples were mixed with 2 ml of KCl buffer solution pH 1 and CH3COONa buffer solution pH 4.5. The mixture was incubated in a dark room for 15 min. The absorbance of the mixture was measured using UV-Vis spectrophotometer (UV1280, Shimadzu, Japan) at wavelength 520 and 700 nm. Total anthocyanin in the extract were measured using the equations below:

$$A = (A_{520} - A_{700})_{pH\ 1} - (A_{520} - A_{700})_{pH\ 4,5} \qquad (1)$$

$$Total\ Anthocyanin\ (\text{mg/L}) = \frac{A \times MW \times DF \times 1000}{\varepsilon \times L} \qquad (2)$$

where A is the absorbance value at different wavelength, MW is the molecular weight of cyanidine-3-glucoside (449.2 g/mol), DF is the dilution factor (20), ε is the molar absorptivity of cyanidine-3-glucoside (26900 L/mol.cm) and L is the cuvet width (1 cm).

2.2.5. Antioxidant activity analysis

Antioxidant activity was measured using the method described in Ahmed et al. (2015). The methanol extract was diluted into 1500 ppm using methanol. Afterwards, 0.3 ml of the diluted sample were reacted with 9 ml of DPPH solution (Merck, Germany) in the dark room for 30 min. Blank solution were prepared using 0.3 ml methanol and 9 ml DPPH solution. After 30 min, the absorbance of the sample (Asample) and blank solution (Ablank) was measured using UV-Vis spectrophotometer (UV1280, Shimadzu, Japan) at 517 nm. The antioxidant activity is calculated using the equation below.

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$$Antioxidant\ activity\ (\%) = \left[\frac{(A_{blank} - A_{sample})}{A_{blank}}\right] \times 100 \qquad (3)$$

2.2.6. Degradation kinetics

The degradation kinetic of the total anthocyanin content and antioxidant activity was fitted into the first order kinetic equation (eq. 4). The degradation kinetic coefficient (k) was obtained from the regression of the experimental data (Fogler, 2006 in Peron et al., 2017).

$$\ln(C_t) = \ln(C_0) - kt \qquad (4)$$

C_t = Concentration of total anthocyanin or Antioxidant activity at time t
C_0 = Initial concentration of total anthocyanin or Antioxidant activity
k = degradation kinetics coefficient
t = time (h)

Furthermore, half-life time (t1/2), the time in which the component's degradation reached half of its initial value, was calculated using eq. 6 below (Peron et al., 2017).

$$t_{1/2} = Ln(\frac{0.5}{k}) \quad (6)$$

$t_{1/2}$ = half-life time
k = degradation kinetic coefficient

2.2.7. Drying kinetics

Water content analysis was done using gravimetric method, which 2.5 g sampel was dried in a porcelain dish at 100°C. Water content analysis was carried out throughout the drying process and the drying kinetic model was done through the moisture ratio (MR) calculation in eq 7 below.

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$$MR = \frac{M_t}{M_0} \quad (7)$$

M_t = moisture content (d.b) at time t
M_0 = initial moisture content (d.b)

The MR data obtained will be used to determine the drying kinetic based on the three types of semi-empirical models (Turan & Firatligil, 2019), which can be seen in Table 1. Mathematical modelling was done using nonlinear regression. Increasing R2 values and increasing RMSE values are factors in determining the relevant kinetic drying model (Vardin & Yilmaz, 2018). RMSE determination was done following eq 8.

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(MR_{exp.i} - MR_{pre.i}\right)^2\right]^{\frac{1}{2}} \quad (8)$$

N = number of observations
$MR_{exp.i}$ = MR experimental
$MR_{pre.i}$ = MR prediction

Table 1. Drying kinetic models

Model	Equation
Lewis	$MR = \exp(-kt)$
Henderson & Pabis	$MR = a \cdot \exp(-kt)$
Page	$MR = \exp(-kt^n)$

2.2.8. Effective moisture diffusivity

Effective moisture diffusivity coefficient (D_{eff}) describes the effectiveness of water diffusion processes in a drying process (Chen et al., 2016). The D_{eff} was calculated based on the value of k (slope) of the linear regression of eq. 9 below.

$$\ln(MR) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}}{r^2}\right)(t) \quad (9)$$

$$k = -\frac{\pi^2 D_{eff}}{r^2} \quad (10)$$

MR = *moisture ratio*
r = material's radius
t = time

Activation energy (E_a) is the minimum energy needed to start the reaction (Syah et al., 2020). The value of E_a of the moisture diffusion process was obtained through a regression of eq 11 below.

$$D_{eff} = D_0 \, . \, e^{\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)} \quad (11)$$

T = temperature (K)
R = ideal gas constant (8.314 J mol^{-1} K^{-1})
D_0 = exponential equation constant

2.2.9. Color intensity

Color intensity measurement was done through digital imaging analysis. The digital images of the *parijoto* fruits during drying was captured using a smartphone (Infinix Note 11 Pro, Infinix Mobile, China). The digital images of *parijoto* fruit were taken every hour during drying inside a modified mini photo studio box. Color intensity measurements of the digital images based on L*, a*, and b* colors are conducted using the eyedropper tool in Adobe Photoshop CS3 software (Adobe, USA). Measurements were taken three times at different points.

2.2.10. Data analysis

Data analysis and model fitting were carried out using Microsoft Excel and SPSS statistical software analysis v.23. Analysis of variance was carried out to measure statistically significant difference at α 0.5.

RESULTS AND DISCUSSION

1.1. Antioxidant activity

Figure 1 shows the antioxidant activity of the *parijoto* fruit before and after drying. The $CaCl_2$ submersion pre-treatment did not significantly influence the antioxidant activity of *parijoto* fruit, while higher drying temperature significantly decrease the antioxidant activity of *parijoto* fruits.

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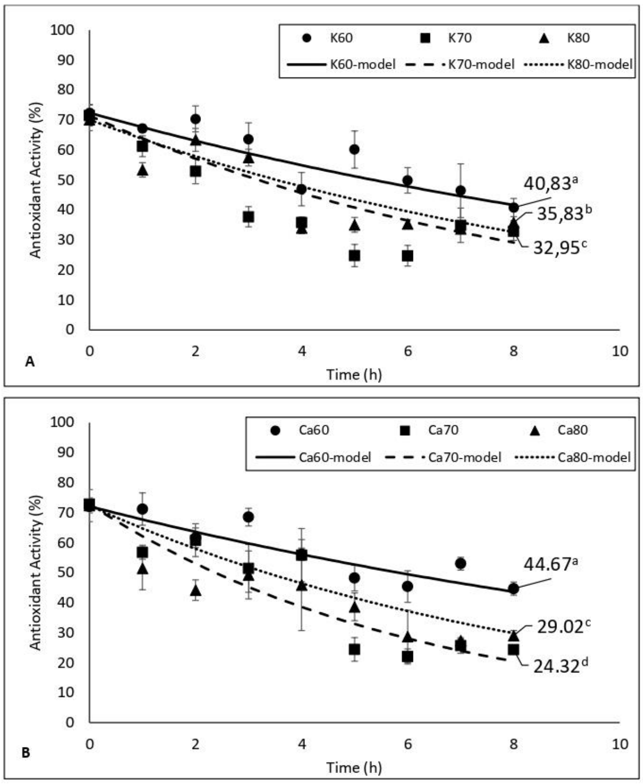

Figure 1. Antioxidant activity of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B)

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High temperatures can damage antioxidant compounds in materials, leading to decreased antioxidant activity (Hwang & Do Thi, 2014). According to research by Aloo et al. (2022), $CaCl_2$ soaking treatment can maintain the ascorbic acid content and antioxidant compounds in bell peppers after 16 days of storage at room temperature. Similar findings can be observed in this study for *parijoto* fruits dried at 60ºC treatment, which shows higher results in the soaked fruit than the control. Calcium ions in $CaCl_2$ can form calcium pectate cross-links with pectin molecules in food materials. This can enhance mechanical properties in *parijoto* fruit, thereby preserving intracellular antioxidant compounds. Goutam et al. (2010) in Aloo et al. (2022) also mentioned that calcium ions could decrease oxidative enzyme activity, thus maintaining antioxidant activity stability against oxidative degradation in *parijoto* fruit. However, the positive effect of the $CaCl_2$ soaking was not observed for drying at 70 and 80ºC, indicating that the high temperature's destructive effect affects the antioxidant activity more than the protection of the $CaCl_2$ pre-treatment.

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1.2. Total anthocyanin content

Figure 2 shows the total anthocyanin content of the dried *parijoto* fruits. Drying caused *parijoto* fruits to lose its anthocyanin content significantly. However, the results show that $CaCl_2$ pre-treatment significantly preserve the anthocyanin content of *parijoto* fruits. On the other hand, the drying temperature did not significantly affect the anthocyanin content of the fruit.

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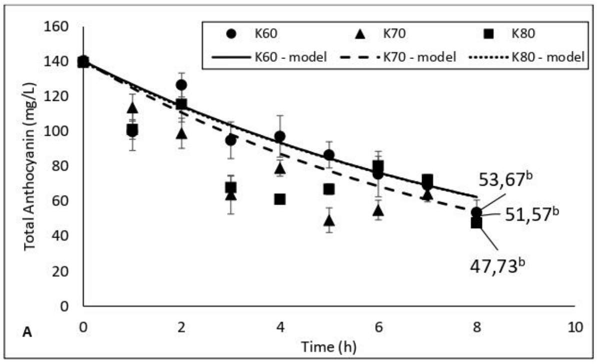

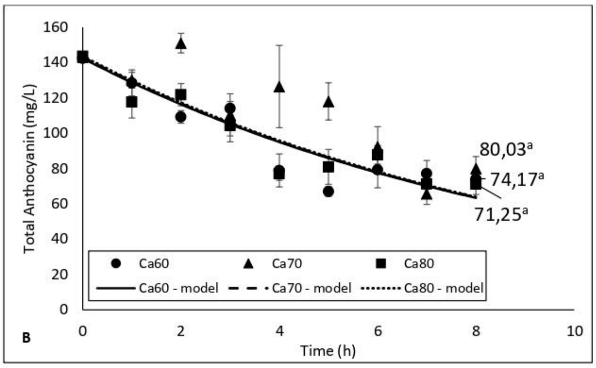

Figure 2. Total anthocyanin content of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B)

Research by Feng et al. (2022) showed that the utilization of $CaCl_2$ solution can preserve the phenolic compounds and stability of antioxidant compounds in luffa (*Luffa cylindrica*). Calcium pectate cross-links may form during the $CaCl_2$ pre-treatment and they can strengthen the interaction between pectin and anthocyanin (Lin et al., 2016) which may protect the anthocyanin content from the heat treatment during drying. Furthermore, the formation of calcium pectate cross-links enhances the integrity of the cell and prevents cellular damage which encourage of enzymatic browning in food materials due to the release of the polyphenol oxidase (PPO). Since anthocyanins are natural compounds in *parijoto* fruit belonging to the phenolic group, damage to anthocyanin compounds from the PPO activity can be prevented. This could explain the higher total anthocyanin content in $CaCl_2$-soaked samples compared to the control.

1.3. Degradation kinetic coefficient of antioxidant activity and total anthocyanin content

The values of k, $t_{1/2}$ and E_a obtained from the first order kinetic regression from the antioxidant activity and total anthocyanin content during drying are presented in Table 2. These values are useful in describing the properties degradation kinetics during drying and to compare the susceptibility of the properties to heat degradation. Higher k value indicates faster degradation and thus, a more susceptible material. On the other hand, higher $t_{1/2}$ showed a slower and more difficult degradation, which indicate a more stable material (Peron et al., 2017).

The results of the antioxidant activity analysis show that the degradation rate constant (k) increases with higher drying temperatures. This indicates a faster decline in antioxidant activity with increasing drying temperature, affecting the time for antioxidant activity to reach half its initial value ($t_{1/2}$). Thus, it can be concluded that the antioxidant activity of *parijoto* fruits is very vulnerable to increase in temperature during drying.

On the contrary, the k value of the total anthocyanin degradation kinetic remained the same with higher drying temperature. This indicate that the temperature difference in this study did not affect the kinetics of the anthocyanin degradation. Interestingly, $CaCl_2$ treatment caused significant reduction in the k value and increase in the $t_{1/2}$ value. This may be due to calcium pectate interactions with anthocyanins as previously discussed (Lin et al., 2016), which can slow down anthocyanin degradation. However, the $CaCl_2$ submersion did not slow down the degradation of antioxidant activity of *parijoto* fruits during drying.

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Table 2. Values of k and $t_{1/2}$

Parameter	Pre-treatment	Temp (°C)	k (h^{-1})	$t_{1/2}$ (h)
Antioxidant activity	Control	60	0.0691	10.03
		70	0.1121	6.18
		80	0.0955	7.26
	$CaCl_2$	60	0.0628	11.04
		70	0.1590	4.36
		80	0.1109	6.25
Total anthocyanin content	Control	60	0.1012	6.85
		70	0.1193	5.81
		80	0.1006	6.89
	$CaCl_2$	60	0.0885	7.83
		70	0.0882	7.86
		80	0.0869	7.98

1.4.Moisture diffusion properties of *parijoto* fruits during drying

The values of D_{eff} and E_a of *parijoto* fruits dried with different conditions are presented at Table 3. Higher value of D_{eff} indicates that moisture could diffuse out of the fruit tissue more effectively during drying (Chen *et al*., 2016). On the other hand, higher E_a indicates that more energy is required to start moisture diffusion out of the tissue.

With higher drying temperatures, a higher diffusion coefficient could be achieved. $CaCl_2$ submersion as pre-treatment also significantly increased the diffusion coefficient and lowered the activation energy. This indicates that moisture more easily escaped from the tissue and cells of *parijoto* fruits. Thus, a more efficient and faster drying occurred for *parijoto* fruits dried with pre-treatment and at higher temperatures. The results correlate well with the drying kinetics in Figure 3, discussed below. The presence of salts such as $CaCl_2$ could induce osmotic dehydration in fruit cells (Udomkun *et al*., 2014). Osmotic dehydration occurred due to the difference in the osmotic pressure between the materials and the salt solutions used to submerge them. Osmotic dehydration can only partially remove water from the materials and usually uses a pre-treatment as the materials require further processing to be shelf-stable (Berk, 2018).

Table 3. *Effective Moisture Diffusivity* and Activation Energy

Pre-treatment	Temp (ºC)	D_{eff} (m^2s^{-1})	E_a (kJ/mol)
Control	60	3.27×10^{-3}	35.53
	70	6.91×10^{-3}	
	80	6.71×10^{-3}	
$CaCl_2$	60	4.49×10^{-3}	29.48
	70	9.00×10^{-3}	
	80	8.13×10^{-3}	

1.5.Drying kinetics of *parijoto* fruits

The change in the moisture ratio during drying for all the different treatments is shown in Figure 3. Based on the drying kinetics, a moisture ratio plateau (which indicate no further moisture reduction) was already reached at approximately 7 hours and 4 hours for 70 and 80ºC, respectively, with a final moisture ratio of about 0.05 for the control sample and about 0.02 for pre-treated samples. On the other hand, *parijoto* fruits dried at 60ºC, both with or without pre-treatment, did not reach the same level of moisture ratio after 8 hours. *Parijoto* fruits with $CaCl_2$ submersion reached a lower final moisture ratio than the control samples at all temperature levels, indicating a more effective drying due to the pre-treatment before drying. As discussed, $CaCl_2$ pre-treatment caused osmotic dehydration, significantly increasing moisture diffusivity out of *parijoto* fruits (Table 3).

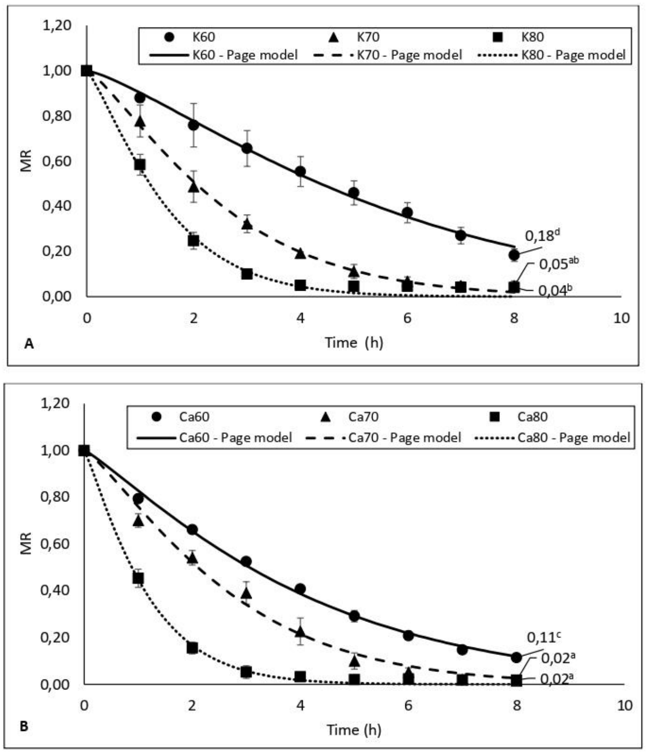

Figure 3. Moisture ratio of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B)

Three models were fitted into the drying kinetics, i.e. Lewis, Henderson & Pabis and Page model. The coefficients obtained from the model fitting are presented at Table 3. Based on the R^2 and RSME values, Page model best describe the drying kinetics of *parijoto* fruits using cabiner dryer. Similar model has been used to describe the drying of gilaburu berries (Dönmez & Kadakal, 2024) and aryl of pomegranate (Vardin & Yilmaz, 2018). The value of k increased significantly with higher temperature and with $CaCl_2$ submersion pre-treatment, which indicate faster drying.

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Table 4. Coefficients of drying kinetics with different models

Pre-treatment	Suhu (°C)	Model	k	n	a	R^2	RMSE
Control	60	Lewis	0.165			0.947	0.099
		Henderson & Pabis	0.174		1.041	0.952	0.119
		Page	0.103	1.292		**0.966**	**0.019**
	70	Lewis	0.379			0.977	0.143
		Henderson & Pabis	0.394		1.045	0.980	0.143
		Page	0.281	1.266		**0.988**	**0.015**
	80	Lewis	0.648			0.986	0.195
		Henderson & Pabis	0.657		1.016	0.986	0.185
		Page	0.566	1.229		**0.989**	**0.027**
$CaCl_2$	60	Lewis	0.239			0.989	0.112
		Henderson & Pabis	0.246		1.023	0.990	0.117
		Page	0.189	1.163		**0.995**	**0.016**
	70	Lewis	0.369			0.974	0.141
		Henderson & Pabis	0.377		1.027	0.975	0.133
		Page	0.275	1.242		**0.984**	**0.032**
	80	Lewis	0.857			0.994	0.223
		Henderson & Pabis	0.864		1.006	0.994	0.210
		Page	0.802	1.158		**0.995**	**0.014**

1.6.Color changes of *parijoto* fruits during drying

Digital image analysis was carried out to the *parijoto* fruits during drying. The visual representations of the color change are shown in Table 5. The results of the analysis (L*, a* and b* values) are shown in Figure 4-6. Heat from the drying immediately caused a change in the color profile of *parijoto* fruits from initially dark purple to reddish color. Slight increase of the L* values were observed after drying and a significant increase of the a* value was observed which indicates the increased intensity of the red color after drying. On the other hand, the value of b* changed from negative to positive, which indicate a change of color hue from dominant blue to yellow after drying.

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$CaCl_2$ pre-treatment seems to have insignificant impact on the color of *parijoto* fruits after drying. The change of the color from purple to reddish color due to drying may be caused by the increase in the acidity level of the fruits, due to the change of the proportion after moisture removal. Anthocyanin color changed at different acidity level, in which it becomes redder at acidic environment.

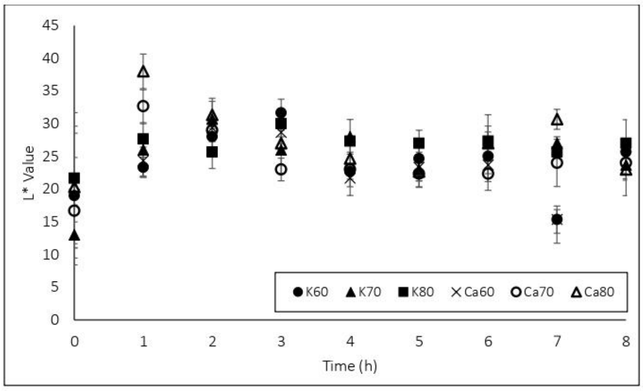

Figure 4. L* values from the digital image analysis of the *parijoto* fruits during drying with different condition

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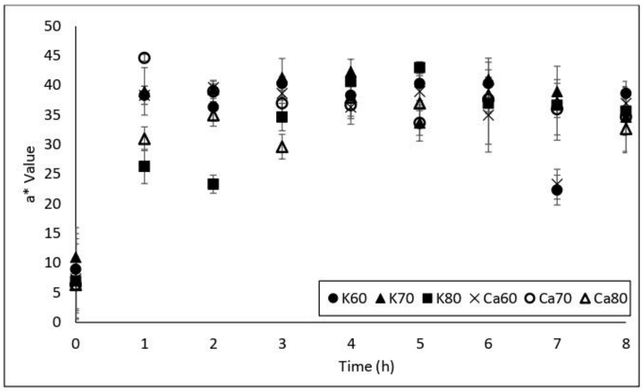


Figure 5. a* values from the digital image analysis of the *parijoto* fruits during drying with different condition

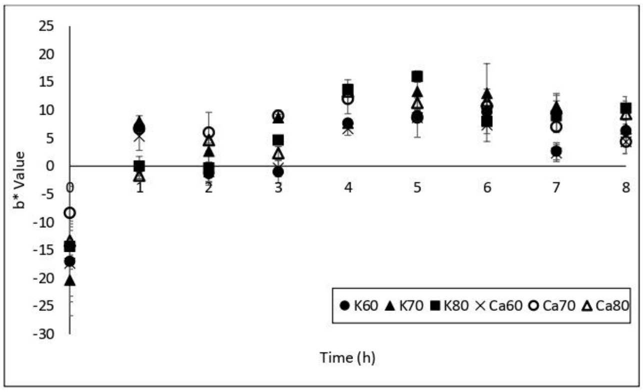
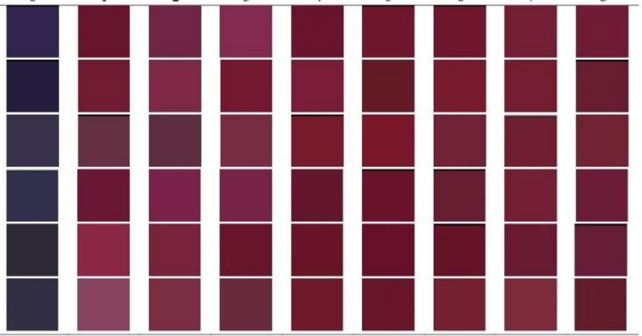


Figure 6. b* values from the digital image analysis of the *parijoto* fruits during drying with different condition

Table 5. Digital color profile of *parijoto* fruits throughout drying with different treatments

Treatment	Drying time (h)								
	0	1	2	3	4	5	6	7	8
K60									
K70									
K80									
Ca60									
Ca70									
Ca80									



CONCLUSIONS

Drying of *parijoto* fruit at 60-80°C may cause significant reduction on its antioxidant activity and total anthocyanin content. The antioxidant activity of *parijoto* fruits is especially susceptible to an increase in temperature during drying. However, with $CaCl_2$ submersion as pre-drying treatment, the degradation of anthocyanin content can be reduced. $CaCl_2$ submersion and higher drying temperature can also increase the drying rate of *parijoto* fruit, which make it possible to dry at a shorter time to prevent further degradation of the anthocyanin content. Higher drying rate correlates to a higher effective diffusion coefficient and the drying kinetics of *parijoto* fruits can best be described by the Page model.

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VI. Accepted Confirmation

Notifications

[jffn] Editor Decision - Manuscript {$articleId}

2024-11-15 04:51 AM

Dear Novita Ika Putri, Bernardus David Lai, Gelbert Jethro Sanyoto, Victoria Kristina Ananingsih,

We have reached a decision regarding your submission to Journal of Functional Food and Nutraceutical, Manuscript {$articleId}, entitled DRYING AND DEGRADATION KINETICS OF THE PHYSICOCHEMICAL CHARACTERISTICS OF PARIJOTO FRUIT (MEDINILLA SPECIOSA) WITH CALCIUM CHLORIDE PRE-TREATMENT.

Our decision is to: Accept Submission

Maria Gunawan Puteri
Swiss German University
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VII. Final Article

Drying and Degradation Kinetics of the Physicochemical Characteristics of Parijoto Fruit (*Medinilla speciosa*) with Calcium Chloride Pre-Treatment

ABSTRACT

Parijoto (*Medinilla speciosa*) is an Indonesian plant rich in bioactive compounds beneficial for human health. However, these compounds are susceptible to high temperatures, which can lead to significant quality degradation during drying. To address this, calcium chloride ($CaCl_2$) pre-treatment is proposed to help maintain cell wall integrity and prevent damage from enzymatic, mechanical, and microbial activities in *parijoto* fruits. The study aims to investigate the impact of soaking with $CaCl_2$ (10 min) and drying temperatures (60, 70, and 80ºC) over 8 hours on the antioxidant activity, total anthocyanin content, and color of *parijoto*. This study also aims to determine the kinetic model of the quality degradation and drying rate of *parijoto*. Moisture ratio, color intensity, antioxidant activity and anthocyanin content of *parijoto* were measured at hourly intervals during drying. The results indicated that soaking in $CaCl_2$ led to accelerating drying rates and preservation of anthocyanin content. Degradation kinetics of anthocyanins and antioxidant activity were established using the first order kinetic equation. The values of k and $t_{1/2}$ showed faster antioxidant activity degradation during drying at higher temperature, while the rate of anthocyanin degradation did not significantly change. $CaCl_2$ soaking decreased the degradation rate of the anthocyanin content. Page model ($MR = \exp(-kt^n)$) was found to be the most suitable drying kinetics model compared to the other models studied. Drying *parijoto* at 80ºC gave the fastest drying rate with insignificant degradation to the anthocyanin and color. The result of this study could be used to determine a suitable drying condition for *parijoto*.

Keywords: *Parijoto* fruit; Degradation kinetic, Drying kinetic, Calcium chloride

Kinetika Pengeringan dan Degradasi Karakteristik Fisikokimiawi Pada Buah Parijoto (*Medinilla speciosa*) dengan Pra-Perlakuan Kaslium Klorida

ABSTRAK

Parijoto (*Medinilla speciosa*) adalah tanaman Indonesia yang kaya akan senyawa bioaktif yang bermanfaat bagi kesehatan manusia. Namun, senyawa ini rentan terhadap suhu tinggi yang dapat menyebabkan penurunan kualitas yang signifikan selama pengeringanUntuk mengatasi hal ini, perendaman dengan kalsium klorida (CaCl2) telah diusulkan sebagai metode untuk membantu menjaga integritas dinding sel dan mencegah kerusakan akibat aktivitas enzimatik, mekanik, dan mikroba pada buah parijoto. Penelitian ini bertujuan untuk menyelidiki dampak perendaman dengan $CaCl_2$ (10 menit) dan pengeringan pada suhu (60, 70, dan 80ºC) selama 8 jam terhadap aktivitas antioksidan, total kandungan antosianin, dan warna buah parijoto. Penelitian ini juga bertujuan untuk menentukan model kinetika untuk degradasi kualitas dan kecepatan pengeringan buah parijoto.Rasio kadar air, intensitas warna, aktivitas antioksidan, dan kandungan total antosianin pada buah parijoto diuji setiap jam selama proses pengeringan. Hasil penelitian menunjukkan bahwa perendaman dalam $CaCl_2$ mempercepat laju pengeringan dan mempertahankan kandungan antosianin. Kinetika degradasi antosianin dan aktivitas antioksidan ditentukan dengan persamaan kinetika reaksi ordo 1. Nilai k dan $t_{1/2}$ menunjukkan bahwa aktivitas

antioksidan terdegradasi lebih cepat ketika suhu pengeringan meningkat, sedangkan kandungan total antosianin tidak mengalami perubahan laju degradasi yang signifikan. Perendaman dengan CaCl2 menurunkan laju degradasi total antosianin. Kinetika pengeringan untuk buah parijoto dengan Model Page ($MR = \exp(-kt^n)$) terbukti menjadi model kinetika pengeringan yang paling relevan dibandingkan dengan dua model lain yang dipelajari. Pengeringan buah parijoto pada suhu 80ºC memberikan laju pengeringan tercepat dengan penurunan kandungan antosianin dan warna yang tidak signifikan. Oleh karena itu, hasil penelitian ini dapat digunakan untuk menentukan proses pengeringan yang sesuai untuk buah parijoto.
Kata kunci: Buah parijoto; Kinetika degradasi, Kinetika pengeringan, Kalsium klorida

INTRODUCTION

Parijoto (*Medinilla speciosa*) is a local Indonesian plant that grows, often uncultivated, in Kudus, Central Java. *Parijoto* is currently often cultivated as a decorative plant. However, the fruit of *parijoto* contains a high number of bioactive compounds such as ascorbic acid, carotenoids, flavonoids, vitamin E, flavonol glycoside and phenolic compounds which may act as antioxidants (Angriani, 2019). Antioxidant compounds play an essential role in the health of the body, as they can protect the body from oxidative damage, inhibit oxidative stress, reduce inflammation, and boost the immune system (Haerani et al., 2018).

Previous research has shown that anthocyanin compound in *parijoto* fruit can be used as a natural blue colorant (Priska et al., 2018). Anthocyanin can also act as antioxidant, anti-cancer, anti-diabetics, and anti-inflammation (Basri, 2021; Tan et al., 2021). However, the bioactive compounds in the *parijoto* fruit are very vulnerable to damage, especially the anthocyanin compound and the antioxidant components such as flavonoids and phenolics (Wachidah, 2013). The damage to such compounds can be caused by high-temperature processes and environmental conditions such as oxygen, light, and pH (Feng et al., 2015). Drying, on the other hand, is a standard preservation method because it can increase the storage life and facilitate the distribution, supply, and ease-of-use. Therefore, it is necessary to prevent the damage of bioactive compounds due to the drying temperature of the *parijoto* fruit, e.g by pre-treatments.

Using organic acid solutions (citric acid, acetic acid) and salt solutions (Na^+, Ca^{2+}) with specific concentrations as a pre-drying treatment can retain bioactive compounds in food materials. Calcium chloride ($CaCl_2$) is a salt classified as a food additive. According to a study by Guo et al. (2023), the lifespan of lychee fruit increased because $CaCl_2$ increased the strength of the cell wall and prevented the activity of polyphenol oxidase (PPO) enzymes and microbes. Looking at the potential of *parijoto* fruit as a novel health-promoting food ingredient, this study aims to firstly examine the effect of $CaCl_2$ and temperature in the drying process of *parijoto* fruit. Secondly, this study also aims to establish the drying and degradation kinetics, which will be useful in developing *parijoto* fruit products that are shelf-stable with optimum bioactive compound activities.

MATERIALS AND METHOD

Materials

Fresh *parijoto* fruits were obtained from Kudus, Central Java. Other materials used in this study are $CaCl_2$ (E. Merck, Germany), KCl (E. Merck, Germany), CH_3COONa (E. Merck, Germany), 2-diphenyl-1-picrylhydrazyl (Sigma Aldrich, USA), and methanol 99.98% (E. Merck, Germany). All the chemicals used are of analytical grade unless specified.

Parijoto fruit preparation and pre-treatment

Parijoto fruits were separated from the branch, sorted and then washed under a running tap water. Half of the cleaned *parijoto* fruits were submerged in $CaCl_2$ 2% solution for 10 min. (sample code: Ca) while the other half were not submerged as a control (sample code: K).

Drying process

Drying was done using a dryer cabinet ED 115 (Binder, Germany) (. *Parijoto* fruits were placed on a tray and were spread evenly. The control and pre-treated samples were dried at 60 ºC (sample code : K60 and Ca60), 70ºC (sample code : K70 and Ca70), and 80ºC (sample code : K80 and Ca80) for 8 hours. During the drying process, the mass of the *parijoto* fruits was weighed every 1 hour. After drying, the samples were grinded with mortar and pestle for further chemical analysis of the antioxidant activity and total anthocyanin.

Ultrasound-assisted methanol extraction for chemical analysis

Five grams of the grinded dried *parijoto* fruit was suspended in 50 ml methanol (Ananingsih et al., 2024). The mixture was subjected to ultrasound in a sonication bath (BioBase, China) at frequency 40 kHz for 30 min and then was let to sit for another 1 h. The mixture was filtered and the filtrate were diluted into 100 ml using methanol. The extract was stored until further analysis for anthocyanin and antioxidant activity analysis.

Total anthocyanin analysis

Anthocyanin analysis was done using pH differential method described in Turmanidze et al. (2016). The methanol extract obtained was further diluted 2x using methanol. Two milliliters of the diluted samples were mixed with 2 ml of KCl buffer solution pH 1 and CH_3COONa buffer solution pH 4.5. The mixture was incubated in a dark room for 15 min. The absorbance of the mixture was measured using UV-Vis spectrophotometer (UV1280, Shimadzu, Japan) at wavelength 520 and 700 nm. Total anthocyanin in the extract were measured using the equations below:

$$A = (A_{520} - A_{700})_{pH\,1} - (A_{520} - A_{700})_{pH\,4,5} \quad (1)$$

$$Total\ Anthocyanin\ (\mathrm{mg/L}) = \frac{A \times MW \times DF \times 1000}{\varepsilon \times L} \quad (2)$$

where A is the absorbance value at different wavelength, MW is the molecular weight of cyanidine-3-glucoside (449.2 g/mol), DF is the dilution factor (20), ε is the molar absorptivity of cyanidine-3-glucoside (26900 L/mol.cm) and L is the cuvet width (1 cm).

Antioxidant activity analysis

Antioxidant activity was measured using the method described in Ahmed et al. (2015). The methanol extract was diluted into 1500 ppm using methanol. Afterwards, 0.3 ml of the diluted sample were reacted with 9 ml of DPPH solution (Merck, Germany) in the dark room for 30 min. Blank solution were prepared using 0.3 ml methanol and 9 ml DPPH solution. After 30 min, the absorbance of the sample (Asample) and blank solution (Ablank) was measured using UV-Vis spectrophotometer (UV1280, Shimadzu, Japan) at 517 nm. The antioxidant activity is calculated using the equation below.

$$Antioxidant\ activity\ (\%) = \left[\frac{(A_{blank} - A_{sample})}{A_{blank}}\right] \times 100 \quad (3)$$

Degradation kinetics

The degradation kinetic of the total anthocyanin content and antioxidant activity was fitted into the first order kinetic equation (eq. 4). The degradation kinetic coefficient (k) was obtained from the regression of the experimental data (Fogler, 2006 in Peron et al., 2017).

$$\ln(C_t) = \ln(C_0) - kt \quad (4)$$

C_t = Concentration of total anthocyanin or Antioxidant activity at time *t*
C_0 = Initial concentration of total anthocyanin or Antioxidant activity
k = degradation kinetics coefficient
t = time (h)

Furthermore, half-life time (t1/2), the time in which the component's degradation reached half of its initial value, was calculated using eq. 6 below (Peron et al., 2017).

$$t_{1/2} = Ln(\frac{0.5}{k}) \quad (6)$$

$t_{1/2}$ = half-life time
k = degradation kinetic coefficient

Drying kinetics

Water content analysis was done using gravimetric method, which 2.5 g sample was dried in a porcelain dish at 100ºC. Water content analysis was carried out throughout the drying process and the drying kinetic model was done through the moisture ratio (MR) calculation in eq 7 below.

$$MR = \frac{M_t}{M_0} \quad (7)$$

M_t = moisture content (d.b) at time t
M_0 = initial moisture content (d.b)

The MR data obtained will be used to determine the drying kinetic based on the three types of semi-empirical models (Turan & Firatligil, 2019), which can be seen in Table 1. Mathematical modelling was done using nonlinear regression. Increasing R^2 values and increasing RMSE (Root Mean Square Error) values are factors in determining the relevant kinetic drying model (Vardin & Yilmaz, 2018). RMSE determination was done following eq 8.

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(MR_{exp.i} - MR_{pre.i}\right)^2\right]^{\frac{1}{2}} \quad (8)$$

N = number of observations
$MR_{exp.i}$ = MR experimental
$MR_{pre.i}$ = MR prediction

Table 1. Drying kinetic models

Model	Equation
Lewis	$MR = \exp(-kt)$
Henderson & Pabis	$MR = a \cdot \exp(-kt)$
Page	$MR = \exp(-kt^n)$

Effective moisture diffusivity

Effective moisture diffusivity coefficient (D_{eff}) describes the effectiveness of water diffusion processes in a drying process (Chen et al., 2016). The D_{eff} was calculated based on the value of k (slope) of the linear regression of eq. 9 below.

$$\ln(MR) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}}{r^2}\right)(t) \quad (9)$$

$$k = -\frac{\pi^2 D_{eff}}{r^2} \quad (10)$$

MR = *moisture ratio*
r = material's radius
t = time

Activation energy (E_a) is the minimum energy needed to start the reaction (Syah et al., 2020). The value of E_a of the moisture diffusion process was obtained through a regression of eq 11 below.

$$D_{eff} = D_0 \, . \, e^{\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)} \quad (11)$$

T = temperature (K)
R = ideal gas constant (8.314 J mol^{-1} K^{-1})
D_0 = exponential equation constant

Color intensity

Color intensity measurement was done through digital imaging analysis. The digital images of the *parijoto* fruits during drying was captured using a smartphone camera (Infinix Note 11 Pro, Infinix Mobile, China) by taking a photo (JPG image file). The photo of *parijoto* fruit were taken every hour during drying inside a modified mini photo studio box to ensure consistent lighting, background and distance between the sample and the camera. Color intensity of *parijoto* fruits is expressed using CIE scale using L*, a*, and b* values. To obtain the L*, a* and b* values, eyedropper tool in Adobe Photoshop CS3 software (Adobe, USA) was used. Measurements were taken three times at different points in the photo.

Data analysis

Data analysis and model fitting were carried out using Microsoft Excel and SPSS (Statistical Package for Social Science) software v.23. Analysis of variance was carried out to measure statistically significant difference at α 0.5.

RESULTS AND DISCUSSION

Antioxidant activity

Figure 1 shows the antioxidant activity of the *parijoto* fruit before and after drying. The $CaCl_2$ submersion pre-treatment did not significantly influence the antioxidant activity of *parijoto* fruit, while higher drying temperature significantly decrease it.

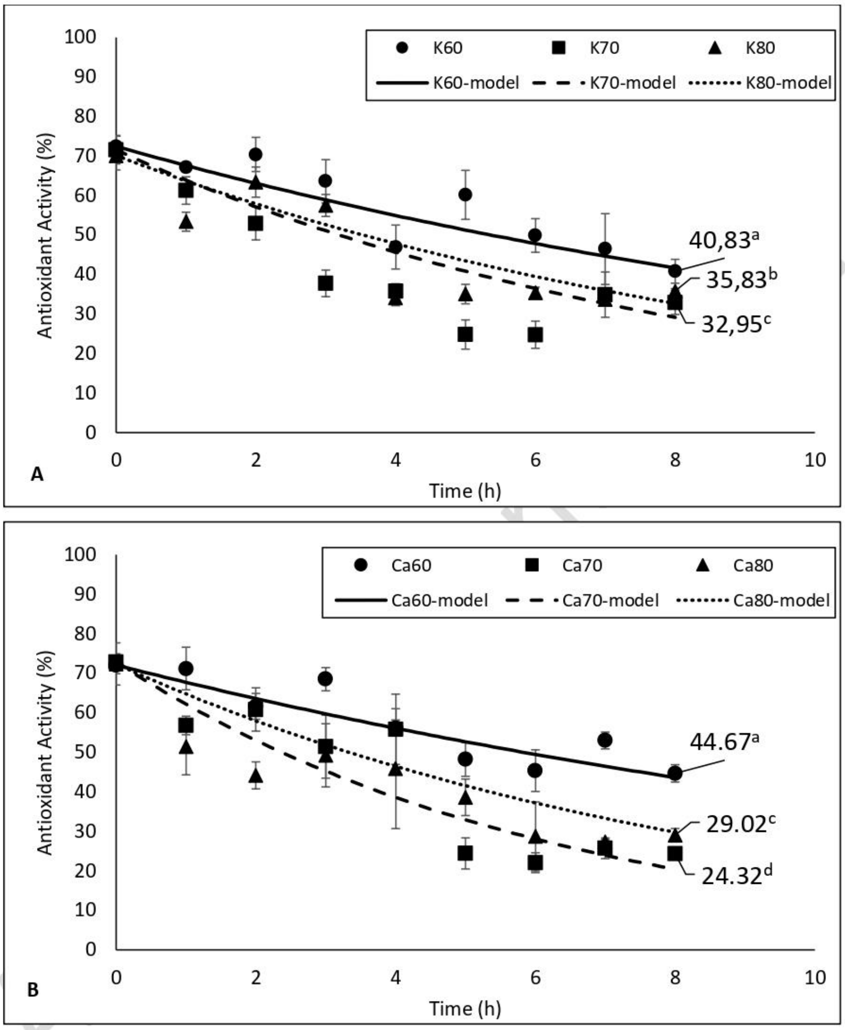


Figure 1. Antioxidant activity of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B). The points indicate the mean observation values and the line indicates the modelled kinetic. The numbers indicate the final value of the antioxidant activity and the superscript letters indicate significant statistical difference ($p < 0.05$).

High temperatures can damage antioxidant compounds in materials, leading to decreased antioxidant activity (Hwang & Do Thi, 2014). According to research by Aloo et al. (2022), $CaCl_2$ soaking treatment can maintain the ascorbic acid content and antioxidant compounds in bell peppers after 16 days of storage at room temperature. Similar findings can be observed in this study for *parijoto* fruits dried at 60ºC treatment, which shows higher results in the soaked fruit than the control. Calcium ions in $CaCl_2$ can form calcium pectate cross-links with pectin molecules in food materials. This can enhance mechanical properties in *parijoto* fruit, thereby preserving intracellular antioxidant compounds. Goutam et al. (2010) in Aloo et al. (2022) also mentioned that calcium ions could decrease oxidative enzyme activity, thus maintaining antioxidant activity stability against oxidative degradation in *parijoto* fruit. However, the positive effect of the $CaCl_2$ soaking was not observed for drying at 70 and 80ºC, indicating that the high temperature's destructive effect affects the antioxidant activity more than the protection of the $CaCl_2$ pre-treatment.

Total anthocyanin content

Figure 2 shows the total anthocyanin content of the dried *parijoto* fruits. Drying caused *parijoto* fruits to lose its anthocyanin content significantly. However, the results show that $CaCl_2$ pre-treatment significantly preserve the anthocyanin content of *parijoto* fruits. On the other hand, the drying temperature did not significantly affect the anthocyanin content of the fruit.

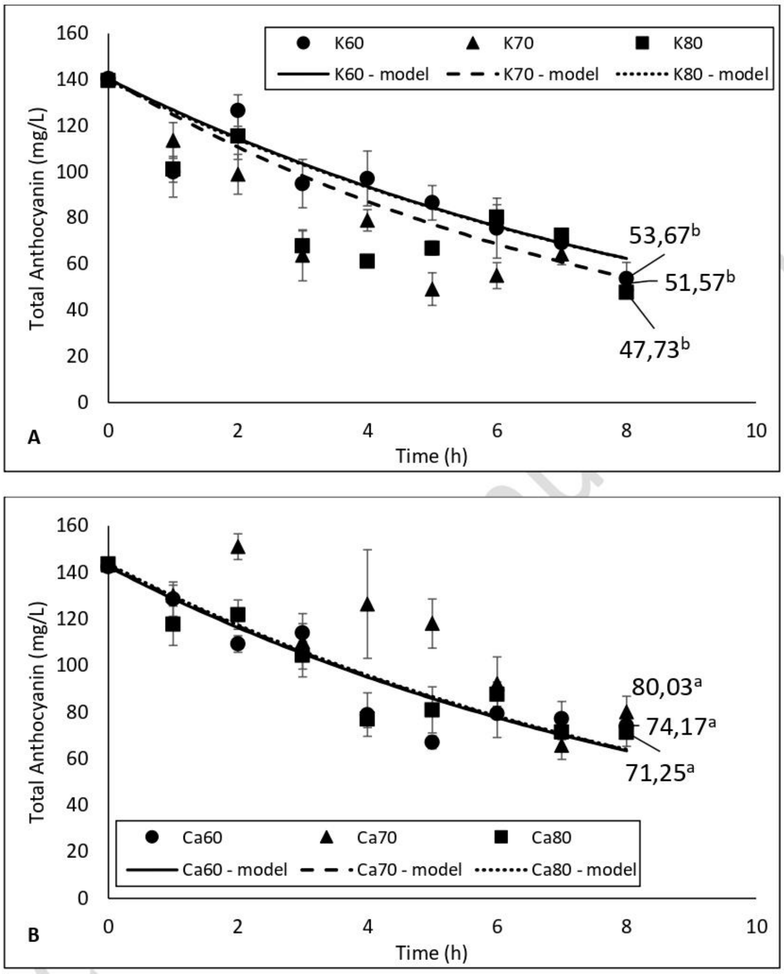


Figure 2. Total anthocyanin content of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B). The points indicate the mean observation values and the line indicates the modelled kinetic. The numbers indicate the final value of the total anthocyanin content and the superscript letters indicate significant statistical difference ($p < 0.05$).

Research by Feng et al. (2022) showed that the utilization of $CaCl_2$ solution can preserve the phenolic compounds and stability of antioxidant compounds in luffa (*Luffa cylindrica*). Calcium pectate cross-links may form during the $CaCl_2$ pre-treatment and they can strengthen the interaction between pectin and anthocyanin (Lin et al., 2016) which may protect the anthocyanin content from the heat treatment during drying. Furthermore, the formation of calcium pectate cross-links enhances the integrity of the cell and prevents cellular damage which encourage of enzymatic browning in food materials due to the release of the polyphenol oxidase (PPO). Since anthocyanins are natural compounds in *parijoto* fruit belonging to the phenolic group, damage to anthocyanin compounds from the PPO activity can be prevented. This could explain the higher total anthocyanin content in $CaCl_2$-soaked samples compared to the control.

Degradation kinetic coefficient of antioxidant activity and total anthocyanin content

The values of k and$t_{1/2}$ obtained from the first order kinetic regression from the antioxidant activity and total anthocyanin content during drying are presented in Table 2. These values are useful in describing the properties degradation kinetics during drying and to compare the susceptibility of the properties to heat degradation. Higher k value indicates faster degradation and thus, a more susceptible material. On the other hand, higher $t_{1/2}$ showed a slower and more difficult degradation, which indicate a more stable material (Peron et al., 2017).

The results of the antioxidant activity analysis show that the degradation rate constant (k) increases with higher drying temperatures. This indicates a faster decline in antioxidant activity with increasing drying temperature, affecting the time for antioxidant activity to reach half its initial value ($t_{1/2}$). Thus, it can be concluded that the antioxidant activity of *parijoto* fruits is very vulnerable to increase in temperature during drying.

On the contrary, the k value of the total anthocyanin degradation kinetic remained the same with higher drying temperature. This indicate that the temperature difference in this study did not affect the kinetics of the anthocyanin degradation. Interestingly, $CaCl_2$ treatment caused significant reduction in the k value and increase in the $t_{1/2}$ value. This may be due to calcium pectate interactions with anthocyanins as previously discussed (Lin et al., 2016), which can slow down anthocyanin degradation. However, the $CaCl_2$ submersion did not slow down the degradation of antioxidant activity of *parijoto* fruits during drying.

Table 2. Values of *k* (degradation kinetic coefficient) and $t_{1/2}$ (half-life) of the antioxidant activity and total anthocyanin content of *parijoto* fruits dried at various conditions

Parameter	Pre-treatment	Temp (ºC)	k (h^{-1})	$t_{1/2}$ (h)
Antioxidant activity	Control	60	0.0691	10.03
		70	0.1121	6.18
		80	0.0955	7.26
	$CaCl_2$	60	0.0628	11.04
		70	0.1590	4.36
		80	0.1109	6.25
Total anthocyanin content	Control	60	0.1012	6.85
		70	0.1193	5.81
		80	0.1006	6.89
	$CaCl_2$	60	0.0885	7.83
		70	0.0882	7.86
		80	0.0869	7.98

Moisture diffusion properties of *parijoto* fruits during drying

The values of D_{eff} and E_a of *parijoto* fruits dried with different conditions are presented at Table 3. Higher value of D_{eff} indicates that moisture could diffuse out of the fruit tissue more effectively during drying (Chen *et al.*, 2016). On the other hand, higher E_a indicates that more energy is required to start moisture diffusion out of the tissue.

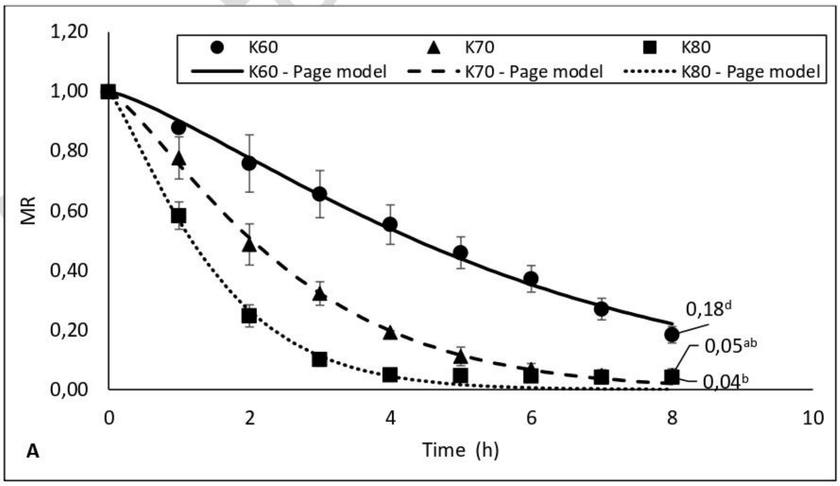
With higher drying temperatures, a higher diffusion coefficient could be achieved. $CaCl_2$ submersion as pre-treatment also significantly increased the diffusion coefficient and lowered the activation energy. This indicates that moisture more easily escaped from the tissue and cells of *parijoto* fruits. Thus, a more efficient and faster drying occurred for *parijoto* fruits dried with pre-treatment and at higher temperatures. The results correlate well with the drying kinetics in Figure 3, discussed below. The presence of salts such as $CaCl_2$ could induce osmotic dehydration in fruit cells (Udomkun et al., 2014). Osmotic dehydration occurred due to the difference in the osmotic pressure between the materials and the salt solutions used to submerge them. Osmotic dehydration can only partially remove water from the materials and usually uses a pre-treatment as the materials require further processing to be shelf-stable (Berk, 2018).

Table 3. *Effective Moisture Diffusivity* (D_{eff}) and Activation Energy (E_a) of parijoto fruits dried at various conditions

Pre-treatment	Temp (ºC)	D_{eff} (m^2s^{-1})	E_a (kJ/mol)
Control	60	3.27×10^{-3}	35.53
	70	6.91×10^{-3}	
	80	6.71×10^{-3}	
$CaCl_2$	60	4.49×10^{-3}	29.48
	70	9.00×10^{-3}	
	80	8.13×10^{-3}	

Drying kinetics of *parijoto* fruits

The change in the moisture ratio during drying for all the different treatments is shown in Figure 3. Based on the drying kinetics, a moisture ratio plateau (which indicate no further moisture reduction) was already reached at approximately 7 hours and 4 hours for 70 and 80ºC, respectively, with a final moisture ratio of about 0.05 for the control sample and about 0.02 for pre-treated samples. On the other hand, *parijoto* fruits dried at 60ºC, both with or without pre-treatment, did not reach the same level of moisture ratio after 8 hours. *Parijoto* fruits with $CaCl_2$ submersion reached a lower final moisture ratio than the control samples at all temperature levels, indicating a more effective drying due to the pre-treatment before drying. As discussed, $CaCl_2$ pre-treatment caused osmotic dehydration, significantly increasing moisture diffusivity out of *parijoto* fruits (Table 3).



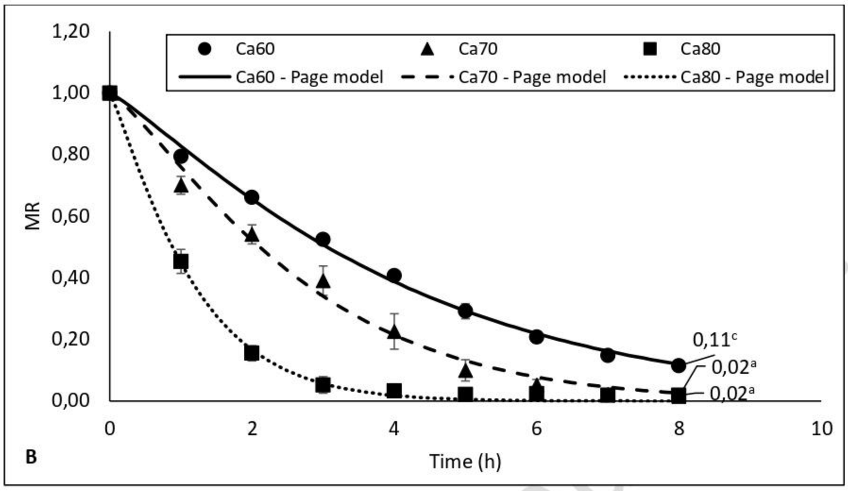


Figure 3. Moisture ratio of *parijoto* fruit dried at different temperature without pre-treatment (A) and with $CaCl_2$ submersion (B). The points indicate the mean observation values and the line indicates the modelled kinetic. The numbers indicate the final value of the moisture ratio and the superscript letters indicate significant statistical difference ($p < 0.05$).

Three models were fitted into the drying kinetics, i.e. Lewis, Henderson & Pabis and Page model (Panchariya et.al., 2002). The coefficients obtained from the model fitting are presented at Table 3. Based on the highest R^2 and lowest RSME values (Table 4), Page model best describe the drying kinetics of *parijoto* fruits using cabinet dryer. Page model was used to estimates the value of k and n. The value of k describes the rate of the drying process which show how fast moisture migrates out of the fruits (Panchariya et.al., 2002), while the value of n does not have significant physical meaning yet. Similar model has been used to describe the drying of gilaburu berries (Dönmez & Kadakal, 2024) and aryl of pomegranate (Vardin & Yilmaz, 2018). The value of k increased significantly with higher temperature and with $CaCl_2$ submersion pre-treatment, which indicate faster drying. With faster drying and insignificant degradation of anthocyanin content observed (Figure 2), drying at 80ºC may be suitable to create functional ingredients from *parijoto* fruits.

Table 4. Coefficients of drying kinetics of parijoto fruits at various conditions from different models

Pre-treatment	Temperature (°C)	Model	k	n	a	R^2	RMSE
Control	60	Lewis	0.165			0.947	0.099
		Henderson & Pabis	0.174		1.041	0.952	0.119
		Page	0.103	1.292		**0.966**	**0.019**
	70	Lewis	0.379			0.977	0.143
		Henderson & Pabis	0.394		1.045	0.980	0.143
		Page	0.281	1.266		**0.988**	**0.015**
	80	Lewis	0.648			0.986	0.195
		Henderson & Pabis	0.657		1.016	0.986	0.185
		Page	0.566	1.229		**0.989**	**0.027**
$CaCl_2$	60	Lewis	0.239			0.989	0.112
		Henderson & Pabis	0.246		1.023	0.990	0.117
		Page	0.189	1.163		**0.995**	**0.016**
	70	Lewis	0.369			0.974	0.141
		Henderson & Pabis	0.377		1.027	0.975	0.133
		Page	0.275	1.242		**0.984**	**0.032**
	80	Lewis	0.857			0.994	0.223
		Henderson & Pabis	0.864		1.006	0.994	0.210
		Page	0.802	1.158		**0.995**	**0.014**

Color changes of *parijoto* fruits during drying

Digital image analysis was carried out to the *parijoto* fruits during drying. The visual representations of the color change are shown in Table 5. The results of the analysis (L*, a* and b* values) are shown in Figure 4-6. Heat from the drying immediately caused a change in the color profile of *parijoto* fruits from initially dark purple to reddish color in the first hour. Slight increase of the lightness (L*) values of the *parijoto* fruits were observed after drying and a significant increase of the a* value was observed which indicates the increased intensity of the red color after drying. On the other hand, the value of b* changed from negative to positive, which indicate a change of color hue from dominant blue to yellow after drying. The change of the color from purple to reddish color due to drying may be caused by the increase in the acidity level of the fruits, due to the change of the proportion after moisture removal. Anthocyanin color changed at different acidity level, in which it becomes redder at acidic environment (Drețcanu, et.al., 2021).

Variations in the visual of *parijoto* fruits and L*, a* and b* values between the different drying conditions are observed during the drying process. However, the final color of *parijoto* fruits after 8 hr of drying was not significantly different between the conditions.

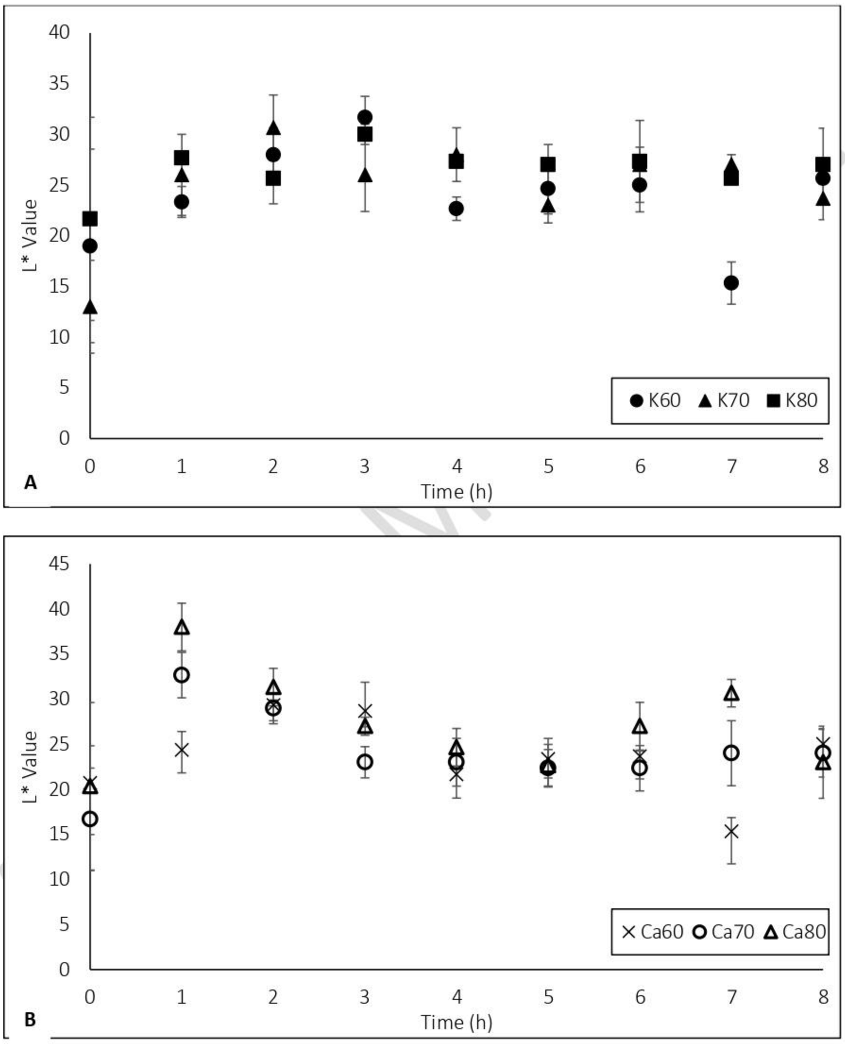


Figure 4. L* values from the digital image analysis of the *parijoto* fruits during drying at different temperature without (A) and with $CaCl_2$ pre-treatment (B)

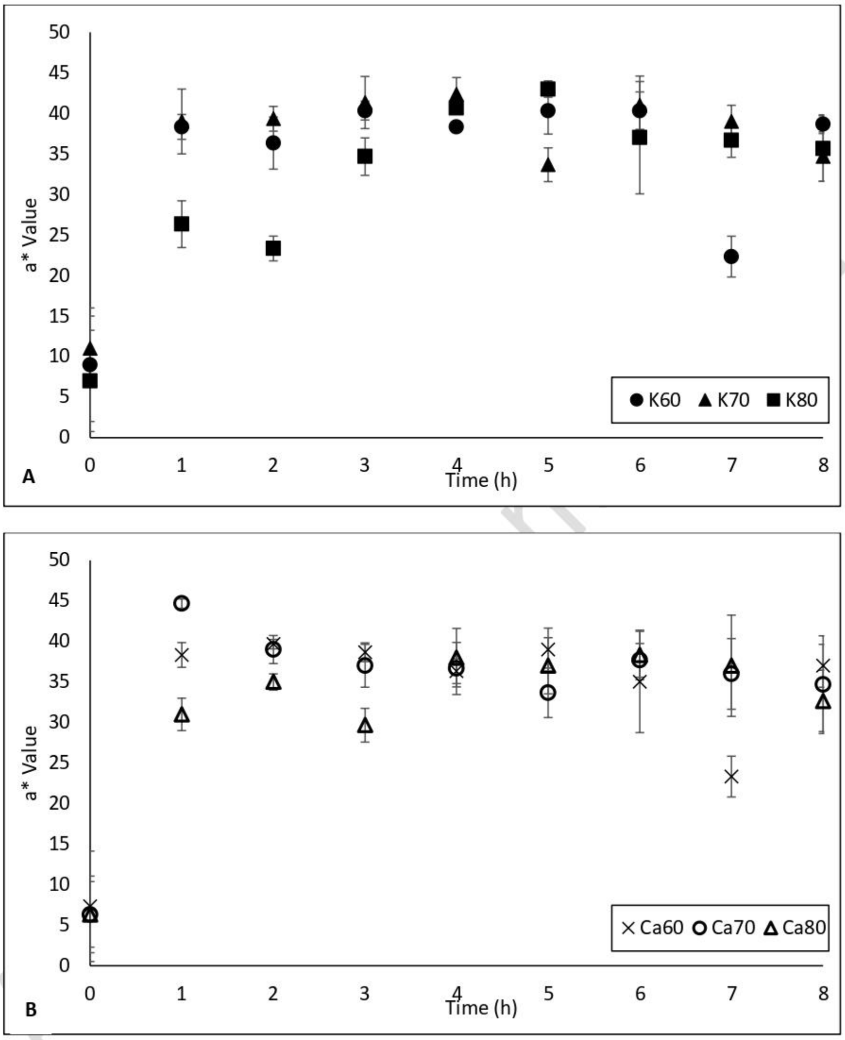


Figure 5. a* values from the digital image analysis of the *parijoto* fruits during drying different temperature without (A) and with $CaCl_2$ pre-treatment (B)

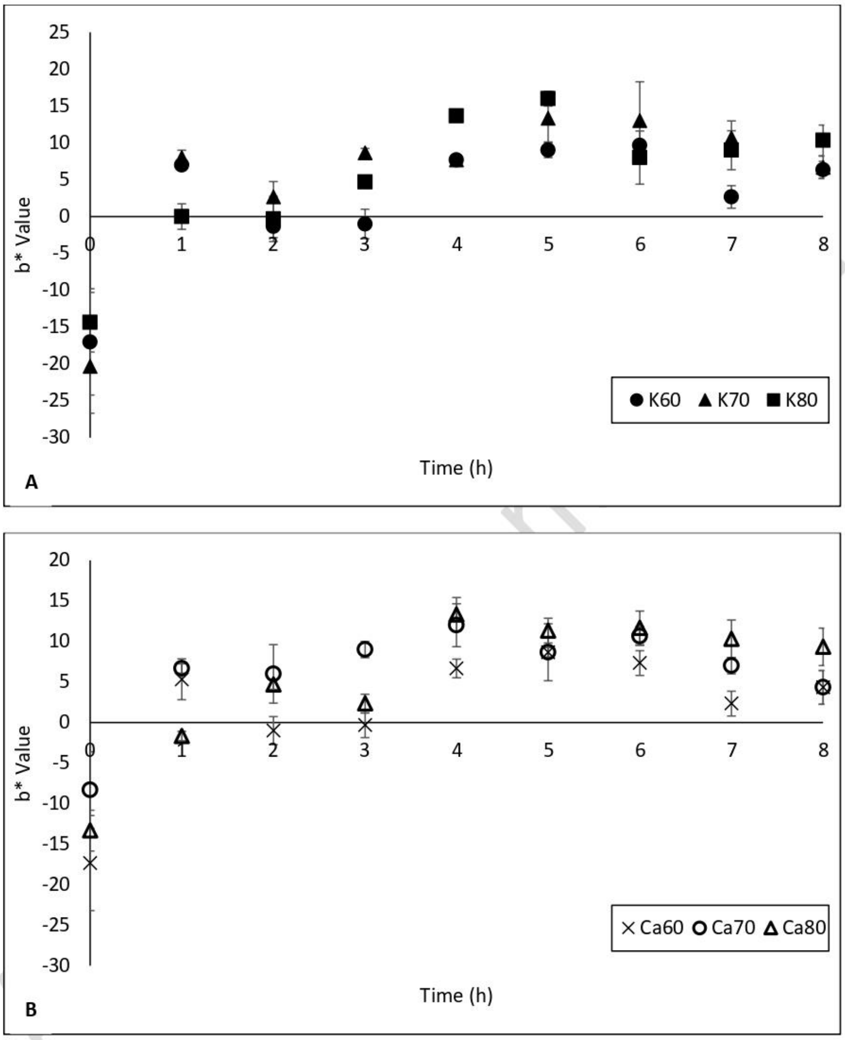
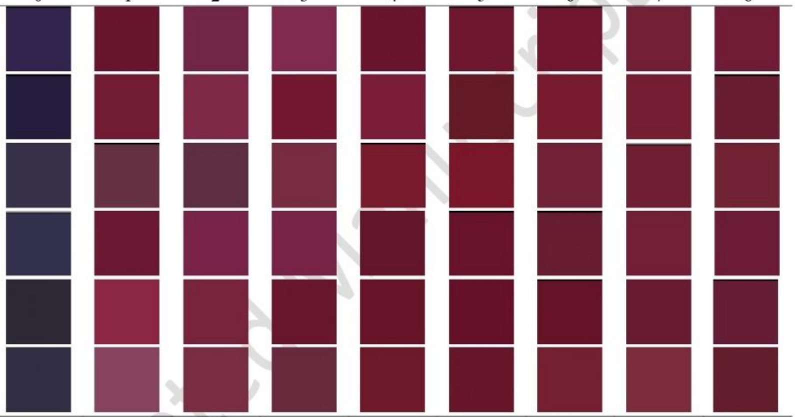


Figure 6. b* values from the digital image analysis of the *parijoto* fruits during drying different temperature without (A) and with $CaCl_2$ pre-treatment (B)

Table 5. Digital color profile of *parijoto* fruits throughout drying with different treatments

Treatment	Drying time (h)								
	0	1	2	3	4	5	6	7	8
K60									
K70									
K80									
Ca60									
Ca70									
Ca80									



CONCLUSIONS

Drying of *parijoto* fruit at 60-80ºC may cause significant reduction on its antioxidant activity and total anthocyanin content. The antioxidant activity of *parijoto* fruits is especially susceptible to an increase in temperature during drying. However, with $CaCl_2$ submersion as pre-drying treatment, the degradation of anthocyanin content can be reduced. $CaCl_2$ submersion and higher drying temperature can also increase the drying rate of *parijoto* fruit, which make it possible to dry at a shorter time to prevent further degradation of the anthocyanin content. Higher drying rate correlates to a higher effective diffusion coefficient and the drying kinetics of *parijoto* fruits can best be described by the Page model($MR = \exp(-kt^n)$). In this research, drying of *parijoto* fruits at 80ºC gave the fastest drying rate with insignificant degradation to the total anthocyanin content and color.

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